MECHANICAL BEHAVIOR
OF 2G REBCO HTS AT 77 AND 300 K

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Mechanical behavior of 2G REBCO HTS at 77 and 300 K

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Στην οικογένειά μου
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Resumen

El gran esfuerzo realizado durante la última década con el fin de integrar los diferentes materiales superconductores en el campo de los sistemas eléctricos y en otras aplicaciones tecnológicas ha dado lugar a un campo de investigación amplio y prometedor. El comportamiento eléctrico de los Superconductores de Alta Temperatura (SAT) crítica (masivo y cintas) depende de diferentes parámetros desde su fabricación hasta la aplicación final como imanes o cables. Sin embargo, las aplicaciones prácticas de estos materiales están fuertemente vinculadas con su comportamiento mecánico tanto a temperatura ambiente (manipulación durante fabricación o instalación) como a temperaturas criogénicas (condiciones de servicio).

En esta tesis se ha estudiado el comportamiento mecánico de materiales masivos y cintas de alta temperatura crítica a 300 y 77 K (utilizando nitrógeno líquido). Se han obtenido la resistencia en flexión, la tenacidad de fractura y la resistencia a tracción a la temperatura de servicio y a 300 K. Adicionalmente, se ha medido la dureza mediante el ensayo Vickers y nanoindentación. El módulo de Young se midió mediante tres métodos diferentes: 1) nanoindentación, 2) ensayos de flexión en tres puntos y 3) resonancia vibracional mediante grindosonic. Para cada condición de ensayo, se han analizado detalladamente las superficies de fractura y los micromecanismos de fallo. Las propiedades mecánicas de los materiales se han comparado con el fin de entender la influencia de las técnicas de procesado y de las características microestructurales de los monocristales en su comportamiento mecánico.

Se ha estudiado el comportamiento electromecánico de cintas comerciales superconductoras de YBCO mediante ensayos de tracción y fatiga a 77 y 300 K. El campo completo de deformaciones en la superficie del material se ha obtenido utilizando Correlación Digital de Imágenes (DIC, por sus siglas en inglés) a 300 K. Además, se realizaron ensayos de fragmentación in situ dentro de un microscopio electrónico con el fin de estudiar la fractura de la capa superconductora y determinar la resistencia a cortante de la intercara entre el substrato y la capa cerámica. Se ha conseguido ver el proceso de la fragmentación aplicando tensión axial y finalmente, se han implementado simulaciones mediante elementos finitos para reproducir la delaminación y el fenómeno de la fragmentación.
Por último, se han preparado uniones soldadas entre las capas de cobre de dos cintas superconductoras. Se ha medido la resistencia eléctrica de las uniones con el fin de evaluar el metal de soldadura y el proceso. Asimismo, se ha llevado a cabo la caracterización mecánica de las uniones mediante ensayos “single lap shear” a 300 y 77 K. El efecto del campo magnético se ha estudiado aplicando campo externo hasta 1 T perpendicular o paralelo a la cinta-unión a la temperatura de servicio (77 K). Finalmente, la distribución de tensiones en cada una de las capas de la cinta se estudió mediante simulaciones de elementos finitos, teniendo en cuenta las capas de la cinta mecánicamente más representativas (Cu-Hastelloy-Cu) que influyen en su comportamiento mecánico.
Abstract

The strong effort that has been made in the last ten years to integrate the different superconducting materials in the field of electrical power systems and other technological applications led to a wide and promising research field. The electrical behavior of High Temperature Superconducting (HTS) materials (bulk and coated conductors) depends on different parameters since their processing until their final application as magnets or cables. However, practical applications of such materials are strongly related with their mechanical performance at room temperature (handling) as well as at cryogenic temperatures (service conditions).

In this thesis, the mechanical behavior of HTS bulk and coated conductors was investigated at 300 and 77 K (by immersion in liquid nitrogen). The flexural strength, the fracture toughness and the tensile strength were obtained at service temperature as well as at 300 K. Furthermore, their hardness was determined by Vickers measurements and nanoindentation and the Young’s modulus was measured by three different techniques: 1) nanoindentation, 2) three-point bending tests and 3) vibrational resonance with a grindsosonic device. The fracture and deformation micromechanisms have been also carefully analyzed for each testing condition. The comparison between the studied materials has been performed in order to understand the influence of the main sintering methods and the microstructural characteristics of the single grains on the macroscopic mechanical behavior.

The electromechanical behavior of commercial YBCO coated conductors was studied. The mechanical behavior of the tapes was studied under tensile and fatigue tests at 77 and 300 K. The complete strain field on the surface of the sample was obtained by applying Digital Image Correlation (DIC) at 300 K. Additionally, in situ fragmentation tests inside a Scanning Electron Microscope (SEM) were carried out in order to study the fragmentation of the superconducting layer and determine the interfacial shear strength between substrate and ceramic layer. The fragmentation process upon loading of the YBCO layer has been observed and finally, Finite Element Simulations were employed to reproduce delamination and fragmentation phenomena.
Finally, joints between the stabilizing Cu sides of two coated conductors have been prepared. The electrical resistivity of the joints was measured for the purpose of qualifying the soldering material and evaluating the soldering process. Additionally, mechanical characterization under single lap shear tests at 300 and 77 K has been carried out. The effect of the applied magnetic field has been studied by applying external magnetic field up to 1 T perpendicular and parallel to the tape-joint at service temperature (77 K). Finally, finite element simulations were employed to study the distribution of the stresses in each layer, taking into account the three mechanically relevant layers of the coated conductor (Cu-Hastelloy-Cu) that affect its mechanical behavior.
Chapter 1

Introduction

1.1 Superconducting materials

Kamerlingh Onnes was a Dutch physicist and the first scientific who liquefied helium. In 1911, he was working in his laboratory on new cryogenic techniques, when he discovered a strange phenomenon affecting the electrical conductivity of Mercury at very low temperature (4 K). Initially he called it suprageleider, translated into English as supraconductor in the first articles. However, later the term superconductivity was adopted for the phenomenon. (Blundell S., 2009).

Superconductivity is an outstanding property that appears in some materials at low temperatures when they lose all electrical resistance and expel magnetic fields from its interior. To understand superconductivity led to thorough knowledge of certain parts of physics and the expectations of controlling superconductivity at higher temperatures promises endless future applications (Blundell S., 2009).

One of the basic phenomena of superconductivity is the Meissner effect that explains the expulsion of the magnetic field from the interior of the superconductor and was discovered in 1933 by Meissner and Ochsenfeld (Meissner W. et al., 1933). It means that a superconductor is not only a perfect conductor it is principally a perfect diamagnetic material. They found that not only a magnetic field is excluded from entering a superconductor, as might appear to be explained by perfect conductivity, but also that a field in an originally normal sample is expelled as it is cooled through the superconducting transition temperature ($T_C$). Superconductivity is a thermodynamic state defined by three state variables: $J$, the electrical current density flowing through the material, $H$, the magnetic field, and $T$, the temperature. This thermodynamic state encloses a state surface defined by three critical values, the critical temperature, $T_C$, the critical current density, $J_C$, and the critical magnetic field, $H_C$, which is related thermodynamically to the free-energy difference between normal
and superconducting states in zero field the so-called condensation energy of the superconducting state.

Then in 1957, the explanation of the superconductivity phenomenon came from Bardeen, Cooper and Schrieffer with the BCS theory. It was shown that even a weak attractive interaction between electrons, such as that caused in second order by the electron-phonon interaction, causes an instability of the ordinary Fermi-sea ground state of the electron gas with respect to the formation of bound pairs of electrons (Cooper pairs) occupying states with equal and opposite momentum and spin (Tinkham M., 1996).

Until this moment only one type of superconductors was known, Type I, that are metallic systems Low-Temperature Superconductors (LTS), when the same year as BCS (1957), Abrikosov predicted a different magnetic behavior for some superconductors. It was shown that the magnetization curve is characterized by the existence of two transition fields \( H_{c1} \) and \( H_{c2} \). While the superconducting state exists for \( H_{c} < H_{c1} \) (being \( H_{c} \) the external applied magnetic field) and the normal state for \( H_{c} > H_{c2} \), a new thermodynamic state, the mixed state, characterized by partial exclusion of the external field, is stable for intermediate fields (Goodman B. B., 1966). Because this behavior is so different from the classic intermediate-state behavior, Abrikosov called these Type II superconductors to distinguish them from Type I (metals). However, it was not until 1964 that this new class of superconductors became standard and universally recognized (Goodman B. B., 1966). This mixed state, the new thermodynamic state, can be observed only in Type II superconductors and this characteristic make them very attractive from technological point of view.

