Escuela Técnica Superior de Ingeniería Aeronáutica y del Espacio

Departamento de Mecánica de Fluidos y Propulsión Aeroespacial

Nanoparticle structures obtained using photovoltaic tweezers and their applications in photonic devices

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PhD Thesis

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*And I know things now,
many valuable things,
that I hadn't known before.*

Stephen Sondheim & James Lapine, Into the Woods

*Of course, it is quite possible to be in the dark in the dark, as well as to be not in the dark not
in the dark, but there are so many secrets in the world that it is likely that you are always in the
dark about one thing or another, [...]*

Lemony Snicket, The End

ნამარიე
(*Namárie*)

John Ronald Reuel Tolkien

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Nomenclature

Symbols

Symbol	Description	Page of definition
A	Stiffness matrix	86
a	Ellipsoid Y axis	36
a	Half of slit width (diffraction grating)	45
a	Node number (Lagrange polynomial)	87
$\mathbf{b}$	Load vector	86
$\mathbf{b}$	Arbitrary vector function	110
b	Ellipsoid X axis	36
$\mathbf{C}$	Constant vector	111
c	Speed of light	29
c	Ellipsoid Z axis	36
$\mathbf{D}$	Dielectric displacement	120
D	Diffusion coefficient	29
D	Distance between plates	40
D	Diagonal matrix	110
D_c	Critical distance between plates	39
$\mathbf{d}$	Piezoelectric coefficient tensor	15
d	Grating displacemnt (SWIFTS)	72
$\mathbf{E}$	Total applied electric field	29
$\mathbf{E}_{ext}$	External electric field	34
E_{sat}	Modulus of the photovoltaic saturation electric field	83
$E_{x,r,z}$	Electric field component along the x , r or z coordinate	83

Symbol	Description	Page of definition
e	Solution error	89
e^-	Electron	22
F_B	Buoyancy	151
F_{Br}	Brownian force	152
F_D	Drag	151
F_{DEP}	Dielectrophoretic force	35
F_{EP}	Electrophoretic force	38
F_G	Gravity	151
f_{be}	Body force	39
f	Focal length (Fresnel zone plate)	48
f	Arbitrary known function	84
f_{CM}	Clausius-Mossotti factor	34
G	Geometric factor matrix	111
G'	Geometric factor matrix multiplied by the local intensity	111
g	Gravitational acceleration	150
h	Arbitrary vector function (decoupled)	110
h	Planck constant	28
I	Photon flux density	28
I_B	Background illumination	122
I_c	Corrected intensity (SWIFTS)	204
$I_{i,m,f}$	Recorded intensity from the interference, the mobile arm or the fixed arm (SWIFTS)	204
I_m	Intensity of the m order of diffraction (diffraction grating)	46
I_m	Mean intensity (sinusoidal light pattern)	58
I_p	Gaussian beam peak intensity	134
I_θ	Angular intensity distribution (diffraction grating)	45
I_0	Incoming intensity (SWIFTS)	70
I_0	Incident intensity	121
$I_{1,2}$	Intensity of the beam 1 or 2 (holographic setup)	58
i	Imaginary unit	34
J	Current density	29
J_R	Current density component perpendicular to the c-axis	129

Symbol	Description	Page of definition
J_z	Current density component parallel to the c-axis	129
J_{z0}	J_z at the beginning of illumination	130
K	Constant (diffraction grating)	45
k	Light source wavenumber	45
k_B	Boltzmann constant	29
$\mathcal{L}$	Arbitrary differential operator	84
L	Distance from diffraction pattern to diffracting object	44
L	Waveguide length (SWIFTS)	70
L	Lagrange polynomial	87
L_{PV}	Photovoltaic transport length	29
$\mathbf{l}$	Arbitrary curve	38
l	Arbitrary length	71
l_D	Debye length	123
l_z	Crystal thickness	122
m	Order of diffraction	46
m	Sinusoidal pattern modulation	58
N	Total impurity concentration in the crystal	27
N	Number of slits (diffraction grating)	45
$(N_{A0}) N_A$	(Initial) Acceptor concentration	28
$(N_{D0}) N_D$	(Initial) Donor concentration	28
$\hat{\mathbf{n}}$	Unit vector perpendicular to a boundary	120
$(n_0) n$	(Equilibrium) charge carrier concentration	28
n	Refractive index	12
n	Integer (Fresnel zone plate)	48
n	Number of nodes (Lagrange polynomial)	87
n_{eff}	Effective refractive index	68
$\mathbf{P}$	Induced polarization	15
P	Eigenvector matrix	110
P_s	Spontaneous polarization	14
$\mathbf{p}$	Dipole moment	35
$\mathbf{p}_{eff}$	Effective dipole moment (spherical, isotropic particle)	34

Symbol	Description	Page of definition
$\mathbf{p}'_{eff}$	Effective dipole moment (arbitrary particle)	36
p_3	Pyroelectric coefficient	14
Q_p	Total charge of a particle	38
q	Electron charge	29
$\mathcal{R}$	Residual	85
R	Reflection coefficient	71
$\mathbf{r}$	Linear electro-optic coefficient tensor	13
r	Particle radius	34
r	Radial spatial coordinate	134
r_n	Radius of a zone (Fresnel zone plate)	48
r_{or}	Oxidation-reduction ratio	27
$\mathbf{S}$	Second order electro-optic coefficient tensor	13
$\mathbf{S}$	Applied stress tensor	15
s	Photoionization cross-section	29
$\mathbf{T}$	Dielectrophoretic torque	36
$\mathbf{T}$	Maxwell stress tensor	39
T	Absolute temperature	14
t	Time	
U	Trial function	85
U_{DEP}	Dielectrophoretic potential energy	35
U_{EP}	Electrophoretic potential energy	38
$\hat{\mathbf{u}}_{PV}$	Unit vector along the polar axis	29
u	Unknown function	84
V	Electric potential	119
V_d	Droplet volume (reservoir)	40
$\mathbf{v}_m$	Medium velocity	151
$\mathbf{v}_p$	Particle velocity	151
W	Incoming light intensity	28
W	Obstacle width	44
$\mathbf{x}$	Arbitrary vector of unknowns (coupled)	110
x	Spatial coordinate	

Symbol	Description	Page of definition
$\mathbf{y}$	Arbitrary vector of unknowns (decoupled)	110
y	Spatial coordinate	
z	Spatial coordinate	
α	Sinus of θ (diffraction grating)	45
α	Absorption coefficient	122
β	Thermal generation rate	29
γ	Recombination constant	29
γ_i	Scalar coefficients	85
δ	Identity tensor	39
$\partial\Omega$	Arbitrary domain boundary	84
ϵ	Relative permittivity tensor	29
$\tilde{\epsilon}$	Complex permittivity	34
$\tilde{\epsilon}_m$	Medium complex permittivity	34
$\tilde{\epsilon}_p$	Particle complex permittivity	34
ϵ_f	Fluid permittivity	39
ϵ_m	Medium permittivity	34
ϵ_p	Particle permittivity	34
ϵ_0	Vacuum permittivity	29
ϵ_{11}	LiNbO ₃ permittivity along X direction	29
ϵ_{22}	LiNbO ₃ permittivity along Y direction	
ϵ_{33}	LiNbO ₃ permittivity along Z direction (parallel to c-axis)	29
ϵ	Induced deformation tensor	15
η	Dinamic viscosity	150
θ	Contact angle	40
θ	Angle between the incident beam and the diffracted one (diffraction grating)	45
θ	Angle between laser beams (holographic setup)	57
κ	Photovoltaic current density	29
Λ	Fringe/grating/pattern period	38
λ	Light wavelenght	29
μ	Mobility	29
ξ	Local coordinate (Lagrange polynomial)	87

Symbol	Description	Page of definition
ξ	Gaussian random number	152
ρ	Space charge density	29
ρ_m	Medium density	150
ρ_p	Particle density	150
σ_D	Dark conductivity tesor	29
σ_{PH}	Photoconductivity tensor	29
σ	Surface charge density	83
σ_G	Gaussian beam radius	83
σ_S	Surface charge density	38
σ_{crit}	Critical surface charge density	38
σ_p	Pyroelectric surface charge density	14
σ_0	Surface charge density (simple model)	83
ς	Conductivity	34
ς_m	Medium conductivity	34
ς_p	Particle conductivity	34
τ	Time constant for J_z time evolution	83
τ_J	Time constant (current density)	130
ϕ	Shape function	84
Ω	Arbitrary domain	84
ω	Frequency of an electric field	34
ω	Weight function	85

Acronyms

Acronym	Meaning	Page of definition
BPVE	Bulk photovoltaic effect	21
CGH	Computer generated hologram	186
DCM	Dichloromethane	197
DEP	Dielectrophoretic, dielectrophoresis	33
DOE	Diffraction optical element	42
DR1	Disperse Red 1	211

Acronym	Meaning	Page of definition
EHD	Electrohydrodynamic	40
EP	Electrophoretic, electrophoresis	33
FDM	Finite difference methods	80
FEM	Finite element methods	80
FIB	Focused ion beam	67
FVM	Finite volume methods	80
HOT	Holographic tweezers	xxiv
IPAG	Institut de Planétologie et d'Astrophysique de Grenoble	xxvi
ISASI-CNR	Istituto di Scienze Applicate e Sistemi Intelligenti	xxvii
MWR	Methods of weighted residuals	84
NP	Nanoparticle	54
ODE	Ordinary differential equation	83
OET	Optoelectronic tweezers	xxiv
OPD	Optical path difference	203
OPL	Optical path length	71
OT	Optical tweezers	xxiv
PDE	Partial differential equation	78
PDI-O	Perylene orange	211
PMMA	Poly(methyl methacrylate)	196
PVT, POT	Photovoltaic optoelectronic tweezers, photovoltaic tweezers, photorefractive optoelectronic tweezers	xxiv
SAW	Surface acoustic waves	15
SHD	Side holographic disperser	67
SLM	Spatial light modulator	56
SWIFTS	Stationary Wave Integrated Fourier Transform Spectrometer	69
ZL	Zeolite	213

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Resumen

Esta tesis se centra en una técnica optoelectrónica de manipulación de partículas llamada «pinzas fotovoltáicas». Esta técnica se emplea para atrapar y estructurar nano- y micropartículas sobre la superficie de cristales de niobato de litio dopado con hierro ($\text{LiNbO}_3\text{:Fe}$) gracias a los enormes campos eléctricos generados por este material cuando es iluminado de forma apropiada. En particular, se han investigado las características de una novedosa configuración basada en cristales de $\text{LiNbO}_3\text{:Fe}$ corte-z. Al contrario que en los sustratos tradicionalmente usados para manipular partículas mediante pinzas fotovoltáicas (corte-x y corte-y), en la configuración corte-z el eje óptico del material es perpendicular a la superficie del cristal, lo que hace posible obtener patrones de nanopartículas bidimensionales y arbitrarios. Atendiendo a su estructura, esta tesis puede dividirse en tres partes:

- En la primera se han llevado a cabo cálculos teóricos del transporte de carga fotovoltáico en cristales corte-z mediante un programa de elementos finitos. Se ha estudiado la evolución temporal del campo eléctrico fotovoltáico y la influencia de distintos parámetros que afectan al proceso de atrapamiento de las partículas.
- En la segunda se han obtenido patrones experimentales de nanopartículas neutras y cargadas eléctricamente. Las características más importantes de las distintas microestructuras de partículas han sido analizadas y explicadas usando los potenciales dielectro- y electroforéticos obtenidos mediante los cálculos teóricos previos.
- Finalmente, algunos de los patrones obtenidos en la parte anterior se han usado como instrumentos ópticos: elementos difractivos y espectrómetros integrados. Estos dispositivos han sido empleados y caracterizados.

En conclusión, esta tesis es un estudio en detalle de cómo pueden obtenerse patrones bidimensionales arbitrarios de nanopartículas usando las pinzas fotovoltáicas, mostrando algunas de sus aplicaciones potenciales. Este trabajo sienta una sólida base teórica y experimental para la técnica, y puede servir de punto de partida para continuar optimizando y mejorando la calidad de los patrones obtenidos mediante pinzas fotovoltáicas.

Abstract

This thesis is focused on an optoelectronic technique for particle manipulation called “photovoltaic tweezers”. This technique takes advantage of the high photovoltaic electric field developed by iron-doped lithium niobate ($\text{LiNbO}_3\text{:Fe}$) crystals when they are properly illuminated to trap and arrange nano- and microparticles on these crystals surface. In particular, the patterning capabilities of a new configuration that uses z-cut $\text{LiNbO}_3\text{:Fe}$ crystals have been investigated. Contrary to the substrates typically used to manipulate particles using photovoltaic tweezers (x- and y-cut), in z-cut configuration the polar axis of the material is normal to the crystal surface, which makes isotropic and arbitrary 2D particle patterning possible. According to its structure, this thesis can be divided in three parts:

- In the first one, theoretical calculations of the photovoltaic charge transport in z-cut crystals have been performed using a finite element software. Time evolution of the photovoltaic electric field and the influence of different factors that affect particle trapping have been studied.
- In the second one, experimental patterns of both electrically neutral and charged nanoparticles have been obtained. The main features of different particle microstructures are analysed and explained using the dielectro- and electrophoretic potentials obtained thanks to the theoretical calculations.
- Finally, some of the patterns shown in the previous section have been used as different optical instruments: diffractive optical elements and integrated spectrometers. The performance of these instruments has been analysed.

In conclusion, this thesis is a thorough study of how arbitrary 2D nanoparticle patterns can be obtained using photovoltaic tweezers and it shows some of the potential applications of this patterning technique. This work provides a sound basis for the theoretical and experimental development of photovoltaic tweezers and lays the groundwork for further pattern optimisation.

Preface

In 1959 Richard P. Feynman gave a lecture at an American Physical Society meeting at Caltech called *There's plenty of room at the bottom* [76]. In his talk, Feynman discussed the possibilities derived from designing devices in progressively smaller and smaller scales and envisaged great advances in science and technology when we were able to accurately manipulate atoms themselves. He was aware of the implicit advantages of miniaturization regarding not only the reduced size of the devices or their portability, but also their faster operation speed, lower raw materials requirements and cost. In short, Feynman tried to inspire physicists and engineers to reach the *submicroscopic* scale, as he called it. Fifteen years had to pass before Norio Taniguchi (谷口紀男) coined the word *nanotechnology* in 1974 [166].

It is curious how Feynman's lecture was barely noticed until the early 1990s, even though it includes many of the key ideas that have captivated the scientific community since the last decades of the 20th century and that have given birth to the nanotechnology as we know it today. For example, in *There's plenty of room at the bottom*, Feynman predicts that conventional manufacturing techniques would not be applicable when working at the nanoscale; in fact, since 1959, many techniques have been developed in order to control and manipulate nanoobjects, to the extent that currently it is possible to make a stop-motion movie using atoms [16].

However, one should note that between the atomic and the macroscopic world there is still *plenty of room*. In particular, nanoparticles (particles between 1 and 100 nm in size) are possibly the most widespread nanoobject among them all [121]. Contrary to bulk materials, whose physicochemical properties are the same regardless of its size, some properties of nanoparticles

are indeed size-dependent due to their large surface to volume ratio. This way, new physical phenomena arise and can be exploited. Currently, nanoparticles are used in a large variety of scientific and technological fields, such as optics, material science, electronics, medicine, biology, energy harvesting and environmental science [121].

One of the most developed, well-known methods for nanoparticle manipulation is the optical tweezers (OT). This technique was first reported by Ashkin in 1970 [31] and it allows precise control and manipulation of particles using a highly focused laser beam. It is based on the interaction of the particles with the electromagnetic field of light and it is typically used to create assemblies up to 100 particles. In order to manipulate larger amounts of particles, a similar technique called holographic tweezers (HOT) uses diffraction patterns to create numerous focal points or “traps” [141].

The main disadvantage of OT and HOT is that these techniques directly depend on the light-particle interaction, and thus very high light intensities are required during particle manipulation ($\sim 10^9 \text{ W/m}^2$). This also limits the throughput of HOT, as the spatial light modulators that are typically used to create the arbitrary trap distribution can stand up to a certain value of incoming light intensity. In 2005 Chiou [59] reported a new optical method for particle manipulation called optoelectronic tweezers (OET), which is capable of achieving high throughput and high resolution, using a light source which intensity is five orders of magnitude lower than that used in OT. OET introduces the concept of “virtual electrodes” and takes advantage of the electric field generated in a biased photoconductive material when illuminated with an arbitrary light pattern.

Finally, in 2007 Eggert and his co-workers used the idea behind OET to develop a new tool [64]; instead of using a biased photoconductive material they used a photovoltaic crystal, capable of developing the required electric field through the space charge field induced in the material under inhomogeneous illumination. This eliminates the need of electrodes or external voltage sources, and thus increases the flexibility and portability of the technique. This method for particle patterning and manipulation is nowadays known as photovoltaic (optoelectronic) tweezers (PVT) or photorefractive optoelectronic tweezers (POT).

PVT takes advantage of the high electric fields (10^6 - 10^7 V/m) generated in some ferroelectric crystals when they are properly illuminated even at low light intensities (~ 10 W/m²) [23]. The physical phenomenon that generates the electric field is called “bulk photovoltaic effect” and consists in a light-induced redistribution of electric charges inside the material due to certain non-symmetries of its crystalline structure [23]. The internal electric field extends outside the crystal as a fringe field, which is capable to trap and structure objects on the crystal surface, no matter its nature -organic or inorganic [46, 103], metallic or dielectric [64], neutral or electrically charged [69], etc., using dielectro- and electrophoretic forces. The technique allows precise and simultaneous trapping of a large number of particles, which makes PVT an excellent technique for parallel manipulation of many objects with very low energy consumption. Other advantages of this method, besides its lack of external electrodes, are the possibility of pattern reconfiguration [85], the exceptional stability of the patterns, and the high achievable resolution, as in principle the size of the motifs is only limited by the exciting wavelength.

The most commonly used ferroelectric crystal for this technique is the iron-doped lithium niobate ($\text{LiNbO}_3\text{:Fe}$), due to its outstanding photovoltaic properties [23, 176]. For PVT operation, it has been typically used in a configuration known as “x-cut” (or y-cut), in which the optical axis of the material is parallel to the crystal surface. That allows very good 1D patterning but has serious limitations when one tries to obtain 2D motifs [28, 67]. To solve this problem, another configuration called “z-cut” (with the optical axis perpendicular to the crystal surface) was introduced in a single publication by Esseling *et al.*, but only to manipulate charged particles [69]. In fact, they indicated that manipulation of neutral particles by DEP forces was not possible because photovoltaic electric fields are not high enough in z-cut. However, this assumption was not true, as will be shown in the present work.

Nowadays, PVT is starting to become a well-established as a technique [81], and it is being used for manipulating inorganic and biological particles [53, 103], liquid droplets [57, 58, 70], liquid crystals [93] and for making different kinds of microstructures [65]. Of course, there is experimental and theoretical work to be done, but as it is shown in this dissertation, the structures

of micro- and nanoobjects obtained using by PVT are good enough to be employed in different scientific fields such as optics [65], biology [103] or microfluidics [58, 70].

Objectives and structure of this thesis

The aim of this thesis work was to perform arbitrary 2D particle manipulation and trapping using photovoltaic optoelectronic tweezers, thus removing the existing limitations that seriously reduced their technological potential. To this end the z-cut configuration proposed by Esseling *et al.* has been investigated in detail from the theoretical and experimental point of view. In particular, the patterning capabilities of z-cut $\text{LiNbO}_3\text{:Fe}$ crystals have been investigated in order to obtain 2D nanoparticle patterns that can be used in different optical devices. The objectives of this research are:

- To obtain high-quality 2D nanoparticle patterns, as they are indispensable for future technique applications.
- To calculate the distribution and time evolution of the fringe field and the dielectro- and electrophoretic potentials generated on the surface of photovoltaic crystals under arbitrary light distributions in order to explain the features of the experimental patterns and to optimize the experimental conditions.
- To develop a nanoparticle pattern transference process from the original $\text{LiNbO}_3\text{:Fe}$ crystal to any arbitrary substrate.
- To fabricate photonic devices based on the nanoparticle patterns and analyse their performance.

The theoretical calculations were performed at the Escuela de Ingeniería Aeronáutica y del Espacio of the Universidad Politécnica de Madrid, whereas the experimental part of this thesis was carried out at the Facultad de Ciencias of the Universidad Autónoma de Madrid. During the course of this work, two research stays were carried out. The first one was at the Institut de Planétologie et d'Astrophysique de Grenoble (IPAG, Grenoble, France) under the supervision of Dr. Guillermo Martín and was focused on characterising two integrated spectrometers previously

fabricated using PVT. The second one was at the Istituto di Scienze Applicate e Sistemi Intelligenti (CNR-ISASI, Naples, Italy) under the supervision of Dr. Simonetta Grilli and Dr. Romina Rega and was focused on learning about the pyroelectric effect and its technological applications.

This dissertation is divided in three different parts: *I. Introduction*, *II. Experimental and theoretical methods* and *III. Results*.

The first part, *I. Introduction*, comprises three chapters that cover the fundamental physical phenomena on which this thesis work is based. In the first one, *1. Lithium niobate*, the structure of this material and its main properties are explained. In addition, different optical waveguides fabricated with LiNbO_3 crystals are briefly described.

In *2. Bulk photovoltaic effect*, this physical phenomenon is first qualitatively explained and afterwards the system of partial differential equations (PDEs) that models the charge transport and space charge distribution inside the photovoltaic material (rate equations) is presented and analysed in detail.

The last chapter of this part, *3. Other electrodynamic and optical effects of interest*, deals with two different topics. On the one hand, the main electric forces that are involved in particle manipulation using PVT (dielectro- and electrophoresis) and their corresponding potential energies are carefully explained, including related effects that are important for particle trapping, such as the dielectrophoretic torque or particle-particle interaction. On the other hand, diffraction phenomenon is qualitatively described and two different diffractive optical elements (DOEs) that are later fabricated using PVT are explained in detail.

The second part, *II. Experimental and theoretical methods*, consists of two chapters. In the first section of chapter *4. Experimental techniques*, all the steps of nanoparticle patterns fabrication using PVT are thoroughly explained and discussed. The second section of this chapter is dedicated to introducing two different kinds of integrated spectrometers, since this thesis includes the fabrication and testing of two prototypes based on our nanoparticle structures.

In the other chapter of this second part, *5. Numerical methods*, an introduction to numerical modelling is made, as well as a description of the most common methods used for solving PDEs. Then, a well-established simple analytical model for describing charge transport in z-cut crystals is explained, since it will be useful for checking the numerical calculations. The last two sections of this chapter are focused on briefly explaining the theoretical foundation of the finite element method (FEM) and describing the commercial software used to perform the theoretical analyses of this work, COMSOL Multiphysics®.

The last part, *III. Results*, is comprised by five chapters and it is dedicated to the original results of this thesis. In *6. Dielectrophoretic z-cut patterning*, the capabilities of x-cut and z-cut crystals for obtaining 1D and 2D particle patterns are compared and some features are explained using the simple analytical model previously presented.

Chapter 7. *Theoretical analysis of the charge transport in z-cut configuration*, starts showing the impossibility of accurately describing the charge transport in z-cut crystals supposing only surface charge accumulation, like all previous models do. This proves the real need of solving the rate equations using FEM. The system implementation in COMSOL® is explained in detail and the time evolution of the space charge and electric field in z-cut crystals under different arbitrary illumination patterns is studied. The role of different experimental parameters is discussed in the last section of this chapter.

In *8. Nanoparticle patterns obtained by dielectrophoretic and electrophoretic forces*, the key features that may appear in patterns obtained with neutral and charged particles are discussed and correlated with the theoretical forces and potential distributions obtained from the FEM analysis performed in the previous chapter. This chapter also has a brief section dedicated to the first results regarding particle trapping simulation.

In chapter 9. *Optical diffractive elements and pattern transference*, actual DOEs that are made using PVT are shown and tested. The problem of optical damage is introduced and two different methods for pattern transference to arbitrary substrates are proposed. Finally, the performance of two kinds of spectrometers, which were made transferring PVT-obtained nanoparticle gratings

on top of LiNbO_3 waveguides, is characterised. This characterisation was carried out during the short research stay at the IPAG.

Finally, *10. Collaborations on applications of photovoltaic and pyroelectric electric fields* is divided in two sections. The first one is dedicated to explaining how partial experimental and theoretical results of this thesis work have been useful for other members of my research group. The second section addresses my three-month research stay at the CNR-ISASI. This stay was focused on learning about the pyroelectric effect in LiNbO_3 crystals, as it can be used for particle patterning in a similar way as the photovoltaic effect. In fact, sometimes both effects appear simultaneously during PVT operation.

I. INTRODUCTION

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Chapter 1: Lithium niobate

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CHAPTER 1

Lithium niobate

The key element of photovoltaic tweezers (PVT) is a material capable of developing a high electric field when it is properly illuminated. This electric field must be strong enough in order to affect nearby particles. Many ferroelectric crystals fulfil this requirement, but among them, lithium niobate (LiNbO_3) stands out for its extremely good properties [172].

In this chapter, the composition and crystalline structure of lithium niobate is presented, paying especial attention to the latter and its dependence on temperature. Most common defects and impurities of LiNbO_3 are described in §1.2, as they have a great influence in LiNbO_3 behaviour and applications. The next section is dedicated to the main physical phenomena that appear in this material. Finally, the last part of this chapter introduces the different kinds of LiNbO_3 waveguides and their properties.

1.1 Composition and crystalline structure

Lithium niobate does not exist in nature. It was first synthesized by Zachariasen in 1928, although it was not until 1949 that Matthias obtained it in its crystalline form [125]. Even if at that time its ferroelectric properties were discovered, the first single crystal was made by Ballman sixteen years later, in 1965, using the Czochralski process [33]. Since then, LiNbO_3 has become the subject of many researches thanks to its excellent electro-optic, acousto-optic, pyroelectric and piezoelectric properties and non-linear optic effects [100, 176, 177]. Nowadays, it is one of

the most widely used electro-optic materials. Some applications of LiNbO_3 include waveguides, optical modulators and holographic memories. It is a key material in current telecommunications (optic fibre networks, mobile phone technology...) but also for developing industries like optoelectronics and integrated optics.

At room temperature, pure lithium niobate is a transparent, shiny solid. It is quite hard (6 in Mohs scale, just a level below quartz) and resistant to chemical attacks, which makes it very stable and easy to manipulate. Its density is 4.64 g/cm^3 and its melting point is around 1253°C , although for every particular crystal both of them depend on its precise lithium to niobium ratio ($[\text{Li}]/[\text{Nb}]$), which is not always the stoichiometric one (1:1).

1.1.1 Composition

Lithium niobate is typically grown from a Li_2O and Nb_2O_5 melt using the Czochralski process. This process consists in introducing a single crystal seed attached to a rod in the melt and pull upwards while rotating. If temperature and pulling and rotating velocities are finely controlled, a monocrystalline, cylindrical ingot can be obtained [107]. The ratio of Li_2O and Nb_2O_5 in the melt determines the final stoichiometry of the ingot. This affects to many LiNbO_3 properties, not only density and melting point, as stated above, but also Curie temperature, lattice parameter, refractive index [40] and absorption edge [78, 111], among others.

The first Li_2O - Nb_2O_5 phase diagram was obtained by Lerner in 1968 [117] and later refined by Svaasand in 1974 [162] (Fig. 1.1). There are two especially interesting compositions in this diagram:

- **Congruent:** the exact Li_2O percentage of this composition depends on the crystal growth direction: 48.47 mol% for crystals grown along Z direction and 48.90 mol% along X one¹[36], but in both cases the crystals have a lithium deficiency compared to the stoichiometric composition. However, as it is the congruent point of the phase diagram, the melt and the solidified material have the same $[\text{Li}]/[\text{Nb}]$; the composition of the melt

¹ The nomenclature of LiNbO_3 directions is explained in §1.1.2.

is preserved during the growth process, and thus that of the ingot. This makes possible to obtain large and homogenous single crystal ingots of several kilograms in weight and up to 4 inches in diameter. Nowadays, most of the crystals used in technological applications have this congruent composition.

- **Stoichiometric:** obtained with 50 mol% of Li_2O in the melt. In these crystals $[\text{Li}]/[\text{Nb}]$ equals 1. However, the difference in composition between molten and solidified material poses problems during growth, and there are usually differences in composition in the final ingot. There are ways to ease the growth of crystals with this composition, such as add K_2O to the melt [158].

Figure 1.1 Li_2O - Nb_2O_5 phase diagram. The ochre line marks the congruent composition.

Adapted from [162].

1.1.2 Crystal Structure

LiNbO_3 exists in two different crystal structures depending on its temperature (Fig. 1.2). On the one hand, the crystal is in its paraelectric phase at temperatures above its Curie point

(1050-1200 °C, depending on the exact composition [47]). In this phase, it has a perovskite-like structure and belongs to the space group $R\bar{3}c$ (point group $\bar{3}m$) [47]; the crystal is made of oxygen octahedra that share their adjacent faces. Inside one in three octahedra there is a Nb^{5+} cation, whereas Li^+ ions are placed at the plane defined by the oxygen triangle that share two empty octahedra (see Fig. 1.2a).

Figure 1.2 $LiNbO_3$ crystalline structures as a function of temperature. Adapted from [176].

On the other hand, for temperatures lower than its Curie point, the crystal is in its ferroelectric phase, which space group is $R3c$ (point group $3m$). The unit cell shrinks, and the niobium and lithium ions are moved from their centred positions. Because the displacement for both ions is in the same direction, a dipolar moment is induced in the material, generating a spontaneous polarization along the straight line defined by the niobium and lithium cations. This line is the crystal polar axis, also called optic, ferroelectric or just c-axis. The polar axis points in the same direction as the ion displacement (Fig. 1.2b). The spontaneous polarization is what provides $LiNbO_3$ with its electrooptic properties, among others [47].

Controlling the direction of the optical axis is extremely important when crystals are being fabricated. Monodomain crystals (also called single crystals) are the ones typically used in technological applications (see Fig. 1.3a). A crystal domain is defined as a region inside the crystal in which the ferroelectric polarization of all its cells points in the same direction. If appropriate actions are not taken during the growth process, what is obtained is a polydomain solid, i.e., the polar axis has different directions in different areas of the material (Fig. 1.3b). To avoid this inconvenience, an electric field may be applied during crystal fabrication, which forces the whole lattice to orientate itself towards a sole direction, usually the growth one.

It should be also mentioned that the direction of the ferroelectric polarization in a crystal can be flipped 180° during fabrication (by an alternating electric field or a temperature gradient) or after it (by means of huge electric fields). This leads to two more kinds of crystals (Fig. 1.3c,d): PPLN (periodic poled lithium niobate) and ODLN (opposite domain lithium niobate), with different applications, including second-harmonic generation and particle trapping [80].

Figure 1.3 Different kinds of LiNbO_3 crystals classified by their domain structure. Arrows point towards c-axis direction.

The direction of the optical axis can be used to set a variety of systems of coordinates for the crystal lattice [176]. Usually, a cartesian coordinate system is used to define the tensor properties of the material:

- Z (or x_3) axis is chosen to be parallel to the polar axis
- X (or x_1) axis is perpendicular to Z and points towards one of the vertices of one oxygen triangle
- Y (or x_2) axis is chosen in such a way that the system is right-handed

LiNbO_3 is typically used in the shape of wafers or plates and this system of coordinates gives rise to a standard nomenclature for them. A LiNbO_3 sample is called x-, y- or z-cut depending on which axis (X, Y or Z, respectively) is perpendicular to its surface. A second letter can be added when needed for completely define the three axes. This letter indicates the direction of the longest dimension of a sample [176] (e.g., zy-cut, see Fig. 1.4).

Figure 1.4 Example of LiNbO_3 sample nomenclature.

As a consequence of LiNbO_3 spontaneous polarization, a surface charge density appear in the crystal faces perpendicular to Z axis. This surface charge density is about 0.80 C/m^2 [88], but under normal circumstances it is screened by mobile charges adsorbed from the ambient [105].

1.2 Defects in lithium niobate

From the structural point of view, lithium niobate is a complex material which properties depend very much on stoichiometry, temperature, residual stresses and growth parameters, among others. It is relatively difficult to obtain a pure, homogeneous crystal, and even if every possible precaution is taken, there will always be defects.

1.2.1 Intrinsic defects

They derive from the non-stoichiometry of the material and/or changes in the material structure during its growth. They are not completely well understood and there are many theories in this regard.

Concerning congruent composition, the one of the crystals used in this work, it has a lack of lithium in relation to the stoichiometric one. The most established model advocates for an excess of Nb^{5+} due to niobium ions placed at Li^+ positions [44]. It is called antisite defect, Nb_{Li} . In order to maintain the crystal charge neutrality, each niobium out of place compensates the lack of four lithium cations. Other models, with less support from the scientific community, suggest that this charge compensation is made either by the removal of niobium or oxygen atoms [21, 123, 163]. Finally, there are also theories that combine hypothesis of the above [73].

1.2.2 Extrinsic defects

Extrinsic defects derive from the addition of external elements atoms to a pure crystal. These atoms or “impurities” can arrive to the crystal lattice from many ways: during the growth process, by surface diffusion and by implantation, among others. These impurities are not always detrimental to the crystal properties, on the contrary, many times they are added on purpose in order to modify or enhance them (doping). Examples of some common metal impurities are listed below. These metals and other impurities, as rare-earth elements, use to be placed at lithium positions in the lattice:

- **Iron:** it increases the photovoltaic and photorefractive sensitivity of LiNbO_3 .
- **Copper:** similar to iron; although the increase in sensitivity is smaller, it helps to maintain the photovoltaic and photorefractive fields longer in time.
- **Manganese:** similar to iron and copper, although with a less intense effect.
- **Magnesium:** it reduces the photorefractive sensitivity of LiNbO_3 .
- **Zinc:** it reduces the photorefractive sensitivity and increases the refractive index of LiNbO_3 .

- **Titanium:** it increases the refractive index, so it is commonly used for waveguide fabrication.

1.3 Lithium niobate properties

1.3.1 Photovoltaic effect

The photovoltaic effect was discovered by Glass *et al.* in 1974 [86]. This effect occurs in non-centrosymmetric ferroelectrics due to the anisotropy of their crystalline lattice. This anisotropy forces a directional excitation of photo-excited electrons along a preferential axis. In the case of uniaxial crystals, this direction matches the one of the optical axis. The charge separation generates an internal electric field in the crystal. This effect is explained in detail in Chapter 2, as it is the most important property of lithium niobate in relation to PVT operation.

1.3.2 Electro-optic and photorefractive effect

Lithium niobate is a birefringent material: it has two refractive indices (ordinary and extraordinary). Which one applies depends on the light direction of propagation and polarization (perpendicular or parallel to the c-axis, respectively). The extraordinary refractive index corresponds to the linearly polarized light that oscillates in a direction parallel to the polar axis; the ordinary refractive index corresponds to the linearly polarized light that oscillates in any direction contained in a plane perpendicular to the c-axis.

The value of LiNbO_3 refractive indices not only depends on the wavelength but also on its stoichiometry, impurities and temperature. This dependence is so strong that a single Sellmeier equation is not enough to accurately describe all the possible cases [177].

When a LiNbO_3 crystal is in presence of an electric field (E), its refractive indices (n) change proportionally to the electric field. This effect is known as Pockels effect and does not depend very much on the particular composition of the crystal [62]. It can be described as a third order tensor but because of the crystal symmetry, only four components of the tensor are independent.

The values of these coefficients (r_{ijk}) are very high [100], which makes lithium niobate one of the widest used materials for electro-optic applications.

For high electric fields ($\sim 10^{10}$ V/m), the second order term of the electro-optic interaction (S_{ijkl}), related to the Kerr effect, should be also taken into account. Therefore, the change of the refractive index due to the presence of an electric field can be expressed as:

$$\Delta\left(\frac{1}{n^2}\right)_{ij} = \sum_k r_{ijk} E_k + \sum_{kl} S_{ijkl} E_k E_l, \quad (1.1)$$

where the second term of the right-hand side is usually negligible compared to the first one, as in most situations this term is much lower than the linear one [120].

An especial phenomenon called “photorefractive effect” occurs when the electric field responsible of the change in the refractive index is generated by illumination due to the photovoltaic effect. This non-linear optical phenomenon was discovered by Ashkin *et al.* in 1966 [30]: when a LiNbO_3 crystal is illuminated by a high-intensity laser beam, it spreads along the c-axis direction (also known as optical damage, Fig. 1.5). The electric field and the associated change in the refractive index remain in the crystal for some time after illumination; they can be tailored through the appropriate light distribution and erased by homogeneous illumination.

Figure 1.5 Schematic of LiNbO_3 photorefractive effect. The laser beam spreads along the c-axis direction. Adapted from [23].

This semi-permanent change in the refractive index is important because it allows reconfigurable applications such as holographic information storage and multiplexing [22, 130], high sensitivity reconfigurable filters [134], second harmonic generation by self-phase matching [140], optical amplification [99, 114] and interferometric applications [144].

1.3.3 Pyroelectric effect

LiNbO_3 spontaneous polarization (P_S) decreases with temperature. As a consequence, a sudden change in the crystal temperature (ΔT) generates a surface charge density (σ_p) associated to non-compensated charges on its surfaces. This is called pyroelectric effect [154] and can be calculated as [34]:

$$\begin{aligned}\sigma_p &= p_3 \Delta T \\ p_3 &\equiv \frac{\partial P_S}{\partial T}\end{aligned}\tag{1.2}$$

The sign of the surface charge is explained in Fig. 1.6. There is no an agreement in literature about the value of the coefficient p_3 , and it ranges between $-(40-95.4) \mu\text{C}/(\text{m}^2\text{K})$ at room temperature [145, 153]. It changes with composition (p_3 is lower as lithium content decreases [89]) and temperature [34], although it may be considered as a constant for a small range of temperatures [83].

Figure 1.6 LiNbO_3 surface charge density generated by the pyroelectric effect when the crystal is heated.

1.3.4 Piezoelectric effect

Lithium niobate is also a piezoelectric material, i.e., when it is deformed an electric field appears in the material and vice versa. The induced polarization or deformation can be calculated as:

$$\begin{aligned} P_i &= d_{ijk} S_{jk} \\ \epsilon_{jk} &= d_{ijk} E_i \end{aligned} \quad (1.3)$$

where $\mathbf{P}$ is the induced polarization, $\mathbf{S}$ the applied stress, $\boldsymbol{\epsilon}$ the induced deformation, $\mathbf{E}$ the applied electric field and $\mathbf{d}$ the piezoelectric constant tensor. These constants vary with the composition in a similar way as the pyroelectric ones do [89]. Some devices rely upon this property, such as piezoelectric mirrors and components [136] or surface acoustic waves (SAW) devices [116].

1.4 Lithium niobate waveguides

Lithium niobate is a material widely used for optical components, such as integrated lasers, holographic systems or frequency multipliers [169]. Among those components, one of the most typical is optical waveguides.

An optical waveguide is a structure capable of confining light in a thickness of just a few micrometres due to total internal reflection phenomenon. For total internal reflection to happen, the material in which light is propagating through must have a larger refractive index than its surroundings. Light propagation inside the waveguide can be described by the ray model of light or using the formal electromagnetic theory [151]. There are different waveguide classifications depending on the confinement dimensions (Fig. 1.7) [50]:

- **1D:** planar waveguides. They can be symmetric, asymmetric or graded-index.
- **2D:** channel waveguides and optic fibres.
- **3D:** photonic crystals.

Figure 1.7 Different confinement dimensions. Retrieved from [50].

As stated above, the part of the waveguide through which light travels is surrounded by one or more materials with lower refractive index. In the case of LiNbO_3 , this is usually achieved by modifying the crystal surface in order to increase one or both refractive indices. This way, the waveguide is located between non-modified LiNbO_3 and the surrounding air. Some of the surface modification processes are:

- **Lithium outdiffusion:** above 900°C , lithium diffuses from the crystal as Li_2O , what slightly increases its refractive index. This effect can be an undesired in other high-temperature fabrication methods of LiNbO_3 waveguides and must be taken into account in these cases. The process can be limited placing the crystal in an oxygen or wet argon atmosphere [54].
- **Metal diffusion:** typically titanium and zinc [38, 49, 156]. In the case of Ti-diffused waveguides, they are made depositing a very thin layer of titanium on top of the LiNbO_3 crystal and heating up to $1000\text{-}1100^\circ\text{C}$ for several hours. One drawback of these waveguides is that they cannot stand high light intensities compared to other kinds of LiNbO_3 waveguides, because of optical damage.
- **Proton exchange:** in this method the material is introduced in a bath of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) at 300°C during several hours or even days. During the process, lithium ions (Li^+) leave the crystal and are substituted by hydrogen ions (H^+) that come from the acid. A superficial layer of $\text{H}_x\text{Li}_{1-x}\text{NbO}_3$ is formed. Up to seven different phases have been identified depending on the molar fraction of hydrogen [109]. These phases have a larger

extraordinary refractive index than LiNbO_3 , but a lower ordinary one. They have very good optical quality and low losses.

- **Ion implantation:** in the superficial layers, the accelerated ions just interact with the lattice electrons and the lattice remains almost intact. It is when those ions are deeper in the material that they collide with the lattice atoms. This makes the material totally or partially amorphous and its diffraction index decreases. The classic way employs light ions and energies up to 2 MeV. However, works have been done with heavy ions at high energies (30-50 MeV) [102].

The waveguides used in this work were made by Ti-diffusion and proton exchange. In particular, the technique used to make the second ones is called soft proton exchange, as the process is softened through the addition of lithium benzoate ($\text{C}_6\text{H}_5\text{COOLi}$) to the benzoic acid. Of the seven phases commented above, the one obtained with this method is the alpha phase, which means the percentage of hydrogen is very low and the material preserves its electro-optic properties [110].

Chapter 2: Bulk photovoltaic effect

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CHAPTER 2

Bulk photovoltaic effect

As stated in the previous chapter, lithium niobate has many properties that involve the generation of internal electric fields. Among them all, the most important one for PVT is, clearly, the bulk photovoltaic effect. Although lithium niobate shares this effect with other non-centrosymmetric materials, such as KNbO_3 or LiTaO_3 , for this crystal it is particularly strong, especially when it is doped with impurities like iron or copper [172]. That is the reason why it is virtually the only material used to carry out PVT experiments.

The bulk photovoltaic effect (BPVE) can be defined as the generation of a very large voltage inside a non-centrosymmetric crystal due to an internal light-induced charge redistribution [39]. BPVE depends on many factors. For iron-doped lithium niobate ($\text{LiNbO}_3\text{:Fe}$) crystals like the ones that have been used for the present work, the most important ones are those related with illumination (light distribution, intensity and exposure time) and those corresponding to the material (doping level and oxidation-reduction state of the crystal).

Although it does not play a key role for the purposes of this work, it is important to bear in mind that LiNbO_3 is also an electro-optic material. Its refractive index changes when it is subjected to an electric field, such as the internal one generated by the photovoltaic effect. This phenomenon is called photorefractive effect and was explained in the previous chapter (§1.3.2). In fact, lithium niobate is better known for its photorefractive effect rather than the photovoltaic one, although the former is somehow a consequence of the last.

This chapter addresses the currently accepted model for bulk photovoltaic effect in $\text{LiNbO}_3\text{:Fe}$ and states and analyses the system of partial differential equations that mathematically represents the process. This model describes well the experimental results for low or moderate light intensities.

2.1 Theoretical description: one centre model

Photovoltaic crystals can have one or more “photovoltaic centres”. In lithium niobate, these centres are usually impurity atoms (iron, copper) or a defect in the crystal lattice (Nb_{Li}). Under illumination, the photovoltaic centres act as sources and sinks of charge, giving rise to a net charge transport and redistribution inside the crystal. For the sake of clarity, the effect will be explained considering only one centre: iron impurities.

The first accepted theoretical model describing the photorefractive effect was presented by Kukhtarev *et al.* in 1979 [113]. Qualitatively, the phenomenon can be described according to the diagram shown in Fig. 2.1a.

In $\text{LiNbO}_3\text{:Fe}$, iron impurities can be present in its two valence states that act as donors (Fe^{2+}) or acceptors (Fe^{3+}) of charge carriers (electrons, e^-). When an area of the crystal is illuminated with light of a suitable wavelength, an electron from a donor (Fe^{2+}) can gain enough energy to jump from the valence to the conduction band. Due to the non-centrosymmetry of the crystal, the electron is excited in a preferential direction (Fig. 2.1b). After moving through the conduction band for some time, it is finally trapped in an acceptor (Fe^{3+}), which becomes a donor. If this new donor is also in an illuminated area, the process recurs. If it is not, then the electron stays trapped in that iron impurity. If the light distribution is steady, after some time a charge redistribution between illuminated and dark areas of the crystal is obtained: in some regions there is an excess of electrons compared to the initial conditions and in others there is a lack of them (Fig. 2.1c). The directional carrier displacement due to the photoexcitation phenomenon is called photovoltaic current, and its direction is essentially determined by the c-axis [23, 75].

Figure 2.1 Qualitative description of the photovoltaic effect. (a) Depiction of the band model. (b) Asymmetry of the potential well. (c) Charge redistribution due to inhomogeneous illumination.

BPVE effect takes place even at low light intensities ($\sim \text{mW}/\text{cm}^2$), although the wavelength required to activate each photovoltaic centre depends on the centre itself. In the case of $\text{LiNbO}_3:\text{Fe}$, the optimum wavelength is around 490 nm, whereas in pure lithium niobate near-UV is needed. This can be correlated with their respective absorption spectra (Fig. 2.2).

Figure 2.2 Absorption spectra of pure and Fe-doped LiNbO_3 .

After illumination, the charge distribution, also known as space charge field, can last months or even years if the crystal is kept under appropriate conditions (e.g., at room temperature and in the dark) [35]. The space charge generates an electric field inside the material that in the case of $\text{LiNbO}_3\text{:Fe}$ can reach values as high as $10^5\text{-}10^7$ V/m [23]. This field spreads outside the crystal (fringe electric field), and even if it decreases rapidly with distance, it is still high enough to make PVT operation possible.

Figure 2.3 Bulk photovoltaic electric field in a x-cut LiNbO_3 sample as a function of illumination time.

It is important to note that the one centre model presented in this chapter is only valid for a certain range of light intensities ($10\text{-}10^5$ W/m² [171]); for lower intensities dark conductivity overcomes photoconductivity (see below) and for higher ones a more complex model, which introduces a second centre, is required to explain the experimental findings [171]. Nevertheless, within that range of intensities, the BPVE is a saturable phenomenon under steady illumination. The electric field inside the material increases until it reaches a certain value called “saturation field” (Fig. 2.3). The value of this field and the exposure time required to reach it depends on many parameters of the crystal and the illumination. However, it has been found experimentally that, within the aforementioned range, exposure time and light intensity play interchangeable roles, and their product can be considered as a single variable, called light exposure.

2.2 Mathematical model

The system of equations published in [113] that describes the photovoltaic charge transport and temporal evolution is known as Kukhtarev or rate equations. It is a system of three partial differential equations. Here they are presented in their most general form [23, 75, 113, 157]:

$$\frac{\partial n}{\partial t} = (sI + \beta)N_D - \gamma n N_A - \frac{1}{q} \nabla \cdot \mathbf{J} \quad (2.1)$$

$$\frac{\partial N_D}{\partial t} = -\frac{\partial N_A}{\partial t} = -(sI + \beta)N_D + \gamma n N_A \quad (2.2)$$

$$\mathbf{J} = (\sigma_{PH} + \sigma_D)\mathbf{E} - qD\nabla n + \boldsymbol{\kappa} \quad (2.3)$$

The meaning of each symbol is listed in Table 2.I, at the end of this chapter (p. 28).

In the equations above, both photoinduced and dark conductivities (σ_{PH} and σ_D) are second order tensors. However, in $\text{LiNbO}_3\text{:Fe}$, these tensor properties can be neglected [157]. Furthermore, even if the photovoltaic current density term ($\boldsymbol{\kappa}$) is a vector quantity, its strong directionality makes it possible to assume that this current density is essentially parallel to the c-axis [75]. Although it is true that photovoltaic currents normal to the optical axis have been measured, they are at least one order of magnitude lower than the parallel one. Also, their value depends on the polarisation of the incoming light² [75]. Finally, the thermal ionization of donors (β) can be disregarded, as its value is negligible for the characteristic light intensities, temperature ranges and time lapses considered for PVT operation. The same happens with the dark conductivity, thus conductivity is solely determined by photoexcited electrons. Taking into account these simplifications, the equations above can be expressed as:

$$\frac{\partial n}{\partial t} = sIN_D - \gamma n N_A - \frac{1}{q} \nabla \cdot \mathbf{J} \quad (2.4)$$

$$\frac{\partial N_D}{\partial t} = -\frac{\partial N_A}{\partial t} = -sIN_D + \gamma n N_A \quad (2.5)$$

$$\mathbf{J} = q\mu n \mathbf{E} - qD\nabla n + q s I L_{PV} N_D \hat{\mathbf{u}}_{PV} \quad (2.6)$$

² In fact, for extremely high intensities (>50 GW/m²) polarization-dependence has been also measured for photovoltaic currents parallel to the c-axis [160].

In Eq. 2.6, the electric field ($\mathbf{E}$) represents the sum of all the electric fields present in the crystal or applied to it. As it was commented in the *Preface*, one of the advantages of PVT over similar techniques is that PVT does not require external sources of voltage. In addition, one can consider that the crystal is excited just by the illumination, so any other phenomena as pyroelectric or piezoelectric effects do not interfere with the space charge generation process³. Thus, the electric field can be easily obtained from Gauss's law:

$$\nabla \cdot (\epsilon_0 \epsilon \mathbf{E}) = \rho = q(N_D - N_{D0} + n) \quad (2.7)$$

New symbols from Eqs. 2.4-2.7 are also included in Table 2.I.

Eq. 2.4 establishes the local time evolution of the free charge carriers, the electrons (n). The first term of the right-hand side stands for the carrier generation due to the light-induced ionization of the donor ions, whereas the second one represents its recombination with acceptors. The third term represents the electron current through the crystal.

Eq. 2.5 is similar to the previous one but concerning the donors/acceptors instead of the electrons. In this case, there is no current term, as the impurities are supposed to be fixed to the crystal lattice.

Finally, Eq. 2.6 is a vector equation. It is equivalent to the conventional drift-diffusion equation [164] plus the photovoltaic term. It shows that the current density in the crystal has three contributions: the drift current, in our case just due to the internal electric field generated by the space charge distribution; the diffusion of electrons, from the areas where there is high concentration to those with less; and the photovoltaic current, generated by the photoexcited electrons.

Solving the system comprised by Eqs. 2.4-2.6 means obtaining the spatial charge distribution in the $\text{LiNbO}_3\text{:Fe}$ crystal and its associated electric field, both inside and outside the material. There are analytic solutions for simple combinations of crystal orientation and illumination

³ Interactions between photovoltaic and other effects during PVT operation is currently under study [147]. First results confirm that such interactions are negligible in the experiments carried out for this work.

distribution [23] but, unfortunately, for an arbitrary light illumination pattern there is no analytic solution, and numerical methods have to be used [28].

Nevertheless, although a general analytical resolution of the system is not possible, some useful information can be deduced from Eqs. 2.4-2.7 without really solving them, and even more can be obtained if a simplified version of the system is solved before performing a complete and rigorous resolution (see §5.3).

First, it is easy to see from Eq. 2.5 that $N_{D0} + N_{A0}$ remains a constant (N): an increase in acceptor concentration means an equal decrease in donor one and vice versa. This way, the crystal remains neutral during the whole illumination process. From this equation one can also estimate the order of magnitude of free charge carriers generated by the light when the crystal is at equilibrium (derivatives equal zero):

$$n_0 = \frac{sIN_{D0}}{\gamma N_{A0}} \quad (2.8)$$

Free charge carriers are somehow proportional to the local light intensity and inversely proportional to the oxidation-reduction ratio, defined as [46]:

$$r_{or} = \frac{N_{A0}}{N_{D0}} = \frac{[Fe^{3+}]}{[Fe^{2+}]} \quad (2.9)$$

So, the higher the intensity and the proportion of donors over acceptors, the more charge carriers are generated. As there are more electrons available, this can be intuitively related to a faster process and a shorter saturation time. This assumption is true and can be confirmed more thoroughly experimentally [23] and also theoretically (see below and §5.3).

If equations 2.4 and 2.5 are properly manipulated one can obtain a continuity equation for the system (Equation 2.10). The local variation of donors plus electrons is proportional to the current density divergence:

$$\frac{\partial(N_D + n)}{\partial t} = -\frac{1}{q} \nabla \cdot \mathbf{J} \quad (2.10)$$

Sometimes this quantity can be more useful than the current density itself to determine whether the photovoltaic effect has saturated or not. For example, in x-cut samples illuminated with a sinusoidal light profile there is a homogeneous current along the c-axis even at saturation. In this case, it is the current density divergence that becomes zero at saturation and not the current density itself [29].

The value of the photoconductivity ($\sigma_{PH} = q\mu n$) can be estimated from Eq. 2.6. It is proportional to the charge carrier concentration, which supports the assumption made above connecting the concentration of electrons and the speed of the photovoltaic effect.

Finally, the parameters that control the photovoltaic current are the light intensity (modulated by the photoionization cross-section), the photovoltaic transport length⁴ and the absolute concentration of donors. Note that it is not the oxidation-reduction ratio, as it was for the electron concentration. It is important to highlight this fact as it will be shown that the component of the photovoltaic electric field parallel to the c-axis is almost proportional to the absolute concentration of acceptors at saturation (see §5.3).

Table 2.I Description of the symbols used in equations 2.1-2.7. Typical values are shown when applicable.

Symbol	Description	Units	Typical value
$(n_0) n$	Charge carrier concentration	m^{-3}	$5.36 \cdot 10^{12} \text{ m}^{-3}$
$(N_{D0}) N_D$	(Initial) Donor concentration	m^{-3}	$5.60 \cdot 10^{24} \text{ m}^{-3}$
$(N_{A0}) N_A$	(Initial) Acceptor concentration	m^{-3}	$4.17 \cdot 10^{25} \text{ m}^{-3}$
$I = \frac{Whc}{\lambda}$	Photon flux density	$\text{s}^{-1} \cdot \text{m}^{-2}$	$5.68 \cdot 10^{20} \text{ s}^{-1} \text{ m}^{-2}$
W	Incoming light intensity	$\text{W} \cdot \text{m}^{-2}$	$100 \text{ W} \cdot \text{m}^{-2}$
h	Planck constant	$\text{J} \cdot \text{s}$	$6.26 \cdot 10^{-34} \text{ J} \cdot \text{s}$ [129]

⁴ This distance represents the mean free path of the electrons along the c-axis once they are photoexcited. For $\text{LiNbO}_3\text{:Fe}$ its value is about 5 Å [23, 160].

Symbol	Description	Units	Typical value
c	Speed of light	$\text{m}\cdot\text{s}^{-1}$	$3\cdot 10^5 \text{ km}\cdot\text{s}^{-1}$ [129]
λ	Light wavelength	M	532 nm
$\sigma_{PH} (= q\mu n)$	Photoconductivity	$\text{S}\cdot\text{m}^{-1}$	$4.29\cdot 10^{-13} \text{ S}\cdot\text{m}^{-1}$
σ_D	Dark conductivity	$\text{S}\cdot\text{m}^{-1}$	$\sim 10^{-16} \text{ S}\cdot\text{m}^{-1}$ [35, 179]
J	Current density	$\text{A}\cdot\text{m}^{-2}$	-
E	Total applied electric field	$\text{V}\cdot\text{m}^{-1}$	-
κ	Photovoltaic current density	$\text{A}\cdot\text{m}^{-2}$	$2.40 \mu\text{A}\cdot\text{m}^{-2}$
$\hat{u}_{PV}$	Unit vector along the polar axis	1	-
s	Photoionization cross-section	m^2	$2\cdot 10^{-22} \text{ m}^2$ [160]
β	Thermal generation rate	s^{-1}	$\sim 10^{-6} \text{ s}^{-1}$ [139]
γ	Recombination constant	$\text{m}^3\cdot\text{s}^{-1}$	$10^{-15} \text{ m}^3\cdot\text{s}^{-1}$ [52]
μ	Mobility	$\text{m}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$	$-5\cdot 10^{-7} \text{ m}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ [52]
$D (= \mu k_B T / q)$	Diffusion coefficient	$\text{m}^2\cdot\text{s}^{-1}$	$1.26\cdot 10^{-8} \text{ m}^2\cdot\text{s}^{-1}$
k_B	Boltzmann constant	$\text{J}\cdot\text{K}^{-1}$	$1.38\cdot 10^{-23} \text{ J}\cdot\text{K}^{-1}$ [77]
T	Absolute temperature	K	293.15 K
L_{PV}	Photovoltaic transport length	m	$5\cdot 10^{-10} \text{ m}$ [160]
ρ	Space charge density	m^{-3}	-
q	Electron charge	C	$-1.60\cdot 10^{-19} \text{ C}$ [72]
ε_0	Vacuum permittivity	$\text{F}\cdot\text{m}^{-1}$	$8.85\cdot 10^{-12} \text{ F}\cdot\text{m}^{-1}$ [129]
ε	Relative permittivity tensor	1	$\varepsilon_{11} = \varepsilon_{22} = 84.6$ [176] $\varepsilon_{33} = 29.1$ [176]

Chapter 3: Other electrodynamic and optical effects of interest

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CHAPTER 3

Other electrodynamic and optical effects of interest

3.1 Dielectrophoretic and electrophoretic forces

All particles experience forces and torques when subjected to electric fields [101]. However, there are many factors that modulate the strength of these forces, like particle composition, size, electric charge or even its surrounding medium. When operating with PVT, the most important electromechanical forces that affect particles are two: dielectrophoresis (DEP) and electrophoresis (EP).

The term “dielectrophoresis” was coined by Pohl in 1951 for describing the forces exerted on uncharged dielectric particles due to their polarizability [101]. In a broad sense of the term, these forces are produced by an external, nonuniform electric field or by other particles also affected by an external field. Regarding electrophoresis, it can be understood as the well-known Coulomb force [108].

3.1.1 Effective dipole moment

Suppose an isolated, spherical, isotropic particle in a dielectric medium subjected to an electric field. In this situation, a dipole moment is induced in the particle along the local direction of the electric field. The effective dipole moment ($\mathbf{p}_{eff}$) induced in the particle is [101]:

$$\mathbf{p}_{eff} = 4\pi r^3 \epsilon_m f_{CM} \mathbf{E}_{ext} , \quad (3.1)$$

where r the particle radius, ϵ_m is the medium permittivity, f_{CM} is the Clausius-Mossotti factor and $\mathbf{E}_{ext}$ the local external electric field in the absence of the particle [108]. The Clausius-Mossotti factor is defined as:

$$f_{CM} = \frac{\tilde{\epsilon}_p - \tilde{\epsilon}_m}{\epsilon_p + 2\tilde{\epsilon}_m} , \quad (3.2)$$

that it is equivalent to the first order polarization coefficient⁵ [108]. For the strict definition of the Clausius-Mossotti factor, the complex permittivity ($\tilde{\epsilon}$) of the particle ($\tilde{\epsilon}_p$) and the medium ($\tilde{\epsilon}_m$) are used. Complex permittivity is defined as:

$$\tilde{\epsilon} = \epsilon + \frac{\varsigma}{i\omega} , \quad (3.3)$$

where ς is the conductivity, i the imaginary unit and ω the frequency of the applied field. This definition better applies when the external field is time dependent, but in the case of PVT all electric fields are stationary. For stationary electric fields, Clausius-Mossotti factor can be expressed only as a function of the particle and medium conductivities [108, 133]:

$$f_{CM} = \frac{\varsigma_p - \varsigma_m}{\varsigma_p + 2\varsigma_m} \quad (3.4)$$

However, when the conductivities of the particle and the medium are both negligible one should use the most common form of the Clausius-Mossotti factor:

$$f_{CM} = \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m} \quad (3.5)$$

⁵ In this work, only first order (dipolar) polarization terms have been taken into account for the calculation of particles polarization and DEP forces. Higher order terms (quadrupolar, octupolar...) are disregarded. It can be done because the scale of the electric field nonuniformity is large compared to the particle size and particle-particle interactions are not considered in numerical calculations [101].

3.1.2 Dielectrophoretic force

Given a dipole, the instantaneous DEP force exerted on it by an applied external field is [101]:

$$\mathbf{F}_{DEP} = \mathbf{p} \cdot \nabla \mathbf{E}_{ext} \quad (3.6)$$

From Eq. 3.6 it is deduced that no net force is applied if the electric field is spatially uniform. Combining Eqs. 3.1 and 3.6 one gets a closed expression for the dielectrophoretic force on a spherical particle:

$$\mathbf{F}_{DEP} = 2\pi r^3 \epsilon_m f_{CM} \nabla (\mathbf{E}_{ext} \cdot \mathbf{E}_{ext}) \quad (3.7)$$

This equation establishes that DEP force is proportional to the particle volume (r^3), the permittivity of its surrounding medium and the gradient of the electric field norm squared. Dielectrophoretic force is conservative, so a dielectrophoretic potential energy can be defined (U_{DEP}):

$$U_{DEP} = -2\pi r^3 \epsilon_m f_{CM} |\mathbf{E}_{ext}|^2 \quad (3.8)$$

Note that the Clausius-Mossotti factor is bounded between -0.5 ($\zeta_m \gg \zeta_p$) and 1 ($\zeta_m \ll \zeta_p$). Therefore, this factor can be positive or negative, so two kinds of dielectrophoresis are defined [108]:

- **Negative dielectrophoresis** ($\zeta_m > \zeta_p \rightarrow f_{CM} < 1$): the particle is repelled from electric field intensity maxima and attracted to minima.
- **Positive dielectrophoresis** ($\zeta_m < \zeta_p \rightarrow f_{CM} > 1$): the particle is attracted to electric field intensity maxima and repelled from minima.

3.1.3 Dielectrophoretic torque

If the particle exhibits some type of anisotropy, either intrinsic (e.g., crystalline) or extrinsic (e.g., shape), it may happen that none of its principal polarization axes is aligned with the applied electric field (Fig. 3.1). Under these circumstances, an orientational torque acts on the particle to align one of their principal axes with the external field:

$$\mathbf{T} = \mathbf{p}'_{eff} \times \mathbf{E}_{ext} , \quad (3.9)$$

where $\mathbf{p}'_{eff}$ is an expression similar to Equation 3.1 but that takes into account the particle anisotropy [101]. Consider, for example, the needle-shaped, ellipsoidal particle depicted in Fig. 3.1: the orientational torque will try to align one of its principal axes (a, b or c) with the external field. The particle is in equilibrium when any of these three axes is parallel to the electric field. Nevertheless, the equilibrium is only stable if it is the longest axis (b) the one aligned with $\mathbf{E}_{ext}$. In general, when the main source of anisotropy is the shape, particles try to align with its longest axis parallel to the external electric field.

Figure 3.1 Dielectrophoretic torque exerted on a needle-shaped particle in the presence of an external electric field. Adapted from [101].

3.1.4 Dielectrophoretic particle chains

In our experiments we deal with suspensions with particle concentrations in the order of $2 \cdot 10^8$ particles per microlitre. Such a high concentration implies that particles can approach very close to each other, especially when they are in the vicinity of the crystal surface.

When a pair of particles is polarized by means of an external electric field, they can strongly interact if they are close enough. This interaction depends on the relative position of the pair of particles respect to the external field and their Clausius-Mossotti factors. If the two particles are similar, or at least their corresponding Clausius-Mossotti factors have the same sign (positive or

negative), they attract to each other when they are aligned parallel to the external field and repel when perpendicular to it (see Fig. 3.2). If their Clausius-Mossotti factors are of opposed sign, then the forces are exerted the other way around.

Figure 3.2 Particle-particle interaction forces depending on their Clausius-Mossotti factors and the relative position of the particles with respect to the external field direction. Adapted from[101].

This behaviour has two complementary explanations. The first one is simple and links this attraction-repulsion action of the particles with the attraction-repulsion forces exerted on one induced dipole by the other (see again Fig. 3.2). The other one is more complex and takes into account the local disturbance of the electric field caused by the particle. When f_{CM} is positive, the local field is increased close to the particle's "poles" and reduced close to its "equator". When f_{CM} is negative, the opposite happens [101]. These changes in the electric field and in the behaviour of the particles is consistent with the negative/positive dielectrophoresis described in §3.1.2.

In the case of the experiments presented in this work, the Clausius-Mossotti factor is always positive, and particles tend to aggregate in the shape of chains or "pearl chains", as they are called in the literature [42, 112, 150]. Due to the shape anisotropy of the chains, they experiment orientational torques and orientate along the external field direction, even if the original particles were isotropic. The larger the number of particles, the larger the DEP force on the chain and on every individual particle that comprises it [101].

3.1.5 Electrophoretic force

Unlike dielectrophoresis, the electrophoretic force is exerted only on charged particles. It is directly proportional to the external electric field and the particle charge (Q_p) [108]:

$$\mathbf{F}_{EP} = Q_p \mathbf{E}_{ext} \quad (3.10)$$

In this work, the medium where particles are suspended is always a nonpolar liquid (see §4.1.2). This way, no double-layer effects are expected [108] and one can assume that positively charged particles are attracted to negatively charged areas of the crystal and vice versa.

Electrophoretic force is conservative, like DEP one, so another potential energy, U_{EP} , can be defined:

$$U_{EP} = - \int_l Q_p \mathbf{E}_{ext} d\mathbf{l} , \quad (3.11)$$

where $\mathbf{l}$ is an arbitrary curve that connects a point where the electrophoretic potential energy is known to the point where this value is required.

3.1.6 Dielectrophoretic vs. electrophoretic force

Charged particles are also polarised in the presence of an external electric field and, as a consequence, dielectrophoretic forces can affect them. Following a procedure similar to that developed by Mokřý *et al.* [131], it can be demonstrated that the minimum surface charge density (σ_{crit}) that a particle must have for EP force to overcome DEP in a configuration similar to the one depicted in Fig. 3.3 is:

$$\sigma_{crit} = \frac{2\sigma_s r(\zeta_p - \zeta_m)}{\Lambda(\zeta_p + 2\zeta_m)} , \quad (3.12)$$

where σ_s is the surface charge density of the surface and Λ the period of the structure.

Figure 3.3 Surface charge distribution generated in a PPLN crystal due to pyroelectric effect. Adapted from [131].

3.2 Electrohydrodynamic jet printing

Assume a configuration like the one depicted in Fig. 3.4a where there is a droplet of a dielectric liquid between two plates. If there is an electric field applied in the space between plates, a force is exerted on the droplet. According to the Kelvin-Helmholtz formulation, the Maxwell stress tensor ($\mathbf{T}$) of a dielectric, incompressible fluid with homogeneous permittivity (ϵ_f) and without any free charges inside it subjected to an external electric field ($\mathbf{E}$) is [108]:

$$T_{ij} = \epsilon_f \left(E_i E_j - \frac{1}{2} \delta_{ij} E_k E_k \right), \quad (3.13)$$

where (δ) is the identity tensor. The body force ($\mathbf{f}_{be}$) can be obtained by taking the divergence of this stress tensor [61]:

$$\mathbf{f}_{be} = \nabla \cdot \mathbf{T} \quad (3.14)$$

This force can be understood as a pressure gradient applied on the liquid surface. If the electric field is the appropriate one, the force will deform the droplet and push it upwards. The droplet will be able to establish a stable bridge between the two surfaces (Fig. 3.4b) only if the distance between them is equal or less than a critical one (D_c) [122]:

$$D_c = \left(1 + \frac{\theta}{4} \right) V_d^{\frac{1}{3}}, \quad (3.15)$$

where θ is the contact angle of the liquid-plate interface and V_d the droplet volume. If the distance between plates is larger than D_c , an instability is generated in the liquid and the drop breaks up, dispensing droplets on the upper surface (Fig. 3.4c). This is the working principle of the electrohydrodynamic (EHD) jet printing.

The mechanism and droplet deformation resembles the Taylor cone formation in conductive liquids subjected to electric fields [167], used in other kinds of EHD jet printing systems [143].

Figure 3.4 Schematic of the setup for EHD. (a) Droplet between two plates subjected to an external electric field. (b) A stable liquid bridge is established between the plates for $D < D_c$, whereas (c) droplet dispensing is achieved for $D > D_c$.

3.3 Triboelectric effect

It is well known that some materials become electrically charged when they come into contact with a different material [181]. This phenomenon is known as triboelectric effect. Its commonly accepted explanation suggests that when two different materials come into contact, a chemical bond is formed between parts of their surfaces. This bond favours the interchange of electrons, protons or even ions [142] in order to equalise their electrochemical potentials. When the materials are separated, certain surfaces tend to keep positive charge and others negative one, giving rise to the triboelectric series (Table 3.I) [174].

Table 3.I Triboelectric series. Materials on top of the table tend gain positive charge and those at the bottom tend to gain negative charge. Adapted from [37, 142].

The table lists materials in a vertical stack, categorized by their tendency to gain positive or negative charge. A red arrow on the left points upwards, labeled 'Positive charge', indicating that materials higher in the list tend to become positively charged. A blue arrow on the left points downwards, labeled 'Negative charge', indicating that materials lower in the list tend to become negatively charged. The materials are color-coded: red for positive, white for neutral, and cyan for negative.

Positive charge ↑	Hair, oily skin
	Nylon, dry skin
	Glass
	Leather
	Quartz
	Aluminium
	Paper (<i>Small positive charge</i>)
	Wool (<i>No charge</i>)
	Steel (<i>No charge</i>)
Negative charge ↓	Wood (<i>Small negative charge</i>)
	Amber
	Rubber
	Resins
	Brass, Silver
	Acetate, Rayon
	Styrene and polystyrene

The triboelectric series is a qualitative table that classifies materials according to their tendency to gain positive or negative charge when they came into contact with others. Triboelectric phenomenon is not completely understood [37, 181] and the triboelectric series just

describes a general trend; the same pair of materials in different situations can become charged in an opposed way than what Table 3.I predicts [37].

What it is clear is that the triboelectric effect is ruled by the materials surfaces. There are some reports of triboelectric charge measurements in which there is sign inversion during the experiment due to material transfer between samples [37]. Electrical conductivity of the material is also important for the final charge distribution. On a conductor the charge spreads homogeneously whereas in an insulator does not [142].

3.4 Light diffraction

A diffractive optical element (DOE) is a device that uses a microstructure pattern to alter the phase of the light propagated through it. If this phase pattern is properly designed, it can shape a light beam into almost any desired intensity profile [14]. Some examples of these elements are multifocal lenses for lasers, homogenizers or beam samplers. They have applications in a multitude of scientific and technological fields: medicine (eye- and microsurgery), laser material processing (laser perforation, micromachining, ablation...), spectroscopy, astronomy, optical communications, cytometry, 3D detection... These elements are based in the diffraction phenomenon, a consequence of the undulatory behaviour of light.

Figure 3.5 Example of DOEs capabilities. With a well-designed DOE a Gaussian beam profile can be shaped into a top hat or a circular intensity profile. Adapted from [14].

3.4.1 Phenomenology of diffraction

Consider first geometrical optics, that is, light propagating through the space as rays. Assume that there are a point light source and a screen where light is projected. If a diaphragm with a small circular aperture is placed between the source and the screen, according to geometrical optics what is projected on the screen is just an illuminated circular spot. However, what is actually observed is a series of alternating dark and light annular regions spreading over the screen (Fig. 3.6). A similar pattern is obtained if an obstacle is placed instead of a diaphragm [55].

Figure 3.6 Straight-ray (left) vs. wave (right) light propagation.

All the events that conflict with the straight ray propagation when light passes through apertures or obstacles are collectively known as “diffraction phenomena” and their origin lies in the undulatory behaviour of light, as it is said above.

Diffraction can be explained using the Huygens-Fresnel principle [55]. This principle considers each point of a wavefront as a point source that reemits the wave and contributes to its propagation. Although each point emits a spherical wave, the interference of all of them creates the appropriate wavefront. However, when the wavefront meets an obstacle, some of the emitters are blocked and cannot emit anymore, and thus the wavefront changes (Fig. 3.7). Its final shape depends on the obstacle [55].

Figure 3.7 Huygens-Fresnel principle. (a) Free wave. (b) Wave through an aperture.

Mathematically, diffraction can be analysed using two different approximations:

- **Fraunhofer diffraction:** or “far field diffraction”. It is used to analyse the diffraction pattern produced by a diffracting object that is at a long distance from the region of study.
- **Fresnel diffraction:** explains the diffraction pattern created in the near field region, i.e., close to the object.