In 1986, the discovery of a new family of superconducting ceramic materials by Bednorz and Müller (Bednorz G. and Müller Z., 1986) introduced the High Temperature superconductivity. They discovered the first cuprate High Temperature Superconductor (HTS), Ba-doped La\(_2\)CuO\(_4\) (214), with \( T_{c} \) of 35 K. Materials of this group are dominated by copper oxide planes and have been discovered with \( T_{c} \) over 100 K. At present, more than 200 cuprates have been found to superconduct at temperatures up to the current \( T_{c} \)-record of 134 K at ambient pressure (Schilling A. et al., 1993) and 164 K at 30 GPa (Gao L. et al., 1994). This higher superconducting transition temperature has opened the way to a broader range of applications because is possible the use of liquid nitrogen, that is much cheaper and easier to handle, instead of helium. After the BaLa\(_2\)CuO\(_4\), more HTS were discovered the next
year (1987). However, the four main cuprates HTS families that have played significant roles in the development of HTS science and technology are (Rogalla H. and Kes P. H., 2011):

- \( \text{RBa}_2\text{Cu}_3\text{O}_7 \) (RBCO, 123, or Cu1212 with \( R= \text{Y or rare-earth (La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu)} \));
- \( \text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4} \) where \( n= 1, 2, 3, ..., [\text{BSCCO or Bi22(n - 1)n}] \);
- \( \text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4} \) where \( n= 1, 2, 3, ... [\text{TBCOO or Tl22(n - 1)n}] \);
- \( \text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3-\delta} \) where \( n=1, 2, 3, ... [\text{HBCCO or Hg12(n - 1)n}] \).

The first cuprate family (\( \text{RBa}_2\text{Cu}_3\text{O}_7 \)) was discovered by Paul C. W. Chu, Maw-Kuen Wu and colleagues in 1987 (Wu M. K. et al., 1987). It was the first HTS family to bring down the liquid nitrogen temperature barrier of 77 K with \( T_C \) of 90 K. After only few years, in 1988 the first cuprate family (\( \text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4} \)) that displays a \( T_C \) up to 110 K at ambient pressure and 135 K at 35 GPa was discovered by Hiroshi Maeda et al., 1988. BSCCO is the material that has been used for the first generation HTS-wires and for spectroscopic studies, due to its graphitic-like behavior. The same year, the second cuprate family (\( \text{Ti}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4} \)) with a \( T_C \) up to 125 K at ambient pressure and 131 K at 7 GPa was discovered by Zhendzhi Sheng and Allen Hermann. However, due to its physical softness and complex synthesis process, TBCCO has limited applications, although there was a lot of optimism regarding its possible use for thin film devices due to its higher \( T_C \) and greater stability. In 1993, \( \text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3-\delta} \) with a \( T_C \) up to 134 K at ambient pressure and 164 K at 30 GPa was discovered by Schilling A. et al., in 1993. The \( T_C \) of 134 K makes this HTS a possible material for HTS devices operable on the Space Shuttle without liquid nitrogen and also may enable the development of a combined HTS/LNG system for the efficient delivery of electrical and chemical energies simultaneously (Rogalla H. and Kes P. H., 2010).

The big surprise of superconducting materials was \( \text{MgB}_2 \) discovered in 2001 (Nagamatsu J. et al., 2001). Before this year, many metal and intermetallic superconductors (LTS) were discovered with the highest \( T_C \) record of 23 K in \( \text{Nb}_3\text{Ge} \) (Gavalier J. R., 1973). The discovery of \( \text{MgB}_2 \) with \( T_C \) at 39 K opened the way for new applications for the intermetallic superconductors.

The idea of converting transparent insulating oxide composed of abundant elements to conducting materials, led in 2007 to the discovery of another superconducting family: The Iron-based superconductors. The first compound was \( \text{LaFeAs(O,F)} \) with
$T_c$ of 26 K. However, since this discovery more iron-pnictide (chalcogenide) superconductors have been processed. Comparing this new family of superconductors with cuprates and MgB$_2$, three special properties make them promising for new applications: robustness to impurity doping, very high upper critical magnetic fields, and low crystallographic anisotropy in physical performances (Rogalla H. and Kes P. H., 2011).

Nowadays, many researchers still work on processing of new superconductors hoping that new materials with higher $T_c$ will be discovered. Although a great progress in this field has been achieved, is also essential the use of tools such as theoretical modelling and experimental characterization, to ensure the reliability and promising role of these materials in materials science field and for several technological applications.

### 1.2 An overview of applications

There are many differences between superconducting and conventional materials in the way that electrons or electric currents move through the material. This characteristic in addition to the unique magnetic properties of the superconductors, differentiate them from all other known conductors and, as a consequence, make them appropriate for several technological applications (figure 1.1).

Among the zero resistance to electrical current and the exclusion of externally applied magnetic field there are more properties that make superconducting materials unique for applications. The extremely high current carrying density and low resistance have an important impact on electric power transmission. Besides, they present high sensitivity to the magnetic field, extremely low resistance at high frequencies, very low signal dispersion, rapid signal flux quantum transfer and close to speed of light signal transmission. Thus, much smaller or more powerful magnets for motors, generators, energy storage and medical equipment can be used. The high sensitivity to magnetic fields provides a unique sensing capability, in many cases 1000x superior to today’s best conventional measurement technology (IEEE Council on Superconductivity 2008).
Fig. 1.1. Present and future applications of superconducting materials (Adapted from IEEE Council on Superconductivity 2008).

Nowadays the commercial applications for superconducting materials are in medical diagnostic field, Magnetic Resonance Imaging (MRI) and in some industrial processing sectors like Nuclear Magnetic Resonance (NMR), high-energy physics accelerators and plasma fusion reactors. Also, the characteristic of superconductor-based products to be normally at least 50% smaller and lighter than other equivalent units rise to the design of more efficient devices and to the open-ended development of new applications in the following fields (IEEE Council on Superconductivity 2008):

**Electric Power.** Superconductors make possible a variety of applications improving the electric power infrastructure. Advances in HTS over the past two decades rise to a new set of technology tools to enhance the capacity, efficiency and reliability of the power system. The high power density and electrical efficiency of HTS wires results in highly compact, powerful devices and systems, like generators, transformers for the grid and wind energy, power cables, synchronous condensers and fault current limiters.

**Transportation.** The incorporation of superconductor technology into transportation sector can improve the performance and efficiency and reduce the weight and fuel
consumption. Within the past 20 years, the ship industry has begun to adopt the electric propulsion system. The HTS marine ship propulsion can be a revolution in ship design. HTS motors and generators are much smaller and lighter than the conventional copper-based electrical propulsion motors and could provide an easier installation. Another application of HTS is the replacement of the copper degaussing coils on military ships to protect the military vessels. Finally, one of the soundest applications in transportation is the magnetically levitated train that could achieve top speed in excess of 500 kmph (IEEE Council on Superconductivity 2008).

**Medicine.** Magnetic Resonance Imaging (MRI) is one of the most effective diagnostic medical methods. Superconducting magnets provide energy efficiency and improve the diagnostic tools not only for MRI but also for Magnetoencephalography (MEG) and Magnetocardiography (MCG). These methods are based on the detector “SQUID” (Superconducting Quantum Interference Device) which enable the detection and measurement of weak magnetic fields, like those generated by the brain.

**Industry.** Superconductor based separators are used in industry, like in kaolin clay sector (IEEE Council on Superconductivity 2008), due to their excellent magnetic properties, as superconducting materials is possible to operate at a field of 5 T, much higher than the field that copper magnets can achieve.

**Communications.** The ultra-low dissipation and distortion are the advantages of the superconductors that led to a remarkable change to satellite communications and advanced filters employed in commercial wireless base stations. Another significant development is the all-digital receivers and transmitters that benefit both military and commercial applications.

**Scientific research.** In the field of High-Energy Physics, superconductors have played a key role to provide new methods in the new energy technologies. In Particle Physics the rings of particle accelerators are made of superconducting magnets (IEEE Council on Superconductivity 2008). Also, the Large Hadron Collider (LHC) includes two concentric rings made up of superconducting magnets (IEEE Council on Superconductivity 2008). Additionally, very important is the role of superconductors in Fusion Energy and ITER Project by generating the high magnetic fields that are necessary to confine and shape the high temperature plasma (IEEE Council on Superconductivity 2008). Another sector is for space related applications, like space telescopes and space-based instruments that include magnetic technologies.
During the last years a continuous effort to develop and commercialize applications of superconducting materials has to overcome four crucial challenges: the cost, the refrigeration system, reliability and acceptance of superconducting devices. The first and most important inconvenience for such applications is the cost of the superconducting materials. To lead this point, superconducting materials should provide high functional and cost efficiency to the system. On the other hand, a solution for some applications was given by the HTS materials that make possible the use of smaller and more efficient cooling systems (Ter Brake H. J. M. and Wiegerinck G. F. M., 2002). However, the acceptance and long term reliability of superconducting devices are great challenges essential to be reached and promise considerable benefits for the society through commercial applications.