All the diffraction patterns studied in this work (and their corresponding mathematical equations) belong to Fraunhofer diffraction. A useful relation that indicates if a diffraction phenomenon is far field diffraction is:

$$\frac{W^2}{L\lambda} \ll 1 , \quad (3.16)$$

where W is the width of the aperture or obstacle, λ the wavelength and L the distance from the diffraction pattern to the diffracting object.

3.4.2 Theory of diffraction gratings: the grating equation

A diffraction grating is a collection of transmitting (or reflecting) elements separated by a distance comparable to the wavelength of the light that is being studied or manipulated [55]. Depending on the design of the diffraction grating, it can modify the amplitude, phase or both of an incident electromagnetic wave in a predictable way. In this work, only amplitude modulation

is considered. A grating is said to be a transmission or reflection grating according to whether it is transparent or mirrored [10]. They are present in many technologies and scientific disciplines. Perhaps the most common application of diffraction gratings is as a fundamental part of monochromators and spectrometers.

For the sake of simplicity, consider first a transmission grating made of a series of N slits, all of them equal in shape, equidistant and parallel. Their width is $2a$ and the period is Λ . If they are illuminated with a collimated light beam of wavelength λ , perpendicular to the plane in which they are contained, the Fraunhofer approximation gives the following expression for the angular intensity distribution (I_θ) of the far field diffraction field [55]:

$$I_\theta = K \cdot \frac{\sin^2\left(\frac{Nk\alpha\Lambda}{2}\right)}{\sin^2\left(\frac{k\alpha\Lambda}{2}\right)} \cdot \frac{\sin^2(ka\alpha)}{(ka\alpha)^2}, \quad (3.17)$$

where K is a constant, k is the wavenumber ($2\pi/\lambda$) and α the sinus of the angle between the incident beam and the considered point measured from the diffraction grating (Fig. 3.8):

$$\alpha = \sin \theta \quad (3.18)$$

Figure 3.8 Geometrical parameters involved in the operation of a diffraction grating.

Equation 3.8 has three well-differentiated terms:

- The first one is a constant (K) that principally depends on the intensity of the incident light and the absorbance and reflectivity of the grating material.
- The second one, $T_2, \left(\frac{\sin^2\left(\frac{Nk\alpha\Lambda}{2}\right)}{\sin^2\left(\frac{k\alpha\Lambda}{2}\right)} \right)$ is an interference term that depends on the grating period and the number of slits. There are some values of α that make zero both the numerator and denominator of T_2 :

$$\alpha = \sin \theta = 0, \frac{2\pi}{k\Lambda}, \frac{4\pi}{k\Lambda}, \dots, m \frac{2\pi}{k\Lambda} \quad m \in \mathbb{Z} \quad (3.19)$$

These are the principal maxima and can be calculated with the incoming wavelength and the grating period alone. The order of the maxima is denoted by m , a positive or negative integer. The shorter the period, the greater these angles, so principal maxima are more distant.

- The third one, $T_3, \left(\frac{\sin^2(ka\alpha)}{(ka\alpha)^2} \right)$ is related with diffraction at each slit. It represents the envelope of the principal maxima and modulates the intensity distribution obtained from the second term. The narrower the slits, the wider the first maximum of T_3 . This means that a greater number of principal maxima are included in it, and thus their intensity is not much lower than the zero order one (usually the highest, Fig. 3.9).

Finally, the ratio between the intensity of an arbitrary order (I_m) and that of the zero order (I_0) can be obtained using T_3 and Eq. 3.19 (Fig. 3.10):

$$\frac{I_m}{I_0} = \frac{\sin^2\left(m\pi \frac{2a}{\Lambda}\right)}{\left(m\pi \frac{2a}{\Lambda}\right)^2} \quad (3.20)$$

It only depends on $2a/\Lambda$. In this work, I_m/I_0 is called “efficiency” of a particular order of the grating⁶.

⁶ Usually, what is called “grating efficiency” is the ratio between the incident light power and the one diffracted in a particular order.

Figure 3.9 Diffraction grating intensities distribution (normalised) $\lambda = 0.633 \mu\text{m}$, $\Lambda = 20 \mu\text{m}$, $a = 5 \mu\text{m}$.

Figure 3.10 Efficiency for different principal maxima as a function of slit width ($2a$) and period (Λ) ratio.

3.4.3 Theory of Fresnel zone plates

Among two-dimensional diffraction patterns, Fresnel zone plate is perhaps the most representative due to its applicability and simplicity [71, 173]. It is used to focus light or other phenomena that exhibit an undulatory behaviour, but instead of taking advantage of refraction, as conventional lenses do, its working principle is based on diffraction.

Typical Fresnel zone plates are made mainly by lithography processes: photolithography, ion- or electron-beam lithography. They are mostly used to bend and focus extreme ultraviolet light and x-ray, as almost every material absorbs those extremely energetic radiations. Other applications include frequency filters and focusing devices for other waves, as sound [48].

A Fresnel zone plate consists in a series of concentric opaque/transparent rings called Fresnel zones. Light diffracts around the opaque zones and interferes constructively if the rings are properly spaced. The adequate radius of each opaque-transparent zone boundary (r_n , see Fig. 3.11) is defined by the following equation [12]:

$$r_n = \sqrt{n\lambda f + \frac{n^2\lambda^2}{4}}, \quad (3.21)$$

where n is an integer, λ the wavelength of the incoming light and f the focal length or distance from the centre of the Fresnel zone plate to the focus. This equation can be approximated to a simpler one if the focal length is large compared to the zone plate itself (as it happens in the case of the devices made for this work):

$$r_n \approx \sqrt{n\lambda f}, \quad (3.22)$$

The equations above are easy to interpret; for a given focal length, the shorter the wavelength, the smaller the Fresnel zone plate should be. Likewise, if the radii are fixed, the larger the wavelength the shorter will be the focal length. This property of having different focuses for different wavelengths is used in some devices to filter in wavelength.

Figure 3.11 Fresnel zone plate.

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Chapter 4: Experimental techniques

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CHAPTER 4

Experimental techniques

This chapter covers the equipment and experimental techniques performed during the development of this work. Special emphasis is made in the first section, where the different components required for PVT operation are presented (crystals, illumination setups, particles...).

An application of PVT which presented in this thesis work involved the fabrication of compact integrated optical spectrometers. They were based on LiNbO_3 waveguides onto which linear particle gratings obtained by PVT were transferred (for more details regarding the transference process see §9.2). The second section of this chapter is dedicated to waveguides and the working principles of this compact spectrometers.

4.1 Photovoltaic tweezers

The main physics involved in a PVT experiment can be summarised as follows:

- 1.- An appropriate photovoltaic crystal (e.g., $\text{LiNbO}_3\text{:Fe}$) is illuminated with a particular light distribution.
- 2.- Due to the bulk photovoltaic effect, inside the crystal a space charge field is generated.
- 3.- This space charge field is the source of an electric field that extends outside the crystal as a fringe electric field.

- 4.- When particles approach to the crystal surface, they are subjected to the fringe field and move accordingly, usually placing on top of the sample following a pattern related to the illumination distribution.

In this section, all the steps and components involved in the process of making and recording a nanoparticle (NP) pattern by PVT are explained in detail.

4.1.1 Crystal samples

Both iron-doped and pure lithium niobate crystals are commercially available in wafers of 2-3 inches in diameter and various thicknesses (typically 0.5-1 mm). The orientation and nomenclature of these wafers is the same as explained in §1.1.2, although rotated orientations can be also found [5].

For this work, wafers were cut in many rectangular (or almost rectangular) samples in sizes ranging from $6.5 \times 10 \text{ mm}^2$ to $18 \times 35 \text{ mm}^2$ (see Fig. 4.1). The experiments were carried out using 0.1 wt%Fe x- and z-cut samples (1 and 0.5 mm thick).

Figure 4.1 Example of two samples of $\text{LiNbO}_3\text{:Fe}$ used in this work.

All samples had one of their faces marked. For x-cut samples, the mark indicated the direction of the c-axis (usually the short edge) whereas for z-cut ones it indicates which was the $\pm c$ face (wafer dependent). Distinguishing between the positive and negative end of the c-axis of the samples was crucial in experiments with charged nanoparticles (§8.3). In order to do so, a setup similar to the one depicted in Fig. 4.2 was used. The procedure is as follows:

- 1.-The sample is connected to a voltmeter and heated.
- 2.-This generates a pyroelectric response.
- 3.-Depending on the sign of the voltage the direction of the c-axis is determined.

Figure 4.2 Experimental setup for $\pm c$ -axis end identification.

4.1.2 Particles and suspensions

A wide range of particles can be manipulated by PVT. In this work, dielectric and metallic particles were used (Fig. 4.3):

- **Aluminium nanoparticles (Al NPs):** metallic, spherical particles. 60-80 nm in diameter. They are the most used particles in this work.
- **Calcium carbonate microparticles (CaCO_3):** dielectric, flake-like particles. 1-6 μm in diameter.
- **Silver nanoparticles (Ag NPs):** metallic, spherical particles. 25 nm in diameter.

Particles were suspended in hexane⁷ (C_6H_{14}). Hexane was chosen because it is a nonpolar liquid, so it does not screen the photovoltaic electric field generated by the lithium niobate crystals. In addition, hexane has a high evaporation rate at room temperature, so after a few seconds only the particles remain on the substrate.

⁷ A reduced number of experiments were performed using heptane (C_7H_{16}), which has properties similar to hexane but with higher density and boiling temperature. Water was also tested as solvent, but not a single experiment was successful. Probably, what prevents particle trapping in water is the electric field screening caused by the spontaneous ionization of water molecules, many orders of magnitude larger than the photovoltaic charge [82]. On the other hand, aluminium NPs were oxidized when suspended in water (sedimented particles turned from metallic grey to alumina white).

Particle concentration of the suspensions depended on each particular experiment. As an example, the standard concentration for Al NPs is around 40 mg/L. All particles came from powder, so suspensions were sonicated prior to use during several dozens of minutes to try to break particle clusters as much as possible and to obtain a fine particle dispersion. Nevertheless, it is almost impossible to completely break nanoparticle aggregates by mechanical means. Most of the nanoparticle suspensions consisted of particles clusters (100 nm - 1 μ m in diameter) along with some single nanoparticles.

Nanoparticle manipulation implies some risks for human health and a potential ecotoxicological impact. One must be careful during the suspension manufacturing, avoiding any contact with the nanoparticles, and ensure a proper disposal [121]. Also, although hexane toxicity is low, it is advisable to manipulate this product in a fume hood.

Figure 4.3 Different kinds of particles used in this work. (a) CaCO_3 microparticles. (b) Aluminum nanoparticles. (c) Silver nanoparticles.

4.1.3 Illumination setups

Sample illumination is the most critical step of the whole PVT process, as the final particle distribution is largely determined by the illumination conditions. The main light source used during this work was a frequency-doubled Nd:YAG laser (Verdi V-2/V-5) emitting at 532 nm (green). Other light sources include a He-Ne laser (Uniphase 1300) at 633 nm (red) and a tuneable argon laser (Omnichrome 543-AP).

Three different illumination setups were used: direct illumination through a mask, two-beam interference, spatial light modulator (SLM).

a) Direct illumination through a mask

This is the simplest of all the illumination methods. It is depicted in Figs. 4.4a,b. The mask was made of aluminium and had two slits of around 2 mm wide, although in practice only one of the slits was used in the experiments. It was painted in black to avoid undesired reflections (see Figs. 4.4c,d). Double sided tape was used to keep the $\text{LiNbO}_3\text{:Fe}$ samples in place.

The Nd:YAG and argon lasers were used interchangeably as light sources in this setup. The incoming light intensity was $10\text{-}100\text{ W/m}^2$ and illumination time was between 5 and 10 minutes.

Figure 4.4. Setup for direct illumination through a mask. (a) Lateral view. (b) Overhead view. Mask was painted in black to avoid light reflections. Compare the differences in light reflexion of the painted and unpainted mask between (c) natural lighting and (d) artificial lighting.

b) Two-beam interference (holographic setup)

This illumination system was used to obtain a sinusoidal light intensity pattern. The setup is shown in Fig. 4.5. Pattern period (Λ) can be calculated from the following equation:

$$2\Lambda \sin\left(\frac{\theta}{2}\right) = \lambda, \quad (4.1)$$

being λ the light wavelength and θ the angle between the beams.

An important parameter of this kind of illumination is the pattern modulation, defined as:

$$m = \frac{2\sqrt{I_1 I_2}}{(I_1 + I_2)} \quad (4.2)$$

I_1 and I_2 are the intensities of the two beams that interfere. When m equals 1 the contrast is perfect, which means that light intensity equals zero in the regions of destructive interference. Although this value of the modulation is usually the desired one, it is impossible to achieve due to reflections on the crystal surfaces and other phenomena like misalignments of the angle of incidence or the fact that beams intensities are not exactly the same. In the best cases m is about 0.95. The final intensity distribution along a direction perpendicular to the fringes (x) is:

$$I(x) = I_m \left[1 + m \sin \left(\frac{2\pi}{\Lambda} x \right) \right], \quad (4.3)$$

where I_m is the mean intensity.

In this case the light source was always the Nd:YAG laser. Typical values for I_m and exposition time were 1250 W/m^2 and 10 minutes, but they are experiment-dependent values.

Figure 4.5 Holographic illumination setup. P: polarizer, BE: beam expander, L: lens, BS: beam splitter, M: mirror. F: Neutral filter. Adapted from [46].

c) Spatial Light Modulator

A SLM is an optical element able to spatially modify the phase and amplitude of a coherent light wavefront. In this work, one (HoloEye LC-R 1080 SLM) was used to easily project arbitrary 2D laser light patterns. It operated in reflexion mode and had a pixel size of $8.1 \mu\text{m}$, although

higher resolutions are theoretically achievable through optical means. It could only work with a wavelength at a time, so light patterns were monochrome (256 levels). The light source was always the Nd:YAG laser.

Figure 4.6 Working principle of the spatial light modulator.

This SLM model is based on liquid crystals, and it works selectively changing the phase of the wavefront. This phase change induces a change in its polarization. Using a pair of crossed polarizers the difference in polarization is translated in a difference in local intensity, and the desired image can be projected. Fig. 4.6 shows this principle of operation. The first polarizer homogenizes the wavefront and polarizes it linearly in one direction (the vertical one in this case). When the laser beam hits the SLM, each pixel of the device modifies or not the polarization of its corresponding part of the wavefront depending on its corresponding intensity level. On the one hand, if a particular pixel is “white”, then the SLM rotates light polarization $\pi/2$ radians. On the other hand, if it is “black”, the polarization is kept unaltered. If the desired intensity corresponds to another intensity level, then the polarization is rotated an angle between 0 and $\pi/2$ radians.

The complete experimental setup is shown in Fig. 4.7. The SLM diffracts the laser beam, so a lens is required to collect as much diffraction orders as possible. In addition, the lens also allowed for obtaining higher spatial resolution than the SLM pixel size through optical demagnification. The iris diaphragm suppressed the diffraction orders coming from the SLM that were unfocused or partially blocked by the lens.

Figure 4.7 SLM illumination setup. P: polarizer, BE: beam expander, SLM: spatial light modulator, L: lens, D: Diaphragm.

The incoming light intensity on the samples was much less than in the holographic setup, in the range of 15-200 W/m², to avoid damaging the SLM. A typical illumination time was about 10 minutes, although longer times were used in some occasions (up to 30 minutes).

4.1.4 Particle deposition

The method used to approach the particles to the crystal has been demonstrated to be a key issue for PVT. Technique results depend on the deposition method, especially pattern cleanliness and definition [46, 135]. The four main methods for particle deposition in PVT are depicted schematically in Fig. 4.8.

- (a) **Particle cloud:** particles are blown into the air to create a cloud in which the crystal is introduced.
- (b) **Blown particles:** particles are deposited homogeneously on the crystal surface. Then, they are blown in order to remove all the non-attached particles.
- (c) **Particle suspension:** the sample is introduced in a suspension that contains the particles.
- (d) **Suspension droplet:** a drop from a suspension that contains the particles is poured on the crystal surface. Depending on the solvent, the droplet may evaporate in seconds or days.

Figure 4.8 Particle deposition methods. (a) Particle cloud. (b) Blown particles. (c) Particle suspension. (d) Suspension droplet. Adapted from [53].

In most cases (Figs. 4.8a, c, d) the deposition method can be simultaneous (while the sample is being illuminated) or sequential (the sample is first illuminated and then the particles are deposited).

In this work, all experiments were performed using the “particle suspension” method (Fig. 4.8c) and sequential operation. Air methods (Figs. 4.8a,b) tend to result in patterns with lower resolution than those obtained with the others [135] and the suspension droplet (Fig. 4.8d) has the disadvantage of not evaporating homogeneously in certain cases. It has been observed that in some occasions the droplet evaporates slower where the sample has been illuminated, probably due to some interaction with the local electric field.

As stated in §4.1.2, the typical solvent used for particle suspensions is hexane, a nonpolar hydrocarbon with a very low dielectric constant ($\epsilon_{hex} = 1.9$ [132]). It also has the advantage of evaporating very quickly. Sequential method is preferred over simultaneous one, with typical immersion times around 15-30 seconds for a suspension with a particle concentration of 40 mg/L. As also explained above, the main issue of this system is that particles tend to aggregate in the suspension. In order to reduce this effect, suspensions are typically sonicated during 10 minutes before the deposition.

4.1.5 Sample recycling

One big advantage of PVT is the possibility of reusing the crystal substrates once the particle patterns are not useful anymore or they have been transferred to other substrate, or even in relation to reconfiguration-based applications [85]. In principle, the pattern “recording-erasing” cycle can be done as many times as desired (about one hundred experiments have been carried out with some of the samples used in this work). This cycle consists in two steps: sample cleaning and photovoltaic field erasure.

a) Sample cleaning

Adhesion forces probably play an important role in pattern stability. Trapped particles can withstand forces perpendicular to the sample very well (e.g., particles are kept in place if the sample is turned upside down). Furthermore, samples can be immersed in water or hexane without fear of destroying the pattern. However, shearing forces (e.g., scratching) can easily remove the particles from the substrate.

The first step in the cleaning process is sonicating the sample inside an acetone or ethanol glass. Sonication removes most of the particles from the crystal surface. Afterwards, the sample is cleaned using a cloth soaked in acetone and another one in ethanol. If the sample is not sonicated first, particle clusters can scratch the crystal surface.

b) Erasure of the electric field

The space charge field recorded by illumination can last months or even years in $\text{LiNbO}_3\text{:Fe}$. In order to remove it and restore a homogenous proportion of donors and acceptors in the crystal, samples are heated up to 230 °C for 10 minutes and then slowly cooled down. While hot, crystal donors are thermally excited and charge redistribution is reached by diffusion, which depends exponentially on the temperature.

When a sample is erased, there are two risks to be avoided:

- **Cracking:** when lithium niobate is heated up or cooled down very quickly, a combination of the pyroelectric and piezoelectric effects can result in mechanical stresses high enough to break the crystal. Z-cut samples are very sensitive to this hazard.
- **Thermal fixing:** between 150-180 °C, H⁺ impurities (protons) move more easily through the crystal lattice than electrons [87]. As they are charged ions, they are affected by the photovoltaic electric field and move towards positions where they compensate it. If this happens, when the crystal is heated at higher temperatures, electrons do not move because the internal electric charge distribution is already stable. Higher temperatures and longer times are required to erase a thermal-fixed sample.

Electric field erasure process is also required for the characterisation of diffractive elements and recommended before performing a pattern transference (§9.1 and §9.2).

4.1.6 Ambient conditions

Ambient relative humidity and temperature are key parameters that must be controlled during a particle trapping experiment. It has been found that levels of relative humidity above 40% can lead to unsuccessful experiments, even if all others experimental parameters are optimal. The explanation is found in the easiness of water molecules to screen the lithium niobate surface charge and therefore the photovoltaic fields.

Regarding temperature, it should be homogeneous during the whole process (illumination and trapping). Otherwise, pyroelectric effects may appear and alter the crystal charge distribution, and so the pattern [147].

4.1.7 Pattern observation and photographic record

Pattern observation and record was made through two devices:

- **Optical microscope** (Nikon Eclipse 80i): capable of working in transmitted and reflected light. It had a set of five objectives (5×, 10×, 20×, 50×, 100×) and an eyepiece (10×). It

also had different filters and polarizers to enhance pattern visualization under certain circumstances (fluorescence, low particle concentration...).

- **Digital camera** (DMK 41BU02): monochrome (black and white). It was used for taking pictures of entire samples or areas larger than those allowed by the microscope.

4.2 Waveguides and compact interferometers

An optical spectrometer is a device used to measure properties of a light source as a function of the wavelength. Typically, and in this work, this property is the intensity, although it can be other, like the polarization state. The spectrometers presented here are compact in the sense that they are small, lack of moving parts and are based on integrated optics. This kind of spectrometers are especially suitable in environments where size and weight are required to be as low as possible, avoiding the more complex setups required by bulk optics.

As said in the introduction of this chapter, linear particle gratings fabricated by PVT have been used to build compact interferometers by transferring these particle structures onto different waveguides. After that, they were characterised first at our laboratory and some of them also at the Institut de Planétologie et d'Astrophysique de Grenoble (IPAG).

4.2.1 Waveguides

In this work, two different kinds of waveguides based on lithium niobate substrates were used:

- **Planar waveguide:** obtained by soft proton exchange in our laboratory. For its fabrication, a z-cut LiNbO_3 sample was immersed for 24 h at 300 °C in a fused melt of benzoic acid buffered with lithium benzoate (3%wt). After the process, the crystalline phase of the sample's surface became α -phase, which retains the electro-optic properties of LiNbO_3 [110].
- **Channel waveguides:** they were Ti-diffused waveguides fabricated from x-cut substrates at FEMTO-ST laboratory (Besançon, France). The fabrication process started with the deposition of a silicon mask on x-cut LiNbO_3 samples. This mask determined the

geometry of the Y-channels (spaced $250\text{ }\mu\text{m}$, see Fig. 4.9). On top the silicon, a thin layer of titanium was deposited and thermally diffused by heating the samples at $1045\text{ }^{\circ}\text{C}$ for 40 h. The resulting waveguides were single mode at $3.39\text{ }\mu\text{m}$.

Figure 4.9 Y-waveguide schematic (not drawn to scale).

4.2.2 Light coupling

Depending on the purpose and characteristics of each waveguide, different setups were used for light injection:

a) Rutile prism

The setup is depicted in Fig. 4.10. A rutile (TiO_2) prism⁸ is used to couple the incoming laser beam into the waveguide. Light propagates through the waveguide and decouples when it reaches the area covered with particles. A camera placed on top the setup is used to record light scattering. For achieving good optical contact between the rutile prism and the waveguide, pressure must be applied with a holder.

b) End-face coupling

Light is injected directly through the sample edge using an optical fibre. This method was used for characterising the two kinds of compact spectrometers fabricated for this work.

⁸ In order to avoid total internal reflexion in the prism-waveguide interface, the material of the prism must have an index of refraction (n) higher than the waveguide. At 633 nm , $n_{\text{TiO}_2} \approx 2.8$.

Figure 4.10 Light coupling in a planar waveguide using a rutile prism.

4.2.3 Spectro-interferometry

The work developed in the IPAG consisted in the study of the viability of particle gratings assembled by PVT to be used in compact spectrometers as scattering centres. According to Blind *et al.* [43], integrated spectrometers can be classified into four families:

- **Grating and phased arrays:** currently, they are the most common and sensitive type of spectrometer. In these devices, the light source is typically injected in a waveguide and then extracted by a DOE. This way, each wavelength of the source interferes constructively on a different position of a detector, allowing to directly observe the spectrum of the signal. Grating spectrometers are the most efficient in terms of signal-to-noise ratio.
- **Fabry-Pérot cavities or interference filters:** in this case, the source wavefront is progressively delayed over reflective surfaces. This allows the elimination of unwanted spectral bands or multiply the signal spectrum by a comb before being recombined and analysed.
- **Fourier transform:** in this family of spectrometers the light source is usually separated in two parts before being recombined in a waveguide with a variable delay, thus creating interference fringes. These fringes are sampled and a digital Fourier Transform of them is performed in order to reconstruct the spectrum.

- **Direct detection:** some detectors are able to measure directly the energy of incident photons. However, nowadays they cannot offer a spectral resolution comparable to that of the other three families.

In this work, spectrometers of the first (grating arrays) and third (Fourier transform) family were fabricated and tested. They were based on the Ti-diffused channel waveguides described in §4.2.1 on top of which gratings of aluminium nanoparticles were transferred.

a) Side Holographic Disperser (SHD)

There are different kinds of SHD spectrometers. On the one hand, in [32], Avrutsky *et al.* show a compact system in which a planar waveguide with a DOE on top of it is coupled directly to a detector without intermediate optics (Fig. 4.11a). With an appropriate detector calibration, the signal spectrum in wavelength can be recovered (Fig. 4.11b). A similar device is also proposed by Dumas *et al.* in [63]. On the other hand, the approach followed in this thesis is more similar to the work developed by Chaganti *et al.* [56], in which relay optics are used to achieve higher resolution.

Figure 4.11 SHD spectrometer propped by Avrutsky *et al.* (a) Experimental setup. (b) Detection of two different wavelengths at two different positions on the detector. Retrieved from [32].

The particular model of SHD spectrometer analysed in this thesis was reported in [124]. In that work, the diffraction grating used as DOE was directly engraved by focused ion beam (FIB) in the LiNbO₃ waveguide. In our case, the DOE is the aforementioned aluminium NP fringes. The experimental setup of the SHD spectrometer is depicted in Fig. 4.12a. A laser beam is injected in

the channel waveguide with the help of a set of micro-actuators, a mirror and a lens. One camera (FLIR SC7000) placed on the opposite side of the sample allows to check whether or not light was coupled to the waveguide. A tuneable laser source centred at 1060 nm (Sacher TEC-1060nm Littman/Metcalf Laser Head) was used. Light extracted from the surface of the waveguide is focused by a cylindrical lens on a CCD camera (Goodrich) placed perpendicular to the sample plane. A second optical stage that consists in two hemi-cylindrical lenses is generally placed between the camera and the cylindrical lens to reduce optical aberrations, disperse laterally diffraction modes and avoid overlapping [124].

The interaction between the light travelling in the waveguide and the grating can be described by the fundamental grating-waveguide structure equation for grazing incidence [124]:

$$\Lambda(n_{eff} - \sin \theta) = m\lambda , \quad (4.4)$$

where n_{eff} is the effective refractive index of the guided mode⁹, θ the decoupling angle (see Fig. 4.12a), m the order of diffraction, λ the wavelength and Λ the grating period. As the camera is placed normal to the sample plane ($\theta \approx 0$), the collected order is high ($m \approx 20$), which implies that the intensity that reaches the detector is low. The dependence of the extraction angle with the wavelength and the effective refractive index makes diffracted light focus on different positions of the detector depending on its wavelength and polarisation state, as the refractive index depends on the polarization (see Figs. 4.12b,c).

According to [124], the longer the diffraction grating, the higher the spectral resolution of the device (i.e., its ability to distinguish between two wavelengths separated by a small amount). In fact, for gratings long enough, the spectral resolution is only related to the focal length of the cylindrical lens, the refractive index of the waveguide and the pixel size of the detector.

⁹ Waveguide modes are the different formats in which an electromagnetic wave can propagate within the waveguide.

Figure 4.12 (a) Setup for characterising the SHD spectrometer fabricated for this work. M: mirror, L: lens, CL: Cylindrical lens. (b) Stack of measurements at different wavelengths. Observe how the light intensity peak (in black) is placed at different positions for different wavelengths. (c) For a fixed wavelength, different polarizations result in different positions on the detector (in white). Retrieved from [124].

b) Stationary Wave Integrated Fourier Transform Spectrometer (SWIFTS)

In these devices, a stationary wave is generated inside a waveguide. Then, the resulting interferogram is sampled through scattering centres placed along the waveguide surface. Performing a discrete Fourier transform of this interferogram the original light spectrum is recovered [115]. Depending on how the stationary wave is generated, two configurations exist:

- **Lippmann:** a mirror is placed at the end of the waveguide so when light travelling in the waveguide is reflected on the mirror, a stationary wave is generated.
- **Gabor (or counterpropagative):** light source is divided upstream the waveguide and injected from its two ends.

Besides, the resulting interferogram is obviously different depending on whether or not the light source is monochromatic:

- **Monochromatic source:** the interferogram is a sinusoidal wave.
- **Polychromatic source:** a Fourier interferogram (Gabor configuration) or a Lippmann one (Lippmann configuration) is obtained. A Lippmann interferogram can be somehow understood as half Fourier one.

All four cases are depicted in Fig. 4.13.

Figure 4.13 Lippmann (left) and Gabor (right) configurations for SWIFTS operation. The resulting interferogram is different whether the source wavelength is monochromatic or polychromatic. Adapted from [115].

The resulting interferograms can be calculated analytically using the well-known formulas for wave interference. For the simplest case, i.e., monochromatic source and disregarding optical absorption, the following equations give the intensity profile along the waveguide according to Fig. 4.14a [168]:

$$I_L^m = I_0 \left\{ 1 + R - 2\sqrt{R} \cos \left[\frac{4\pi}{\lambda} n_{eff} (z - L) \right] \right\} \quad (4.5)$$

$$I_F^m = 2I_0 \left\{ 1 - \cos \left[\frac{4\pi}{\lambda} n_{eff} \left(z - \frac{L}{2} \right) \right] \right\} \quad (4.6)$$

I_L^m and I_F^m are Lippmann and Fourier intensity distributions of a monochromatic source respectively, L the total length of the waveguide and R the reflection coefficient in the interface waveguide/air given by:

$$R = \left(\frac{n_{eff} - 1}{n_{eff} + 1} \right)^2 \quad (4.7)$$

Reflection can be increased by attaching a mirror at the end of the waveguide. Observing the period of the stationary wave, and according to the Nyquist-Shannon sampling theorem [115], for obtaining a faithful reconstruction of the interferogram using discrete scattering centres, the distance between centres must not be larger than $\lambda/4n_{eff}$. Furthermore, in order to perform a correct sampling of the signal and not a convolution, the size of the scattering centre has to be much smaller than this distance, typically $\lambda/40n_{eff}$. This is one of the main reasons that motivated the use of nanoparticle structures for making this kind of device.

For a polychromatic source, the intensity profile is obtained through the summation of the corresponding intensities for each wavelength. Note that n_{eff} is wavelength dependent and can be computed with the Sellmeier equations [104]:

$$I_L^p = \sum_{\lambda} I_0(\lambda) \left\{ 1 + R(\lambda) - 2\sqrt{R(\lambda)} \cos \left[\frac{4\pi}{\lambda} n_{eff}(\lambda)(z - L) \right] \right\} \quad (4.8)$$

$$I_F^p = \sum_{\lambda} 2I_0(\lambda) \left\{ 1 - \cos \left[\frac{4\pi}{\lambda} n_{eff}(\lambda) \left(z - \frac{L}{2} \right) \right] \right\} \quad (4.9)$$

In the case that the grating is “displaced” from the middle of the waveguide (for Gabor configuration) or the edge (for Lippmann one), the grating and the interferogram of a polychromatic source would not match (Fig. 4.14b). This is especially critical for Lippmann configuration. In order to make grating and interferogram match again, the optical path length (OPL) of the input beam (one of them for Gabor configuration) must be modified. The OPL is given by:

$$OPL = l \cdot n_{eff}(\lambda) , \quad (4.10)$$

where l is the distance travelled by a wave of wavelength λ in a medium with refractive index n_{eff} . As the OPL depends on the wavelength, a perfect match cannot be done at the same time for all the wavelengths of a polychromatic source. If this source is a gaussian beam, the wavelength chosen for matching is the central one (λ_c). This way, Eqs. 4.8 and 4.9 become:

$$I_{Ld}^m = \sum_{\lambda} I_0(\lambda) \left\{ 1 + R(\lambda) - 2\sqrt{R(\lambda)} \cos \left[\frac{4\pi}{\lambda} [n_{eff}(\lambda_c)d + n_{eff}(\lambda)(z - L)] \right] \right\} \quad (4.11)$$

$$I_{Fd}^p = \sum_{\lambda} 2I_0(\lambda) \left\{ 1 - \cos \left[\frac{4\pi}{\lambda} [n_{eff}(\lambda_c)d + n_{eff}(\lambda) \left(z - \frac{L}{2} \right)] \right] \right\} \quad (4.12)$$

Figure 4.14 Depiction of the waveguide-grating configurations represented by Eqs. 4.8-4.12. (a) Centred grating. (b) Displaced grating.

For this work, MATLAB routines were programmed for adjusting the OPL in our experiments. One should note that the chromatic dispersion of the wave packet (due to the dependence of the refractive index with the wavelength) can be high for very displaced gratings.

The experimental setup for SWIFT spectrometry is depicted in Fig. 4.15. The laser source is split in a Michelson interferometer and injected in the waveguide from one (Lippmann) or both (Gabor) ends. In the case of Lippmann configuration, a mirror is attached to the free edge of the waveguide. Optical fibres were used to couple the light coming from the interferometer into the waveguide. Their position was controlled by ultra-high-resolution piezoelectric actuators (Newport NanoPz). Light scattering was recorded on a CCD camera (SBIG ST3200-ME) through a microscope (Mitutuyo VM L4) with an objective of $5\times$ magnification. Two SLED lasers were

used as light sources at 635 nm (red) and at 850 nm (infrared, 10 nm of linewidth). In addition to splitting the source beam, the Michelson interferometer was used to adjust the OPL of the coupled beams in both configurations.

Figure 4.15 Setup for characterising the SWIFTS spectrometer fabricated for this work. BS: beam splitter, M: mirror, MM: Mobile mirror, OF: optical fibre. The camera (not shown) was placed above the grating.

Chapter 5: Numerical methods

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CHAPTER 5

Numerical methods

The problem of solving Kukhtarev equations (Eqs. 2.4-2.6) is not a new issue. Since their publication in 1979, analytical solutions arose, mainly driven by the potential applications of the photorefractive effect. However, due to the high non-linearity of these equations, analytical solutions were only obtained for restricted cases such as x-crystals illuminated by low-modulation sinusoidal light patterns [23].

Regarding numerical methods, some work has been done in the past years. Numerical models developed by some authors like Gazzetto [82] and Arregui [27] have studied in detail x-cut configuration, but z-cut is not so well explored.

For the theoretical section of this thesis one first tried to follow in Arregui's footsteps, who developed an extremely good model of finite differences for x-cut crystals and also made some advances in the modelling of charge transport for z-cut crystals [29]. However, this finite difference approach turned out to be more difficult to implement for z-cut configuration than originally predicted, so it was decided to change the way of coping with the problem and solve the equations making use of the finite element method, taking advantage of a commercial software, COMSOL Multiphysics®.

5.1 Steps in numerical modelling

The following flowchart represents the numerical modelling process (Fig. 5.1). This work is mostly focused on the “numerical solution” box and related ones, as there is an existing mathematical model generally approved that describes very well the experimental observations, despite it has some limitations (as will be shown in this and following sections).

Figure 5.1 Stages of modelling. Adapted from [126].

As this work deals with numerical methods and numerical solutions, two concepts must be kept in mind: verification of the numerical method and validation of the results. They will be especially important in Chapter 7.

On the one hand, verification consists in comparing the solution of the governing system of partial differential equations (PDEs) with an analytical or numerical benchmark solution approved by the community [126]. It is an essential step that gives a sound base for the whole numerical implementation of the system. Of course, it does not guarantee that the solution obtained for the case of interest is correct or that it will match experimental results, but it is useful to discard unadvertised implementation errors.

On the other hand, validation is defined as the comparison between the numerical solution of the mathematical model and experimental observations [126]. In fact, validation is not exclusive of numerical methods but should be done every time an analytical or numerical model is solved. Validation is necessary to reject unphysical solutions since even if the implementation of the mathematical model is correct, some physics may be missing, the boundary conditions not the appropriate ones, etc.

5.2 Numerical methods for solving PDEs

As stated in Chapter 2, the system of equations that describes the bulk photovoltaic effect does not have a general, analytical resolution. Finding the solution for a particular situation involves using numerical methods for computing the temporal evolution of the space charge and its associated electric field. In general terms, numerical methods for solving systems of PDEs can be classified in two groups: stochastic and deterministic [126]. This classification is based in how the output solution changes according to the input data.

The first type embraces methods based on statistical principles, such as Monte Carlo, which results can be somewhat different depending on certain factors, like how many times the calculation is performed [126]. Nonetheless, the solution is always bounded by the statistical error. Stochastic methods can be very powerful for certain areas of physics and engineering. For example, they are appropriate for solving high dimensional PDEs (with six or more independent variables) or those that involve very complex physics with an intrinsic randomness (e.g. Boltzmann transport equation, clustering in materials or transport equations in turbulent reacting flows) [126]. Stochastic methods are also especially suited for parallel computing. However, due to the need of performing a series of calculations (because of their general dependence on the statistical sample size), deterministic methods are usually preferred over stochastic ones and they are not used unless there is a clear reason for doing so [126].

In the case of deterministic methods, for a given problem, discretization and method, the solution is the same every time it is performed. Many deterministic methods have been developed

for solving systems of partial differential equations, each one with their own advantages and disadvantages. The most common are:

- **Finite difference methods (FDM):** these methods solve PDEs by approximating the derivatives to difference series, usually using a Taylor series expansion. The simulation domain in which the equations are being solved is discretised in a number of interconnected points called nodes [126]. In FDM the equations are solved in their “strong form”, so called because the governing PDE is forced to be completely fulfilled at the nodes after being discretised [7].
- **Finite element methods (FEM):** Although they are many families of methods that could be called by this name, it is commonly restricted to the Galerkin Method of Weighted Residuals using piecewise polynomial trial spaces [149]. Contrary to FDM, the differential operators are not approximated but maintained, although the PDEs are manipulated in order to satisfy them in an integral sense, known as the “weak form” [7]. In order to do so, the domain is discretised in a mesh or grid made up by finite elements and the solution is approximated using test or shape functions (typically polynomials) defined within each element. Solutions calculated by FEM can achieve high accuracy easily if the mesh and shape function are correctly chosen. In fact, the exact solution can be obtained if it can be described by one of these shape functions. One of the major advantages of FEM is that it can handle complex geometries easily [7].
- **Finite Volume Methods (FVM):** In this case the problem domain is also discretised in a mesh formed by control volumes and PDEs are satisfied over the cells that it defines. The governing equations are first integrated over the control volume and after that approximated and solved. Like in the case of FEM, the solution is obtained in its weak form [7]. In FVM quantities are computed as flux balances between elements. In fact, an important characteristic of FVM, which is missing in all other methods described in this section, is their inherent conservation property. FVM are appropriate for problems that deal with transport, like fluid dynamics or heat transfer [126].

- **Spectral methods:** Unlike the methods above, spectral methods do not require the simulation domain to be discretised. These methods work well for PDEs with smooth solutions in relatively simple domains. Spectral methods consist in choosing a certain group of basis functions (Fourier series, Legendre polynomials, among others [149]) defined across the whole simulation domain and then obtaining a set of coefficients for them that satisfies the PDEs. Although it is complicated to implement, high-precision solutions can be obtained if the exact one is smooth enough.

Other deterministic methods include meshless methods (for moving boundaries problems [126]) and the boundary element method (when the solution in the bulk is not of interest). However, they are usually restricted to certain kinds of problems.

5.2.1 Why FEM?

The election of the appropriate numerical method for a certain real-life problem is a crucial step in the modelling process. Although many methods can provide equivalent, good results, parameters such as computational time or flexibility to adapt the model to different situations must be taken into consideration.

Regarding the numerical methods presented in the previous section, stochastic ones were out of the question. Although some works have been published dealing with photovoltaic charge transport using Monte Carlo methods, they are focused on micro- or even nanometre crystals, which is not feasible for our purposes [25]. FDM was the method chosen by previous group members and gave really good results for x-cut crystals, but the program in its current state could not properly handle z-cut and its associated surface charge accumulation. Some work was done in this direction, but the results were not as good as expected.

So, although some effort was made in readapting the FDM code and trying to fix these issues, finally we decided to try a new route. We acquired a commercial software, COMSOL Multiphysics®, able to handle both FEM and FVM. The level of optimization and versatility that COMSOL® offered were by far more powerful than the available resources at that time.

The next dilemma was choosing between FEM and FVM. When the different methods for solving PDEs were explained in the previous section, FVM was described as the most appropriate for transport problems. Paying attention to Kukhtarev equations (Eqs. 2.4-2.6), one can see that they are very similar to the convection-conduction equations that describe semiconductor physics, and for solving charge transport in semiconductor materials, COMSOL® make use of FVM. However, for us, this choice implied two major disadvantages:

- **Surface physics of LiNbO₃ are not well known:** although there are some studies about charge compensation and redistribution in z-cut crystals [152], they have been developed for very specific situations and some results are not fully understood. Therefore, although some efforts were done, it was impossible to adapt the pre-set semiconductor physics module to lithium niobate and the custom equation modelling module only offered working with FEM (in §5.5.1 there is an explanation of how COMSOL® is structured).
- **Multiphysics coupling:** LiNbO₃ is an extremely electroactive material which pyroelectric and piezoelectric properties are as important as the photovoltaic effect is. For future simulations involving coupling of these physical properties, FEM was more suitable than FVM.

On the other hand, FEM lacks any intrinsic conservation property, neither local nor global. Although it is true that this is a major disadvantage, special care has been taken in order to ensure total charge conservation inside the crystal. So, finally, FEM turned to be the chosen option.

5.3 Analytical approximation

Before dealing with FEM and COMSOL Multiphysics®, the fundamentals of the analytical approach used in the early stages of this work will be described. First, let us introduce the simplest model for z-cut charge transport.

Consider a z-cut LiNbO₃:Fe crystal and assume that the space charge is concentrated at both crystal faces as a surface charge density ($\pm\sigma$). Disregard light absorption and diffusion. Then, consider the current density equation (Eq. 2.6) at the crystal centre; due to symmetry conditions,

the electric field at the centre is parallel to the c-axis. Under this approximation, the temporal evolution of σ can be described as a first order ordinary differential equation (ODE)¹⁰:

$$|J| = \frac{d\sigma}{dt} = q\mu \frac{sIN_{D0}}{\gamma N_{A0}} E_z + qsIN_{D0}L_{PV} \quad (5.1)$$

As all the space charge is accumulated on the surface, the concentration of donors and acceptors does not change in the bulk and n can be considered a constant equal to n_0 (Eq. 2.8). In the simplest case, when the whole crystal is illuminated with the same light intensity, the electric field generated by σ is parallel to the c-axis and there is no transversal charge transport. This electric field can be approximated to that of a parallel plate capacitor ($E_z = \frac{\sigma}{\epsilon_0 \epsilon_{33}}$), so Eq. 5.1 becomes:

$$\frac{d\sigma}{dt} = q\mu \frac{sIN_{D0}}{\gamma N_{A0} \epsilon_0 \epsilon_{33}} \sigma + qsIN_{D0}L_{PV} , \quad (5.2)$$

which analytical solution is:

$$\sigma = \pm \sigma_0 \left(1 - e^{-\frac{t}{\tau}} \right) \quad (5.3)$$

$$\sigma_0 = \frac{\gamma N_{A0} L_{PV} \epsilon_0 \epsilon_{33}}{\mu} \quad \tau = \frac{\gamma N_{A0} \epsilon_0 \epsilon_{33}}{q\mu sIN_{D0}}$$

A few years ago, a more complex model was developed by Arregui *et al.* [28, 29]. It analytically solves the problem of a square-shaped illumination in x-cut and z-cut crystals. The model provides an analytical formula for the calculation of the electric field (E_z) at the centre of a LiNbO₃:Fe sample as a function of the square side length and the crystal thickness. This field is then equated to the saturation electric field (E_{sat}) to obtain the surface charge density. E_{sat} field can be calculated from Eq. 5.1 as current density equals zero at saturation:

$$E_{sat} = \frac{\gamma N_A L_{PV}}{\mu} \quad (5.4)$$

¹⁰ This system is defined for one face of the crystal. The surface charge distribution of the other face would be the same but with the opposite sign.

However, the main drawback of the model presented in [28] is that it only considers isolated pixels which means it is not valid for complex illumination patterns. In this thesis, an extension of the work developed by Arregui *et al.* to arbitrary patterns is presented.

5.4 The Finite Element Method

It is not the aim of this dissertation to explain in detail the mathematics behind FEM but give the reader a minimum basis to understand the theoretical part of this work and its nomenclature. For a detail explanation the reader can consult [149] in which the method and its implementation is explained in detail.

FEM were born in the 1950's in a structural mechanics context. They belong to a broad group of techniques used to solve PDEs called methods of weighted residuals (MWR). MWR include methods such as Collocation, Subdomain and Galerkin [149]. What it is actually called FEM is a particular case of the Ritz-Galerkin MWR using piecewise polynomial trial spaces [149].

5.4.1 Theoretical background

Suppose a general differential equation:

$$\mathcal{L}u(\mathbf{x}) = f(\mathbf{x}), \quad \mathbf{x} \in \Omega, \quad (5.5)$$

where $\mathcal{L}$ is a differential operator, $u(\mathbf{x})$ is the unknown solution and $f(\mathbf{x})$ is a known function (both dependent on a series of independent variables, $\mathbf{x}$) and Ω the domain where the equation applies. In addition, a set of appropriate boundary conditions must be specified along the domain boundary, $\partial\Omega$.

If one is interested in obtaining an approximate solution of this differential equation, a set of basis or shape functions that belong to an arbitrary function space, called trial space, can be used $\{\phi_1, \phi_2, \dots, \phi_N\}$, where N is the dimension of the space. So, the approximate function can be defined as:

$$U(\mathbf{x}) = \sum_{i=1}^N \gamma_i \phi_i(\mathbf{x}), \quad (5.6)$$

where $U(\mathbf{x})$ is called the trial function and γ_i are scalar coefficients. The problem now lies in obtaining a set of $\{\gamma_i\}$ so that $U(\mathbf{x})$ is a good approximation to the actual solution $u(\mathbf{x})$.

As commented above, FEM belongs to a family of methods known as Method of Weighted Residuals. These methods try to minimize the error between the approximate and the actual solution defining a residual:

$$\mathcal{R}(\mathbf{x}) = \mathcal{L}U(\mathbf{x}) - f(\mathbf{x}), \quad (5.7)$$

and minimizing it by forcing it to be zero in a weighted average sense over the whole domain:

$$\int_{\Omega} \mathcal{R}(\mathbf{x}) \omega_j(\mathbf{x}) d\mathbf{x} = 0, \quad (5.8)$$

where ω_i is one of a set of weight or test functions $\{\omega_1, \omega_2, \dots, \omega_M\}$. The total number of weight functions (M) is related to the trial space dimension and the number and type of boundary conditions. Depending on the chosen weight functions, different methods appear, such as Collocation method or Subdomain method [149]. In the case of Ritz-Galerkin method, weight functions are equal to the shape functions of the trial space:

$$\int_{\Omega} \mathcal{R}(\mathbf{x}) \phi_j(\mathbf{x}) d\mathbf{x} = 0 \quad (5.9)$$

For performing this integral a set of shape functions has to be defined. In order to do so, Ω is first divided in smaller, non-intersecting subdomains (Ω^e), i.e., the mesh. In FEM, the shape functions are usually piecewise polynomial functions defined within each element in such a way that they equal 1 at one element node and 0 at the rest of the nodes (see §5.4.3). This way, the integral in Eq. 5.9 turns into multiple integrals that together with the boundary conditions form a system of algebraic equations which solution is the values of $\{\gamma_i\}$, and so the approximation to the differential equation solution:

$$A\boldsymbol{\gamma} = \boldsymbol{b} \quad (5.10)$$

A and $\boldsymbol{b}$ are the stiffness matrix and load vector, respectively. These names came from the structural mechanics-related origin of FEM. This system of equations can be solved by direct or iterative methods, like LU decomposition [6] or Conjugate gradients [161].

5.4.2 Meshing

Probably, one of the most important steps, if not the most important one, when solving a problem by FEM is meshing the domain or geometry within the problem is being solved. No matter how complicated this domain is, FEM can describe it as a collection of subdomains, which altogether conform the grid or mesh. Usually, “grid” refers to the set of lines and nodes that define the elements whereas “mesh” refers to the spaces enclosed by the lines. In this work, however, both terms will be used as synonyms [126]. Mesh elements must be convex, nonintersecting and their union must cover all the domain.

Mesheres are classified in two broad groups: structured and unstructured (see Fig. 5.2). Structured meshes are always ordered and they have a better performance regarding memory usage and solving time, however, their lack of flexibility to modify the element distribution is a serious drawback when meshing certain geometries or performing mesh refinement¹¹. In this work, both kind of meshes are used.

Figure 5.2 Comparison between a structured and an unstructured mesh.

¹¹ Usually, finer meshes (i.e., more and smaller elements) are used where important gradients of the dependent variable are expected or in areas where high precision is desirable (like close to boundaries with periodic conditions).

The shape of the elements depends on the dimension of the problem (1D, 2D, 3D) and the problem itself, as some elements are more appropriate than others for certain equations. In Fig. 5.3, different elements shapes are shown. In this work, most of them will be used as each one is appropriate for a specific part of the geometry.

Figure 5.3 Different kinds of elements used in FEM analysis. In bold the ones used in this work. Adapted from [126].

5.4.3 Shape functions

For a single mesh element, many shape functions can be used to approximate the unknown solution. As commented above, in FEM these functions are usually piecewise polynomial functions defined for each node within an element. The most used shape functions are piecewise Lagrange polynomials of first and second degree. The general form of a Lagrange polynomial of arbitrary degree (d) for a 1D element is:

$$L_a^{d=n-1} = \frac{\prod_{\substack{i=1 \\ i \neq a}}^n (\xi - \xi_i)}{\prod_{\substack{i=1 \\ i \neq a}}^n (\xi_a - \xi_i)} , \quad (5.11)$$

where a is the node number, ξ a local coordinate defined within the element and n the total number of nodes. In the simplest case of a first order 1D element, one obtains two linear Lagrange polynomials (Fig. 5.4a):

$$\begin{aligned}
L_1^1 &= \frac{1}{2}(1 - \xi) \\
L_2^1 &= \frac{1}{2}(1 + \xi) ,
\end{aligned}
\tag{5.12}$$

whereas a second order 1D element has three nodes and the polynomials are quadratic (Fig. 5.4b):

$$\begin{aligned}
L_1^2 &= \frac{1}{2}\xi(\xi - 1) \\
L_2^2 &= \frac{1}{2}\xi(\xi + 1) \\
L_3^2 &= 1 - \xi^2
\end{aligned}
\tag{5.13}$$

Figure 5.4 1D Lagrange shape functions. (a) First-order element (2 nodes). (b) Second order element (3 nodes).

As a rule of thumb, the larger the order of the element, the better the approximate solution, as it can “fit” better the shape of the exact solution. However, this also increases the number of degrees of freedom of the system and therefore the size of the matrix and vectors in Eq. 5.10. Thus, larger memory allocation and computational time. Usually, second order elements, together with an appropriate mesh refinement where required, exhibit the best performance-computational complexity ratio for most equations.

The extension of Equations 5.12 and 5.13 to 2D and 3D elements is straightforward. Fig. 5.5 depicts the shape functions of a quadrilateral 2D element. Note that $L_a^d = 0$ in every node except one.

Figure 5.5 2D Lagrange shape functions. (a) First-order element (4 nodes). (b) Second order element (9 nodes). Retrieved from [7].

Although Lagrange are the most commonly used elements, there are others like Hermite, Argyris and infinite elements. These elements are used with certain equations and boundary conditions [20].

5.4.4 Error estimation

When a PDE is solved by numerical methods, the obtained solution seldom matches the real one due to the discretisation made and the numerical method itself. When talking about FEM, ideally the finer the mesh the closer the approximate solution is to exact one. The process of successively solving a problem with finer meshes is known as mesh refinement and the error (e) in the solution can be approximated as:

$$e = U_{i+1} - U_i , \quad (5.14)$$

being U_i the solution for which one wants to know the error and U_{i+1} the solution computed with a finer mesh. Applying this procedure, a sort of convergence curve can be plotted to analyse the solution evolution and check that the error function is monotonically decreasing [7].

Although mesh refinement is the easiest way to obtain an error estimation in FEM, two major drawbacks are associated with it:

- **Increase in computational cost:** the finer the mesh, the larger the computation time and the computer memory allocated for the simulation. A way to deal with this problem is also decreasing the order of the elements instead of just refining the mesh. This way, the increase in memory and time is counterbalanced by the lower number of degrees of freedom. However, the convergence curve is usually steeper when the order of the elements is larger.
- **Singularities:** sometimes the exact solution of a PDE at certain points of the domain is a singularity, which leads to unphysical results like infinite electric field at a very sharp metallic tip. When this occurs, mesh refinement around the singularity would only increase its effect. Nevertheless, the influence of the singularity over the rest of the simulation domain is usually restricted to a small region close to it.

Finally, it is worth mentioning that, in terms of error in the solution, second order shape functions are equivalent to third order finite differences approximations, whereas lineal elements to second order ones [149].

5.5 COMSOL Multiphysics®

COMSOL Multiphysics® is a general-purpose software for modelling and simulating [10]. Its major advantage is that every step of the modelling process can be configured from the program interface: defining the problem geometry, material properties and physics involved, meshing the domain, choosing a solver and analysing the results with post-processing tools. In this thesis, COMSOL® Version 5.2a and Version 5.3a have been used.

5.5.1 COMSOL® tree

A COMSOL® project is divided in different sections or branches:

- **Geometry:** 1D, 2D, 2D axisymmetric and 3D. The program has tools for defining from simple to complex geometries. Also, it allows to import geometries from files of different formats.

- **Physics:** pre-set physic interfaces include a large number of physical phenomena grouped by areas of Physics, Chemistry and Engineering. Each one has its own set of equations and boundary conditions. In addition, the software also offers the possibility of introducing user-defined equations and conditions, something that has been done in this work.
- **Mesh:** element type and distribution can be controlled with great detail.
- **Solvers:** COMSOL® includes different solvers for different problems and physic interfaces. Although the predefined solver is usually good enough for most applications, sometimes it is necessary to adjust its parameters in order to obtain a better performance.
- **Post-processing:** the program has different tools for analysing the simulation results.

5.5.2 The Method of Lines

Strictly speaking, when solving the temporal evolution of the Kukhtarev equations COMSOL® is not applying a pure FEM scheme. COMSOL® solves time dependent problems using the Method of Lines. This method for solving PDEs consists in discretising all the independent variables on which a PDE depends except one. Typically, spatial coordinates are the ones discretised and time is the one to remain continuous. This way, the system shown in Eq. 5.10 is not of algebraic equations but of ODEs, and it can be solved numerically [155].

5.5.3 COMSOL® solvers

Numerical methods and solvers used of obtaining the solution of Eq. 5.10 can be classified as direct or iterative. Direct solvers are those that provide the exact solution (in the absence of rounding errors) by computing it in a finite number of operations. Iterative methods start with an initial guess of the solution and compute iteratively a sequence of better approximations, rather than in one large computational step [45, 79]. Each family of methods has its own advantages and disadvantages [2]:

- **Direct solvers:** in general, they have larger memory requirements, but they are also robust.

- They require about $O(n^2)$ - $O(n^3)$ numerical operations, being n the number of degrees of freedom¹².
- Memory allocation is approximately of the same order, $O(n^2)$ - $O(n^3)$.
- Their algorithms are robust, even with most of stiff problems.
- **Iterative solvers:** typically, their memory requirements and computation time are lower than direct solvers ones. However, they require a good initial guess and a preconditioner, which is very problem dependent.
 - Solution time is $O(n)$ - $O(n^2)$ and it depends on the preconditioner.
 - Memory usage is also $O(n)$ - $O(n^2)$.
 - Their robustness is very problem and preconditioner dependent.
 - Different equations require different iterative methods.

In view of these properties, direct solvers were our choice. Although iterative solvers offer an interesting combination of low computation time and memory requirements, they are less robust than direct ones. Furthermore, whether obtaining a good solution or not with an iterative method usually depends on a well-chosen preconditioner. Ill-conditioned problems can be difficult to solve, and the previous experience solving Kukhtarev equations with FDM pointed toward that direction (§7.1). In addition, we were not able to find any reference that used iterative solvers for similar problems, neither in COMSOL® documentation nor in the literature [19, 137]. The choice of a direct solver implied that we had to be careful when meshing, in order to keep the number of nodes as low as possible.

COMSOL® has three main direct solvers. All of them are based on LU decomposition [6, 79]: MUMPS, PARDISO and SPOOLES. After some tests, PARDISO exhibited the best performance in terms of computation time. More information about COMSOL® solvers, can be found in [20].

¹² Roughly speaking, in our case n is three times the number of nodes because there are three independent variables (see §7.2).

III. RESULTS

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Chapter 6: Dielectrophoretic z-cut patterning

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CHAPTER 6

Dielectrophoretic z-cut patterning

First PVT experiments were carried out using x- and y-cut $\text{LiNbO}_3\text{:Fe}$ crystals [53, 64]. The rationale behind this choice was their widespread use in photorefractive applications and the existing deep knowledge of their internal photovoltaic electric fields. Although NP fringe patterns can be obtained easily through sinusoidal illumination, these samples have an important limitation regarding particle trapping: their surface anisotropy. The optical axis is parallel to the crystal surface, and so it is the charge transport. This led to the impossibility of obtaining proper 2D patterns, as will be shown below.

It took a few years to start using z-cut crystals. When this thesis work started, there was only one paper reporting PVT experiments using z-cut $\text{LiNbO}_3\text{:Fe}$ crystals as substrates [69]. This work deals with charged glassy carbon microparticles and the authors state that z-cut crystals are not expected to develop an electric field gradient high enough to trap neutral particles, so they use charged particles instead, obtaining fairly good results.

However, the impossibility of DEP trapping on z-cut seems strange. In this cut, charge accumulates on the crystal surface, so there should be a large field gradient at least in the boundaries between illuminated and non-illuminated areas. On this basis, we started a series of experiments that led to dielectrophoretic PVT patterning on z-cut crystals for the first time.

May this chapter serve as a first approach to the patterning capabilities of z-cut $\text{LiNbO}_3\text{:Fe}$ crystals. A complete theoretical description of the PV electric field generation and its associated

potentials is developed in the following chapter. For the moment, the simple model presented in §5.3 is good enough to explain these first experiments. Fig. 6.1 shows the tentative charge distribution for x- and z-cut under the same illumination pattern.

Figure 6.1 Schematic of the charge distribution obtained in a (a) x-cut and (b) z-cut LiNbO₃:Fe crystal due to a single beam illumination. Observe how in both cases there is charge accumulation at both ends of the optical axis.

This simple depiction will be useful for explaining the results presented in this chapter. The experiments were carried out using the highly doped x- and z-cut LiNbO₃:Fe samples (0.1 wt%Fe) in order to ensure a strong photovoltaic effect. The particles used in the first experiments are CaCO₃ microparticles.

6.1 One-dimensional patterns

As stated above, when this work started all DEP trapping PVT experiments were carried out with x- or y-cut crystals. Due to the crystal asymmetry, which allows proper patterning only in one direction (perpendicular to c-axis), and the photorefractive experience regarding holographic setups (like the one presented in §4.1.3b), first PVT experiments were carried out using these kinds of illumination distributions [64, 67].

When these patterns were tested in z-cut crystals, they were expected to give similar particle arrangements to those made with x-cut crystals: for times close to τ (see Eq. 5.3), the simple theory for z-cut charge distribution predicts DEP potential minima to be located at illumination maxima, with the same periodicity as the light pattern, λ (Fig. 6.2d); the well-developed theory

for x-cut crystals [29] also predicts potential minima with a periodicity Λ , although in this case located at illumination minima, that is where charge accumulation occurs (Fig. 6.2c).

Figure 6.2 Comparison between PVT nanoparticle patterning using a x-cut or a z-cut $\text{LiNbO}_3\text{:Fe}$ sample and a sinusoidal light intensity profile. (a) Donor redistribution in x-cut (adapted from [29]). (b) Surface charge density in z-cut obtained using the model explained in §5.3 at $t = \tau$. DEP potentials along a line perpendicular to the fringes for (c) x-cut and (d) z-cut crystals at different heights from their surface. Experimental patterns made of CaCO_3 microparticles on (e) x-cut and (f) z-cut samples.

Roughly speaking, patterns on both crystal cuts are similar (Fig. 6.2e,f). However, particle lines obtained on x-cut tend to be thinner and better defined than those on z-cut, leaving aside experimental variability.

6.2 Two-dimensional patterns

It has been shown that there is not much difference between x- and z-cut patterning regarding 1D sinusoidal patterns, but the situation may be different when 2D patterns are tested. One of the simplest 2D patterns that can be conceived is a rectangle (Fig. 6.3c). The experimental setup for obtaining a rectangular light distribution was described in §4.1.3a. The same highly doped crystals used in the previous section were also used to perform this experiments.

In this case, the corresponding x- and z-cut DEP potentials are dissimilar or, at least, more dissimilar than they are for the sinusoidal illumination profile (Figs. 6.3a,b). In the case of x-cut, two narrow potential wells are located at the edges of the illumination, whereas for z-cut there is a plateau of low potential that covers almost all the illuminated region, although the potential is even lower at the boundaries of the illumination. This difference in the potential shape is translated into the particle pattern, as is evident from Figs. 6.3d,e. For x-cut the particles are arranged in two parallel strips that are perpendicular to the c-axis, independently of the sign of the charge distribution. This pattern is typical of dielectrophoretic trapping of neutral particles and can be found in previous works [46]. In the case of z-cut, the whole illuminated area is covered with particles, reproducing exactly the light pattern.

As a matter of fact, in both configurations particles are trapped in the regions where charges are accumulated, that are precisely where the electric field gradient is the highest and potential minima occur (compare Fig. 6.1 and Figs 6.3a,b). The impossibility for charges in x-cut to accumulate parallel to the optical axis is the origin not only of the absence of particles in that direction (like the horizontal side of the rectangle in Fig. 6.3d), but also of the contouring effect, i.e., the fact that the particle patterns do not reproduce the light pattern but only its outline. Both effects are more evident in a pattern with radial symmetry, such as a Fresnel zone plate (Fig. 6.4a);

we choose this pattern because it will prove to be useful in terms of applicability and for studying PVT technique itself. This light distribution was achieved using the SLM presented in §4.1.3c.

Figure 6.3 Comparison between PVT nanoparticle patterning using a x-cut or a z-cut $\text{LiNbO}_3\text{:Fe}$ sample and a rectangular light intensity profile. DEP potentials for (a) x-cut and (b) z-cut crystals at different heights from their surface. (c) Illumination profile. (d, e) Experimental patterns made of CaCO_3 microparticles on (d) x-cut and (e) z-cut samples.

Figs. 6.4b,c show the result of the trapping experiment for x- and z-cut. The first striking difference between both patterns is the lack of particles in the x-cut one in its upper and lower part. In particular, the area without trapping is delimited by two straight lines at 70° from the c-axis direction. This angle is greater than others measured in similar trapping experiments [67], which implies that it is dependent on the experimental conditions. The contouring also appears in this pattern; although it can go unnoticed in the general view, it is clear in the inset (Fig. 6.4d).

On the other hand, z-cut particle pattern is a faithful representation of the light pattern. Again, the particles cover all the illuminated area in such a way that the illumination distribution acts as a template for them with really good fidelity.

Figure 6.4 Comparison between PVT nanoparticle patterning using a x-cut or a z-cut LiNbO₃:Fe sample and a Fresnel zone plate light intensity profile. Experimental patterns made of CaCO₃ microparticles on (b) x-cut and (c) z-cut samples. (d) Inset showing the contouring effect in the x-cut case.

A problem with the patterns above is the size of the CaCO₃ microparticles ($\sim \varnothing 3.5 \mu\text{m}$). As their mean diameter is relatively large, the definition of the smallest motifs of the pattern, the outer circles, is not good. To show the patterning capabilities of z-cut crystals, the same Fresnel zone plate made with CaCO₃ microparticles and two additional patterns have been obtained using Al NPs ($\sim \varnothing 70 \text{ nm}$). They are shown in Fig. 6.5. The definition is notably increased, especially when both Fresnel zone plates are compared (Fig. 6.4c and Fig. 6.5a). The inset (Fig. 6.5b) is also a demonstration of the resolution achievable in our laboratory. More than 25 rings are perfectly

defined, the thinnest having a radii difference of just some dozens of microns. Another point to note is the remarkable large sizes that can be patterned in a single operation with good quality and homogeneity. The chequered pattern shown in Fig. 6.5c has a surface extension of $5.7 \times 6.4 \text{ mm}^2$.

Figure 6.5 Different patterns made of Al NPs fabricated on z-cut LiNbO_3 samples by PVT.

- (a) Fresnel zone plate. (b) Inset showing the extraordinary definition of the rings.
(c) Chequered pattern covering a large area of the sample. (d) Triangle mosaic.

6.3 Discussion and conclusions

The main result of this chapter is the successful DEP trapping of neutral particles on z-cut $\text{LiNbO}_3\text{:Fe}$ crystals for the first time. Furthermore, it has turned out to be an excellent template for arbitrary 2D PVT trapping due to the isotropy¹³ of its surface, overcoming previous limitations

¹³ Strictly speaking, the surface of z-cut LiNbO_3 samples is not isotropic due to its crystalline structure (§1.1.2). However, for the purposes of this work, it can be considered so.

related to the exclusive use of x-cut crystals. Contrary to x-cut samples, z-cut ones allow obtaining particle patterns that are a faithful representation of the illumination profile. It is important to highlight that z-cut crystals *allow* obtaining such patterns, as experimental conditions can be modified in order to obtain different results (see Chapter 8).

The extension of the patterns is also remarkable, as they have good quality and homogeneity over areas as large as 36.5 mm^2 . Such throughput is difficult to achieve with other techniques, such as optical or holographic tweezers. Furthermore, the patterns can be designed at will, as the only limitation is the resolution of the SLM, and even this inconvenience can be avoided up to certain extent by optical means (§4.1.3c). It should be also noted that although micro- and nanoparticles are equally trapped, the size of the particles has an influence in the final pattern. Smaller particles are preferred for obtaining well-defined patterns. When motifs are around one order of magnitude larger than the particles, the sharp definition and faithful replica of the light pattern can be compromised.

It has been also shown and explained the impossibility of obtaining arbitrary 2D patterns using x-cut samples. The rationale behind this limitation is the optical axis being parallel to the crystal surface. As charge displacement basically follows c-axis direction, only certain space charge distributions are possible. When talking about particle patterning, crystal anisotropy is translated in a contouring effect, and only the outline of the illumination profile is reproduced. Moreover, if the direction of a certain edge of the light profile is parallel or close to the direction of the c-axis, then there is no trapping at all, which is the main limitation of x-cut configuration. In this sense, the single slit and the Fresnel zone plate are very representative examples of the x-cut 2D pattern capabilities.

The results obtained with x- and z-cut crystals are only equivalent when using a 1D sinusoidal light profile. In fact, depending on the desired result, x-cut can result more appropriate than z-cut, as it tends to produce thinner and better-defined fringes (§9.1.1).

The simple theory developed in §5.3 has proved to be enough for describing the main features of DEP trapping in z-cut configuration. It shows an appropriate DEP potential distribution and

presents one of the key features of DEP trapping: the edge enhancement, related to the fact that the potential at the edges of the illuminated area is the lowest (see §8.2.2). In the next chapter a complete theoretical model for z-cut is developed in depth. This complete model not only ratifies the results obtained with the simple one, but also provides a better description of the space charge distribution and time evolution inside z-cut crystals, which will be required for a deeper understanding of other experimental features (Chapter 8).

In conclusion, the results presented in this chapter are a significant progress in the PVT development, as 2D DEP trapping was one of the key capabilities that PVT lacked. Now, this technique is ready to become a competitive tool among other optoelectronic procedures for simultaneous manipulation of a large number of particles.

Chapter 7: Theoretical analysis of the charge transport in z-cut configuration

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CHAPTER 7

Theoretical analysis of the charge transport in z-cut configuration

The photorefractive and photovoltaic effects in x- and y-cut $\text{LiNbO}_3\text{:Fe}$ crystals have been investigated for a long time due to the applicability of these cuts in non-linear optics [23, 113], but z-cut was left out of most studies due to the poor use of its photovoltaic fields for such purposes. However, it has been shown in the previous chapter that this late configuration is fundamental in order to make PVT a competitive optoelectronic tool for particle manipulation, as it is the only one that allows isotropic patterning. In fact, nowadays most applications of PVT require the use of z-cut crystals [81]. This means that the study and understanding of the charge transport in z-cut crystals is fundamental for improving this particle manipulation technique.

In this chapter, the photovoltaic charge transport in z-cut crystals is investigated in depth. In the first section, an analytical model is developed based on the work of Arregui *et al.* [28]. This model considers that all the generated space charge density is accumulated on the crystal surfaces as surface charge density. However, the analysis of the results shows that this assumption is a key limitation of the model and motivated the development of a complete FEM model.

The FEM model was implemented using a commercial simulation software called COMSOL Multiphysics®. The second part of this chapter is dedicated to explaining this implementation and the accent is placed on the most important issues, like meshing.

Finally, the time evolution of the space charge and the photovoltaic currents and electric field inside the crystal is studied for three basic illumination patterns. The influence of certain crystal and illumination parameters is also analysed in detail.

The results presented in this chapter will be used in the following ones to compute the DEP and EP forces and potentials outside the crystal, which are what ultimately determines the particle distributions on the crystal surface during PVT operation. Actually, the importance of this chapter lies in the fact that these DEP and EP forces and potentials cannot be properly calculated without an accurate description of the photovoltaic effect inside the crystal, and therefore it is impossible to truly describe and predict the experimental patterns.

7.1 Analytical model

Let suppose a non-homogeneous first-order linear system of ODEs:

$$\mathbf{x}' = A\mathbf{x} + \mathbf{b} \quad (7.1)$$

In which $\mathbf{x}$ is the column vector of unknowns, A a $n \times n$ square matrix and $\mathbf{b}$ a given vector function. The independent variable is time (t). If A is a diagonalizable matrix with constant values which n eigenvectors (e_i) are independent and its n eigenvalues ($1/\tau_i$) are real, the solution of the system can be obtained analytically. First, a change of variables is made using the matrix P of eigenvectors [24]:

$$\mathbf{x} = P\mathbf{y} \quad (7.2)$$

Left multiplying Eq. 7.1 by P^{-1} transforms A into a diagonal matrix (D). The elements of the diagonal are the eigenvalues of A :

$$\mathbf{y}' = D\mathbf{y} + \mathbf{h} , \quad (7.3)$$

where $\mathbf{h} = P^{-1}\mathbf{b}$. As D is diagonal, the system is decoupled, and n independent equations are obtained:

$$y'_i = \frac{y_i}{\tau_i} + h_i \quad i = 1, n, \quad (7.4)$$

which solution is:

$$y_i = C_i e^{\frac{t}{\tau_i}} - \frac{h_i}{\tau_i} \quad i = 1, n \quad (7.5)$$

Once the vector $\mathbf{y}$ is obtained, $\mathbf{x}$ can be simply calculated using Eq. 7.2. The constants C_i depend on the initial conditions.

Following the analytical approach made by Arregui *et al.* [28], it is possible to discretize a z-cut LiNbO₃:Fe sample illuminated with a complex light pattern into a grid of pixels (Fig. 7.1a). This way we can take advantage of their formula for the calculation of the electric field in the centre of the sample and combine it with the exponential model described by Equation 5.2 to obtain a system of ODEs:

$$\frac{d\sigma_{ij}}{dt} = \frac{q\mu s N_{D0} I_{ij}}{\gamma N_{A0} \epsilon_0 \epsilon_{33}} \sum_k^N \sum_l^M \sigma_{kl} G_{|(k-i)||l-j|} + q s I_{ij} N_{D0} L_{PV}, \quad (7.6)$$

where G is a matrix that contains the geometric factors that modulate the influence of one pixel over the others [28, 29]. The surface charge density (σ_{ij}) is supposed constant in each cell¹⁴. This system can be solved using the algorithm explained above by just identifying $\mathbf{x}$ and $\mathbf{b}$ vectors and A matrix:

$$\mathbf{x} = \boldsymbol{\sigma} \quad (7.7)$$

$$\mathbf{b} = q s N_{D0} L_{PV} \mathbf{I} \quad (7.8)$$

$$A = \frac{q\mu s N_{D0}}{\gamma N_{A0} \epsilon_0 \epsilon_{33}} G' \quad (7.9)$$

Note how the matrix formulation of Eq. 7.6 can be restructured into a vector formulation (Fig. 7.1b). In addition, note also that G' is a matrix made by multiplying the components of G by

¹⁴ This system is defined for one face of the cristal. The surface charge distribution of the other face would be the same but with the opposite sign.

the local intensity of each cell (I_{ij}). This is very important to notice because the algorithm above is valid only when A matrix fulfils the condition of being diagonalizable with real eigenvalues and n independent eigenvectors. G is a real symmetric matrix, which means that always fulfils this condition [28, 29], but an arbitrary light distribution can make G' non-symmetric and so the algorithm above cannot be applied. In fact, similar methods exist for general cases in which A is not diagonalizable, it has imaginary eigenvalues, $\mathbf{b}$ is a time dependent vector function, etc. [24]. Nevertheless, there is no need to worry about this, as the light distribution chosen for the example shown in this chapter makes G' symmetric, and this case perfectly illustrates the behaviour of the photovoltaic charge transport, so more complicate models are not necessary.