1.3 REBaCuO system

In spite of the many cuprate HTS subsequently discovered since 1986, REBCO (where RE= rare earth such as Y, Nd, Sm, Gd etc) remains the most attractive HTS material for applications due to its physical characteristics and superior superconducting behavior in high magnetic fields (Table 1.1). The irreversibility field, $B_{irr}$, represents the magnetic field applied to the superconductor at which the flux pinning centers become ineffective and then the critical current density of the superconductor becomes zero. In general, HTS are characterized by an irreversibility line that defines the field/temperature phases’ space above which the material becomes useless for current carrying applications (Cardwell D. A. and Ginley D. S., 2003). These compounds exhibit the highest irreversibility fields and therefore are the most promising for applications at high current and magnetic fields. For most applications, large critical current densities of the order of $10^4$ to $10^5$ Acm$^{-2}$ are required and REBCO family fulfill the necessary characteristics. One of the most studied and relevant cuprate HTS is YBa$_2$Cu$_3$O$_{7-8}$ compound. This HTS is one of the more stable-four element compound with a $T_C$ above 77 K. Additionally, does not include toxic neither volatile elements and is quite easy the processing of single-crystals. Also it is less anisotropic, compared with the other HTS cuprate families, and presents high critical current density, $J_C$, at high magnetic fields.
Table 1.1. Superconducting characteristics of REBCO single grains  
(Cardwell D. A. et al., 2006)

<table>
<thead>
<tr>
<th>RE in REBa₂Cu₃O₇</th>
<th>Y</th>
<th>Gd</th>
<th>Nd</th>
<th>Sm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point (± 5°C)</td>
<td>1005</td>
<td>1030</td>
<td>1068</td>
<td>1054</td>
</tr>
<tr>
<td>T_c (K)</td>
<td>92 air</td>
<td>92.5 pO₂</td>
<td>95 pO₂</td>
<td>93.5 pO₂</td>
</tr>
<tr>
<td>J_c at 77 K (KA/cm²)</td>
<td>20-30</td>
<td>50-60</td>
<td>40-50</td>
<td>40-50</td>
</tr>
<tr>
<td>B_{irr} (T) at 77 K</td>
<td>5-6</td>
<td>6-7</td>
<td>8-10</td>
<td>6-8</td>
</tr>
</tbody>
</table>

Another promising candidate of the REBCO family is the GdBa₂Cu₃O₇-δ compound. Gd is a Light Rare Earth (LRE) element and exhibits very good superconducting properties such as high critical current density, J_c, and high irreversibility fields, B_{irr}. Although the superconducting behavior of GdBa₂Cu₃O₇ is better than that of the YBa₂Cu₃O₇ (Babu N. H. et al., 1999; Nakiri S. et al., 2004), has not been investigated so much such as others HTS compounds because of the difficulty of processing of single grains by cold seeding method, due to the lack of availability of a suitable seed crystal and the need to apply reduced oxygen partial pressure during processing (Cardwell D. A. and Babu N. H., 2006). However, the slightly better superconducting behavior of GdBa₂Cu₃O₇ has been suggested to be because of the higher critical temperature, T_c (Iguchi T. et al., 2002) and some extra defects, such as stacking faults that provide less anisotropic magnetic field angle dependence of J_c (Takahashi K. et al., 2005) than in the case of YBa₂Cu₃O₇.

1.3.1 Crystallographic structure

In the first cuprate family, YBa₂Cu₃O₇-δ compound, also known as YBCO or phase Y123, presents an orthorhombic perovskite structure refined in the centrosymmetric Pmmm space group with lattice parameters a = 3.823 Å, b = 3.886 Å, and c = 11.680 Å (Beno M. A. et al., 1987). The perovskite unit cell consists of ordered Y and Ba cations and an unspecified number of oxygen atoms. Particularly, is a planar structure of stack layers with the following order: CuO/BaO/CuO₂/Y/CuO₂/BaO/CuO and all layers are perpendicular to the c-axis. The ordering and occupancy of the oxygen atoms determine the unit cell structure which can be tetragonal (non-superconducting) or orthorhombic (superconducting), as is shown in figure 1.2.
When oxygen atoms are randomly distributed along $a$-$b$ axis, the structure is tetragonal of the space group $P4/mmm$ and the material behaves as an insulator. On the other hand, when the positions of oxygen atoms in the CuO layer along the $a$-axis are empty, the unit cell is orthorhombic and therefore superconducting. The tetragonal structure is characterized by a partially occupied, almost octahedral Cu-O arrangement, in contrast with the orthorhombic structure which has one-dimensional Cu-O chains (Jorgensen J. D. et al., 1987). The deficiency of O atoms depending on the stoichiometry composition is represented by the letter $\delta$ in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ formula. When $\delta$=0, the structure is orthorhombic and when $\delta$=1, passes from orthorhombic to tetragonal. The YBCO orthorhombic unit cell is formed by three Cu centered perovskite cubes with both O vacancy ordering and Y-Ba ordering along $c$-axis. Each O vacancy occurs in every CuO layer, along $a$-axis at site (1/2, 0, 0). The Y and two Ba ions are positioned along $c$-axis, and the other O vacancy occurs in the Y plane (figure 1.2).

Fig. 1.2. Schematic of the tetragonal and orthorhombic unit cell of YBCO.

The GdBa$_2$Cu$_3$O$_{7-\delta}$ compound, also known as GdBCO or phase Gd123 has the same unit cell and structure as YBCO, but presents a different ionic radius (GdBCO: 1.053 Å and YBCO: 1.019 Å (Andreouli C. and Tsetsekou A., 1997) and minor differences in the lattice parameters. The lattice parameters for GdBCO are: $a = 3.859$ Å, $b = 3.885$ Å and $c = 11.759$ Å (Cao L. X. et al., 2002). For both compounds, the
orthorhombic perovskite structure contains CuO chains along the b-axis. These chains appear in the basal plane of the perovskite. The CuO chains and the CuO₂ planes contribute to the superconducting properties of the material (orthorhombic structure). The occupancy of the oxygen atom in structures that contains CuO chains could be variable. Also, these chains act as charge carriers of superconductivity creating vacancies in the CuO₂ planes. In the case of the tetragonal structure oxygen vacancies appear in the CuO chains (Jorgensen J. D. et al., 1987).

1.3.2 Processing techniques

1.3.2.1 (RE)BaCuO bulk superconductors

The ability of (RE)BaCuO to carry current and hence, to generate magnetic field, is severely limited by the presence of grain boundaries in the sample microstructure which is manifested as a rapid decrease in $J_c$ with applied field. For this reason, is necessary to process (RE)BaCuO materials in the form of large, single grains if the grain boundary problem is to be avoided (Cardwell D. A. and Ginley D. S., 2003).

A variety of melt processing techniques has been developed for the fabrication of large grain REBCO. These are all based on a peritectic reaction (equation 1.1), occurring in these systems between 1000 and 1080 °C (the peritectic temperature, $T_p$), in which the (RE)Ba₂Cu₃O₇-₅ (RE-123) phase is formed from solid (RE)BaCuO₅ (RE-211), a Ba-Cu-O based liquid phase (L) and oxygen gas (G) (Cardwell D. A. and Ginley D. S., 2003):

$$\text{(RE)}_2\text{BaCuO}_5 + \text{Ba}_2\text{Cu}_3\text{O}_{6.72} + 0.42\text{O}_2 \rightarrow 2\text{(RE)}\text{Ba}_2\text{Cu}_3\text{O}_{6.28}$$

(L) (G) (RE-123)

(1.1)

The non-superconducting RE-211 phase and the liquid in this reaction can be produced by rapidly heating a pre-sintered green body of the desired composition to a temperature well above $T_p$. In principle, formation of the required RE-123 phase is then achieved by cooling the peritectically molten (RE)BCO sample slowly through the peritectic temperature-hence the name of the process.
In this thesis, the studied materials were processed by two different techniques: 1) Top Seeded Melt Growth (TSMG) and 2) Bridgman. TSMG is one of the most well-known methods to produce high performance (RE)BCO single grain samples (Yoo S. I. et al., 1994; Cardwell D. A. and Babu N. H., 2006), in which a small single crystal with lattice parameters similar to that of the target RE-123 material is placed on the top surface of the pre-sintered pellet to provide a heterogeneous grain nucleation site, often under a thermal gradient. Typical large single grains of YBCO and GdBCO/Ag grown by this technique are shown in figure 1.3. In both cases, the seed crystal must necessarily have a higher peritectic temperature than the bulk (RE)BCO sample if it is to remain undecomposed during the melt process. Sm-123 and Nd-123 crystals provide suitable seeds for the growth of YBCO and GdBCO, whereas MgO is frequently used as a seed for other (RE)BCO materials.

During the growth of the single (RE)BCO grain, the RE-211 inclusions remain trapped within the bulk RE-123 phase matrix to form a distribution of unconnected inclusions. Enrichment of the starting stoichiometry with RE-211 has two main beneficial effects to the sample processing and properties. Firstly, the excess RE-211 sustains peritectic solidification over greater sample sizes so that larger grain specimens may be produced by the melt process technique. Secondly, the RE-211 inclusion density correlates with an increase in effective flux pinning sites, which enhance $J_c$, of the fully processed sample and yield higher trapped fields. Therefore, a general processing aim is to generate a fine distribution of the second phase RE-211 inclusions in a large, homogeneous superconducting RE-123 matrix. The latter may be achieved by the addition of a variety of dopants to the precursor materials, such as Pt or CeO$_2$ which have proved particularly effective in refining the size and distribution of the RE-211 phase (Cardwell D. A. and Ginley D. S., 2003).

![Fig. 1.3. Batch-processed YBCO (left) and GdBCO/Ag (right) single grain samples prepared in the University of Cambridge, Bulk Superconductivity Group [Konstantopoulou K. et al., 2014].](image-url)
The Bridgman technique was developed by the Harvard physicist Percy Williams Bridgman in 1925. Is one of the simplest methods for growth of crystals from melts and is a directional solidification process (Granados X. et al., 1994; Piñol S. et al., 1995). Many novel organic single crystals and certain semiconductor crystals such as gallium arsenide have been grown by this method. The method involves heating of the material to be grown in a container having the required gradient for growth. After melting the material, the growth ampoule is moved from hot zone to cold zone gradually. Single crystal material is progressively formed along the length of the container. The process can be carried out in a horizontal or vertical geometry.

1.3.2.2 (RE)BCO coated conductors

Many alternative modified combinations are being investigated worldwide in the field of processing to achieve high performance and low cost coated conductors (CCs). However, at present, complex conductor architectures are the main choice in commercial CCs (with multiple buffer layers). Processing steps for REBCO coated conductors include different techniques in order to deposit the multiple layers. Different types of substrate (IBAD and RABiTS) and deposition techniques (PLD, MOCVD, CSD) are used by the industrial leadership (Obradors X and Puig T., 2014).

Usually the substrates are based on Ni and Ni-W alloys, although new developments are still required to decrease their ferromagnetic behavior. Polycrystalline metallic substrates support an oxide template textured through Ion Beam Deposition Approach (IBAD). Another option as metallic substrates is based on the RABiT (Rolling Assisted Biaxially Textured substrates) approach. These substrates form the basis of most studies of multilayered growth in this area. However, a desirable objective is to make available non-magnetic substrates to reduce ac losses (Obradors X and Puig T., 2014). Hastelloy C-276 alloy is often used as a substrate for the RE-123 coated conductors because of their resistance to high temperature. During the fabrication of the coated conductors, the substrate should be heated up to 1073 K (Selvamanickam V. et al., 2001; Truchan T. G. et al., 2001). Therefore, thermal stability and inertness to the buffer layer are required for the substrate material.

Hastelloy C-276 is Ni-Cr-Mo-W alloy developed in 1960s (Tawancy H. M. et al., 1983). Compared to Hastelloy C alloy developed in 1930s, Hastelloy C-276 alloy includes a low content of carbon and silicon atoms and this results in the
improvement of corrosion resistance at the heat affected zone after welding, since precipitation of the carbides at the grain boundaries can be suppressed (Tawancy H. M. et al., 1983). Electropolishing is used to achieve the smooth, clean surface for Hastelloy-based substrate, as a prerequisite for the successful addition of the buffer and superconductor layers.

Chemical Solution Deposition (CSD) growth of buffer layers on RABiT substrates has been widely explored; however, further understanding of nucleation and growth process is still needed (Zhao Y. et al., 2012).

In Europe two key technologies have a large tradition and they are foreseen to be widely investigated, Pulsed Laser Deposition (PLD) and Chemical Solution Deposition (CSD), although some effort based on evaporation (EV) and MOCVD is also being made. In all cases, YBCO and GdBCO, or mixed RE ions such as (Gd, Y)BCO, are being considered as attractive superconducting phases.

![Diagram of HTS coated conductor](image)

**Fig. 1.4.** Schematic illustration of the laminate structure of a HTS coated conductor. The characteristics of the different layers for two HTS coated conductors are shown (SCS4050 and SF12100).
In this thesis, two commercial HTS coated conductors have been studied and their laminate structure is shown in figure 1.4. Usually, the IBAD technique or sputtering for a stack of buffer layers is applied that act as a template layer to introduce the biaxial texture for the superconductor material. Afterwards, the superconductor growth, based on yttrium copper oxide (YBCO) or other rare earth materials, is performed by Metal Organic Chemical Vapor Deposition (MOCVD) and sputtering of a thin cover layer of silver to provide electrical contact is finally applied. Depending on the application, electroplating can be performed to completely surround the wire (Surround Copper Stabilizer, or SCS).

1.3.3 Oxygenation process

During the oxygenation process the oxygen diffuses from the surface of the material to the inside, in order to transform the material from the no superconducting tetragonal phase to the orthorhombic (superconducting) (Diko P. et al., 2007). At the initial stage of this process, the formation of a/b macrocracks starts at the sample surface due to the difference in the microstructure lattice parameter between the two structures (Cava R. J. et al., 1990; Rothman S. J. et al., 1991; Diko P. et al., 2003). The oxygenated layer has lower c-lattice parameter than the matrix and as a consequence is under tensile stresses perpendicular to the ab-plane of the Y/Gd-123 lattice (Diko P., 2004). Therefore, the oxygenation process is of critical importance and should be performed in a particularly careful manner.

1.3.4 Microstructural defects produced during fabrication

During fabrication of HTS bulk superconductors there are several parameters that control the final microstructural characteristics of the single crystals. Unfortunately, the REBCO compounds are inherently brittle and therefore sensitive to cracking. However, cracks and other defects are formed in HTS bulk superconductors even during their fabrication, particularly during solidification and oxygenation process. Some of the defects, such as cracks are not desirable as deteriorate the mechanical properties of the materials but others like RE-211 particles act as pinning centers improving the superconducting behavior. The microstructural defects mentioned below are present in bulk as well as in thin film HTS superconductors.
The main reasons for cracking are mechanical stresses, which arise in the sample during its fabrication. Two main sources of stresses have been identified (Diko P., 2004). Firstly, due to the different thermal expansion coefficient of 123 and 211 phases and secondly, due to the dependence of 123 phase lattice parameters on the oxygen stoichiometry of 123 phase. The a/b-microcracking (microcracks in the ab-planes) is formed due to the microstresses induced by the 211 particles (figure 1.5) arising from the lower thermal expansion coefficient compared with the matrix (RE-123) (Diko P. et al., 1997; Sakai N. et al., 1997; Diko P., 1998). Macrocracking is also induced by macroscopic inhomogeneity of the 211 particles concentration during the solidification process. This inhomogeneity lead to a complicated picture of residual stresses after cooling from processing temperature. An approximation profile of the residual thermal macrostresses in two different sections of a single-grain sample is depicted in figure 1.6.

Diko P. and Krabbes G., (2003) discovered that the formation of a/b-macrocracks (parallel to the ab-plane) starts on the sample surface at the initial stage of oxygenation. The c-macrocracks parallel to the ab-plane that are formed in the first stages of oxygenation provide a passage for oxygen delivery to the sample interiors (Diko P. et al., 2007).

In some cases, to improve the mechanical behavior of the superconductors, Ag-doped bulk superconductors can be prepared. The Ag-addition suppresses cracking and the reason can be associated with microstresses introduced by the Ag particles during cooling down from the processing temperature. The thermal expansion coefficient of the RE-123 phase is lower in the ab-plane and is higher in the c-axis than the thermal expansion coefficient of Ag (Diko P., 2004). Consequently, Ag particles introduce a completely different stress field into the matrix when compared with 211 particles. This field is schematically shown in figure 1.5.
Fig. 1.5. Schematic illustration of the stress fields introduced by 211 and Ag particles. ($\sigma_R$)-radial, ($\sigma_\theta$) tangential stresses. (Diko P., 2004).

Fig. 1.6. The approximation profile of the residual thermal macrostresses in two different cross sections of a single-grain sample (Diko P., 2004).

On the other hand, contributions to flux pinning comes from most defects present in RE-123 superconductors and generated at different steps of processing, such as RE-
211 inclusions, dislocations, low angle grain boundaries, twin boundaries, stacking faults and random effects associated to oxygen or cation vacancies (Krabbesc G. et al., 2006; Palau A. et al., 2006).

1.4 Mechanical properties of HTS of YBCO and GdBCO compounds

The mechanical properties of REBCO superconductors have been studied by means of different techniques during the last ten years. In the case of the HTS single domains, the mechanical behavior of the compounds is critical for their functional use especially in applications such as magnets where high magnetization of the samples is required and at the same time is limited by the stresses due to the Lorenz forces. On the other hand, HTS coated conductors have been widely studied to achieve both long length and high critical current simultaneously for several applications (Iijima Y. et al., 2004; Schoop U. et al., 2005). However, the study of their mechanical behavior at room temperature and the electromechanical properties at service temperature is essential for large scale applications such as cables, fault current limiters (FCL), magnets etc.