Figure 7.1 (a) Pixel discretization of an arbitrary light pattern. (b) Visual representation of the change between matrix and vector formulation of Eq. 7.6.

The algorithm was programmed and solved in Fortran 90 using the LAPACK library [3]. As input, the program requires the illumination pattern (intensity distribution, size) and the crystal parameters (thickness, doping level, oxidation-reduction ratio...). The outputs are the values of

the surface charge density, the electric field at the crystal centre and current density for each pixel as a function of time, and the eigenvalues and eigenvectors of the system.

To illustrate this method, it is applied to a simple illumination pattern consisting in a simple slit of illumination or rectangular light profile (Fig. 7.2). The size of the slit and the crystal parameters different to those of Table 2.I are listed in Table 7.I. Following the discretization shown in Fig. 7.2, a system of three equations is obtained, as the contribution to the current and the electric field of all the non-illuminated cells is zero.

Figure 7.2 Rectangular light profile.

Table 7.I Parameters used for performing the calculations using the analytical model.

Symbol	Description	Units	Typical value
N_{D0}	Initial donor concentration	m^{-3}	10^{24} m^{-3}
N_{A0}	Initial acceptor concentration	m^{-3}	10^{25} m^{-3}
L	Square side length	m	10^{-4} m

The analytical solution for the surface charge evolution in the central and the lateral cells¹⁵ are:

$$\begin{aligned}\sigma_C &= \left[0.412 \left(1 - e^{-\frac{-t}{6.17 \cdot 10^3 \text{ s}}} \right) - 2.23 \cdot 10^{-29} \left(1 - e^{-\frac{-t}{7.09 \cdot 10^5 \text{ s}}} \right) - 46.1 \left(1 - e^{-\frac{-t}{1.60 \cdot 10^8 \text{ s}}} \right) \right] \frac{\text{C}}{\text{m}^2} \\ \sigma_L &= \left[0.410 \left(1 - e^{-\frac{-t}{6.17 \cdot 10^3 \text{ s}}} \right) - 3.54 \cdot 10^{-15} \left(1 - e^{-\frac{-t}{7.09 \cdot 10^5 \text{ s}}} \right) + 23.2 \left(1 - e^{-\frac{-t}{1.60 \cdot 10^8 \text{ s}}} \right) \right] \frac{\text{C}}{\text{m}^2}\end{aligned}\quad (7.10)$$

¹⁵ For symmetry reasons, the solution for the two lateral cells is identical.

The evolution of the surface charge density for each cell is the sum of three exponential functions, which resembles Eq. 5.3 very much. Fig. 7.3 shows the time evolution of the surface charge density and the electric field at the centre of each cell. There are some features of the surface charge density temporal evolution that stand out. First, it seems to evolve very slowly until $t \sim 10^6$ s. Second, the sign of the surface charge density of the lateral cells at saturation is the opposite to that of the central one, and their absolute value is very high considering the results given by other models ($\sim \text{mC/m}^2$). Finally, the required time to reach saturation is extremely long (31 years).

Figure 7.3 Time evolution of the surface charge density and the electric field at the centre of the crystal using the analytical model and the illumination profile shown in Fig. 7.2. The subindices “C” and “L” correspond to the central and lateral cells, respectively.

So, even though Eq. 7.10 is the exact solution to the system of PDEs, it is evident that it does not describe the physics of the photovoltaic effect. Saturation time is extremely high and it has never been observed positive and negative surface charge density at the same face of a z-cut crystal. This model is not validated by the experimental observations (see §5.1) and it should be modified.

In order to figure out why the model fails, let us analyse the surface charge density and its relationship with the evolution of the internal electric field. It can be seen in Fig. 7.3 that the electric field almost reaches its theoretical saturation value (Eq. 5.4) long before surface charge density starts to dramatically increase. However, from that point ($t \sim 10^4$ s) until it reaches the exact saturation value ($t \sim 10^9$ s) the electric field is slightly lower in the lateral cells than the central one. Both values only match when the saturation surface charge density is reached.

A closer look to the “flat” zone of the surface charge evolution (on the left side of Fig. 7.3) is plotted in Fig. 7.4. This graph reveals that the surface charge evolution seems appropriate at the beginning: it matches a saturable exponential function (in agreement with the simple model described by Eq. 5.3) and its magnitude and the time until saturation are closer to what may be expected. In addition, the surface charge density is higher in the lateral cells than in the central one, what seems appropriate due to the fact that the electric field that opposes the photovoltaic charge transport is higher in the centre. However, as soon as the surface charge density appears to reach a plateau (i.e., to saturate) it starts to diverge.

Figure 7.4 Close-up view of Fig. 7.3. Time evolution of the surface charge density and the electric field at the centre of the crystal using the analytical model and the illumination profile shown in Fig. 7.2. The subindices “C” and “L” correspond to the central and lateral cells, respectively.

The origin of this divergence of the surface charge density from its apparent saturation value can be found in the electric field. In Fig. 7.4, the value of the theoretical saturation electric field (100 kV/cm) is plotted in black. This figure shows how the central cell reaches this value before lateral ones do. From this moment, the current density associated to surface charge accumulation (the first term in the right-hand side of Eq. 7.6) is larger than the photovoltaic one in the central cell. As a consequence, the surface charge density in the central cell (σ_c) starts to decrease, which accelerates the growth of σ_L . This process continues until the saturation electric field is reached simultaneously in all the cells, leading to the surface charge density evolution shown in Fig. 7.3.

Another way to understand this behaviour is through the eigenvalues and eigenvectors of the system. The eigenvalues and eigenvectors of this particular crystal, light distribution and discretization are listed in Table 7.II. When these values are compared with the analytical expression for the surface charge evolution (Eq. 7.10) it becomes evident that the eigenvectors are related to the shape of the solution and the eigenvalues to its temporal evolution.

Table 7.II Eigenvalues and eigenvectors of the system represented in Fig. 7.2.

Eigenvalues, $1/\tau_i$ (s ⁻¹)	Eigenvectors, e_i
$-1.62 \cdot 10^{-4}$	(0.576, 0.580, 0.576)
$-1.41 \cdot 10^{-6}$	(0.707, $4.41 \cdot 10^{-15}$, -0.707)
$-6.24 \cdot 10^{-9}$	(0.410, -0.814, 0.410)

An apparent correct solution of the problem is the one determined by just the first eigenvector-eigenvalue pair. This solution has been represented in Fig. 7.4 and although it seems valid, it is not. The first eigenvector determines that the surface charge density in the central cell is larger than in the lateral ones, and this is not possible. As commented above, the electric field opposing the photovoltaic charge transport is the largest in the central cell, so its surface charge density should be the lowest. This subtle but important behaviour is indeed observed in the complete solution.

Then, a sensible reasoning could be keeping the complete solution but either using it only for calculating short periods of illumination or setting manually a saturation point and neglect the rest of the time evolution. Even though this procedure could work for simple illumination patterns like this one, it would be difficult or even impossible with larger or more complex patterns. Furthermore, the problem would not be really solved.

Under the assumption that the origin of the problem was forcing the surface charge density to be homogeneous within each cell, we tried to smooth its distribution with different interpolating functions, but the alternation of the positive and negative charge continued. In fact, the key point was understanding what this solution was really telling us: the only way to obtain a homogeneous electric field at the centre of the crystal using only an arbitrary surface charge distribution is alternating the sign of this surface charge from one cell to another.

However, this has never been observed experimentally, and it is highly counterintuitive; we had to recognise that a model based only in a surface charge distribution was unable to properly describe the photovoltaic charge transport in z-cut $\text{LiNbO}_3\text{:Fe}$ crystals. The complete system of Kukhtarev equations (Eqs. 2.4-2.6) must be solved in order to obtain an appropriate space charge distribution capable to generate a homogeneous saturation electric field inside the crystal.

7.2 Finite element model implementation

It was said in the introduction that the solution of the complete system of Kukhtarev equations for z-cut crystals could have been done using a finite differences scheme, like the one previously developed by Arregui to solve x-cut configuration [29]. However, whereas for x-cut the problem can be considered 2D [27], calculating the photovoltaic transport in z-cut crystals requires a complete 3D discretization. We took this option into consideration, but it was discarded as it seemed unfeasible with our available resources, as explained in §5.2.1. Therefore, we decided to use a FEM commercial software, COMSOL Multiphysics®. The different steps of modelling our problem with COMSOL® are explained in this section. Note that most of this analysis can be also applied when using any other FEM software.

7.2.1 Geometry

The geometry is the physical entity where the equations are solved. It is made of different “domains”. The end of a domain or the intersection between two domains is called a “boundary”. In our case, there are two main domains: the $\text{LiNbO}_3\text{:Fe}$ crystal and a surrounding fluid, typically air or hexane.

As was the case when considering using a finite differences scheme, one of the biggest problems faced when applying FEM to Kukhtarev equations in z-cut is the high number of elements that are required. That is why symmetries are applied as much as possible in order to reduce the total number of elements. In this work, geometries (or models) are classified in three different groups or levels (Fig. 7.5):

- **2D:** for 1D light distributions in which the crystal can be supposed to be “infinite” in one direction. Examples: single slit, sinusoidal light distribution (§7.3.3).
- **2D axisymmetric:** a special case of 2D geometry for revolution illumination patterns. Examples: circular or gaussian spots (§7.3.1, §7.3.2) or Fresnel zone plates.
- **3D:** for arbitrary or periodic 2D patterns. Example: chequered illumination (§8.3.2).
- It can be seen in Fig. 7.5 that in every model there are two material domains: crystal (D1) and air —or hexane, for trapping simulations §8.4— (D2), as commented above. This is an important advance with respect to previous models, as none of them took into consideration the effect of the fluid surrounding the crystal on the electric field distribution, and thus on the photovoltaic charge transport.
- The different domain boundaries have been also labelled in Fig. 7.5. The crystal-air interface (B1) and the outer boundary (B2) are common to the three kinds of geometries, whereas periodic boundary (B3) and symmetry/revolution axis (B4) are specific of certain configurations.

Figure 7.5 Schematic of different geometries used in this work for performing the numerical calculations: (a) 2D periodic, (b) 2D axisymmetric and (c) 3D arbitrary geometry.

7.2.2 Physics

As explained in §5.5.1, in COMSOL® physical phenomena, i.e., the equations that describe them, are implemented through physic interfaces. These interfaces allow the user to introduce the equations and their initial and boundary conditions. In principle, nine equations are required to calculate the values of the nine dependent variables (n , N_A , N_D , J_X , J_Y , J_Z , E_X , E_Y , E_Z), but currently only seven equations have been presented (Eqs. 2.4-2.7)¹⁶. However, it will be soon demonstrated that the number of variables and equations can be reduced significantly.

First of all, let us pay attention to the electric field, as their equations apply on both crystal and air domains. In FEM, electric field is not computed directly but through a scalar variable, the electric potential (V):

$$\mathbf{E} = -\nabla V \quad (7.11)$$

Eq. 7.11 introduces a new variable (V) but also three more equations, as it is actually a vector equation. So we are facing a system of ten dependent variables and ten equations. However, it is possible to reduce this number.

¹⁶ Eq. 2.5 counts as two equations, as it includes the time evolution of N_A and N_D , and Eq. 2.6 is a vector equation with three components.

Recall Kukhtarev equations, that only apply to the LiNbO₃:Fe crystal (D1). Current density (Eq. 2.6) can be easily introduced into Eq. 2.4, removing in one step three equations and three dependent variables. In addition, using the relation $N_A = N - N_D$ (derived from Eq. 2.5) another variable and equation are gone. Finally, substituting the electric field by Eq. 7.11 in Eqs. 2.4 and 2.7 a system of only three equations and three variables (N_D, n, V) is obtained:

$$\frac{\partial n}{\partial t} = sIN_D - \gamma n(N - N_D) - \nabla \cdot (-\mu n \nabla V - D \nabla n + sIL_{PV} N_D \hat{\mathbf{u}}_{PV}) \quad (7.12)$$

$$\frac{\partial N_D}{\partial t} = -sIN_D + \gamma n(N - N_D) \quad (7.13)$$

$$-\nabla \cdot (\epsilon_0 \epsilon \nabla V) = q(N_D - N_{D0} + n) \quad (7.14)$$

Table 7.III Initial and boundary conditions for Eqs. 7.12-7.14. Boundaries are labelled according to Fig. 7.5. $\mathbf{D}$ is the dielectric displacement field, $\mathbf{D} = \epsilon \cdot \mathbf{E}$.

Equation	Initial conditions	Boundary conditions			
		B1 Crystal-air interface	B2 Outer	B3 Periodic	B4 Symmetric
7.12 Charge carriers (n)	$n = n_0$	$\hat{\mathbf{n}} \cdot \mathbf{J} = 0$	-	$n^{left} = n^{right}$	<i>Symmetry:</i> $n^{left} = n^{right}$ <i>Antisymmetry:</i> $n = n_0$
7.13 Donors (N_D)	$N_D = N_{D0}$	-	-	$N_D^{left} = N_D^{right}$	<i>Symmetry:</i> $N_D^{left} = N_D^{right}$ <i>Antisymmetry:</i> $N_D = N_{D0}$
7.14 Electric potential (V)	$V = 0$	$\hat{\mathbf{n}} \cdot \epsilon_0 (\mathbf{D}_{cry} - \mathbf{D}_{air}) = \sigma$ $\hat{\mathbf{n}} \times (\mathbf{E}_{cry} - \mathbf{E}_{air}) = 0$	$V = 0$	$V^{left} = V^{right}$	<i>Symmetry:</i> $\hat{\mathbf{n}} \cdot (\epsilon_0 \epsilon \mathbf{E}) = 0$ <i>Antisymmetry:</i> $V = 0$

All the other variables of interest ($N_A, \mathbf{J}$ and $\mathbf{E}$) can be derived from these three. COMSOL® has a predefined module for electrostatic calculations that includes Eq. 7.14. The other two must be introduced in the program as user-defined equations. Eqs. 7.12 and 7.13 (and their dependent

variables) are only defined in the crystal domain (D1), whereas Eq. 7.14 is defined in the whole simulation space (D1 and D2).

Initial values and boundary conditions for Eqs. 7.12-7.14 are listed in Table 7.III. Strictly speaking, Eq. 7.13 is an ODE and not a PDE, but the program computes better results if it is treated as PDE and periodic or symmetric boundary conditions are introduced when applicable. For the sake of completeness, boundary conditions for the crystal-air interface (B1) are shown for Eq. 7.12, although this condition has not to be introduced explicitly in the program as it is automatically fulfilled between elements.

7.2.3 Light profiles

Many different illumination profiles are studied in this work. Experimentally, most of them are generated with the SLM (§4.1.3c) and they are intended to be well-defined areas of light and darkness with sharp boundaries. However, no matter how well-adjusted the SLM setup is, there will be also a small transition zone between illuminated and non-illuminated areas plus a low background illumination. This relatively smooth transition between the illuminated and non-illuminated zones is actually good for the numerical resolution of Eqs. 7.12-7.14. If sharp light patterns are directly introduced in the simulation, they tend to produce numerical problems due to unrealistic charge accumulation in the light-darkness boundaries. So in order to avoid these numerical problems and to try to reproduce as much as possible the experimental conditions, binary light patterns are always smoothed and a background illumination (I_B) is introduced (see Fig. 7.6). The value of I_B is usually about 0.1% of the incident intensity (I_0).

On the other hand, there is another group of patterns, like a Gaussian beam or a sinusoidal light distribution, that do not require any special treatment from the point of view of numerical modelling, as their intensity gradients are smooth enough by themselves.

Finally, light absorption by the crystal has been also taken into account. Light absorption by the crystal is a parameter that has been always disregarded by previous models. At 532 nm (the only wavelength considered in this work), the absorption coefficient (α) of $\text{LiNbO}_3\text{:Fe}$ is directly

proportional to the donor concentration, being the photoionization cross-section the constant of proportionality:

$$\alpha = sN_{D0} \quad (7.15)$$

The intensity decay from the illuminated to the non-illuminated face is about 50% in a $\text{LiNbO}_3\text{:Fe}$ sample 1 mm thick with a typical doping (0.25 wt%Fe) and oxidation-reduction state ($r_{or} = 10$)

Considering the whole previous discussion, the light intensity at a particular point of the crystal produced by a static, arbitrary illumination distribution is:

$$I(x, y, z) = [I_B + I_0(x, y)]e^{-\alpha z} \quad (7.16)$$

where $z = 0$ is the illuminated surface of the crystal and $z = l_z$ the non-illuminated one. Absorption is particularly important when comparing the illuminated and non-illuminated faces of the crystal.

Figure 7.6 Comparison between a sharp and a smoothed light intensity profile.

Also note that lithium niobate has a relatively high refractive index (around 2.3), which will interact with the illumination beam. This high refractive index also results in a high coefficient of reflection (Eq. 4.7), so this phenomenon should be taken into account when comparing

experimental results and theoretical calculations. The reflected intensity in the lithium niobate-air interface is around 16% of the incident one (at 532 nm and normal incidence).

As final remark, it should be commented that there are two phenomena that have not been considered for the calculations. The first one is the multiple reflections of the incident beam inside the crystal. The second one is the photorefractive effect (§1.3.2), which can modify the intensity profile inside the crystal; however, in a first approximation, it can be neglected for z-cut samples, as the photorefractive effect is mostly along the c-axis, which does not strongly influence the light beam.

7.2.4 Meshing

As commented in §5.4.2, meshing is probably the most important step in FEM modelling. If the mesh is not properly defined, there is no possible way to obtain a correct solution. For the present case, there are some key points to take into account when meshing the geometry:

- **Debye length:** it is defined as $l_D = \sqrt{k_b T \epsilon_0 \epsilon_{33} / q^2 N_{A0}}$. This length represents the distance at which charges are screened, and it is around 2 nm for the usual set of parameters used in this work [23]. In principle, the mesh should resolve this length [17, 20]. However, this is not feasible for calculations involving macroscopic patterns of dozens or hundreds of microns, as the number of elements would be extremely high. Luckily, it was possible to overcome this requirement and use a mesh coarser than theoretically required based on a mesh convergence analysis (Appendix A).
- **Surface and bulk of the crystal:** the closer to the surface, the finer the mesh. Although we already know that there is space charge distributed in the bulk of the crystal, it is true that most of the charge accumulation occurs very close to the surface. In fact, in the analysis below (§7.3) a surface charge is considered. The definition of this surface charge can be also found in the mesh convergence analysis performed in Appendix A.
- **Illumination transition zones:** as commented above, the boundaries between illuminated and non-illuminated areas of the crystal are critical points where numerical

errors tend to appear. Transition zones should be fine meshed in order to avoid these problems.

- **Periodic boundaries:** for improved accuracy, it is also important to mesh carefully close to the boundaries where periodic conditions are set.
- **Infinite domains:** in order to avoid spurious results in the electric field calculation due to a small simulation domain, a special kind of element called “infinite element” is used for the four or five elements that are the closest to the outer boundary. In these elements, the coordinates are rescaled in order to simulate that the domain stretches out toward infinity or that it is much larger than it really is [20].

In addition, general rules of thumb related to meshing in FEM are also considered:

- Apply symmetry or periodic conditions when possible.
- Element growth rate¹⁷ should not be larger than 20%.
- Elements should have a low aspect ratio¹⁸ (<4). In this case, this is not always applied to the elements inside the crystal in order to reduce the number of elements where the main direction of the charge transport is known.

Fig. 7.7 shows an example of meshing for 2D and 3D geometries considering all the explained above. In all geometries, three different kind of mesh elements can be distinguished:

- Rectangular (hexahedron) elements for meshing the crystal in 2D (3D). This part of the mesh is structured. We also tried using triangular (tetrahedral) elements, but there were problems with charge density accumulation at random points due to an inappropriate description of the intensity distribution by the shape function.
- Triangular (tetrahedral) elements for meshing the surrounding medium. This part of the mesh is unstructured. In 3D, coupling between the prismatic elements of the crystal and the tetrahedral ones of the medium is made by means of pyramidal elements.

¹⁷ The difference in size between two neighbour elements.

¹⁸ The aspect ratio is defined as the longest dimension of an element divided by the shortest one.

- Quadrilateral (hexahedron) elements for the infinite domains. This part of the mesh is also structured.

Figure 7.7 Examples of meshes used for performing the numerical calculations. They are coarser than the actual ones in order to properly show the elements shape and distribution.

Regarding the shape functions, we used quadratic Lagrange shape functions (§5.4.3) for all the three dependent variables (N_D , n , V), although each variable could have been discretised with different shape functions.

Finally, recalling the rescaled coordinates of the infinite domains, we kept the predefined COMSOL® settings. These settings do not make these elements theoretically infinite. Instead they are stretched approximately 10^3 times their length, which is enough for our purposes and avoids numerical difficulties related to real infinite domains. Furthermore, the predefined stretching exhibits a $1/r$ decrease for the dependent variables defined in the element, where r is the distance from inhomogeneities. The only dependent variable defined in those domains is the electric potential (V), which precisely decreases as $1/r$.

7.2.5 Solver

It was commented in §5.5.2 that as we are solving a time dependent problem, COMSOL® applies the Method of Lines. This means that a FEM scheme is used to obtain the values of N_D , n and V at each time step and a numerical integration scheme is used to compute the time evolution.

As explained in §5.5.3, the direct solver PARDISO was the one chosen for solving the part related to the spatial discretization. PARDISO is a direct method for solving linear systems of equations, like the one that results from applying FEM (§5.4.1). Using this solver computation time is orders of magnitude lower than with the predefined one, MUMPS.

For temporal integration we selected the backward differentiation formula (BDF), which are a family of implicit methods for solving ODEs. The order of the scheme is automatically adapted by the software [20]. BDF is robust, but it tends to damp the solution, especially if the order of the method is low. In our case, we checked that the order is kept high and the solution behaves as expected, so in principle we do not have to worry about this issue.

BDF was chosen instead of more efficient iterative methods as it is especially appropriate for solving stiff systems. Although there is not a precise definition of stiffness in literature, the problem solved in §7.1 matches one of the descriptions of a stiff problem: “A linear problem is stiff if all of its eigenvalues have negative real part and the ratio of the magnitudes of the real parts of the largest and smallest eigenvalues is large” [4]. Also, some attempts of solving Eq. 7.6 by numerical methods instead of the analytic approach presented in §7.1 pointed toward that direction, as the solution exhibited an oscillatory behaviour dependent on the time step size. Although the system defined by Eq. 7.6 is not the same as the one made up by Eqs. 7.12-7.14, they certainly share the same origin and exponential behaviour. This suggests that the complete system is also stiff. Furthermore, another attempt to define a stiff problem is: “A problem is stiff if it contains widely varying time scales” [4], which also happens in our case, as time evolution of the free charge is much faster than that of the donor/acceptor concentration [23]. Finally, it is worth

mentioning that some attempts of solving a general case by iterative methods were made, but they were not successful.

7.2.6 Verification

When the flowchart of the numerical modelling was presented in §5.1, two concepts were defined: verification and validation. It has been stated that the analytical model shown in §7.1 was not validated by experimental results, mainly by the non-consistent result of charge inversion at the crystal surface.

Figure 7.8 Depiction of the parallel plate capacitor approximation.

In the case of the FEM model, the first step was to test it against a well-known benchmark solution: the parallel plate capacitor approximation (Eq. 5.2). In this configuration, the crystal is supposed infinite and illuminated with a homogeneous light intensity. For modelling, a 3D geometry with periodic boundary conditions has been used (see Fig. 7.8)¹⁹. To be faithful to the original problem, light absorption by the crystal was not taken into account in this particular case. The values of all crystal parameters have been taken from Table 2.I. Crystal thickness is $l_z = 0.5$ mm.

¹⁹ In fact, a simpler 2D geometry could have been done to simulate this particular illumination pattern. However, we were interested in test this more complicated case.

Time evolution of the surface charge density has been plotted in Fig. 7.9 together with the analytical simple solution (Eq. 5.3). In the light of the results, we can consider the model verified.

Figure 7.9 Comparison of the time evolution of the surface charge density between FEM and the simple models.

7.3 Analysis of basic illumination patterns

In this section, the FEM model developed in COMSOL® is used to study the photovoltaic charge transport in z-cut $\text{LiNbO}_3\text{:Fe}$ crystals illuminated with three different patterns: a single circle, a Gaussian spot and a sinusoidal periodic pattern. These three basic illumination patterns have been selected for their simplicity and wide use in practical applications of PVT [57, 65, 66]. The study is focused on the time evolution of the space charge distribution associated to each illumination pattern at the illuminated and the non-illuminated face of the crystal. The crystal is supposed to be in air and the values of the crystal parameters are those of Table 2.I, except when explicitly stated.

7.3.1 Single circle

Among all the possible illumination patterns, a single circular spot presents some features that make it interesting for a first analysis: it is simple, symmetric and its intensity distribution is homogeneous and has a well-defined limit. The crystal and light distribution are depicted in Fig. 7.10. The calculations are carried out for typical experimental parameters: a 0.5 mm thick z-cut $\text{LiNbO}_3\text{:Fe}$ crystal illuminated by a $\varnothing 250\ \mu\text{m}$ single circular spot ($I_0 = 160\ \text{W/m}^2$).

Figure 7.10 Schematic of a $\text{LiNbO}_3\text{:Fe}$ crystal illuminated by a circular light intensity profile indicating the coordinate system. Odd numbers correspond to the central axis of the cylinder defined by the illumination, whereas even numbers are placed at the transition zone between the illuminated and non-illuminated areas (see Fig. 7.6).

Attention has been paid to different variables in order to study the temporal distribution of the space charge and the electric field inside the crystal. The first one is the electric current (J), which has been evaluated at the six points labelled in Fig. 7.10. The components of the electric current parallel (J_z) and radial or transversal (J_R) to the c-axis are shown in Fig. 7.11. Note how the time evolution of each component is absolutely different. On the one hand, J_z follows an exponential decay law for all the six points:

$$J_Z = J_{Z0} e^{-\frac{t}{\tau_J}} \quad (7.17)$$

From Eq. 2.6 it can be deduced that the initial value (J_{Z0}) only depends on the local light intensity and the absolute concentration of donors, as at $t = 0$ both the drift and the diffusion current densities are null. However, looking at Fig. 7.11a it can be observed how the time constants value (τ_J) does not only depend on the local intensity and crystal doping but also on how close the point is to one of the crystal surfaces. Time evolution of the points that are at the surfaces is much faster than those at the centre of the crystal; even if at the centre the local intensity is higher than in the non-illuminated face, its evolution is noticeably slower.

Figure 7.11 Current components at different points in the crystal due to a circular light profile. Plots are labelled according to Fig. 7.10. (a) Current parallel to c-axis (b) Current perpendicular to c-axis.

On the other hand, Fig. 7.11b shows that the time evolution of J_R behaves in a completely different way. First, this component is null for the points belonging to the central axis of the illumination (points 1, 3, 5) due to the symmetry of the light pattern. Second, it is not monotonic: at the surfaces, it increases (in absolute value) until it reaches a maximum and then decreases; at the centre it has two relative maxima (again, in absolute value). As this component represents the migration of charge perpendicular to the c-axis, this behaviour leads to charge accumulation at the boundaries of the illumination pattern. Furthermore, the value of the integrals of J_R for points 2 and 6 are equal in absolute value, whereas the integral of J_R at the centre (point 4) equals zero.

This indicates that despite the different time evolutions of the illuminated and non-illuminated face, the total charge accumulation at saturation is antisymmetric about the central plane of the crystal. Moreover, note that it is at the centre of the crystal where the photovoltaic charge transport takes more time until it reaches saturation. Finally, it is worth remarking that J_R is lower but comparable to J_Z , i.e., the transversal current component (usually neglected) plays a relevant role in the charge transport dynamics.

The current density is directly related to the space charge accumulation at the surface and in the bulk of the crystal. Fig. 7.12 shows the space charge distribution after a couple of minutes of illumination and at saturation. Observe that at saturation there is space charge accumulation inside the crystal (at the edges of the illumination) and not only at the surface, as it has been always supposed by simpler models. This confirms the statement made in the last paragraph of §7.1: a surface charge distribution is not always a solution of the Kukhtarev equations for z-cut $\text{LiNbO}_3\text{:Fe}$. More precisely, it requires of space charge density accumulation in the bulk of the crystal at the boundaries of the illumination.

Figure 7.12 Space charge density distribution at two different illumination times due to a circular light profile.

However, as explained in Appendix A, we can still define a surface charge density (σ) at the crystal surface if we integrate the space charge density along a line perpendicular to the crystal surface. Thus, we can compare this with the simple model presented in §5.3 (Eq. 5.3), as shown in Fig. 7.13a. As for J_Z , the time evolution of the surface charge density also fits an exponential

decay function. Comparing both models, the value of τ for the FEM model increases by 43% respect to the simple one for the illuminated face and by 55% for the non-illuminated one.

In addition, lateral charge accumulation is most noticeable comparing the surface charge distribution early in the illumination and after a long time. Fig. 7.13b shows the surface charge density in the crystal at three different moments. For short times, charge distribution closely follows the illumination pattern, as the simplest models predict. However, for longer times, charge increases at the boundary more than in the centre of the pattern, resulting in peaks of surface charge density.

Figure 7.13 (a) Surface charge density time evolution due to a circular light profile at the centre of the illuminated area according to the simple and the complete FEM models. (b) Surface charge density at three different illumination times at the illuminated and non-illuminated faces. In grey the light intensity distribution.

The space charge accumulation at the boundaries between the illuminated and non-illuminated areas of the crystal is what compensates for the finite size of the crystal and the illumination, and produces a uniform electric field inside the material. This is better explained in Figs. 7.14a,d. They show the electric field distribution inside the crystal at two different times considering the charge distribution given by Eq. 5.3 (Figs. 7.14a,c) or the complete FEM model (Figs. 7.14b,d). The arrows point towards the local electric field direction, whereas the background colour represents the electric field Z component (E_z). Note how in Fig. 7.14d

(complete model) the electric field is homogeneous and equals the saturation one (417 kV/cm, Eq. 5.4) in the whole illuminated area of the crystal whereas in Fig. 7.14c (simple model) saturation value is only reached close to the surfaces.

Figure 7.14 E_z at the beginning of the illumination and at saturation according to (a, c) the simple and (b, d) the complete FEM models. Illumination profile is depicted above and below the plots. (e) Time evolution of E_z at 6 points of the crystal labelled according to Fig. 7.10.

It is worth mentioning that the internal electric field of the simple model shown in Fig. 7.14c very much resembles the complete model's solution at short illumination times (Fig. 7.14b). Actually, one important aspect of the temporal evolution of the electric field is the fact that the saturation field is first reached at the crystal surfaces and last at its centre (Fig. 7.14e). This is of special interest because for PVT trapping and manipulation the field that matters is the one at the surface, so there is no need for the crystal to be completely saturated to develop an electric field high enough for trapping particles.

Finally, Fig. 7.15 shows the radial component of the electric field (E_R). Observe the difference between Fig. 7.15a, in which E_R is not null inside the illuminated region at the surface, and Fig. 7.15b, where this component is almost zero in the illuminated region of the crystal at saturation. In both cases, its maximum value is comparable to E_Z .

Figure 7.15 E_R at the beginning of the illumination and at saturation according to the complete FEM model. Illumination profile is depicted above and below the plots.

7.3.2 Gaussian beam

The next illumination pattern is a Gaussian beam profile, like the one described by Eq. 7.18:

$$I_0(r) = I_p e^{-\frac{r^2}{2\sigma_G^2}}, \quad (7.18)$$

where I_p is the peak intensity and σ_G the beam radius. This light profile is of special importance because it is the most common laser beam shape, so it is likely to be used in different kinds of experiments. In this section, a $I_p = 7.64 \text{ W/cm}^2$, $\sigma_G = 7 \text{ μm}$ beam has been studied.

Figs. 7.16a,b show the resulting space charge density distribution at two different illumination times. As it happened in the previous case, for short times almost all the space charge is concentrated at the crystal surfaces, whereas for long times there is also space charge accumulation inside the crystal. However, in this case the space charge accumulated far from the surface is less localised than in the case of a circular spot (Fig. 7.12), probably due to the smooth intensity gradient of the Gaussian beam profile. For the same reason, the peak of surface charge that appears in Fig. 7.16c is broader but also lower than in the case of circular illumination.

Figure 7.16 (a, b) Space charge density at two different illumination times due to a Gaussian beam light profile. (c) Surface charge density at three different illumination times at the illuminated and non-illuminated faces. In grey the light intensity distribution.

Observe that the space charge density extends a few times σ_G relatively soon. When surface charge density peaks start to occur, an “influence radius” can be defined as the distance between the centre of the Gaussian beam and the point where surface charge density is maximum (Fig. 7.17). This radius increases with time, although its growth rate decays exponentially due to the very low light intensity of the Gaussian tails. Providing the beam has not been stopped by any

previous optical element, space charge would increase indefinitely until it reaches the end of the crystal so, strictly speaking, one cannot talk about “saturation”; however, for practical purposes, a “virtual influence radius” can be defined as the influence radius at a sensible exposure time (around 15 minutes) at usual intensities. This radius depends on σ_G and I_p , and it is different for the illuminated and the non-illuminated face.

Figure 7.17 Distance from the centre of the Gaussian at which the maximum surface charge density occurs (influence radius) for three different light peak intensities.

Regarding the internal electric field distribution, its time evolution is very similar to that of the circular illumination profile (Fig. 7.18).

Figure 7.18 E_z (left) and E_R (right) at three different illumination times due to a Gaussian beam light profile. Illumination profile is depicted above and below the plots.

7.3.3 Sinusoidal light profile

The last light profile analysed in this chapter is a periodic sinusoidal light illumination, like the one obtained by two-beam interference (§4.1.3b). The intensity profile is repeated here for the sake of clarity:

$$I_0(x) = I_m \left[1 + m \sin\left(\frac{2\pi}{\Lambda} x\right) \right] \quad (7.19)$$

In this section, a sinusoidal grating of period $\Lambda = 100 \mu\text{m}$, modulation $m = 0.95$ and mean intensity $I_m = 1250 \text{ W/m}^2$ was analysed.

Regarding the space charge distribution, there is no space charge accumulation in the bulk at any time, probably due to the smooth light profile and its periodicity. The surface charge density peaks associated to the transversal charge transport are low, and the model predicts a homogeneous surface charge density for long illumination times (Fig. 7.19). The evolution of the internal electric field is similar to the previous patterns, although much more homogeneous (Fig. 7.20). The reason can be found again in the light profile. Another important difference is the fact that the transversal component of the electric field (E_x) is significantly lower. In fact, this component is null at saturation, precisely because the surface charge density is homogeneous.

Figure 7.19 Surface charge density at three different times due to a sinusoidal light profile according to the simple and the complete FEM models at the (a) illuminated and (b) non-illuminated faces. In grey the light intensity distribution.

Figure 7.20 E_z (left) and E_R (right) at three different illumination times due to a sinusoidal light profile. Illumination profile is depicted above and below the plots.

7.4 Role of doping, crystal thickness and pattern size

As it was explained in §2.2 and §5.3, it is well-known that some crystal parameters have a key influence in the magnitude and time evolution of the photovoltaic effect in $\text{LiNbO}_3\text{:Fe}$. It was also commented that light intensity and illumination time play interchangeable roles, so their product can be considered as a single variable (light exposure) for a certain range of intensities. However, there are other parameters that have not received so much attention in the literature, like illumination and pattern size, crystal thickness and light absorption. The first two were partially considered as a single variable by Arregui *et al.* in [28] but the influence of absorption has not been reported yet.