1.4.1 HTS YBCO and GdBCO single domains

Bulk, melt processed high temperature superconducting materials (HTS) exhibit enhanced magnetic properties compared to conventional permanent magnets due primarily to their ability to trap large magnetic fields at temperatures that can be achieved using commercially available, cryo-cooler technology. This ability makes bulk HTS, such as (RE)BCO (where RE is a rare earth element) particularly attractive for a variety of large scale applications, including bulk magnets, flywheel energy storage systems, magnetic bearings, magnetic separators and fault current limiters (Murakami M., 1992; CampbeJ A. M. and Cardwell D. A., 1997). YBCO and GdBCO have emerged over the past twenty years within the (RE)BCO family of bulk HTS as the most promising for practical applications, and numerous studies have been performed to improve the single grain fabrication process for these materials (Cardwell D. A., 1998; Shi Y. et al., 2007). GdBCO generally exhibits higher critical current density, $J_c$, in the presence of applied magnetic fields than YBCO, which makes it more suitable for many applications (Babu N. H. et al., 1999; Nakiri S. et
al., 2004). Unfortunately, the world record fields of up to 17.6 T that have been produced recently by these remarkable materials are limited, ultimately, by the mechanical properties of the bulk superconductor (Durell J. H. et al., 2014; Nakiri S. et al., 2005). The Lorentz force generated within a bulk superconductor in the presence of a large magnetic field is sufficient to cause internal fracture of the single grain, although relatively little research has been performed on the magnitude of the stresses generated during the magnetization process. Bulk (RE)BCO single grains tend to fracture when the internal electromagnetic stresses exceed values of 10-30 MPa (Sakai N. et al., 1999). Although \( J_c \) and the irreversibility field, \( H_{irr} \), are higher for GdBCO than YBCO, the latter remains a very good candidate for a variety of applications and has consequently been subject of numerous studies on its superconducting and mechanical properties (Yoshimo Y. et al., 2001; Okudera T. et al., 2003; Shi Y. et al., 2009; K. Konstantopoulou et al., 2014). Relatively few studies, on the other hand, have been performed on the mechanical behavior of GdBCO single grains. Tables 1.2-1.4 show information about the mechanical characteristics of YBCO and GdBCO compounds obtained from the literature.

**Table 1.2.** Flexural strength values of REBCO (Literature data).

<table>
<thead>
<tr>
<th>Material</th>
<th>( \sigma_F ) (MPa)</th>
<th>Method</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBCO</td>
<td>91 ± 19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>YBCO + 10 wt% Ag</td>
<td>109 ± 34</td>
<td>Three-point bending</td>
<td>Fujimoto H., 2003</td>
</tr>
<tr>
<td>YBCO + 20 wt% Ag</td>
<td>134 ± 28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd-123/G-211 + 10 wt% Ag + 0.5 wt% Pt Standard bulk</td>
<td>88</td>
<td>Three-point bending</td>
<td>Fujimoto H. and Murakami M., 2012</td>
</tr>
<tr>
<td>Gd-123/G-211 + 10 wt% Ag + 0.5 wt% Pt Densified bulk</td>
<td>105</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 1.3. Fracture toughness values of REBCO (Literature data).

<table>
<thead>
<tr>
<th>Material</th>
<th>$K_{IC}$ (MPa.m$^{1/2}$)</th>
<th>Method</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-123 without Y-211</td>
<td>0.88-1.2</td>
<td>Vickers Indentation</td>
<td>Fujimoto H. et al., 1992</td>
</tr>
<tr>
<td>Y-123 with Y-211</td>
<td>1.6-2.1</td>
<td>Vickers Indentation</td>
<td></td>
</tr>
<tr>
<td>Y-123 + 30 mol% Y-211</td>
<td>1.01</td>
<td>Vickers Indentation</td>
<td>Leenders A. et al., 1999</td>
</tr>
<tr>
<td>Y-123 + 60 mol% Y-211</td>
<td>1.44</td>
<td>Vickers Indentation</td>
<td></td>
</tr>
<tr>
<td>Y-123/Y-211</td>
<td>0.4-1.3</td>
<td>Vickers Indentation</td>
<td>Yoshino Y. et al., 2001</td>
</tr>
<tr>
<td>Y-123 + 28.6 mol% Y-211 + 15 wt% Ag</td>
<td>1.6-2.1</td>
<td>Three-point bending</td>
<td>Okudera T. et al., 2003</td>
</tr>
<tr>
<td>Y-123</td>
<td>1.43</td>
<td>Vickers Indentation</td>
<td>Foerster C. E. et al., 2008</td>
</tr>
<tr>
<td>Y-123 + 10 wt% Ag$_2$O</td>
<td>1.6</td>
<td>Vickers Indentation</td>
<td></td>
</tr>
<tr>
<td>Gd-123/G-211 + 10 wt% Ag + 0.5 wt% Pt Standard bulk</td>
<td>2.27</td>
<td>Three-point bending tests</td>
<td>Fujimoto H. and Murakami M., 2012</td>
</tr>
<tr>
<td>Gd-123/G-211 + 10 wt% Ag + 0.5 wt% Pt Densified bulk</td>
<td>2.44</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 1.4. Hardness and Young’s modulus values of REBCO (Literature data).

<table>
<thead>
<tr>
<th>Material</th>
<th>E (GPa)</th>
<th>H (GPa)</th>
<th>Method</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-123</td>
<td>154 ± 16</td>
<td>10.3 ± 1.7</td>
<td>Indentation</td>
<td>Lucas B. N. et al., 1991</td>
</tr>
<tr>
<td>Y-211</td>
<td>213</td>
<td>14</td>
<td>Nanoindentation</td>
<td>Goyal A. et al., 1992</td>
</tr>
<tr>
<td>YBCO texturized</td>
<td>182</td>
<td>10.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y-123/Y-211</td>
<td>185</td>
<td>18 ± 2.5</td>
<td>Vickers Indentation</td>
<td>Yoshino Y. et al., 2001</td>
</tr>
<tr>
<td>Y-123</td>
<td>177</td>
<td>5.2</td>
<td>Vickers Indentation</td>
<td>Foerster C. E. et al., 2008</td>
</tr>
<tr>
<td>Y-123 + 10 wt% Ag₂O</td>
<td>149</td>
<td>4.1</td>
<td>Vickers Indentation</td>
<td>Roa J. J. et al., 2010</td>
</tr>
<tr>
<td>Y-123/Y-211</td>
<td>123.5 ± 3.4</td>
<td>-</td>
<td>Nanoindentation</td>
<td>Fujimoto H. and Murakami M., 2012</td>
</tr>
<tr>
<td>Gd-123/G-211 + 10 wt% Ag + 0.5 wt% Pt Standard bulk</td>
<td>123</td>
<td>-</td>
<td>Three-point bending tests</td>
<td>Fujimoto H. and Murakami M., 2012</td>
</tr>
<tr>
<td>Gd-123/G-211 + 10 wt% Ag + 0.5 wt% Pt Densified bulk</td>
<td>156</td>
<td>-</td>
<td>Three-point bending</td>
<td></td>
</tr>
</tbody>
</table>

### 1.4.2 HTS YBCO coated conductors

Since the discovery of the HTS coated conductors, a strong effort has been made in order to integrate these coated conductors in the field of the electrical energy power systems and coil manufacturing (Granados X. et al., 2008; Gamble B. et al., 2011; Soika R. et al., 2011; Hobl A. 2013; Lazić Z. et al., 2013). Coated conductors based on YBCO are a new enabling technology with a strong potential for the development of efficient electrical power applications that appear to be ready at the right time (Obradors X. and Puig T., 2014).

To be successful in the need for such a new electrical engineering paradigm, HTS materials need to demonstrate their capabilities in fully integrated real systems,
including reliable cryogenic cooling. Many different power demonstrators and real
systems based on HTS conductors have been built and demonstrated at present. In
all cases it becomes clear that while huge advances have been made in the
development of the novel materials, there are still more challenges to tackle in order
to improve their performance.

For the magnet applications, not only high critical current density under magnetic
field but high strain endurance are essential. During fabrication and/or operation of
a magnet, the conductors experience various mechanical-electromagnetic strains.

Depending on the magnetic field range, the possible applications change, taking into
account the service temperature. Firstly, Low magnetic field range (< 1 T) is suitable
for cable and Fault Current Limiter (FCL) systems that could work at around 77 K.
Second, a high magnetic field range (3-5 T) at present would require placing CCs at
temperatures in the range of 30-60 K to achieve high enough electric currents.
Power systems that could be include these conductors would be mainly rotating
machines and Superconducting Magnetic Energy Storage (SMES). Finally, ultrahigh
magnetic fields (> 15 T) to build magnets could only be achieved cooling at lower
temperatures (∼ 5 K) (Obradors X. and Puig T., 2014).

In addition, the development of wires with HTS coated conductors requires
considering in details several issues related to the development of a welding process,
accurate wire tooling, the deposition and stability of buffer and superconductivity
layers, electrical and thermal protection, mechanical properties and ac losses, etc.

An intrinsic strain effect on the critical current, $I_c$, has been reported for RE-123
coated conductors (Cheggour N. et al., 2003; Sugano M. et al., 2005 and Sugamo M.
et al., 2005). For YBCO coated conductors, $I_c$ increases with increasing the applied
strain, has a maximum and decreases for further strain (Sugano M. et al. 2005,
Cheggour et al., 2005). Within a certain limit, the $I_c$ value can recover reversibly
when applied strain is relieved. Such an intrinsic strain effect on $I_c$ has also been
observed in other HTS coated conductors (Sugano M. et al., 2005).

It has been reported that buffer layers, superconducting materials and residual strain
in superconductors are not responsible for the value of the strain at quenching. On
the other hand, all the coated conductors that are grown on the Hastelloy C-276
substrate depend on the mechanical properties of the substrate materials for the
allowable strain limit.
Another parameter that is important during applications is the limited length of the superconducting coated conductors that does not exceed the kilometer range. Therefore, for applications such as SMES and superconducting cables, is essential the tape splicing in order to produce long tapes. According to the literature (Celentano G. et al., 2010), there are mainly three techniques for jointing the superconducting tapes: 1) superconducting joints, 2) non-superconducting joints and 3) diffusion joints. For power applications, the most usual jointing type is by soldering with a soft welding metal. However, the jointing technique should fulfill important requirements, such as to be an easy and simple technique and to provide low electric resistance to the joint.

As it is well-known, the mechanical characteristics of the coated conductors are crucial for their functional use and the electrical behavior of the wires. The superconducting layer has the leading role and although its thin thickness (~ 1 µm), the degradation of the critical current of the tape is directly related with the fracture of the HTS layer. Additionally, when spliced joints between superconducting coated conductors are need to be performed, the high strain due to the Lorenz forces and the external magnetic field that could be applied can affect both the superconductor and the joint, and as a consequence, the electromechanical behavior of the HTS coated conductors.

Although a lot of studies have been performed about the effect of the strain on the coated conductors under axial stress or bending, the fracture process of the superconducting layer and the interfacial properties between the layers of the coated conductors are not enough investigated. Finally, a deeper study about the effect of the external magnetic field and strain to the electromechanical behavior of the spliced joints between HTS coated conductors is also essential.
1.5 Objectives

The progress of the applied superconductivity during the last decade has brought HTS bulk and coated conductors to the field of magnet applications and electric power systems. However, to be successful in the need for such big variety of technological applications, HTS materials need to demonstrate their mechanical and electromagnetic capabilities in fully integrated real systems, including certain cryogenic conditions. The main aim of this thesis is to perform: 1) a thorough characterization of the mechanical properties of GdBCO/Ag and YBCO bulk, melt-processed samples at 77 and 300 K and 2) an electromechanical characterization of single commercial YBCO HTS coated conductors. Particularly, the HTS bulk samples were fabricated in laboratory by different methods and the effect of the processing and the microstructure on the mechanical behavior was studied and analyzed. The commercial HTS coated conductors were chosen in order to study the fracture process of the superconducting layer that leads to the degradation of the critical current, $I_c$, of the tape. Numerical predictions were able to reproduce the fracture of the superconducting layer and the delamination of the interface between substrate and ceramic layer of a single HTS coated conductor. Finally, spliced joints between YBCO coated conductors using a soft welding metal were prepared to evaluate the welding process through the electromechanical characterization of the joints under self-field and/or by applying external magnetic field up to 1 T. This study is focused on the essential role of the mechanical and electromechanical properties of the HTS bulk and coated conductors that are critical for their functional use under cryogenic condition, emphasizing to the behavior of the superconductor as bulk and thin layer.
Chapter 2

Mechanical properties of (RE)-BCO single crystals

2.1 Introduction

Second generation superconducting bulk materials show high critical current density and high trapped magnetic field at cryogenic temperatures, $T_c$. The development of these materials that present a superconducting behavior at temperatures above 77 K ($T_c \approx 92$ K) is of great technological and scientific interest.

The excellent performance as magnets of HTS single crystals makes them attractive for several large scale applications, such as bulk magnets, flywheel storage systems, magnetic bearings, magnetic separation and fault current limiters (Murakami M. et al., 1992; Campbell A. M. and Cardwell D. A., 1997; Granados X. et al., 2002; Obradors X. et al., 2002). The compound system of (RE)-BCO is still the most interesting for applications, standing out the YBCO and GdBCO compounds. Particularly are significant potential at 77 K presenting high current density, $J_C$, up to $5 \times 10^4$ A/cm$^2$ at 1 T and high trapped field, $B_{trap}$, up to 1~1.5 T for YBCO and over 2 T for (RE)-BCO.

Practical applications of these materials are strongly related with their mechanical performance at room temperature (handling) as well as at cryogenic temperatures (service conditions). For example, the field-trapping capability of melt-textured materials can be improved by enlarging the sample size; though this is not easily achieved since intense magnetic fields can produce strong magnetic forces, which can lead to complex stress fields generated by the flux density gradients that will in turn give rise to an undesired fracture of the material (Ren Y. et al., 1995; Gonzalez-Arrabal R. et al., 2003). As a consequence, further improvements are limited by their current mechanical properties. Besides, YBaCuO and GdBCO single crystals are
brittle ceramics, whose mechanical properties and maximum trapped fields, commonly tend to degrade due to weak regions in the microstructure such as cracks, which are inherent in the growth process and induce local stress concentrations and eventual cracking of the samples (Diko P., 2000). Furthermore, microcracks are always present in such materials, given the fact that they are associated with the stress induced in the superconducting matrix by the microstructure of the oxide compound, while cooling down from the processing temperature, and also due to the oxygenation process (Zmorayova K. et al., 2006; Roa J. J. et al., 2012). Therefore, the study of not only their macroscopical mechanical properties, but also their local mechanical properties is crucial for their industrial application.

These high temperature superconducting materials (HTSC) present an intrinsic anisotropy in its microstructure because of the perovskite structure (Roa J. J. et al., 2012). For this reason, strength and toughness show a macroscopically anisotropic behavior. Hence, the study of their mechanical properties is a key point in achieving structural reliability. Moreover, optimization (mechanical and functional) is highly relevant for their potential applications as bulk high-temperature superconductors in generating large magnetic fields.

As a consequence of industrial requests, both low costs and high stability of the superconducting properties are desired. Low costs are not only related to the material manufacturing, but also to the operating conditions, e.g., the number of broken elements during production, transport, installation and operation. It is therefore necessary to produce highly reliable structural materials, something that is only possible if a good knowledge of the relationship between the properties and the microstructure of these materials is provided.

In some works the mechanical behavior of these materials at low temperature has been studied partially by different methods but mainly by indentation (Yu F. et al., 1997; Yoshimo Y. et al., 2001). Unfortunately the indentation and nanoindentation mechanical measurements are quite local and not completely representative of the macroscopic structural behavior of the material, since the indentation size is similar to the microstructural size of the material.

In this chapter the mechanical behavior at 300 and 77 K (by immersion in liquid nitrogen), of YBaCuO (sintered by two different methods) and GdBCO/Ag 15 wt% is thoroughly and critically examined, by means of macroscopical and microscopical
mechanical tests. The fracture and deformation micromechanisms have been also carefully analyzed for each testing condition. The comparison between the studied materials has been performed in order to understand the influence of the main sintering methods and the microstructural characteristics of the single grains on the macroscopic mechanical behavior.

2.2 Processing of the materials

Four high temperature superconducting bulk materials were processed involving two different methods: i) YBCO-1, ii) YBCO-2, iii) YBCO-3 and iv) GdBCO/Ag 15 wt%. The YBCO-1 and YBCO-3 were processed in the Department of Materials Science and Metallurgy Engineering, University of Barcelona by top seeded melt growth (TSMG) method and Bridgman method, respectively. The other two materials, YBCO-2 and GdBCO/Ag 15 wt% were fabricated in Bulk Superconductivity Group, University of Cambridge, both by top seeded melt growth technique. The YBCO-1 samples were rectangular-shaped whereas the rest of the samples were obtained as cylinders. The density of the single domain was calculated taking into account the mass and the dimensions of the samples. The nominal dimensions of the samples as-received after processing and the corresponding density values are shown in Table 2.1.

<table>
<thead>
<tr>
<th>Material</th>
<th>YBCO-1</th>
<th>YBCO-2</th>
<th>YBCO-3</th>
<th>GdBCO/Ag 15 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process</td>
<td>TSMG</td>
<td>TSMG</td>
<td>Bridgman</td>
<td>TSMG</td>
</tr>
<tr>
<td>Shape</td>
<td><img src="image" alt="YBCO-1 Shape" /></td>
<td><img src="image" alt="YBCO-2 Shape" /></td>
<td><img src="image" alt="YBCO-3 Shape" /></td>
<td><img src="image" alt="GdBCO/Ag 15 wt% Shape" /></td>
</tr>
<tr>
<td>Dimensions (mm)</td>
<td>20 x 20 x 40</td>
<td>h= 15 d= 25</td>
<td>h= 30 d= 6</td>
<td>h= 15 d= 25</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>6.026 ± 0.006</td>
<td>6.081 ± 0.009</td>
<td>5.86 ± 0.02</td>
<td>7.039 ± 0.004</td>
</tr>
</tbody>
</table>

Table 2.1. Characteristics of the four single domains.
2.2.1 Top Seeded Melt Growth method (TSMG)

The top seeded melt growth process is the most effective method to fabricate single grains of RE-BBCO superconductors, mainly YBCO and GdBCO (Cardwell D., 1998; Shi Y. et al., 2007; Babu N. et al., 2006). Until now, very good superconducting properties have been achieved and high $J_c$ and $T_c$ values have obtained for REBCO samples (Yoo S. I. et al., 1994; Cardwell D. A. and Babu N. H., 2006). In this process a generic seed (Nd-Ba-Cu-O or Sm-Ba-Cu-O) is placed on the top surface of the pellet (Shi Y. et al., 2005). The $ab$-plane of the seed is in contact with the top surface of the pellet to obtain the appropriate orientation of the grain. Then, the pellet with the seed is melt-processed under air atmosphere and finally the peritectic solidification of the melt provides the required single grains. During the peritectic solidification the peritectic reaction is carried out starting from the growth of a liquid phase (Ba$_2$Cu$_3$O$_8$) and a solid stage (Y-211 or Gd-211) in order to obtain the crystal.