7.4.1 Light absorption and crystal thickness

A great variety of doping levels and oxidation-reduction ratios can be found in the samples used for conducting PVT experiments [57, 68, 93, 128, 182]. Experimentally, it has been found a minimum electric field required for trapping particles [147] and as it is known that the value of the saturation electric field is proportional to the absolute concentration of acceptors in the crystal (Eq. 5.4), it seems interesting to study the time evolution of the crystal electric field as a function of the doping and the oxidation-reduction ratio. Simple models predict a direct dependence of τ on the oxidation-reduction ratio (Eq. 5.3); however, it has been demonstrated in §7.3.1 (circular illumination) that this relation is not accurate, as absorption slows down the process in the whole crystal, especially at the non-illuminated face.

Fig. 7.21 shows τ as a function of the reduction-oxidation ratio for two different crystals 0.5 mm and 1 mm thick²⁰. The rest of the crystal and illumination parameters are those of §7.3.1 (circular illumination). As the absorption coefficient is directly proportional to the absolute donor concentration (Eq. 7.15) and the iron concentration is fixed, the higher the reduction-oxidation

²⁰ The value of τ has been calculated using the time evolution of the current density parallel to the c-axis (J_z see Fig. 7.11), as $\tau \approx \tau_J$.

ratio, the higher the absorption. The value of τ is represented for three different points of the crystal in the central axis of the illumination (points 1, 3, 5 from Fig. 7.10).

Figure 7.21 Time constant (τ) as a function of the oxidation reduction ratio for two different crystals (0.5 mm and 1 mm thick) with a total Fe concentration $N = 0.1$ wt%Fe. Point labels are referred to Fig. 7.10.

On the one hand, the plots for both crystal thicknesses almost match for the illuminated face, so one can conclude that light absorption by the crystal has little influence in the time evolution of that face (points corresponding to the illuminated face of each sample do not fit, but the difference is almost imperceptible.). On the other hand, light absorption is very important for the non-illuminated face. Although at first τ decreases when increasing the donor concentration, above a certain value it starts to grow. For highly reduced crystals, τ in the non-illuminated face is even higher than in the centre. Also note that thicker crystals are related to larger values of τ at the centre of the crystal, even at low donor concentrations, in which absorption could almost be neglected.

Moreover, in Fig. 7.21 an analytical expression of τ has been also plotted:

$$\tau = \frac{\epsilon_0 \epsilon_{33} \gamma}{\mu q s I} \left(\frac{N}{N_{D0}} - 1 \right) e^{s N_{D0} z} \quad (7.20)$$

This equation can be obtained introducing absorption (Eq. 7.15) in the definition of τ (Eq. 5.3) and substituting N_{A0} for $N - N_{D0}$. It relates the value of τ to the local light intensity at the crystal surfaces when absorption is considered. Note how Eq. 7.20 fits relatively well for both crystal surfaces. Although it underestimates the value of τ , it can be used for obtaining a first approximation. In all cases However, Eq. 7.20 is not valid for the crystal centre. If it were so, the plot for the centre (point 3) of the 1 mm thick crystal would match the graph of the non-illuminated face (point 5) of the 0.5 mm crystal, and it does not. This confirms that the time evolution of the electric field at the crystal centre cannot be described by simple models.

7.4.2 Pattern size and crystal thickness

It has been shown that an accumulation of space charge is produced in the limits of the illumination. This charge is responsible of compensating the finite size of the crystal and the light pattern in order to reach the saturation electric field through all the crystal thickness. It has been also shown that the sharper the illumination profile, the higher and more concentrated the space charge accumulation.

It seems reasonable to assume that the size of the pattern and the thickness of the crystal have some influence in this effect. Again, to perform the study we use the circular light profile analysed in §7.3.1. Fig. 7.22 shows the increment in surface charge at the centre (Fig. 7.22a) and boundary (Fig. 7.22b) of the illumination for different pattern sizes and crystal thicknesses, taking as a reference the case with the largest pattern ($\varnothing 300 \mu\text{m}$) and the thinnest crystal ($l_z = 0.25 \text{ mm}$). It can be seen how the thicker the crystal or the smaller the pattern, the higher the surface charge. This result was also described in [28], although they obtained a larger variation of the surface charge density with the crystal and pattern size. Note that the increase is larger for the charge peak in the boundary than for the charge in the centre. Again, this is because this charge at the boundary have to compensate the finite size of the illumination and the crystal.

Figure 7.22 Surface charge density increment at (a) the centre and (b) the boundary of the illumination as a function of the crystal thickness and circle diameter. The case with the largest pattern ($\varnothing 300 \mu\text{m}$) and the thinnest crystal ($l_z = 0.25 \text{ mm}$) has been taken as reference.

At first sight, this slight variation in the surface charge may not seem important. For example, it is not relevant when performing a pure PVT experiment and the crystal is saturated, as the electric field at the surface, which is the one that matters, is the same regardless the size of the crystal or the pattern. However, the 5-10% increase can become important in terms of coupling

with other effects if the interaction depends on the absolute value of the surface charge density. Two examples of this situation are the pyroelectric effect (§10.2) [147] and the particle charging (§8.3).

7.5 Analysis and conclusions

In this chapter, the FEM model used to solve the Kukhtarev equations in z-cut $\text{LiNbO}_3\text{:Fe}$ crystals has been explained in detail and applied with three different illumination patterns. We decided to use FEM after realising that simple models that only consider surface charge density accumulation in the crystal cannot produce a homogenous electric field in the bulk. Therefore, the FEM model developed in this chapter allows space charge density accumulation through all the crystal thickness. This model also deals with the current density components perpendicular to the c-axis and light absorption by crystal, for the first time in a z-cut model.

During FEM model development, special care was taken in reducing the number of elements and dependent variables (i.e., the degrees of freedom of the system). The mesh was also carefully designed, as some parts of the geometry require a very fine meshing and certain elements in order to achieve proper solutions. The model was verified against the parallel plate capacitor approximation shown in §5.3, with excellent results.

The first illumination pattern that has been analysed was a circular light profile, as the most relevant physical phenomena can be explained using this simple pattern. It was found that the time evolution of the components of the current density parallel (J_Z) and perpendicular (J_R) to the c-axis is completely different. Whereas J_Z starts from a maximum and has an exponential decay-like evolution towards zero, J_R increases from zero to a maximum and then decreases as the crystal saturates. The time evolution of J_R in the central plane of the crystal is noteworthy, as it changes its sign in order to reach zero space charge accumulation in the central plane of the crystal at saturation. The results also show that the magnitude of J_R is lower but comparable to J_Z .

Our hypothesis of space charge accumulation in the bulk was confirmed by the model: peaks of space charge appeared localised in the boundaries of the illumination. This space charge distribution is responsible for the homogeneous saturation electric field in the whole illuminated volume of the crystal. Surface charge density peaks also appeared at the edges of the light profile for the same reason. Nevertheless, the saturation electric field is almost always reached at the crystal surfaces long before its whole volume is saturated. This is important for PVT operation, as the electric field that matters is the one on the surface.

The other two analysed patterns (Gaussian beam and periodic sinusoidal intensity distribution) showed a similar behaviour in terms of internal electric field evolution. However, their smooth light profile caused the space and surface charge density peaks to be lower in magnitude and less localised than those of the circular illumination. In fact, in the case of the sinusoidal intensity distribution there was no internal space charge distribution at all. This makes sense if one considers the sinusoidal distribution as a special case of the parallel plate capacitor: an infinite crystal completely illuminated. Although the time evolution is different, the final charge distribution it is not. In a real, finite crystal probably there is charge accumulation at the edges of the sample.

As stated above, the influence of light absorption has been studied for the first time. Calculations showed that absorption is responsible of increasing the time constant (τ) of the non-illuminated face of the crystal but that it has little influence on the illuminated face. Nevertheless, in both faces the values of τ obtained with the simple analytical model are lower than FEM predictions. This is critical for experimental applications, as the differences between models are of the order of typical illumination times (minutes). If the non-illuminated face is the one of interest (e.g., due to the experimental setup, see [57]), the simple model predictions can be extremely inaccurate.

In view of the results of this chapter, simple approximations for z-cut charge transport can be used only for small values of light exposure. For medium and high values, the components of the current density perpendicular to the c-axis become important and play a major role in the migration and accumulation of charge at the illumination boundaries. In fact, simple models tend

to be more accurate when used with light patterns with a smooth intensity profile, as this charge-accumulation phenomenon is not so strong.

According our study, the influence of the crystal and pattern sizes in the space charge distribution is limited. Although the surface charge increases with smaller patterns and thicker crystals, this difference is not relevant for most common applications. However, it should be taken into account when the interaction with other charge-dependent phenomena (like the pyroelectric effect) are required.

Note that within a certain range of intensities the product of light intensity and illumination time is a single variable, the light exposure (§2.1). This means the calculations performed with this model using a particular intensity value can be easily compared with other intensities by just adjusting the time scale accordingly. This remark is important for avoiding unnecessary calculations of large models with many elements.

In addition, as there is evidence that suggests that there is a minimum electric field required for trapping particles [147], this FEM model is very useful for the design of experiments. It can be used to know *a priori* whether or not a crystal can develop an electric field high enough for particle trapping and if it does, the required value of light exposure.

Finally, as mentioned in the introduction of this chapter, the results presented above are used in the following chapters to calculate the DEP and EP forces exerted on the particles during PVT operation and their corresponding potential energies.

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CHAPTER 8

Nanoparticle patterns obtained by dielectrophoretic and electrophoretic forces

This chapter is dedicated to the characterisation and analysis of various experimental patterns obtained by PVT on top of z-cut $\text{LiNbO}_3\text{:Fe}$ samples. In the first section, the most important forces that affect a nanoparticle inside a fluid that is being manipulated by dielectrophoresis are explained and their order of magnitude is compared. Then, different NP patterns obtained by dielectrophoresis are shown and the main features of this kind of particle trapping are analysed. The influence of some experimental parameters is also studied in pursuit of pattern optimization and the obtention of *ad hoc* structures. The FEM model developed in the previous chapter is used to understand these structures through calculations of the dielectrophoretic potential energy profiles.

The next section is dedicated to the comparison of patterns obtained by electro- and dielectrophoresis (EP and DEP). The possibility of patterning and trapping charged and neutral particles increases the versatility and potential applications of PVT, so it is interesting to study the differences of DEP and EP patterns in terms of particle density distribution and fidelity to the original light profile.

Finally, there is a brief demonstration of the COMSOL® Multiphysics capabilities to reproduce experimental NP patterns through particle dynamic simulations.

8.1 Forces acting on nanoparticles

As explained in §4.1.4, the most common way to approach the NPs to the crystal surface during PVT operation is introducing the crystal in a liquid suspension that contains the particles or placing a droplet of that very suspension on the crystal surface. This way, NPs are not only subjected to dielectrophoretic forces but to a variety of hydrodynamic forces illustrated in Fig. 8.1 and analysed below. The order of magnitude estimates is made considering the crystals, aluminium nanoparticles and ambient conditions that are typically used in our experiments (see again §4.1.2 and Table 8.I). Note that the electrophoretic force is not considered in this section, as a thorough analysis of this force is made in §8.3.

Table 8.I Physical properties of the suspensions (particles and solvent medium) used in this work.

Parameter		Value
Particles (spherical clusters of Al NPs)	Radius (r)	0.25 μm
	Density (ρ_p)	2700 kg/m ³ [159]
	Conductivity (ζ_p)	37.7 MS/m [159]
Medium (hexane)	Density (ρ_m)	678 kg/m ³ [10]
	Dynamic viscosity (η)	0.3131 mPa·s [8]
	Relative permittivity (ϵ_m)	1.9 [132]
	Conductivity (ζ_m)	10 pS/m [15]
Gravitational acceleration (g)		9.81 m/s ² [96]

Figure 8.1 Forces acting on a neutral nanoparticle immersed in a fluid and subjected to an electric field: buoyancy (F_B), gravity (F_G), drag (F_D), Brownian motion (F_{Br}) and dielectrophoresis (F_{DEP}).

8.1.1 Buoyancy and gravity

The most obvious forces exerted on a particle immersed in a fluid are buoyancy and gravity. For a spherical particle, these forces are [121]:

$$F_B + F_G = \frac{4\pi r^3}{3}(\rho_p - \rho_m)g \quad (8.1)$$

They are proportional to the volume of the particle, so for our NP clusters its magnitude is expected to be small. Using the parameters in Table 8.I we obtain an order of magnitude of $F_B + F_G \sim 10^{-15}$ N.

8.1.2 Drag

Drag forces reduce the velocity of the particles in a fluid. Assuming a laminar flow in a incompressible, Newtonian fluid, the drag force on a sphere can be calculated using the Stoke's law [121]:

$$F_D = 6\pi\eta r(v_m - v_p) , \quad (8.2)$$

where are the $\mathbf{v}_m$ medium and $\mathbf{v}_p$ particle velocities respectively. We consider the medium to be at rest, so $\mathbf{v}_m = \mathbf{0}$. From Eqs. 8.1 and 8.2 the terminal or settling velocity of the particles in the suspension can be obtained. In our case, this velocity is around 1 $\mu\text{m/s}$.

8.1.3 Brownian motion

The Brownian motion is the random movement of particles suspended in a fluid due to collisions with the fluid molecules [121]. The Brownian force exerted on a particle during a period of observation Δt can be approximated to:

$$\mathbf{F}_{Br} = \xi \sqrt{\frac{12\pi k_B T \eta r}{\Delta t}} , \quad (8.3)$$

where ξ is a Gaussian random number with a zero mean and unit standard variation; independent values for ξ have to be chosen in all the three spatial directions [106]. In order to overcome the Brownian motion and move a particle in a deterministic manner, the DEP or EP forces must be greater than $\mathbf{F}_{Br}$. For $\Delta t = 10 \text{ s}$ (the order of magnitude of a typical deposition time) and our experimental parameters, $F_{Br} \sim 10^{-15} \text{ N}$.

Although this force scales with the square root of the radius of the particle, the particle mass is proportional to the third power of the radius, so the particle acceleration is inversely proportional to $r^{5/2}$. This means that the smaller the particle, the larger the importance of the Brownian motion.

8.1.4 Dielectrophoretic force

This is the most important force, as it is the responsible of the final particle distribution. If DEP force is not high enough, particles will move to unintended locations or they will not even move at all [121]. Its expression was deduced in §3.1.2 and it is repeated here for the sake of clarity:

$$\mathbf{F}_{DEP} = 2\pi r^3 \epsilon_m f_{CM} \nabla |\mathbf{E}_{ext}|^2 , \quad (8.4)$$

Supposing $f_{CM} \sim 1$ and $\nabla|\mathbf{E}_{ext}|^2 \sim 10^{18} \text{ N}^2\text{m}^{-1}\text{C}^{-2}$ (obtained through COMSOL® calculations), the DEP force on our particles is $F_{DEP} \sim 10^{-12} \text{ N}$, which is three orders of magnitude larger than all the previous forces. As is F_{DEP} the largest force, this means that F_D should be equated to it, and thus the terminal velocity when particles are subjected to DEP forces is around 1 mm/s.

8.2 Main features of dielectrophoretic trapping

This section is dedicated to the analysis of the main features that appear in patterns obtained by PVT using neutral particles. Although the statement made in §6.2 is still true and DEP patterns made on z-cut substrates can be a faithful representation of the illumination profile, the DEP potential distribution and the particle-particle interaction produce some side effects in the final particle arrangement that deserve some attention. Note that most of the patterns shown here are limiting cases used to illustrate particular features. All of them were made on z-cut crystals with 0.25 wt%Fe.

The first pattern to be analysed is a single square illumination or “pixel” which side is 1.8mm long (Fig. 8.2). The experimental parameters are listed in Table 8.II. Fig. 8.2a shows a photograph of the whole pattern on the illuminated face and Fig. 8.2b on the non-illuminated one. Observe that in both faces there is a halo without particles all around the squares that extends for around a 120µm from their sides. Further from the square, there is uniform trapping for around half millimetre.

A closer look to the patterns reveals that the particle distribution in each case is very different (Figs. 8.2c,d), except for the long chains of particles that are distributed across the halo between the square and the uniform trapping area. On the one hand, the square on the illuminated face is completely covered by a thick layer of nanoparticles. Also note that most of the particles of this layer are arranged as chains pointing towards the square sides, whereas the particles on the other side of the halo are basically isolated clusters. On the other hand, on the non-illuminated face particles are concentrated on the sides of the square. In addition, the few particles inside the square do not exhibit any kind of structure.

Table 8.II Experimental parameters used to make the patterns shown in Fig. 8.2.

	Parameter	Value
Illumination (532 nm)	System	SLM
	Incoming intensity	1.55 mW/cm ²
	Exposure time	10 min
	Pattern	Single square (side 1.8mm long)
Suspension (Hexane + Al NPs)	Concentration	46 mg/L
	Immersion time	30 s
Crystal	Thickness	1 mm

Figure 8.2 Single square pattern made of Al NPs. (a, c) Illuminated face. (b, d) Non-illuminated face. The experimental parameters are listed in Table 8.II.

The explanation for these features can be found in the dielectrophoretic potential energy and forces outside the crystal. Fig. 8.3 shows them at the illuminated and non-illuminated face from two different perspectives: parallel to the crystal surface at 10 μm from the sample (Figs. 8.3a,c),

and perpendicular to the crystal, crossing the square centre and parallel to one of its sides (Figs. 8.3b,d). They have been calculated using the FEM model analysed in the previous chapter.

Note the difference in DEP potential energy magnitude between the illuminated and non-illuminated face. The fact that they are different reveals that the crystal has not saturated for the light intensity and exposure time chosen. Although DEP potential energy distributions are similar and their minima are located at the square sides, the absolute value in the non-illuminated face is one order of magnitude lower than in the illuminated one, as the space charge density is also lower due to light absorption (recall the analysis made in §7.3). In a similar manner, DEP force is also lower (Figs 8.3e,f). This explains why in the non-illuminated face particles are only at the square sides: it is simply where DEP force is high enough to trap them. Note that this means that some failed experiments reported in the literature may have their origin in inappropriate exposure times or intensities.

The halo without particles around the square is also related to the strong DEP potential minima at the edges of the light pattern. Figs. 8.3a,b show the potential energy and force for the illuminated face. While inside the square there is an important component of the DEP force that is perpendicular to the crystal surface, outside the illumination the force is more parallel to it. This way, particles that are initially “above” the square are trapped inside it, and those that approach from “outside” the illumination are attracted to the illuminated area. The halo is the region where DEP forces are strong enough to introduce the NPs into the square, and thus this area remains locally empty. The particle chains in the halo are made of those particles that reached the crystal in the middle of this process, probably because they were initially close the surface. The same applies to the non-illuminated face, but in this case, as the forces are lower due to the lower light exposure, the halo is less defined, and the number of NP chains inside it increases.

DEP potential

Illuminated

Non-illuminated

DEP force

Illuminated

Non-illuminated

Figure 8.3 Dielectrophoretic potential and force calculations due to a single square light distribution on (a, b, e) the illuminated face and (c, d, f) the non-illuminated one. (a, c, e, f) are calculated at $10 \mu\text{m}$ from each crystal surface. The arrows indicate the direction of the DEP force. In (b,d) illumination profile is depicted above and below the plots. The parameters for the simulation were taken from Table 8.II.

8.2.1 Particle-particle interaction

NP particle chains are related to the particle-particle interaction, as explained in §3.1.4. Their orientation is not determined by the direction of the DEP force but by the electric field. However, as shown in Fig. 8.4, for the case above, the direction of both almost match. Note that where the electric field is stronger (areas 1, 2 and 5 from Fig. 8.4) particles form chains orientated with the local field, whereas where it is lower (areas 3, 4, 6) particles are trapped as independent clusters.

Figure 8.4 Electric field modulus at 10 μm from the crystal surfaces. The arrows indicate the direction of the electric field. Each calculation has three numbered zones: (1, 4) centre of the light pattern, (2, 5) edges of the illumination, (3, 6) area far away from the illumination. The parameters for the simulation were taken from Table 8.II.

In fact, dielectrophoretic chains appear in almost all DEP patterns, giving them a particular texture (as shown above) or even modifying the pattern itself. Look at Fig. 8.5, where a fringe pattern is shown (experimental parameters in Table 8.III). Particle chains arise from the fringes at regular intervals. Observe that the angle of these branches depends on their position: on the left side of Fig. 8.5a the angle between the chains and the fringes is the largest but on the right side of the image there are virtually no chains, as they are almost parallel to the fringes.

Figure 8.5 Periodic fringes made of Al NPs. (a) General view of the pattern and two insets showing the different orientation of the particle chains inside the sample and close to the edge. The experimental parameters are listed in Table 8.III. (b) DEP potential energy due to a sinusoidal light distribution at 10 μm from the crystal surface. The arrows indicate the direction of the electric field. The parameters for the simulation were taken from Table 8.III.

Table 8.III Experimental parameters used to make the pattern shown in Fig. 8.5.

	Parameter	Value
Illumination (532 nm)	System	Two-beam interference
	Incoming intensity	40 mW/cm ²
	Exposure time	10 min
	Pattern	Sinusoidal ($\lambda = 30 \mu\text{m}$, $m = 0.95$)
Suspension (Hexane + Al NPs)	Concentration	670 mg/L
	Immersion time	1 min
Crystal	Thickness	1 mm

This clear example reveals the influence on the final particle distribution of the pattern position on the sample. In this case, the edge of the sample matches the right side of the image, whereas the left side is closer to its centre. Fig. 8.5b shows the calculated DEP potential energy and the direction of the local electric field. As the electric field tends to be perpendicular to the closest edge of the sample, in this case chains spread at the crystal centre and “disappear” at the sample edge. The fairly homogeneous separation of the chains is also caused by the particle-particle interaction (chains repel each other, see §3.1.4) and this feature should be taken into account when small motifs are patterned. In fact, this structure very much resembles other structures obtain by DEP forces using different techniques [42].

Table 8.IV Experimental parameters used to make the pattern shown in Fig. 8.6.

	Parameter	Value
Illumination (532 nm)	System	Two-beam interference
	Incoming intensity	40 mW/cm ²
	Exposure time	10 min
	Pattern	Sinusoidal ($\lambda = 40 \mu\text{m}$, $m = 0.95$)
Suspension (Hexane + Al NPs)	Concentration	20 mg/L
	Immersion time	1 min
Crystal	Thickness	1 mm

Figure 8.6 Periodic fringes made of scattered Al NP clusters. The experimental parameters are listed in Table 8.IV.

If the particles (or particle clusters) are comparable in size with the pattern motifs, the particle-particle repulsion makes difficult to obtain a continuous pattern (Fig. 8.6, experimental parameters in Table 8.IV). One way to alleviate this effect is increasing the particle concentration of the suspension. However, this also increases the probability of cluster formation.

8.2.2 Edge enhancement effect

There is another typical DEP patterning feature that has been briefly presented above but deserves further attention as it appears in most patterns made of neutral particles. It is the “edge enhancement effect” of the motifs.

When the DEP potential energy distributions of the illuminated and non-illuminated faces were compared in Fig. 8.3, it was said that in both cases the potential minima were located at the edges of the square. This is not a distinctive feature of this pattern; in fact, in almost every pattern the absolute potential energy minimum is located at the outermost edge of the motif or, if the pattern covers the whole crystal, at the very sample end. The physical explanation is evident: those are the boundaries of the charged regions themselves, so the electric field gradient is the highest there. This phenomenon can affect the intended particle distribution, as even if the light intensity profile is homogeneous, the final particle concentration may be larger at the edges of the motifs

(local edge enhancement, examples are shown below and in the next section, Fig. 8.11) or even the very sample edges (global edge enhancement, Fig. 8.7, experimental conditions in Table 8.V).

Table 8.V Experimental parameters used to make the pattern shown in Fig. 8.7.

	Parameter	Value
Illumination (532 nm)	System	SLM
	Incoming intensity	20 mW/cm ²
	Exposure time	10 min
	Pattern	Chequered pattern (square side 240 µm long)
Suspension (Hexane + Al NPs)	Concentration	30 mg/L
	Immersion time	1 min
Crystal	Thickness	1 mm

Figure 8.7 Chequered pattern made of Al NPs. The edges of the sample are brighter because there is a higher particle density than in the centre. The experimental parameters are listed in Table 8.V.

An extreme example of this edge enhancement effect is shown in Fig. 8.8 (experimental parameters in Table 8.VI). In this case, the edge enhancement due to the finite size of the light motif (periodic fringes) and the crystal appear simultaneously and produce a distortion of the intended pattern. Observe the evolution of the fringes definition from left to right: (1) first, close to the sample edge, particles are trapped only on the left side of the fringes; (2) then, left and right

edges are defined as the pattern gets into the sample; (3) finally, the fringe is filled with particles (3).

Table 8.VI Experimental parameters used to make the pattern shown in Fig. 8.8.

	Parameter	Value
Illumination (532 nm)	System	SLM
	Incoming intensity	16 mW/cm ²
	Exposure time	13 min
	Pattern	Sinusoidal ($\lambda = 33 \mu\text{m}$, $m = 0.95$)
Suspension (Hexane + Al NPs)	Concentration	80 mg/L
	Immersion time	30 s
Crystal	Thickness	1 mm

Figure 8.8 Periodic fringes made of Al NPs. Illumination profile is depicted above the pattern. Note the gradual change in the pattern definition from left to right. The experimental parameters are listed in Table 8.VI.

Particle concentration in the suspension can also modify this phenomenon to some extent. In fact, particle concentration cannot be addressed independently from immersion time, as increasing immersion time can produce similar results as increasing particle concentration in the suspension. However, experimentally it has been found that it is easier to fix immersion time and modify the particle concentration than the other way around. Fig. 8.9 shows three patterns made with the same crystal and illumination parameters but three different suspensions with different nanoparticle concentrations (Table 8.VII). In the case low NP concentration (Fig. 8.9a) particles

are trapped only at the circles' circumferences; for medium concentrations (Fig. 8.9b) the circles are completely filled, but the particle density is higher at the circumferences; finally, when the suspension with the highest NP concentration is used (Fig. 8.9c) the particle density of the resulting pattern is the same in the whole circle. Furthermore, in this last case the texture of the pattern reveals a high density of dielectrophoretic chains, related to the high concentration of particles in the suspension.

Table 8.VII Experimental parameters used to make the patterns shown in Fig. 8.9.

	Parameter	Value
Illumination (532 nm)	System	SLM
	Incoming intensity	1 mW/cm ²
	Exposure time	20 min
	Pattern	Array of circles (Ø250 µm)
Suspension (Hexane + Al NPs)	Concentration	10-40-200 mg/L
	Immersion time	40 s
Crystal	Thickness	1 mm

Figure 8.9 Arrays of circles made of Al NPs. They were made using suspensions with different particle concentration: (a) 10 mg/L, (b) 40 mg/L, (c) 200 mg/L. The experimental parameters are listed in Table 8.VII.

Nevertheless, for certain sets of experimental parameters, local and global edge enhancement effects can become almost unnoticeable, as it happened in the square pattern shown at the beginning of this section (Fig. 8.2a) or the large chequered pattern shown in Fig. 6.5.

8.3 Electrophoretic trapping

Based on the few available studies on the subject [108, 131], patterns obtained by electrophoresis are expected to exhibit different features than those obtained by dielectrophoresis. Exploring the differences between both configurations is interesting not only to understand the patterns made of naturally electrically charged objects (such as DNA and other biological or inorganic particles), but also to increase the patterning possibilities and versatility of PVT, as some particles (like our Al NPs) can be used both electrically neutral or charged.

8.3.1 Particle charging mechanism

Over the course of this thesis work, it was found that after using a particular suspension of aluminium NPs in hexane for several trapping experiments, sometimes the resulting patterns were different than expected. Particles were trapped in less defined, fading shapes. In principle, this behaviour could be addressed to multiple causes: experimental variability, pollution of the suspension by external agents or the simple fact that there were very few particles available in the suspension. However, when this happened, a particular feature also appeared: patterns were obtained only on one of the two z-cut crystal faces. As sometimes the face was the non-illuminated one, the reason could not be the lower electric field associated to this face. A very reasonable explanation was that the particles were electrically charged.

In order to check the charge state of the particles we developed a simple system based on x-cut crystals and the single slit illumination profile (§4.1.3a). Charge accumulation in x-cut crystals under this light pattern was sketched in Fig. 6.1. The result is two well-defined strips of positive and negative charge.

Figure 8.10 Comparison between DEP and EP patterning on x-cut $\text{LiNbO}_3\text{:Fe}$ samples after single slit illumination. (a) DEP and (b) EP potentials at different heights from the crystal surface. (c) Illumination profile. Experimental patterns made of (d) neutral or (e) charged Al NPs.

EP and DEP potentials for x-cut crystals and this illumination profile are shown in Figs. 8.10a,b. DEP potential is symmetric and has two well-defined potential minima, whereas EP potential is clearly antisymmetric, with a single potential minimum. This means that neutral particles are expected to be trapped in two parallel strips at the edges of the illumination whereas charged particles should trap in a single line at the maximum or minimum of EP potential, depending on the sign of their charge.

We performed this simple test with the suspensions that were apparently charged and new ones that were used as control (Figs. 8.10d,e). As expected, a single line of particles was obtained with the former and two parallel strips of NPs were trapped with the latter. Thus, we confirmed that the nanoparticles can acquire charge.

The next step was identifying the sign of the NP charge. We measured the direction of the c-axis in x-cut and z-cut samples using the method described in Fig. 4.2. This technique was easy to perform with z-cut samples, but with x-cut ones the small area available to place the electrodes (the lateral of the samples, around $6 \times 1 \text{ mm}^2$) increased a lot the difficulty of the measurements. In order to obtain repeatable results, we had to paint the laterals of the samples with silver paint, and thereby enhance the conductivity at the sample/electrode interface. The results of the experiments on z-cut and x-cut were consistent: particles acquired positive charge after long series of experiments using the same suspension. The physical mechanism is still not fully understood, but it probably relies on electron transfer from the metallic particles to the crystal. Regarding charge stability, it was variable; particles remained charged from one to several days.

These experiments prove that the single slit experiment performed in x-cut crystals is an easy and efficient way to check the charge state (and sign) of the NPs.

We also considered measuring the total charge of the nanoparticles, but it was not possible due to lack of proper equipment. So, we decided to perform simple theoretical calculations in order to estimate the surface charge density on the particles (σ_{crit}) required for EP forces to overcome DEP ones. It was based on Eq. 3.12, repeated here for the sake of clarity:

$$\sigma_{crit} = \frac{2\sigma_s r(\zeta_p - \zeta_m)}{\Lambda(\zeta_p + 2\zeta_m)}, \quad (8.5)$$

We used the parameters of Table 8.I and supposed $\sigma_s = 1 \text{ mC/m}^2$ (a typical value of the surface charge density on the crystal surface due to the photovoltaic effect) and $\Lambda = 100 \text{ }\mu\text{m}$ (the characteristic size of our structures). The result is $\sigma_{crit} = 55 \text{ }\mu\text{C/m}^2$. This means that for a spherical cluster like the one defined in Table 8.I the total charge (Q_p) that the whole cluster should acquire is $Q_p \sim 10^{-17} \text{ C}$. For the calculations shown below we have used $Q_p = 10^{-16} \text{ C}$, thus considering that EP force is one order of magnitude larger than DEP one.

As a final remark, we also found that particles can also become electrically charged after long periods of sonication, probably due to the triboelectric effect (§3.3). However, when particles are charged using this procedure the sign of their electric charge is not predefined, as they can

become positively or negatively charged. This explains why most suspensions do not charge: as experiments with one suspension are spread over several days, particles can neutralize through sonication. Although we did not use this technique for particle charging, it must be taken into account, as particles can become charged even if it is not our purpose²¹.

8.3.2 Electrophoretic versus dielectrophoretic patterning

The simplest way to compare both kinds of trapping is analysing NP patterns obtained with the same light distribution. Fig. 8.11 shows two 7×9 chequered patterns obtained with charged and neutral nanoparticles (experimental parameters in Table 8.VIII). DEP pattern (Fig. 8.11b) consists of similar, well-defined squares with size matching the illumination profile, as blank and filled squares are equal in size. Also, as may be expected in a DEP pattern, the particle density is larger at the edges of the motifs, faintly visible in the central ones but noticeable in the outer squares. In contrast, EP pattern (Fig. 8.11d) shows a clear particle density gradient from the edges towards the centre; the squares at the corners are barely defined, whereas the inner ones are completely full of particles, although their size seems a bit smaller than the illuminated area. Finally, the number of particles out of place seems to be larger in the pattern made with neutral particles. Particle density profiles in Fig. 8.11 confirm and highlight these differences. It is interesting how the profile for the DEP pattern shows perfectly the edge enhancement of the motifs and the particles out of place, and how the profile for the EP squares exhibits a smooth decrease in particle density at two different scales: across the whole pattern and inside each square.

As with the previous section, for better understanding of the patterns the corresponding DEP and EP potential energy distributions and forces have been calculated (Figs. 8.11c,e). On the one hand, the DEP potential is similar to those presented in the previous section: equally deep potential energy wells for all the squares delimited by thin regions of much lower potential energy. On the other hand, the EP potential energy profile softly varies from the edges of the illumination

²¹ Remember that sonicating the suspensions once in a while is advisable in order to obtain a fine nanoparticle dispersion.

towards the centre, where the absolute minimum is located. This is in good accordance with the fading particle density and definition observed in the experimental pattern.

If EP and DEP potentials are observed in detail at different heights from the crystal surface (Fig. 8.12), they also explain the different density of background particles in each pattern. In both cases, the potential far from the surface is essentially flat, thus particles are distributed homogeneously, like they are in the suspension. As DEP and EP are attractive potentials, both are lower closer to the surface, but EP shows a gentle decrease that starts higher from the surface than DEP one. This means that charged particles far away from the crystal start to move towards the illuminated squares before neutral ones do. Nevertheless, observe how the general shape of the patterns is already defined at 50 μm for both cases. Also note that EP forces must be larger than DEP ones, which for sure contributes to the lower presence of particles out of place.

Table 8.VIII Experimental parameters used to make the patterns shown in Fig. 8.11.

	Parameter	Value
Illumination (532 nm)	System	SLM
	Incoming intensity	1 mW/cm ²
	Exposure time	20 min
	Pattern	Chequered pattern (square side 250 μm long)
Suspension (Hexane + Al NPs)	Concentration	40 mg/L
	Immersion time	40 s
Crystal	Thickness	1 mm

Figure 8.11 Comparison between DEP and EP patterning. (a) Light profile. (b) Chequered pattern made of neutral Al NPs. (c) DEP potential energy calculation at 1 μm from the crystal surface. (d) Chequered pattern made of positively charged Al NPs. (e) EP potential energy calculation at 1 μm from the crystal surface. The parameters for the simulation were taken from Table 8.VIII.

Figure 8.12 DEP and EP potential energies calculations of the patterns in Fig. 8.11 at different heights from the crystal surface.

Another comparison between EP and DEP particle trapping is shown in Fig. 8.13; in this case, the light profile was an array of circles. The DEP picture is the same as in Fig. 8.9b, but it is repeated here for better comparison. Experimental conditions were those of Table 8.IX. In this case, the difference in size between both patterns is evident: even if they were illuminated with exactly the same light profile, the circles made of charged particles are clearly smaller than those made of neutral ones due to the global and local particle density gradient explained above.

Table 8.IX Experimental parameters used to make the patterns shown in Fig. 8.13.

	Parameter	Value
Illumination (532 nm)	System	SLM
	Incoming intensity	Array of circles ($\varnothing 250 \mu\text{m}$)
	Exposure time	$1 \text{ mW}/\text{cm}^2$
	Pattern	20 min
Suspension (Hexane + Al NPs)	Concentration	40 mg/L
	Immersion time	40 s
Crystal	Thickness	1 mm

Figure 8.13 Comparison between DEP and EP patterning of an array of circles. (a) Pattern made of neutral Al NPs. (b) DEP potential energy calculation at 1 μm from the crystal surface. (c) Pattern made of positively charged Al NPs. (d) EP potential calculation at 1 μm from the crystal surface. The parameters for the simulation were taken from Table 8.IX.

8.3.3 Electrophoretic patterns analysis

Up to this point, it seems evident that DEP patterns are a more accurate reproduction of the light profile than EP ones, as the motifs keep their size, are better defined and more homogeneous. However, the large number of parameters involved in the process makes PVT a flexible technique. As it was demonstrated in §8.2, the user is provided with some degrees of freedom (e.g., light exposure or particle concentration) that allows them to modify the patterning capabilities of their system. In this section, two experimental findings regarding EP trapping and improved pattern fidelity to the light profile are explained.

The first one is based on increasing the immersion time, and thus allowing more particles to reach the sample and “fill” the EP potential energy wells. As explained above, for DEP patterning it is more advisable increasing the particle concentration of the suspension than the immersion time. However, a larger particle concentration makes the charging process more difficult, so we preferred this procedure for EP patterning. Fig. 8.14 shows a pattern made with the same

chequered illumination profile and experimental conditions as that of Fig. 8.11d but increasing the immersion time to 90 seconds (Table 8.X). The definition of the motifs is better, although the number of particles out of place has also increased.

Table 8.X Experimental parameters used to make the pattern shown in Fig. 8.14.

	Parameter	Value
Illumination (532 nm)	System	SLM
	Incoming intensity	1 mW/cm ²
	Exposure time	20 min
	Pattern	Chequered pattern (square side 250 μ m long)
Suspension (Hexane + Al NPs)	Concentration	40 mg/L
	Immersion time	90 s
Crystal	Thickness	1 mm

Figure 8.14 Chequered pattern made of positively charged Al NP. This pattern was made on a 1 mm sample and increasing the immersion time in the suspension compared to usual PVT operation. The experimental parameters are listed in Table 8.X.

The second result was obtained using thinner samples. Usually, but not always, EP experiments performed with thin samples showed better fidelity to the original light pattern. Fig. 8.15 shows again a chequered pattern but in this case the sample was 0.5 mm thick instead 1 mm. The rest of the experimental conditions are the same as in Fig. 8.11d (Table 8.XI). The pattern in Fig. 8.15 is more homogeneous and resembles the light profile almost as much as Fig. 8.14, but with less background particles. Nevertheless, a certain fading in particle

concentration is still noticeable, especially in the bottom row or in squares at the corners, which are somehow distorted.

Table 8.XI Experimental parameters used to make the pattern shown in Fig. 8.15.

	Parameter	Value
Illumination (532 nm)	System	SLM
	Incoming intensity	Chequered pattern (square side 250 μm long)
	Exposure time	1 mW/cm^2
	Pattern	20 min
Suspension (Hexane + Al NPs)	Concentration	40 mg/L
	Immersion time	40 s
Crystal	Thickness	0.5 mm

Figure 8.15 Chequered pattern made of positively charged Al NP. This pattern was made on a 0.5 mm sample. The experimental parameters are listed in Table 8.XI.

This finding has not a clear explanation. At first, we thought that the EP potential energy distribution was flatter in the crystals 0.5 mm thick compared to the case of 1 mm samples, as the proximity of positively and negatively charged faces could decrease the total electric field exerted on particles far away from the crystal. As a consequence, the gradient (i.e., the force) would be also lower. However, theoretical calculations provide similar EP potentials and forces for both thicknesses (Fig. 8.16).

Another possible explanation is indeed based on the theoretical calculations. As the crystal approaches to saturation, the EP potential minimum extends outside the illuminated area due to

the space charge density peaks that were analysed in the previous chapter (§7.3). This way, the fading effect in EP patterns can be counteracted by larger potential wells (Fig. 8.17). Also, as samples 1 mm and 0.5 mm thick come from different wafers, it is reasonable to assume that their oxidation-reduction ratio (and maybe Fe doping) is not the same²². Thus, under the same illumination conditions, the temporal evolution of each sample can be different.

Figure 8.16 Comparison of the EP potential and electric field calculations of two samples with different thickness (1 mm and 0.5 mm). There is barely any difference between them apart from the value of the potential energy. The parameters for the simulation were taken from Tables 8.IX and 8.XI.

Nevertheless, the key idea is that it is possible to obtain an accurate reproduction of the light profile by PVT using charged particles, although the experimental conditions must be controlled more carefully than with neutral ones. May serve as final example the pattern shown in Fig. 8.18 together with its corresponding light profile (experimental conditions in Table 8.XII). Although

²² In fact, the difference in oxidation-reduction ratio is sometimes visible within a single sample: $\text{LiNbO}_3\text{:Fe}$ is darker for higher donor concentrations, and some of the samples used in this work showed a clear colour fading.

it may seem that the high particle density at the boundaries is caused by a dielectrophoretic edge enhancement effect, the truth is that the particles were highly charged, according to the total absence of particles on the non-illuminated face (Fig. 8.18c) and the charge test explained in 8.3.1. Note the grainy texture of the pattern: there is a total absence of dielectrophoretic chains due to electrostatic particle-particle repulsion.

Figure 8.17 EP potential due to a circular light profile after ten minutes of illumination and at saturation. The same parameters as in §7.3.1 were used to perform the calculations.

Table 8.XII Experimental parameters used to make the pattern shown in Fig. 8.18.

	Parameter	Value
Illumination (532 nm)	System	SLM
	Incoming intensity	Single square (side 1.5 mm long)
	Exposure time	3.78 mW/cm ²
	Pattern	5 min
Suspension (Hexane + Al NPs)	Concentration	50 mg/L
	Immersion time	30 s
Crystal	Thickness	0.5 mm

Figure 8.18 Single square pattern made of positively charged Al NPs. (a) The pattern on the illuminated face is a faithful reproduction of the (b) light intensity profile. (c) As the particles are positively charged, they are repelled from the illuminated area in the c^- face, which is positively charged. The experimental parameters are listed in Table 8.XII.

As a final remark, it has not been observed that crystal thickness plays a role in DEP patterning, at least in the typical range of thickness used in our laboratory (1-0.5 mm). Theoretical calculations only predict sharper DEP potential minima at crystal saturation (Fig. 8.19).

Figure 8.19 DEP potential due to a circular light profile after ten minutes of illumination and at saturation. The same parameters as in §7.3.1 were used to perform the calculations.

8.4 Particle patterning simulations

One of the advantages of using COMSOL® Multiphysics is that this software includes a particle tracing module, which allows us to simulate the process of particle trapping. Different forces can be selected in order to simulate the nanoparticle dynamics. We only considered the dielectrophoretic force for the calculations shown in this section. Buoyancy and drag can be disregarded for the time periods considered in the simulations (less than a second), whereas the Brownian force increased too much the computation time of the simulations. For this last reason, particle-particle interaction was not included either.

In this module, particles are treated as individual entities, and their trajectory is computed by solving the Newton's second law of motion [18]. At each time step, the forces acting on each particle are computed based on their current position. Then, the particle position is updated based on the resulting velocity and acceleration vectors. This loop is repeated until a specified end time is reached for the simulation [18]. Unfortunately, during the development of this thesis work it was not possible to explore all the capabilities of this module, but some promising results were obtained. In the simulations below we used the particle parameters listed in Table 8.I.

The first one is related to the sinusoidal illumination pattern. As shown in the previous chapter (§7.3.3), the time evolution of the space charge distribution due to this light profile starts as a replica of the illumination and ends as a homogeneous surface charge density. This is translated into broader potential wells as exposure time increases, which experimentally is observed as wider fringes (Figs. 8.20a-c, experimental parameters in Table 8.XIII). This effect has been perfectly reflected in the particle trapping simulations (Fig. 8.20e). This plot shows the particle density distribution on the crystal surface for three particle trapping simulations. They were performed using the DEP potential distribution after different exposure times. Note how the particle distribution is broader for longer exposure times in Fig. 8.20e.

Table 8.XIII Experimental parameters used to make the pattern shown in Fig. 8.20.

	Parameter	Value
Illumination (532 nm)	System	Two-beam interference
	Incoming intensity	125 mW/cm ²
	Exposure time	10 s, 30 s, 3 min, 10 min, 30 min, 40 min
	Pattern	Sinusoidal ($\Lambda = 60 \mu\text{m}$, $m = 0.95$)
Suspension (Hexane + Al NPs)	Concentration	40 mg/L
	Immersion time	30 s
Crystal	Thickness	1 mm

Figure 8.20 Time evolution of the fringe width depending on the illumination time.

(a-d) Experimental patterns and plot of the fringe width vs. time that indicates a saturable exponential tendency. (e) Results of three different particle trapping simulations that shows progressively wider fringes as illumination time increases. Experimental parameters are listed in Table 8.XIII.

The second simulation shows the particle distribution due to a small array of light squares (Fig. 8.21a). Symmetry is exploited and only one quarter of the pattern was simulated. Note the initial preferential trapping at the outer edges of the illumination (Fig. 8.20c) and the great

similitude between the experimental (Fig. 8.21b and Table 8.VIII) and the final simulated pattern (Fig. 8.21d), including the particle bridge between squares.

Figure 8.21 (a) Theoretical light intensity profile. (b) Experimental Al NP pattern. Particle distribution (c) at the beginning and (d) at the end of the simulation.

8.5 Discussion and conclusions

The key features of the experimental patterns obtained by PVT have been explained in this chapter. The main forces exerted on the nanoparticles have been analysed and compared with DEP one, and it has been found that for our typical experimental parameters, DEP force is at least three orders of magnitude larger.

The FEM model developed in the previous chapter has been used to understand different NP features that appear in almost all DEP patterns to a greater or lesser extent. The edge enhancement effect of the motifs (global and local) and the dielectrophoretic chains, oriented in the direction of the local electric field, are especially relevant, as they appear in many DEP structures and produce a particular NP distribution and pattern texture. It has been shown that particle concentration in the suspension can drastically modify the final structure, so they should be carefully controlled during experiments.

The theoretical model has been also used to explain the differences between patterns of charged and neutral particles. In general, patterns made of charged particles show a gradient in both trapped particle density and pattern definition: they are lower at the edges of the pattern and higher in the centre. Also, in this patterns NP chains do not occur. In the case of neutral particles, the definition of the whole pattern is approximately the same, without forgetting the larger particle density at the edges of each individual motif due to the edge enhancement effect.

However, although it is easier to obtain a more faithful representation of the illumination profile by DEP patterning, it is also possible with charged particles. Long immersion times of the crystal in the suspension or the use of thin samples can provide NP structures which are an excellent replica of the original light intensity distribution. However, there is not a definite explanation for this to occur.

It has been found that illuminated $\text{LiNbO}_3\text{:Fe}$ crystals are able to charge aluminium particles with positive charge. Also, a simple test to check whether the particles of a suspension are charged or not was developed based on x-cut $\text{LiNbO}_3\text{:Fe}$ crystals. This method also provides the sign of the charge.

The comparative analysis between DEP and EP patterns presented in this chapter provides routes for PV patterning optimization when the particle of interest can be either charged or neutral. In those cases, one may choose which configuration (EP or DEP) is better for a particular application. Furthermore, the features explained here probably appear regardless the method used for creating the electric field. In particular, we refer to related optoelectronic and non-optical

electronic deposition techniques on ferroelectric substrates that take advantage of charge distributions similar to PVT ones for particle arranging, such as pyroelectric particle manipulation (see §10.2.1 and [80, 147]), ferroelectric domain-based trapping of biological [90] and inorganic [131] particles, or even conventional optoelectronic tweezers [59].

Some simulations of particle trapping were shown in the last section of this chapter. The results are still preliminary, but they are promising, as some particular experimental features are replicated in the simulations. Nevertheless, we are aware that further work is required in this direction. For example, we also tried to simulate large motifs, but the results did not match the experimental patterns; there is a large migration of particles towards the boundaries of the simulation domain, which leaves the centre empty. A better description of the system is probably required in order to obtain a really useful tool. Particle-particle interaction and Brownian forces have not been considered in the simulations above, and neither have been particle concentration in the suspension or the immersion time of the sample, which are parameters that have a great influence on the experimental patterns. Our ultimate goal is being able to design trapping experiments *in silico* and get rid of the trial and error in the laboratory.

Chapter 9: Optical diffractive elements and pattern transference

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CHAPTER 9

Optical diffractive elements and pattern transference

Nanoparticle patterns and structures made by PVT may find application in different technologies, like charge sensors [69], bio-microfluidics [103, 127] or plasmonic platforms [65]. In this chapter, an actual application is demonstrated: their capability of acting as diffractive optical elements (DOEs). This application takes advantage of 2D patterning capabilities of z-cut substrates and the great stability of the NP structures, even after the photovoltaic field has been erased.

However, there is a serious drawback when using the patterns for optical applications directly on the original $\text{LiNbO}_3\text{:Fe}$ substrate: the photorefractive damage. This is why two methods for transferring patterns from their original substrate to arbitrary ones have been also developed, and explained in this chapter. The transference processes allowed us to go one step further and fabricate two kinds of integrated spectrometers based on channel waveguides. These devices were developed and tested in collaboration with the Institut de Planétologie et d'Astrophysique de Grenoble (IPAG) in France.

9.1 Diffractive optical elements

As commented in §3.4, a diffractive optical element is a device with a micro- or nanostructure pattern that produces arbitrary light distributions by means of interference [14]. They are used in many scientific and technological fields like medicine, laser material processing, spectroscopy, astronomy, optical communications, 3D detection... [10]. DOEs can be also used for the same purposes as refraction-based devices (lenses, prisms...), and they are much smaller and lighter [10].

Typical DOEs include diffraction gratings, beam shapers, multi-spot beam splitters, tuneable filters, grating couplers or Fresnel zone plates [178]. There are different methods to fabricate these components, such as engraving by mechanical methods (electron and ion irradiation), laser writing and different lithography techniques [9, 175]. More flexible methods include photorefractive-induced gratings [51] and computer generated holograms (CGH) [60].

In this chapter, 1D and 2D DOEs have been made using PVT, and their optical performance has been characterised. In Table 9.I, PVT is compared with similar but established methods for DOE fabrication. From the table it can be conclude that although PVT cannot currently offer an optimal precision, it presents a good trade-off between cost, speed and resolution.

Table 9.I Different techniques for DOE fabrication. FIB stands for “focused ion beam”, a well-established mechanical method.

	FIB	Lithography	Laser writing	PVT
Precision	Excellent	Very good	Excellent	Very good
Time consumption	Large	Large	Low	Low
Reconfigurable	No	Partially	No	Yes
Area extension	Small	Large	Large	Large
Cost	Very high	High	High	Medium

9.1.1 1D DOEs. Diffraction grating

Two main conclusions can be derived from the theory of diffraction gratings presented in §3.4.2:

- The grating period should be as short as possible in order to spatially separate the different orders, as the angle of the principal maxima increases when grating period decreases.
- The width of the silts should be as narrow as possible. This way the envelope of the principal maxima is wide, and the intensity of the lower orders is comparable to that of the zero order, that is usually the highest.

For diffraction gratings fabrication, we decided to use x-cut $\text{LiNbO}_3\text{:Fe}$ crystals (instead of z-cut ones) and the holographic setup (§4.1.3b), as this is a well-known configuration and the results tend to be more repetitive. Most of the gratings, like the one analysed in this section, were made of aluminium nanoparticles. After fabrication and before measuring their diffraction efficiency, the photovoltaic electric field of the substrate was thermally erased to avoid competition of the refractive index grating and the particle grating [23], as explained in §4.1.5.

Gratings performance was measured in transmission and reflexion configurations (see Fig. 9.1a). It seems pretty obvious that in transmission the uncovered regions of the substrate act as the slit ($2a$ in Fig. 9.1b) and the NPs as the opaque element (W in Fig. 9.1b). However, due to the high reflectivity of the metallic particles, we thought that the roles may be exchanged in reflexion configuration.

Figure 9.1 (a) Diffraction grating working in transmission and reflexion configurations.
(b) Grating parameters.

Fig. 9.2a shows the grating analysed in this work. It is made with aluminium nanoparticles, has a period of $\Lambda \sim 15.2 \mu\text{m}$ and the width of the particles strip is $W \sim 10.7 \mu\text{m}$. For performing the measurements we used a He-Ne laser (Uniphase 1300). We kept exposure times as short as possible in order to avoid photorefractive damage as much as possible (see §9.1.3). The intensities of the spots corresponding to the different diffraction orders were measured using a silicon photodetector (Coherent LM-2). The measurements for the two first orders and the theoretical intensity distribution are plotted in Fig. 9.2b. Theoretical curves are plotted for two possible cases: the slit being the particles (continuous line) or the substrate (dashed line). The results are conclusive: in transmission and reflection configurations the particles act as the opaque element and the lithium niobate as the slit. Metallic NPs act just as incoherent light scattering points and do not contribute to the intensity of the diffraction orders.

Figure 9.2 (a) Diffraction grating made of Al NPs. (b) Calculated diffraction intensity profile of a linear grating with period $\Lambda = 15.2 \mu\text{m}$ and fringe width $W = 10.7 \mu\text{m}$ (solid red line) or $W = 4.5 \mu\text{m}$ (dashed blue line). The experimental intensity data of the 1st and 2nd diffraction orders for reflection and transmission configurations are indicated. (c) Transmission diffraction pattern.

Tables 9.II-9.IV provide the experimental measurements done in order to obtain Fig. 9.2b. The mean grating period has been obtained by two ways. In the first one, it was measured directly on

Fig. 9.2a. The second method consisted in measuring the experimental position of the intensity maxima and solve for Λ in Eq. 3.19. Both periods differ only by 300 nm, which gives an idea of the great homogeneity of the grating. As it may be expected, the experimental efficiency of the grating is lower than the theoretical one. The most important features that decrease this grating efficiency are the irregular thickness of the NP strips and the presence of particles out of place between them.

The use of metallic nanoparticles in diffraction gratings is interesting due to the possible additional effects associated to plasmonic resonances (see §10.1.1), such as increasing the coupling efficiency in whispering gallery resonators [183].

Table 9.II Intensity values and efficiencies (transmission).

				Efficiency	
	Right side (μW)	Left side (μW)	Mean (μW)	Experimental	Theoretical
Zero order	96.33		96.33	—	
First order	63.80	58.50	61.15	0.63	0.74
Second order	10.10	10.05	10.08	0.11	0.25

Table 9.III Intensity values and efficiencies (reflection).

				Efficiency	
	Right side (μW)	Left side (μW)	Mean (μW)	Experimental	Theoretical
Zero order	26.20		26.20	—	
First order	13.30	13.10	13.20	0.50	0.74
Second order	3.03	3.00	3.02	0.11	0.24

Table 9.IV Grating period calculated from the diffraction maxima positions. The first three columns indicate relative distances. This way, the diffraction angle of each order (θ_m) is calculated and thus Eq. 3.19 is solved for Λ .

	Right side (cm)	Left side (cm)	Mean (cm)	Period (μm)
Grating to screen	72.7		72.7	—
Zero to first order	3.10	3.10	3.10	14.85
Zero to second order	6.20	6.20	6.20	14.89
			Mean	14.9

9.1.2 2D DOEs. Fresnel zone plate

For the fabrication of 2D DOEs we used z-cut substrates, as it has been demonstrated in previous chapters that they guarantee isotropic particle trapping and patterning over the whole crystal surface. For obtaining the light profiles we used the SLM (§4.1.3c). We made two different patterns: a chequered pattern and Fresnel zone plate.

The chequered pattern is presented in Fig. 9.3a, the same presented in Fig. 6.5c. Each square side is $135\ \mu\text{m}$ long and the pattern homogeneously covers a large area of the sample, around $36.5\ \text{mm}^2$. The corresponding diffraction pattern, obtained again with a He-Ne laser, is shown in Fig. 9.3b. Many well-defined diffraction orders were obtained.

Figure 9.3 (a) Chequered pattern made of Al NPs. (b) Diffraction pattern in transmission configuration using a He-Ne laser.

The Fresnel zone plate (§3.4.3, Fig. 9.4a) was already shown in Fig. 6.5a. Its focalisation properties were tested due to its extraordinary quality and definition (more than 25 rings were patterned). We passed a He-Ne laser beam through the centre of the pattern and measured its intensity profile with a laser beam profiler (Newport, LBP2-HR-VIS) in a plane parallel to the sample at three different distances from it (Figs. 9.4b-d). We found the highest focalization peak at 39 cm from the sample plane. The theoretical distance is 39.49 cm, obtained from solving for f in Eq. 3.22 using $n = 1$, $r_1 = 500\mu\text{m}$ and $\lambda = 0.633\mu\text{m}$. The relative error in the focal length is 1.24%, which is small and can be addressed to various reasons such as imperfections of the pattern and experimental errors in the measurement of the plate radius and the distance to the detector.

Figure 9.4 (a) Fresnel zone plate made of Al NPs. (b-d) Intensity profiles of a He-Ne laser beam at different distances from the zone plate.

9.1.3 Optical damage

The biggest issue when one envisages actual applications for the patterns above, especially for applications in the visible range of the electromagnetic spectrum, is the fact that they remain on their original $\text{LiNbO}_3\text{:Fe}$ substrate. Recall the absorption spectrum of iron-doped lithium niobate (Fig. 2.2): it shows high absorption in the visible range compared to, for example, pure lithium niobate. In a non-photorefractive material this would be a “minor” problem, as it would only imply a decrease of the intensity of the travelling wave. However, lithium niobate is indeed photorefractive and a phenomenon called “optical damage” is very likely to appear for high light intensities or long exposure times.

In short, photorefractive optical damage is the defocusing of a light beam as it passes through the LiNbO_3 crystal (see again Fig. 1.5). This phenomenon degrades the beam intensity profile; the wavefront undergoes a distortion as the beam propagates through the material [171]. If the optical damage is high enough it can lead to beam instabilities, i.e., the beam profile is not constant over time [23].

As optical damage is ultimately caused by the combination of the photovoltaic and the electro-optic effect (§1.3.2), it depends on the same parameters. Here, the most important ones are light intensity and illumination time. As usual operation of DOEs involve long exposure times, this becomes an important concern: in fact, $\text{LiNbO}_3\text{:Fe}$ can exhibit optical damage even for low light intensities and short periods of illumination. Take as an example the diffraction pattern shown in Fig. 9.5, which was obtained after illuminating during a few minutes one of our diffraction gratings on an x-cut sample with a He-Ne laser at 14 mW/cm^2 . The optical damage appears as an obvious spreading of the light spots along the polar axis.

Figure 9.5 The diffracted laser beam spreads along the c-axis direction due to the optical damage.

Although this effect can be minimized or delayed in time using low doped samples, this is not a definite solution. In the first place, the phenomenon does not disappear, it is only delayed. In the second place, the electric field that a $\text{LiNbO}_3\text{:Fe}$ sample is able to develop is dependent on the acceptor concentration (Eq. 5.4). If doping level is below a certain value [147], it would be possible for the photovoltaic electric field to become too low to even trap particles.

9.2 Pattern transference

It has just been shown that if patterns are kept on their original substrate, PVT technique has an important limitation regarding their application in photonic and integrated optics devices due to optical damage and absorption. Of course, one option is avoiding their use when PR-sensitive wavelengths or those highly absorbed by the crystal are required, but this is not a proper solution. Finding a real alternative to this problem was the main motivation to develop a process for transferring the patterns to other substrates. In addition, pattern transference also offers additional possibilities and increases the versatility of the micro- and nanoparticle structures created by PVT. Silica glass and polymers are two examples of very convenient and common substrates that can be used as new supports for PVT-fabricated structures.

Early transference attempts were made using simple adhesive tape, but even if particle patterns were removed completely from the $\text{LiNbO}_3\text{:Fe}$ sample, there was no way to peel the tape off the new substrate without removing the particles with it. In short, once the particles were stuck to the adhesive tape it was impossible to detach them from it.

Trying to elaborate a transference method which final result was leaving the particle pattern on the new substrate without any residue we developed two different processes. Both are based on a thermal release tape (REVALPHA, from Graphene Laboratories Inc.), typically used to manipulate graphene or temporary fixing electronic components during production. This thermal release tape is very similar to a conventional adhesive tape, but with the difference that when it is heated up to a certain temperature (100 °C in our case) the adhesive layer foams. This reduces the contact area of the adhesive layer and can be easily detached from the surface where

it was stuck. This first method is very simple and has practically no limitations regarding the substrates to which the particles can be transferred. However, the percentage of transferred particles is around 50%. The second method is partially based on one developed by Li *et al.* [118] and its transference throughput is extremely high, although it cannot be applied on certain substrates as it requires the use of solvents.

9.2.1 Simple transference method

This method consists of six steps which are depicted in Fig. 9.6:

1. The photovoltaic field of the sample is thermally erased following the procedure described in §4.1.5.
2. The thermal release tape is firmly stuck onto the $\text{LiNbO}_3\text{:Fe}$ sample surface with the pattern and peeled off. The particles are now attached to the tape.
3. The tape is firmly stuck on the new substrate.
4. The new substrate with the tape attached to it is slowly heated up to 150-200 °C for 5 minutes. Some pressure (3 kPa) is applied using a weight. It prevents the tape from detaching too early, as actual detaching temperature of the tape is around 100 °C.
5. The weight and the tape are removed before the new substrate cools down. The pattern has been transferred.
6. In most occasions there are no residues left. If they are, they can be removed immersing the sample in a hot acetone bath.

Two images of a pattern before and after the transference process are shown in Fig. 9.7. Increasing the temperature beyond the actual detachment temperature of the thermal tape proved to increase the efficiency of the method. Although no particles remain on the original sample, particle transference density is not as high neither as homogeneous as one may desire. Usually, 50% of the particles remain on the thermal release tape after detachment, which is the reason this method is only used when the one below (§9.2.2) cannot be applied.

Figure 9.6 Schematic of the simple transference method. Numbers are referred to the steps in the text.

Figure 9.7 Simple transference method example. Fresnel zone plate pattern made of Al NPs (a) on the original $\text{LiNbO}_3\text{:Fe}$ substrate and (b) on a silica glass.

9.2.2 Full-transference method

The second method is by far more complex than the previous one. It consists in four different stages which are depicted in Fig. 9.8:

1. PMMA film spin coating

1. Few drops of a PMMA²³-acetone solution (6 %wt) are spin coated on the LiNbO₃:Fe sample surface with the pattern (at 3000 rpm for 6 seconds). When poured on the crystal, the solution must cover its whole surface without overflowing.
2. The sample is left undisturbed for 3-4 minutes in order to ensure the complete evaporation of the acetone.

2. PMMA film + pattern transfer

1. The edges of the PMMA film are scratched to facilitate its future detachment from the LiNbO₃:Fe sample. A thermal release tape is firmly stuck on the PMMA film.
2. The crystal is introduced in a suitable lidded dish, like a Petri dish, which is filled with deionised water. The PMMA film + thermal release tape ensemble detaches from the crystal by itself.
3. The ensemble is put on a hot plate at 45 °C for a few minutes to evaporate the water on the PMMA film. The thermal release tape should be the one in contact with the hot plate to avoid pattern contamination.
4. The ensemble is placed onto the new substrate and light pressure is applied.

3. Thermal tape removal

1. The new substrate + PMMA film + thermal tape ensemble is put on the hot plate and heated up to 80-85 °C.
2. After some minutes, the thermal tape detaches from the PMMA film. If some part of the tape is still stuck to the film, gently remove it manually.

²³ Poly(methyl methacrylate) (C₅O₂H₈)_n.

4. PMMA film dissolution

1. In a fume hood, the new substrate + PMMA film ensemble is immersed in a glass of dichloromethane (DCM) for 15 seconds.
2. Let it rinse.
3. If there is still some PMMA residues, repeat steps 4.1-4.2.
4. Finally, the substrate with the transferred pattern is immersed in hot acetone (at 40 °C) to remove final residues.

Figure 9.8 Schematic of the full-transference method. Numbers are referred to the steps in the text.

In Fig. 9.9 there is an example of a NP grating transferred onto a channel waveguide. It can be observed the high fidelity to the transferred grating. The typical percentage of transferred particles is around 95% when this method is used.

Figure 9.9 Full-transference method example. Al NP grating (a) on the original LiNbO₃:Fe substrate, (b) on a LiNbO₃ waveguide previous to removing the PMMA film and (c) on a LiNbO₃ waveguide without the PMMA film.

When possible, the second method is obviously preferred over the first one. Even if it is by far more complex, it pays off with a much higher transference quality. However, as will be shown in this work (§10.1.1), it cannot be applied when the new substrate has certain kinds of polymeric layers, as acetone and DCM can dissolve them.

9.2.3 Transference analysis

Particle distribution and the pattern itself remain the same after being subjected to any of the two transference processes. They also remain stable on the new substrate, which can be easily handled without fear of removing the pattern. This reinforces the idea that adhesion forces play a key role in the stability of the PVT patterns, in particular when the photovoltaic electric field is erased.

However, two important limitations apply to both transference methods. The first one is related to the new substrate, as it must stand the temperatures required for the thermal release tape to detach. This is especially important in the first method, as it requires a higher temperature in order to optimize the transference process. However, one must be careful on how much time the tape is heated, as it can reattach to the new substrate (see Fig. 9.10) or even burn.

The second limitation seems to be intrinsic to both processes. Although a lot of work has been done in order to optimize the methods, the fact is that transference of the pattern at the edges of

the sample is not always possible, as both particles (in the first method) and the PMMA film (in the second one) tend to remain attached to the thermal release tape no matter how the processes are performed. This should be taken into account from the moment the pattern is recorded on the $\text{LiNbO}_3\text{:Fe}$ crystal: if it contains particularly important motifs, they should be at least 1-2 mm away from the sample edge in order to ensure their correct transference.

Figure 9.10 Re-adhesion problems of the thermal release tape at high temperatures.

Retrieved from [11].

9.2.4 Transferred diffractive optical elements

As an example of the capabilities of the transference process, Figs. 9.11a,b show a Fresnel zone plate before and after its transference to a silica glass substrate. In this particular case, we used the simple method for the transference. The great quality of the transferred pattern can be observed, although there is a loss of particle density, specially at the bottom right of the second inner circle, where the pattern disappears.

However, its focusing properties were unaffected. We performed the same measurements as for the zone plate in §9.1.2 using the transferred pattern and we found a sharp focalisation peak at 14 cm from the sample (Fig. 9.11d). The theory predicts this distance to be 14.22 cm ($n=1$, $r_1 = 300 \mu\text{m}$ and $\lambda = 0.633 \mu\text{m}$), so in this case the relative error in the focal length is 1.56%.

Figure 9.11 Fresnel zone plate made of Al NPs (a) on the original $\text{LiNbO}_3\text{:Fe}$ substrate and (b) transferred on a silica glass. (c-e) Intensity profiles of a He-Ne laser beam at different distances from the transferred zone plate.

9.3 Integrated spectrometers

This section is dedicated to a direct application of the NP patterns obtained by PVT in the field of integrated optics. They are used together with channel waveguides to fabricate integrated spectrometers. As said in the introduction of this chapter, these devices were fabricated in our laboratory and characterised at IPAG.

It was commented in §4.2 that integrated spectrometers have great advantages compared to bulk optics systems, like reduced weight and size, simpler setups or lower maintenance. In addition, their low power consumption and great stability make them perfect for space and UAV applications. Two good examples of integrated spectrometers applications are PIONIER and GRAVITY, currently operating at the Very Large Telescope of the European Southern Observatory in Chile; both were partially developed at IPAG [1, 13]. The project presented here consisted in using linear NP gratings made by PVT for the fabrication of the two different compact spectrometer configurations presented in §4.2.3: Side Holographic Disperser (SHD) and Stationary Wave Integrated Fourier Transform Spectrometer (SWIFTS); the gratings would act

as diffraction gratings and scattering points respectively in each configuration. The major advantages of using PVT-fabricated gratings are their reconfigurability and the low-cost, quick process. Typically, the gratings are engraved in the waveguide by FIB or laser writing (not reconfigurable) or deposited by lithography processes (time consuming).

We first developed a proof-of-concept device based on a soft proton exchange planar waveguide made from a z-cut pure LiNbO_3 sample and a NP grating ($\Lambda = 20 \mu\text{m}$) transferred on top. The idea was checking if light decouples when it travels through the regions where particles are deposited (Fig. 9.12a). Particle fringes are perpendicular to the propagation direction and were transferred from an x-cut $\text{LiNbO}_3\text{:Fe}$ sample using the simple transference method.

The experimental setup of the experiment was similar to that shown in Fig. 4.10. Fig. 9.12b shows a photograph of the experiment. There are three well-defined zones regarding light intensity: 1) A bright spot corresponding to the laser beam injection in the waveguide, 2) where there is no particles nor light extraction and 3) where light decouples from the sample due to the presence of the particles. So, the experiment was a success: light clearly decouples when travelling through the region where the grating is placed. This result supported the development of the two more complex devices.

Figure 9.12 (a) Al NP grating. (b) Light decoupling from a planar waveguide due to the presence of the particles.

9.3.1 SHD

The physics of this device and the experimental setup for the measurements were explained in §4.2.3a. The device was made from one of the Ti-diffused channel waveguides described in §4.2.1 on top of which a NP grating was transferred using the full-transference process. The grating is shown in Fig. 9.13a. It consisted of Al NP fringes with a period of $28\text{ }\mu\text{m}$ and a total extension of more than 1 mm, as the longer the grating, the better the performance of the device.

The grating successfully extracted the injected laser beam and a diffraction pattern was obtained on the CDD detector. However, it was a periodic pattern of lines instead of the expected single bright line (compare Fig. 9.13b with Figs. 4.12b,c). This pattern changed and moved along the focalisation line as we modified the input wavelength from $1.03\text{ }\mu\text{m}$ to $1.077\text{ }\mu\text{m}$, which means that the device worked at least partially.

There are some reasons why we did not get a single line. Perhaps the most probable is that the channel waveguide was single mode for $3.39\text{ }\mu\text{m}$ and we used a source centred at $1.06\text{ }\mu\text{m}$, so many modes and different polarizations (TM and TE) are expected to be injected in the waveguide and thus extracted, diffracted, and recorded by the detector.

Figure 9.13 (a) Al NP grating before being transferred to a LiNbO_3 Y-waveguide to make the SHD spectrometer. (b) Two different diffraction patterns obtained using two different incoming wavelengths.

9.3.2 SWIFTS

The obtention of good results with this configuration was more difficult than with the SHD system. Once more, the theoretical background and the experimental setup were described in §4.2.3b. We used the same sample of the previous case.

Figure 9.14 (a) Light extraction capabilities of the NP grating. (b) Fourier interferogram of the polychromatic light source. (c) Schematic of the NP cluster on the waveguide (not drawn to scale) and photograph of the cluster.

First, as SWIFTS is based on the measurements of the light intensity extracted by the different scattering points, we checked if light extraction by the particles was enough, and so was it (Fig. 9.14a). We started working with the infrared laser source (850 nm); as it has a relatively broad linewidth (10 nm), it can be used as a polychromatic source. First, without injecting the laser beam in the sample, we adjusted both arms of the Michelson interferometer to find the OOPD (zero optical path difference) of the system itself, i.e., the position in which the optical path length of both beams is equal. Fig. 9.14b shows interference fringes of the resulting Fourier interferogram. Then, we tried to replicate this result inside the channel waveguide, injecting light from its both ends (Gabor configuration). However, after many attempts, we realised that the fringes were too thick for the device to work properly, and no interference pattern could be recorded. As it was impossible to remake the pattern at IPAG, we decided to work with a particle

cluster placed just after the junction of one of the Y-channels of the waveguide, at 1.16 mm and 18.84 mm from each sample end (Fig. 9.14c).

We tried Gabor and Lippmann configurations and performed some calculations using Eqs. 4.11-4.12 to adjust the OOPD of our system to the cluster position, but we were not able to record any interference pattern. Finally, we had to accept that we could not make the device work with this laser source, probably due to the chromatic dispersion of the beam inside the waveguide. The cluster was too far from the centre of the sample for using Gabor configuration, but also too far from any of the edges, so Lippmann approach did not work either.

Safe in the knowledge that the main problem was the chromatic dispersion of the source beam in the waveguide, we tried using a monochromatic source (LED laser at 635nm). This source was not affected by the chromatic dispersion, and using Gabor configuration we were able to record the blinking light extracted by the cluster. The recorded light intensity versus the interferometer arm displacement is plotted in Fig. 9.15. These intensity values have been corrected using the following formula:

$$I_c = \frac{I_i - I_f - I_m - D}{2\sqrt{(I_f - D)(I_m - D)}} , \quad (9.1)$$

where I_c is the corrected intensity, I_i is the intensity obtained from the interference of the fixed and mobile arm, I_f and I_m are the intensities of the fixed and mobile arm respectively and D is the background illumination.

The original scatter plot has been adjusted using a sinusoidal regression:

$$I(d) = I_0 \cos \left[\frac{2\pi}{\lambda} n_{eff}(d + l_0) \right] , \quad (9.2)$$

where d is the arm displacement and l_0 depends on the cluster position.