For the preparation of YBCO-1 single domains, the YBaCuO powders (Y-123 and Y-211) were prepared by the polyvinyl alcohol (PVA) method (Serradilla I. G. et al., 2002). The used ratio of 69 wt% Y-123, 30 wt% Y-211 and 1 wt% CeO$_2$H$_2$O was chosen to maximize critical current density (Piñol S. et al., 1993). The standard composition of the starting material was Y-123 with an excess of 30 wt% Y-211. CeO$_2$ was added to improve the distribution of Y-211 particles. The calcined powder was de-agglomerated by ball milling in an agate mortar and finally green bulk pieces were obtained by cold isostatic pressure (CIP).

In the case of YBCO-2 single domains, oxide powders of Y-123 and Y-211 were thoroughly mixed with a starting composition of 70 wt% Y-123, 30 wt% Y-211 and 1 wt% CeO$_2$ using a mortar and pestle. Then the green bulk pieces were obtained by uniaxially pressing into pellets 30 mm in diameter under a pressure of 5 MPa and finally by cold isostatic pressure.

The GdBCO/Ag 15 wt% single domains were prepared by mixing oxide powders with the recommended composition of 75 wt% Gd-123, 25 wt% Gd-211 and an excess of 15 wt% Ag$_2$O, 1 wt% BaO$_2$ and 0.1 wt% Pt (Shi Y. et al., 2010). The role of Pt is to inhibit the grain growth of the Gd-211 phase in the presence of molten Ba$_2$Cu$_3$O$_8$ liquid. The precursor powder was then pressed uniaxially into pellets 30 mm in diameter under a pressure of 5 MPa and finally by cold isostatic pressure to obtain the green bulk pellets.
A cold seeding process was used for all samples with a NdBa2Cu3O7-δ generic seed to nucleate and grow single grains of all materials. The melt-processing was carried out via a thermal profile that is described in figure 2.1. Different thermal profiles were applied for each case taking into account the different melting temperatures of the compounds (YBCO: 1005 °C, GdBCO/Ag: 1000 °C and GdBCO: 1030 °C). Also the crystallization, \( T_{s1} \), and crystal growth, \( T_{g2} \), temperatures varied, depending on the material (YBCO or GdBCO). The melting temperature was higher than the melting point of the powder and lower than the melting point of the seed. The crystallization temperature was 1010~1015 °C and the crystal growth temperature was 960~970 °C. Finally the cooling rate for the samples of 25 mm in diameter was 0.4 °C/min.

![Fig. 2.1. Thermal profile for melt-processing (TSMG).](image)

### 2.2.2 Bridgman technique

The YBCO-3 material was processed via Bridgman method. The preparation of the YBCO powders and the ratio used for each component were the same as in the case of YBCO-1. After mixing, the powder was pressed under isostatic pressure as a bar and inserted in the furnace at the peritectic temperature (1010 °C). The semisolid bars were hung inside the furnace and displaced through a thermal gradient (20 K cm\(^{-1}\)) from a higher temperature than the \( T_p \) to a lower one at a constant rate of 1 mm/h (Roa J. J. et al., 2012). A solid-liquid interface that produces a directional growth through the cylinder was established. The crystal growth occurs via a competition process between the nucleated grains on the warmer edge of the cylinder (polydomain zone) (Piñol S. et al. 1999).
2.2.3 Oxygenation process (annealing)

All single domain melt-processed samples were annealed in order to transform their crystallographic structure from tetragonal (non-superconducting) to orthorhombic (superconducting). The samples YBCO-1 and YBCO-3 were annealed in a kiln with a 99.9% pure oxygen flow, at 0.4 l/min, during 240 h at 450 °C (Serradilla I. G. et al., 2002). The other two materials, YBCO-2 and GdBCO/Ag 15 wt% were placed in a cylindrical kiln in a flowing oxygen atmosphere and were annealed at 400 °C for 168 h.

2.3 Microstructure

Samples of the four single domains were characterized micro-structurally with the aim of linking microstructural variations with the changes in the mechanical properties and the fracture behavior. For each compound, the $ab$-plane (longitudinal section) and the plane perpendicular to the $ab$-plane (transversal section) were embedded to resin and then polished up to 1 μm. The microstructure of the polished surfaces was revealed by etching with a solution of 95% of 2-butoxietanol and 5% of percloric acid, at 273 K during 1-3 min depending on the material. The microstructure was studied for all compounds by SEM and optical microscopy.

In case of YBCO-1, 3 a heterogeneous distribution of a secondary phase, Y$_2$BaCuO$_5$ (Y-211) can be observed in figures 2.2-2.3. This phenomenon is more noticeable in the case of YBCO-3, producing denser superconductor grains, because the particles of Y-211 typically improve the growth of the crystal and by preventing the liquid flow, the amount and size of the pores could decrease (Roa J. J. et al., 2010). Also, the heterogeneous distribution of fine Y-211 particles in Y-123 matrix acts as pinning centers under superconducting conditions and increases the current density of the material (Piñol S. et al., 1993).
Fig. 2.2. Microstructure of the YBCO-1 single grain. a) Longitudinal section where microcracking and the distribution of the Y-211 particles can be observed. b) Transversal section where macrocracking perpendicular and parallel to the $ab$-plane can be seen in the micrograph.
Fig. 2.3. Microstructure of the YBCO-3 single grain. a) Longitudinal section where the size and the distribution of the secondary phase Y-211 are indicated. b) Transversal section where the propagation of the crack parallel to the \(ab\)-planes can be seen.
In addition, according to figure 2.2b and 2.3b (transversal sections), it can be observed that during the oxygenation process cracks form smaller and narrower areas in the structure of the YBCO-1 superconducting domain than in the case of the YBCO-3. Micro and macro cracking for both materials were also observed produced during the oxygenation and the crystallization process. The two main sources of mechanical stresses during fabrication that lead to the cracking phenomena are a) the different thermal expansion coefficient of Y-123 and Y-211 phases and b) the dependence of Y-123 phase lattice parameters on the oxygen stoichiometry (Diko P., 2004).

For the YBCO-2 samples the matrix, Y-123 and the secondary phase, Y-211 are readily apparent in figure 2.4. The size of Y211 particles is homogeneous and between 1-4 μm. In the case of GdBCO/Ag there are three phases: Gd-123, Gd-211 and Ag particles (figure 2.5). The shape of the silver particles is almost cylindrical and the diameter varies between 20-60 μm, whereas the Gd-211 phase is quadratic and much smaller than Y-211 in the YBCO single crystals.

The presence of cracking has been observed previously in both YBCO and GdBCO/Ag single grains (figures 2.4–2.5). GdBCO/Ag, however, typically contains lower porosity and the voids are smaller than in the case of YBCO-2 samples. Macrocracking parallel to the ab-plane generated during the oxygenation process is shown in figures 2.4c and 2.5c. In addition, cracks oriented perpendicular to each other, are also observed within the ab-plane. The propagation of the cracks occurs around, rather than through, the Y-211 and Gd-211 secondary phases (K. Konstantopoulou et al., 2014). Moreover, for GdBCO/Ag single grains, cracks that interconnect the Ag particles are present due to a mis-match in the thermal expansion coefficients of silver (1.8 x 10^-6 K^-1) and superconductor (10^-5 K^-1).
Fig. 2.4. Microstructure of the YBCO-2 single grain. a) Longitudinal section where cracking perpendicular and parallel to the ab-plane can be seen, b) Longitudinal section where the size of a void is indicated and c) Transversal section where the density of cracking parallel to the ab-plane and the secondary phase Y-211 are shown.
Fig. 2.5. Microstructure of the GdBCO/Ag 15 wt% single grain. a) Longitudinal section where small cracks, voids and the size of Ag particles are indicated. b) Longitudinal section where the secondary phase Gd-211 and the size of Ag particles are shown and c) Transversal section where cracking parallel to the ab-plane and around the Ag particles can be seen.
2.4 Experimental procedure

2.4.1 Preparation of specimens for mechanical testing

The rectangular and cylindrical shaped samples obtained by TSMG and Bridgman processes were embedded in epoxy resin to enable cutting them in smaller prismatic specimens suitable for mechanical characterization. The as-grown cylinders and the rectangular samples were cut with a diamond wire parallel to the ab-plane to obtain the desirable prismatic-shaped specimens for the three-point bending tests. After several steps, prismatic specimens with nominal section 2 x 2 mm² were obtained. In order to remove the epoxy resin, the embedded samples were heated at 400 °C in air atmosphere for 30 minutes.

2.4.2 Mechanical characterization at room temperature (300 K)

The oxide compounds, YBCO and GdBCO/Ag were characterized via three-point bending (TPB) tests to determine their flexural strength and fracture toughness. In order to check the effect of the microstructural anisotropy on the mechanical properties, all tests were performed for loading directions parallel to the c-axis and parallel to the ab-plane. Only in the case of YBCO-3 single grain the tests were performed in a single loading direction (parallel to the ab-plane), because of the radial microstructural anisotropy of the grain. Prismatic specimens have been used for the TPB tests and the span between the test supports, Ls, was 8.5 mm and 16 mm for fracture toughness and flexural strength, respectively (figure 2.6).