Considering the period of the sinusoidal regression (8.14 μm) and the value of the ordinary refractive index of LiNbO_3 at 635 nm ($n_{eff} = 2.28$), one can solve for λ in Eq. 9.2, obtaining a value of $\lambda = 18.55 \mu\text{m}$. This value is larger than the actual wavelength, which means that the

cluster is too big for sampling visible wavelengths and what we obtained is a convolution (aliasing) of the actual interferogram.

Figure 9.15 Interference of a monochromatic source obtained recording the light scattered by the NP cluster shown in Fig. 9.14c.

9.4 Discussion and conclusions

In this chapter we have studied the possibilities of using PVT structures to create *ad hoc* 1D and 2D DOEs. This is one of the first actual applications of the NP patterns made by PVT. This DOEs fabrication technique has some important advantages over traditional ones, as it is low-cost and no time-consuming and offers reconfiguration capabilities. In fact, an interesting line of research is the *in situ* reconfiguration of these DOEs, as it has been proved that PVT patterns can be dynamically manipulated [85]. Currently, the main drawback of PVT-fabricated DOEs is their lack of precision and homogeneity when compared to devices fabricated using well-established techniques.

Two methods to transfer PVT-fabricated patterns from their original substrate to other passive or active substrates have been also developed. The first one is quite simple and can be

applied on any substrate, whereas the second one offers much better results (around 95% of the particles are transferred) in the exchange for higher complexity and the impossibility of transferring patterns to certain materials. Nevertheless, both offer excellent results in terms of pattern stability and fidelity to the original. The main motivation for developing these transference methods was avoiding the optical damage exhibited by $\text{LiNbO}_3\text{:Fe}$; however, they can become a tool for increasing the applicability of PVT patterns in photonics and other fields. Examples of potential applications are as integrated optical components, such as couplers and uncouplers in optical waveguides (as shown), or as tracks for photonic integrated circuits. It should be also mentioned that these transference methods can be applied not only to PVT patterns but also to other structures fabricated using different techniques [80].

Finally, the transference process allowed us to fabricate two kinds of integrated spectrometers which were tested at IPAG in France. Despite the advantages of fabricating these devices using PVT, like large area coverage and low-cost, their present performance was not as good as expected. However, the results were promising, and important sources of error were detected. Unfortunately, it was not possible to improve the nanoparticle gratings and perform a second stay at IPAG with better devices. However, if dedicated work is done in this line, it is expected that the capabilities of these devices can be highly improved.

Chapter 10: Collaborations on applications of photovoltaic and pyroelectric electric fields

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CHAPTER 10

Collaborations on applications of photovoltaic and pyroelectric electric fields

The present chapter is divided in two different sections. The first one deals with techniques that are directly related to the main topic of this thesis: the generation and study of microstructures of nano- and microparticles on z-cut $\text{LiNbO}_3\text{:Fe}$ crystals. It shows two applications of PVT for which part of the experimental procedures and theoretical calculations developed throughout this thesis work were useful to other members of my research group. The applications include the generation and study of plasmonic microstructures and the orientation of zeolites subjected to $\text{LiNbO}_3\text{:Fe}$ photovoltaic electric fields.

The second section shows some experiments and theoretical calculations performed during my stay in the Institute of Applied Sciences and Intelligent Systems (CNR-ISASI) in Pozzuoli, Italy. This section is focused on the manipulation of particles and liquid droplets using the pyroelectric effect of pure LiNbO_3 crystals. The techniques shown below are closely related to PVT, as pyroelectric and photovoltaic effect share some similarities. Even more, in our $\text{LiNbO}_3\text{:Fe}$ samples both phenomena can occur simultaneously when performing experiments, so it is interesting to learn about the pyroelectric effect in order to exploit an undeniable, potential synergy between pyroelectric and photovoltaic electric fields.

10.1 PVT applications

This section shows two applications of PVT for which part of the experimental and theoretical results of this thesis were of particular interest. The first application consisted in generating NP microstructures to enhance the luminescence of organic molecules through plasmonic resonance [65]. The second one studied the patterning distribution and orientation of anisotropic objects like zeolites on x- and z-cut LiNbO₃:Fe crystals [66].

10.1.1 PVT plasmonic microstructures for fluorescence enhancement

In this case, the main objective was studying the enhancement in fluorescence of luminescent of organic and biological molecules using NP patterns made by PVT. The enhancement was achieved through localized surface plasmon resonances (LSPR). *Plasmons* are collective oscillations of free electrons in metals and LSPR can occur at the interface between metallic NPs and a dielectric medium [26]. LSPR are known to strongly enhance the linear (e.g., absorption, luminescence, Raman scattering) and nonlinear (e.g., second harmonic generation) optical responses of a medium placed close to the NPs [84, 94]. The wavelengths for which the enhancement is the strongest depend on the properties of the particle (composition, size, shape...) and the surrounding medium itself. The plasmonic resonances of the metallic structures generated by PVT cover a broad spectral range (400-700 nm) due to the size dispersion of the particles and clusters that comprise them.

Typical techniques for making metallic nano- and microstructures are based on bottom-up strategies, like the deposition from metal colloids. However, they tend to be complex and require many steps. Some of them even lack of enough repeatability or do not offer the possibility of obtaining *ad hoc* structures [98]. Top-down strategies are similar to those explained in §9.1 (FIB, lithography...), which deliver great results in exchange of sophisticated equipment and time-consuming processes. In this work, PVT was proposed as a low-cost, easy, quick alternative for the assembly of NP microstructures. Furthermore, pattern reconfigurability is also an advantage of PVT over similar techniques, like NP precipitation in the boundaries of periodically polled ferroelectrics [90, 119].

My contribution to this work consisted in the fabrication of a chequered pattern of silver nanoparticles ($\varnothing 25$ nm) and the transference (§9.2) of a linear grating (made of the same NPs) on an organic planar waveguide. Note the use of silver NPs instead the aluminium ones used throughout most of this thesis. This is because silver and gold are the most commonly used metals in plasmonic applications due to its large plasmonic resonance in the visible region of the light spectrum.

The chequered pattern was obviously made on a z-cut $\text{LiNbO}_3\text{:Fe}$ substrate, taking advantage of the 2D patterning capabilities of this kind of substrate (§6.2). Each square side was $200\text{ }\mu\text{m}$ long. The pattern was not continuous, as different isolated regions and clusters can be observed (Fig. 10.1a), what makes it interesting for broad-band applications. After fabrication the pattern was covered with Disperse Red 1 (DR1, $\text{C}_{16}\text{H}_{18}\text{N}_4\text{O}_3$, an organic dye used in optical switching and optical data storage [138]) by simply immersing the z-cut sample with the microstructure on top of it in a solution of ethanol and DR1 (1 g/L). The great stability of the patterns makes possible this procedure, as particles remain attached to the substrate. The enhancement measurements were performed by other members of the group using a microfluorescence setup based on a confocal microscope and a laser source at 488 nm. The scan was made parallel to a square side and the results are shown in Fig. 10.1b. An enhancement factor in luminescence of around 10 can be observed in the areas matching the NPs pattern, which is a great value considering that similar systems achieve values between 6 and 10 [165]. This efficient fluorescence enhancement can be probably addressed to the broad resonance band of the microstructure, which overlaps the absorption and emission bands of DR1 [65].

As commented above, my second contribution to this work consisted in transferring a Ag NP grating onto a planar organic waveguide. The waveguide consisted of a glass substrate with a PMMA film on top. The PMMA film contained another organic dye, perylene orange ($\text{C}_{48}\text{H}_{42}\text{N}_2\text{O}_4$, PDI-O), homogeneously distributed (1 wt%). PDI-O is used in waveguide-based organic lasers and biological sensors [148]. We had to choose the simple transference process of the two explained in §9.2, as DCM would have dissolved the PMMA film containing the dye. In fact, the process had to be done with extreme care. As the PMMA film could not stand the $200\text{ }^\circ\text{C}$

required for an optimum transference process, the working temperature had to be reduced to 110 °C, which yielded to a lower number of transferred particles. However, the amount was enough to observe an increase of the fluorescence at the regions in the vicinity of the particles (Fig. 10.2). The exciting laser wavelength was 532 nm, close to the absorption peak of PDI-O [65]. This simple experiment suggests that metallic structures could be designed to improve the lasing efficiency of these systems or increase their versatility in integrated optical systems.

Figure 10.1 (a) Al NP chequered pattern. (b) Overall FL intensity as a function of the position along the line indicated in (a). Retrieved from [65].

Figure 10.2 Ag NP fringe pattern transferred on top of a planar organic waveguide. Retrieved from [65].

10.1.2 Study of zeolite orientation

The goal of this second work was studying the patterning of anisotropic objects by PVT, like elongated zeolites (ZLs) type L. ZLs are a broad class of microporous ceramic materials based on an aluminosilicate structure [180]. The term “zeolites” encompasses many families of particles with different structures and applications in technology, as catalysts, containers or filters for molecule separation [41]. The ZLs type L used in this work are elongated cylindrical structures ($1.5 \times 4 \mu\text{m}^2$) with nanochannels ($\varnothing 1.26 \text{ nm}$) aligned along their longitudinal axis (Fig. 10.3). This type of ZLs has high capabilities to be functionalized. They have been used in biotechnological applications such as nanocontainers attached to self-propelling bacteria or loaded with luminescent labels for imaging purposes [146, 170]. Furthermore, some applications of ZLs type L require of a large number of particles to be aligned in a particular direction in order to take advantage of their strict orientation. For example, this is a critical requirement for increasing the efficiency of solar cells [97].

Figure 10.3 Zeolites type L structure. Retrieved from [180].

The intrinsic and extrinsic anisotropy of ZLs made them an interesting particle to be studied, as most PVT experiments have been carried with isotropic, spherical particles. The ZLs used in this work were electrically neutral and had an aspect ratio of 2.6, so under the influence of an electric field they are subjected to a dielectrophoretic torque in addition to the dielectrophoretic force. As explained in §3.1.3, this torque tends to align one of the main axes of the particle with

the local electric field. This phenomenon was previously observed in living *Escherichia coli* bacteria in x-cut samples [128], but it had not been investigated in z-cut crystals.

My contribution to this work was calculating the electric field and dielectrophoretic potential distribution in the vicinity of z-cut $\text{LiNbO}_3\text{:Fe}$ crystals after illumination in order to compare them with the experimental trapping of ZLs. The experiments were carried out by other members of the group using two different light profiles: a circular and a Gaussian spot. The DEP potentials are shown in Figs. 10.4a,b.

Regarding the circular spot, the electric field is essentially perpendicular to the crystal above the illuminated area and it bends as it approaches to the boundary of the illumination. Outside the illuminated area the electric field is almost parallel to the crystal surface. This change in the electric field direction is clearly observed in the ZLs orientation of Fig. 10.4c. On the one hand, those trapped in the centre of the circle have their longitudinal axis perpendicular to the crystal. See in Fig. 10.4d how most of the ZLs show a circular profile, which matches the base of a cylinder. The orientation of these ZLs was further confirmed as, a constant cross-section was observed while focussing with the microscope at different heights from the crystal surface. On the other hand, particles outside the illuminated area were trapped in radial chains that lay on the crystal.

In the case of particle trapping after Gaussian illumination, the particle chains were even longer (Fig. 10.4e). A possible explanation is the fact that this light pattern generates an electric field which always points towards the centre of the illumination, what favours chain formation and deposition on the crystal surface. These two examples show that the long axis of the ZLs was almost always aligned with the local electric field, which is the only stable configuration predicted by theory. This work proves how useful theoretical calculations are not only to predict where particles trap but also their orientation in the case they exhibit some kind of anisotropy.

Figure 10.4 (a) DEP potential due to a circular light profile. (b) DEP potential due to a Gaussian beam light profile. (c) Partial view of a ZLs pattern after a circular light profile illumination. The inset shows a small chain of ZLs. (d) ZLs in the centre of the circular pattern shown in (a). (e) Long chains of ZLs obtained using a Gaussian light distribution. Retrieved from [66].

10.2 Pyroelectric effect

The pyroelectric effect was described in §1.3.3 as a change in the spontaneous polarization of LiNbO_3 due to a change in its temperature. This change in the spontaneous polarization can be modelled as a surface charge density accumulation on the crystal surfaces, which is usually screened by ambient ions. However, the electric fields associated to this surface charge density can be used to trap or structure particles in a similar way to PVT.

Occasionally, during the performance of standard PVT experiments, strange patterns like the one shown in Fig. 10.5 appeared. This pattern was obtained after illuminating a z-cut sample with the light profile shown in Fig. 8.11a. However, the particle distribution is completely different to the expected one, as there are particles trapped on illuminated and non-illuminated squares. It took us some time to realize that those kinds of patterns were the result of the addition of the photovoltaic and the pyroelectric electric fields. When a sample is cooled down a few degrees

after illumination (for example, if the NP suspension is at lower temperature than the crystal), the surface charge density that appears in both crystal faces due to the pyroelectric effect is of the order of that generated by the photovoltaic effect, but has the opposite sign. This new charge distribution produces these curious patterns. The interaction between pyroelectric and photovoltaic effect is currently being investigated in our lab and interesting results have been already obtained [147].

Figure 10.5 Chequered pattern made of Al NPs which shows a combination of photovoltaic and pyroelectric trapping.

Within this framework, it seemed beneficial to establish a collaboration with the group of Pietro Ferraro at the CNR-ISASI, as one of their lines of research deals with exploiting the LiNbO_3 pyroelectric effect in several fields such as microfluidics, particle trapping, polymer poling or bacteria manipulation [74, 90, 91]. I conducted a three-month research stay at their laboratory in order to get a deeper learning on the pyroelectric effect and its associated experimental techniques and systems. For the purposes of this thesis, two are the most important works I developed: nanoparticle patterning using PPLN crystals and droplet manipulation through an electrohydrodynamic (EHD) jet printing system.

10.2.1 Magnetic nickel nanostructures

Direct, fast obtention of arbitrary patterns through pyroelectric effect is not an easy task. A precise control on the local temperature change, and thus the pyroelectric surface charge, is

difficult due to heat transfer within the crystal. There are indeed techniques able to do so, and arbitrary 2D structures have been printed using the pyroelectric effect and a point heat source, like a hot tip [74], but, as one may imagine, these methods are time consuming and require a precise control of the setup. In this work another approach was studied. It achieves high-throughput particle trapping based on z-cut LiNbO_3 crystals polling.

Polling consists in making domains in a crystal where the c-axis points towards the opposite direction than in the rest of the sample. When these crystals are heated the areas where c-axis points “upwards” (c^+) become negatively charged, as there is a decrease of the spontaneous polarization, and therefore an excess of negative screening charge. For the same reason, the areas with c-axis pointing “downwards” (c^-) become positively charged. This process is depicted in Fig. 10.6 and can be used to trap particles taking advantage of the DEP and EP potential distributions that appear due to the positive-negative charge pattern on the surface.

Figure 10.6 Pyroelectric effect in a poled LiNbO_3 crystal due to a sudden increase (top) or decrease (bottom) in temperature.

The goal of this work was to create patterns of magnetic NPs embedded in PDMS films using the pyroelectric effect of pure z-cut LiNbO_3 crystals polled with hexagonal domains. These films have different applications in microfluidics and biomedicine, as they result attractive due to both their flexibility and their magnetic properties. For example, they can be used to detect, trap and sort other magnetic micro- and nanoparticles.

For making the films, a solution of PDMS with nickel NPs ($\varnothing 250$ nm, 12 wt%) was used. It also contained a curing agent (Sylgard 184, 10 wt%); this way, the heating process required to stimulate the pyroelectric effect in the sample also triggers the cross-linking reaction. As substrates, three z-cut LiNbO_3 samples (0.5 mm thick) were subjected to electric field poling in order to obtain an array of hexagonal domains with reversed polarization direction. The total modified area was the same in all of them ($2 \times 2 \text{ cm}^2$), but with different hexagon sizes and periodicities (50, 200 and $400 \mu\text{m}$).

The experiment consisted in spin-coating the LiNbO_3 samples with the Ni-PDMS solution and heat them for 1 minute at 170°C on a hotplate. As commented above, this activates in a single step the pyroelectric effect and the cross-linking of the PDMS (Fig. 10.7).

Figure 10.7 Pyroelectric NP patterning based on PPLN crystals. (a) The Ni-PDMS solution is spin coated at 7000 rpm for some dozens of seconds. (b) The sample is heated up to 170°C for a minute to activate the pyroelectric effect and the PDMS cross-linking. (c) Particles are arranged according to the PPLN pattern. (d) When cooled down, the PDMS film with the embedded NP structure can be easily removed.

Nickel particles were supposed to be neutral, so identical patterns were expected to be obtained independently of the sample face chosen to carry out the experiments. However, it was found that patterns were indeed face-dependent and very different. On the one hand, if the experiments were performed on the c^- face of the crystal (c^+ within the hexagonal domains) the particles filled the hexagons (Fig. 10.8a). On the other hand, if they were carried out using the c^+ face (c^- within the hexagonal domains) the particles were trapped outside the hexagons (Fig. 10.8b). These results seemed to indicate that NPs were not neutral, but positively charged.

Figure 10.8 Patterns of Ni NPs in PDMS obtained by (a,b) heating or (c,d) cooling z-cut PPLN crystals. Different results are obtained depending on whether the c-axis was pointing (a, c) downwards or (b, d) upwards outside the inverted hexagonal domains. The theoretical (e) DEP and (f) EP potentials are depicted for an arbitrary change in temperature.

The experiments above were performed prior to my stay. When I arrived, I was asked to carry out a calculation in COMSOL® in order to obtain the DEP and EP potential distributions of the system, compare them with the experimental patterns and check the hypothesis of the particles being positively charged. The results of such calculations are shown in Figs. 10.8e,f. DEP potential predicts that Ni particles should be trapped in the boundaries of the hexagons no matter which

face is being used, whereas EP potential predicts the particles to be outside/inside the hexagonal domains when the experiment is performed on the c^+/c^- face, exactly as experimentally happened.

Even though theoretical calculations confirmed the charge state of the particles, it was still uncertain where the charge came from. In order to double-check the charge state of the particles and clarify its origin, we performed the same experiment, but instead of heating the samples, they were cooled down (3-18 hours at -20°C). This method has the disadvantage of not activating the PDMS cross-linking, which is the reason it had not been used before. The results agreed with the hypothesis that the particles were positively charged (Figs. 10.8c,d), but in this case the particles seemed to have less electric charge, as some DEP features, like preferential trapping at the hexagons edges and NP chains, were evident. This was a key fact that helped us to find out why particles were charged.

Prior to the first set of experiments (those heating the sample), the solution of PDMS with the Ni NPs was subjected to magnetic stirring and ultrasound treatments for 5h in order to obtain a homogeneous distribution. However, when we performed the experiments cooling the sample, this treatment was much shorter, of around 30 minutes. The fact that the particles subjected to long ultrasonic baths seemed to have more electric charge than those only sonicated for half an hour suggested that the ultrasound treatments were responsible of charging the particles. Moreover, this hypothesis is supported by the fact that this charging procedure was also observed in our laboratory (§8.3.1).

10.2.2 EHD jet printing

This second work deals with “patterning” in a different sense than the rest of this thesis, as it consists in dispensing droplets from a reservoir using a EHD system. These systems are useful for dispensing liquid droplets of very small diameters and volumes (nano- and picolitres). The ability of obtaining such small droplets finds applications in microfluidic equipment such as lab-on-a-chip devices or sensors and in the manipulation of particles and biological material too fragile to be patterned by conventional lithography techniques [74]. In this work, a pyro-EHD jet printing system was used as a “pyro-concentrator”, a device capable of detecting very low

concentrations of molecules in a little amount of a liquid sample, which implies higher resolutions than conventional methods [92].

Figure 10.9 EHD jet printing experimental setup.

The theoretical background of this system was explained in §3.2. In this case, the electric field that affects the liquid is generated by the pyroelectric effect of a pure LiNbO₃ crystal. The experimental setup is depicted in Fig. 10.9. A continuous-wave CO₂ laser at 10.6 μm was used to heat a z-cut LiNbO₃ sample (500 μm thick) that lies on top a microscope slide²⁴. The liquid reservoir was placed on top of a gold tip on a moving platform controlled by mechanical micro-actuators. Pulses of 50-100 ms long and 80 W/cm² were emitted by the CO₂ laser while the reservoir was being approached to the microscope slide. At a certain distance (dependent on the drop composition, shape and volume) micro-droplets were ejected from the reservoir towards the slide. A 10 $\times$ microscope objective was placed between the sample and a high-speed CMOS camera (Motion Pro Y3-S1) for image and video recording.

²⁴ Regarding the microscope slides, the used ones had one side covered with positive charged, reactive amino groups (NH³⁺) (SuperAmine 2 from Arrayit). In principle, these slides were used for better attachment of some biological species, but it was found during the performance of the experiments that common glass slides screened the electric field of the LiNbO₃ sample.

We performed the EHD jet printing with different liquid samples:

- A commercial lactose solution with a fluorescent tag. The aim was obtaining a calibration curve of the lactose concentration based on later fluorescence measurements.
- A suspension of gold nanoparticles ($\varnothing 21$ nm) in aqueous solution plus a solution of Thiram ($C_6H_{12}N_2S_4$, a fungicide used in crops) in ethanol or water ($10\mu M$). In this case, the idea was dispensing gold nanoparticles and Thiram on the same place looking for an enhancement of the Thiram signal in Raman measurements.

Part of the work consisted in the development of a new reservoir deposition system on the gold tip. This step was used to be performed with a micropipette (Gilson F144801), but the control of the droplet volume, shape and placement was not precise. So instead of the micropipette, we used a digital syringe (Hamilton 7000.5H, resolution $0.005\mu L$). Droplets dispensed on a microscope slide with both tools are compared in Fig. 10.10. The greater repeatability of the digital syringe over the traditional micropipette is evident.

Figure 10.10 Comparison of droplets of polystyrene deposited using a digital syringe (left) and a micropipette (right).

As stated in Eq. 3.15, the volume of the droplet is a key parameter for droplet dispensing, but it is also its shape. Experimentally, it had been found that in order to obtain properly dispensed microdroplets (Fig. 10.11d), the shape of the reservoir has to be similar to that depicted in Fig. 10.11b. Otherwise, the ejected droplet tends to be too big (Fig. 10.11e). This shape was

obtained with an appropriate combination of tip height ($\sim 500\ \mu\text{m}$) and reservoir volume ($0.2\ \mu\text{L}$ for lactose and water-based samples).

Figure 10.11 (a, c) Different reservoir shapes depending on the gold tip height. (d, e) A comparison between a properly dispensed droplet and a droplet that is bigger than required.

Regarding the reservoir shape, evaporation plays an important role when working with volatile liquids like the Thiram-ethanol solution. Due to the experimental setup, a non-negligible amount of time passes between reservoir deposition and the ejection, so part of the reservoir evaporates and its volume and shape changes. In those cases, we were forced to a compromise solution that consisted in depositing three droplets of $0.3\ \mu\text{L}$ instead of one of $0.2\ \mu\text{L}$. We were aware that there would be an important change in the Thiram concentration due to ethanol evaporation, but as in this case the research was in the early stages of investigation, we disregarded this fact. Finally, it should be mentioned that evaporation can also affect to lactose and water-based reservoirs if the experiment is performed slow enough, as their small volume increases their evaporation rate (Fig. 10.12).

Figure 10.12 Lactose droplet evaporation. The time lapse between (a) and (f) is about 2 minutes.

The EHD system was successfully tested with the lactose solution using three different nominal concentrations of lactose: 0, 10 and 30 ng/mL. After deposition, the droplets fluorescence was measured using a microarray reading scan emitting at 532 nm (InnoScan 710). The calibration curve obtained from various sets of experiments is presented in Fig. 10.13. It shows a linear relation between the luminescence and the lactose concentration.

The experiment regarding the enhanced detection of Thiram using gold NPs produced good results concerning Thiram detection, but the drop sizes required for detection were similar to those obtained by traditional methods.

Figure 10.13 Calibration curve plotting spot luminesce versus lactose concentration. Spot examples are shown for each concentration. Their mean diameter is around 180 μm .

10.3 Conclusions and final remarks

This final chapter had two different purposes. First, it showed the applicability of the theoretical and experimental results discussed throughout this thesis in works of other members of my research group. It has been proved the use of 2D patterns on z-cut crystals as platforms for plasmon enhancement and the versatility and applicability of the “simple” transference process when the destination substrate is too delicate. Also, the developed theoretical model has been proved useful not only to estimate where particles are trapped as a result of a certain illumination pattern but also their orientation in case they exhibit some kind of anisotropy. Furthermore, the fact that the experimental patterns matches so well the theoretical calculations can be interpreted as an additional validation of the model.

The second purpose was introducing the pyroelectric effect. It is a phenomenon also exhibited by our samples and could compete with the photovoltaic charge transport under certain circumstances, what should be kept in mind when performing PVT experiments. In fact, this interaction between pyroelectric and photovoltaic effect is being studied [147], and some efforts

have been made to adapt the FEM model presented in this work to also take into account the pyroelectric effect.

The familiarisation with the pyroelectric effect was the aim of my stay at CNR-ISASI. During that stay, I was mostly involved in two experimental works. The first one is a technique for making structures of magnetic NPs embedded in PDMS. It is a three-step method based on PPLN crystals which electro- and dielectrophoretic potentials and particle distribution resemble those of PVT. This suggests an intimate relation between both methods, and it is possible that they share other experimental features and trapping limitations. The second work consisted in dispensing droplets of very small volumes (nano- and picolitres) from a reservoir taking advantage of the pyroelectric effect of LiNbO_3 . Recently, some works dealing with liquids manipulation using PVT and z-cut crystals have been published [57, 58, 82]. Learning from well-established systems based on the pyroelectric effect is important, as one may expect the behaviour of liquids subjected to photovoltaic electric fields to be similar.

Conclusions

Summarizing, the main contributions of this thesis work are *i)* to provide and consolidate a novel capability for PVT: arbitrary 2D trapping and patterning based in z-cut substrates instead of traditional x- or y-cuts, and *ii)* the application of the technique to fabricate functional 2D microstructures of nanoparticles such as diffractive devices or plasmonic platforms. This general result has required multiple steps, including fundamental and technological aspects and requiring theoretical and experimental work. The specific conclusions are the following:

Regarding the theoretical analysis, a very accurate analysis has been developed. The system of partial differential equations that determine the photovoltaic charge transport in $\text{LiNbO}_3\text{:Fe}$ has been solved using the finite element method. It has been found that the whole system must be solved in order to obtain an accurate time evolution of the current density, electric field and space charge distribution inside the crystal. For the first time, current density components perpendicular to the c-axis and light absorption have been considered in a theoretical model for z-cut crystals. Both play an important role in the time evolution of the space charge and distribution, especially when illuminated and non-illuminated faces are compared.

Contrary to the assumptions of the previous models, charge accumulation in z-cut is not limited to a surface charge density at the crystal surfaces but requires of an internal space charge accumulation at the boundaries of illumination so saturation electric field is reached in the whole illuminated area. The sharper the light profile, the narrower and higher this space charge accumulation.

Time constants of space charge evolution obtained with simple models are lower than those obtained with the complete model. Because the differences are of the order of typical experimental times, the complete model should be used when accurate predictions are required. On the contrary, the mean surface charge density at saturation can be predicted using simple models within a reasonable margin of error.

From the point of view of experimental patterns, it has been demonstrated that using z-cut samples enables obtaining a faithful reproduction of any light pattern, no matter the charge state of the particles. The precision, simplicity and high throughput of this technique makes PVT a competitive tool, particularly advantageous to produce functional microstructures.

Patterns of neutral and charged particles have been investigated and compared, finding that they exhibit some different features. In particular, dielectrophoretic patterns tend to show a global and local edge enhancement, i.e., the particle concentration at the edges of the pattern and the individual motifs is larger. In addition, when the fringe electric field or the particle concentration of the suspension is high, particle chains tend to appear, which affects to the pattern texture and look. This effect can be used to obtain different patterns using the very same light distribution but different suspension concentrations.

In the case of patterns made with charged particles, they usually show a fading in particle concentration and pattern definition, being the concentration larger and the definition better in the centre than in the edges of the illumination. However, it has been found that using thin crystals (0.5 mm) this phenomenon seems to be attenuated, and almost perfect reproductions of the light profile have been obtained using charged particles and thin crystals. In electrophoresis there are not visible nanoparticle chains.

It should be also mentioned that if particle size is comparable to motif size, the definition of the final pattern is worse and the presence of areas with a lack or excess of particles inside the pattern is more probable due to particle-particle interaction.

Most of the experimental features of the nanoparticle patterns can be explained using the finite element model developed in this thesis. Analysing the potential energy and forces distribution, particle distribution and orientation can be predicted up to a major extent.

Paying attention to the possible applications of our nanoparticle patterns, two methods for pattern transference from the original $\text{LiNbO}_3\text{:Fe}$ crystal to an arbitrary substrate have been developed. The first one is very simple and can be used in almost any kind of destination substrate; however, only around 50% of the particles are transferred. The second one is more efficient and complex and cannot be applied on every substrate as it requires the use of organic solvents. Using this second transference method results are outstanding, reaching a 95% of particle transference.

Different devices based on our nanostructures have been fabricated. On the one hand, 1D and 2D diffractive optical elements exhibited a great performance, as their experimental capabilities have been compared with the theoretical ones. Unfortunately, the integrated spectrometers characterised during a research stay at IPAG did not work as expected, although the results pointed towards the possible reasons of their malfunction.

Finally, exploiting the pyroelectric effect for particle and liquid manipulation was also investigated during a research stay at the CNR-ISASI, due to its close relation with the photovoltaic effect. In fact, sometimes they occur together during the performance of PVT trapping experiments. As the charge distribution obtained from both phenomena can be compared in certain situations, there is a possible technological transfer between both manipulation techniques.

To conclude, I would like to point out which should be, from my point of view, the next steps in the research of PVT. First, a proper description of the physical (and probably chemical) processes that occur in the $\text{LiNbO}_3\text{:Fe}$ crystal surfaces is required to obtain better predictions of the PVT trapping. This is of high relevance for z-cut samples, as in this thesis it has been demonstrated that rate equations are not enough to describe the photovoltaic phenomenon at the very sample surface and that charge transfer between the crystal and the nanoparticles is possible. Including the complete photovoltaic tensor in the rate equations is less important, but

it also deserves attention; certain terms of the photovoltaic current perpendicular to the optical axis can arise for high light intensities, thus breaking the pseudo-isotropy of z-cut surfaces. When this is done, proper particle dynamic simulations can be performed in order to accurately predict the experimental patterns and thus reaching submicrometric patterning. Regarding experimental particle trapping and manipulation, special attention should be paid to certain parameters that have been somehow disregarded since the beginning of the technique: the ambient conditions (it has been already proved that ambient humidity have a great influence during technique operation), concentration and dispersion of the particles in the suspensions, immersion time and the exact doping level and oxidation-reduction state of the $\text{LiNbO}_3\text{:Fe}$ samples used to performed the experiments. This would help to reduce the experimental variability.

Publications

The studies carried out in this thesis work have been published in different scientific journals and presented in international conferences.

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Appendix A

For the sake of clarity, let the system of equations analysed in §2.2 be repeated here:

$$\frac{\partial n}{\partial t} = sIN_D - \gamma nN_A - \frac{1}{q} \nabla \cdot \mathbf{J} \quad (\text{A.1})$$

$$\frac{\partial N_D}{\partial t} = -\frac{\partial N_A}{\partial t} = -sIN_D + \gamma nN_A \quad (\text{A.2})$$

$$\mathbf{J} = q\mu n\mathbf{E} - qD\nabla n + qsIL_{PV}N_D\hat{\mathbf{u}}_{PV} \quad (\text{A.3})$$

$$\nabla \cdot (\epsilon_0 \epsilon \mathbf{E}) = q(N_D - N_{D0} + n) \quad (\text{A.4})$$

According to the literature, when this system of equations is solved using FEM the mesh should resolve the Debye length (around 2nm) in order to obtain an appropriate description of the space charge distribution²⁵ [17, 20]. However, this entails a high computational cost, as the number of resulting elements is huge, especially for 3D geometries.

Luckily, there is no need to use such a fine mesh. Let us look at Fig. A.1, which shows the space charge at the vicinity of the c^+ face of a homogeneously illuminated crystal for four mesh sizes and a typical set of crystal parameters (Table 2.I) at saturation. It can be seen that both the spatial distribution and value of the space charge are clearly different in each case (and, although not shown, it is antisymmetric about the central plane of the crystal). Nevertheless, if these various space charge distributions are integrated along a line perpendicular to the crystal surface (i.e., if

²⁵ Furthermore, this condition can be related to certain instabilities that appear in drift-diffusion-reaction equations like Eq. A.1 [95], related to the Péclet and Damköler numbers. However, that kind of problems have never been observed in our calculations, so they are not considered in this discussion.

one computes the areas under the curves in the plot depicted in Fig. A.1), it is found that from a certain mesh refinement all the results are equal to -10.7 mC/m^2 . This line integration defines a new variable that does not depend on the mesh. As the variable has units of C/m^2 , it can be understood as an “equivalent surface charge density”, which can be used to compare the results of the calculations with previous models (as it is done in §7.3) or with other physical phenomena that arise in $\text{LiNbO}_3\text{:Fe}$, like the pyroelectric effect [147].

Figure A.1 Space charge density distribution in a z-cut $\text{LiNbO}_3\text{:Fe}$ crystal at saturation due to a homogeneous illumination using different meshes. Only half the simulation domain has been plotted. (a) Schematic of the geometry. (b-e) Space charge density distribution for different mesh resolutions. (f) Space charge density distribution as a function of the Z coordinate for (b-e).

Moreover, the main variables that are involved in the photovoltaic charge transport (e.g., electric field or current density) are also independent on the mesh size, as long as the mesh is not too coarse (see Fig. A.2). The appropriate mesh size depends on the crystal and illumination parameters, so usually a mesh refinement analysis is required to ensure a correct solution. This mesh refinement process is also done in FEM for calculating the solution error (§5.4.4), so it can be performed for both purposes simultaneously.

Figure A.2 Component of the electric field parallel to the optical axis (E_z) in a z-cut LiNbO₃:Fe crystal at saturation due to a periodic illumination of fringes using different meshes. Only half the simulation domain has been plotted. Illumination profile is depicted above the plots.

Of course, it is possible to use a mesh whose elements are close or even reach the Debye length. In fact, for extremely fine meshes the obtained space charge distribution no longer depends on the mesh, but also an unexpected effect arises. The space charge distribution for the case of homogeneous illumination is shown in Fig. A.3. This plot shows an asymmetric distribution of the space charge about the central plane of the crystal at saturation (all the previous ones were symmetric), although the value of the equivalent surface charge density is the same for both faces and matches the previous one ($\pm 10.7 \text{ mC/m}^2$).

Unfortunately, even if this result might be interesting due to the asymmetry of the solution, a problem arises when one considers the origin of Eqs. A.1-A.4. These equations are the mathematical translation of a microscopic model for the photovoltaic charge transport [23], and some parameters are defined using statistical values, such as the photovoltaic drift length (L_{PV}).

This means that rate equations can be applied as long as the crystal volume that is considered is big enough to contain an appropriate number of iron impurities. However, if a $\text{LiNbO}_3\text{:Fe}$ sphere whose radius equals the Debye length is considered, and supposing a typical iron concentration ($N = 10^{25} \text{ m}^{-3}$), it turns out that the mean number of iron impurities in that sphere is about $3 \cdot 10^{-2}$! This means that some of the assumptions made to obtain Eqs. A.1-A.4 are no longer applicable. Besides, if one takes into account that these calculations are focused on the crystal surface, it is probable that at that nanometric scale other effects that have been disregarded play an important role (e.g., surface states due to the finite size of the crystal). Thus, the numerical results shown in Fig. A.3 may not be faithful to reality.

Figure A.3 Space charge density distribution in a z-cut $\text{LiNbO}_3\text{:Fe}$ crystal at saturation due to a homogeneous illumination using a mesh that resolve the Debye length of the crystal. Abscissa represents the distance from the corresponding crystal surface.

To sum up, it is possible to perform the numerical calculations using a mesh so fine that it resolves the Debye length of the crystal. However, this is not worth the associated computational cost, as one cannot be sure of the precision of the results due to the formulation of the rate equations. For practical purposes it is better to use coarser meshes, as the global results do not differ from those obtained using an extremely fine discretization.

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