All tests were carried out using an electromechanical testing machine, (Instron 5866), with the applied load and the displacement of the loading point recorded constantly during the test with a load cell of ±1 kN and a linear variable differential transducer (LVDT) of ±1 mm of displacement range (±1 μm resolution).

The three-point bending tests were performed using displacement control at a constant cross-head speed of 100 μm/min.
Fig. 2.6. Schematic illustration of the three-point bending tests for the evaluation of the flexural strength and fracture toughness.

Flexural strength was computed from the measured maximum load using established equations of strength of materials (Timoshenko S., 1955):

$$\sigma_F = \frac{3L_\varepsilon F_{\text{max}}}{2BD^2}$$  \hspace{1cm} (2.1)

Where $F_{\text{max}}$ is the maximum applied load, $L_\varepsilon$ is the distance between the rollers, $B$ is the width of the specimen and $D$ the height of the specimen.

To determine the fracture toughness, a notch was machined in the central section of the beams with a thin diamond wire (Well 3241, Swiss), to a notch tip radius of 65 $\mu$m. The length of the notch was nominally 35% of the thickness of the sample in all cases. Introduction of longer notches or V-notch was not considered practical, due to the small residual force necessary to break the notched specimens.

Finally, the fracture toughness, $K_{IC}$, was calculated from the measured maximum load and the post-measurement notch length using the equation reported by Guinea et al., 1998:
\[ K_c = \frac{3L SF_{\text{max}}}{2BD^{3/2}} \left( \frac{a}{D} \right)^{1/2} \left\{ \frac{A - B \left( \frac{a}{D} \right) + C \left( \frac{a}{D} \right)^2 - D \left( \frac{a}{D} \right)^3 + E \left( \frac{a}{D} \right)^4}{\left( 1 - \frac{a}{D} \right)^{3/2} \left( 1 + 2 \frac{a}{D} \right)} \right\} \]  

(2.2)

\[ A = 1.989 - 0.356 \frac{D}{L_S} \quad D = 3.222 - 0.020 \frac{D}{L_S} \]

\[ B = 1.217 + 0.315 \frac{D}{L_S} \quad E = 1.226 - 0.015 \frac{D}{L_S} \]

\[ C = 3.212 + 0.705 \frac{D}{L_S} \]

Where \( D \) is the height of the specimen, \( L_S \) is the distance between the rollers, \( F_{\text{max}} \) is the maximum applied load, \( B \) is the width of the specimen and \( a \) is the length of notch.

After testing all the samples, their surfaces were analyzed with a SEM, in order to find the micro mechanisms responsible for the macroscopically mechanical behavior of these materials.

2.4.3 Mechanical characterization at service temperature (77 K)

Three point bending tests have been performed at service temperature. The test device used at low (77 K) and room temperature was similar in both cases. The main difference between the two test conditions was that an additional cryogenic chamber was attached to the electromechanical testing machine (INSTRON 5866) in the vicinity of the loading device in the low temperature tests (figure 2.7). The bottom of the vessel and its load application point were connected to the actuator and the load cell of the machine, respectively, via hollow bars of stainless steel to prevent excessive cooling of the measurement instrumentation during the test. The cryogenic vessel was coated with polyurethane and cryogenic foam to insulate the system, and to maintain a constant temperature during the experiment. The
cryogenic tests were performed by immersing the specimens in boiling liquid nitrogen (i.e. at a temperature of 77 K), with the temperature stabilized for around 10 minutes before each test was performed. The level of liquid nitrogen in the cryogenic vessel was maintained throughout the low temperature test by refilling as necessary to keep the specimen and part of the loading device completely immersed during the measurement. This process was monitored to ensure it did not affect either the measurement of the load or the displacement. As in the case of the tests at 300 K, the load and the displacement were recorded constantly during the test with a load cell of ±1 kN and a linear variable differential transducer (LVD) of ±1 mm of displacement range (±1 μm resolution), respectively.

The positions of all test devices and specimens were fixed prior cooling. A constant, compressive load of low magnitude (4 N) was applied throughout the cooling and measurement process to keep the system in balance, and avoid any movement of the sample or the supporting rollers and plates.

At service temperature as well as at 300 K, the three-point bending tests were performed using displacement control at a constant, cross-head speed of 100 μm/min.

![Experimental set-up for TPB at 77 K.](image)

**Fig. 2.7.** Experimental set-up for TPB at 77 K.
Brazilian tests (Carneiro F. L. L. and Barcellos A., 1953) were carried out to obtain the splitting tensile strength, $\sigma_f$, of the YBCO and GdBCO/Ag samples. This experimental method has been applied widely to characterize both structural and functional materials, such as concrete (Planas J. and Bažant Z. P., 1998), graphite (Salazar A. et al., 2002) and functional ceramics (Pastor J. Y. et al., 1999). The samples tested were of cylindrical geometry (i.e. as-processed after annealing) with nominal dimensions of 20 mm in diameter and 12 mm in thickness and each one was compressed with its axis horizontal between the plates of the testing machine. The load was distributed by two bearing strips positioned parallel to the growth facet lines characteristics of the TSMG process on the upper surface of the bulk, superconducting samples. According to Rocco et al., 1999, when the behavior of the tested material is linear-elastic, the stress distribution becomes more uniform as the loading-bearing strips become narrower. So, in all cases, the load was distributed by two narrow bearing strips 1.5 mm in thickness, to prevent multiple cracking and crushing at the loading point. In the case of the YBCO compounds, the study has been performed only for the YBCO-2 samples, given the fact the lack of material for YBCO-1, 3 and that the cylindrical shaped samples of YBCO-2 had the same dimensions as GdBCO/Ag samples. After annealing, the top and bottom surfaces of the samples were polished up to 3 µm in order to take off any irregularity produced during the melt-processing. To carry out the Brazilian tests it was essential to design a device to center the samples and the two bearing strips in order to apply the load parallel to the facet lines. Then splitting tests were performed at 77 K in a servohydraulic machine (INSTRON 8501) with a load cell of ±10 kN (figure 2.8).

Fig. 2.8. Schematic illustration of the experimental set-up for Brazilian tests.
Additionally, a chamber was attached to the servohydraulic machine that was coated with polyurethane and cryogenic foam to insulate the system, and keep the temperature constant during the experiment. The tests were carried out at displacement control at a constant cross-head speed of 100 μm/min. A schematic illustration of the Brazilian tests is shown in figure 2.9

![Schematic illustration of the Brazilian tests](image)

**Fig. 2.9.** Schematic illustration of the splitting test for the evaluation of the tensile strength.

As the tested specimens presented a linear-elastic behavior, the schematic geometry and loading ensure a nearly uniform tensile stress state in the center plane of the specimen. As a consequence, the expected failure mode is the split of the samples in two halves across the loading direction (figure 2.10). The splitting tensile strength, $\sigma_T$, was obtained by the following expression:

$$\sigma_T = \frac{2P}{\pi BD}$$  \hspace{1cm} (2.3)

where $P$ is the maximum load, $B$ is the specimen thickness and $D$ is the specimen diameter.
2.4.4 Elastic modulus and Hardness

Nanoindentation is one of the most common methods to obtain the elastic modulus and the hardness of different low volume materials at nanoscale. During the measurements, a small diamond tip is pressed into the specimen until a fixed penetration depth. The load and the displacement of the tip into the surface are recorded constantly with high precision instruments and finally, the load-displacement curve is obtained. The hardness of the material is defined as the ratio between the applied load, $P$ and the projected area, $A$,

$$ H = \frac{P}{A} \quad (2.4) $$

In order to determine the elastic properties (hardness and elastic modulus) of the materials by the load-displacement curves obtained during tests, the analytical model developed by Oliver and Pharr (1992) was implemented. This method relates the initial slope of the unloading curve, $S$ in figure 2.11 with the contact area and the reduced elastic modulus, $E_r$ by the expression:

$$ E_r = \frac{1}{\beta} \frac{\sqrt{\pi} S}{2 \sqrt{A}} \quad (2.5) $$
Where $S$ is the initial slope of the unloading curve, $A$ is extracted by the geometrical characteristics of the tip and the record of the displacement into the surface and $\beta$ is related with the type of the tip. For Berkovich tip $\beta$ is 1.034.

![Load-Displacement Curve](image)

**Fig. 2.11.** Schematic of the load-displacement curve obtained by nanoindentation.

The reduced elastic modulus, $E_r$, takes in account the effect of a non-rigid indenter and is computed by

$$E_r = \frac{1}{\frac{1 - \nu_l^2}{E_l} + \frac{1 - \nu^2}{E}}$$

(2.6)

Where the symbol “$l$” indicates the tip properties and $E$ and $\nu$ are the elastic modulus and the Poisson’s ratio of the material, respectively. In the case of a diamond indenter $E_l$ is 1140 GPa and $\nu_l$ is 0.07 whereas for YBCO and GdBCO/Ag $\nu$ is 0.3 (Bartolomé E. et al., 2010).

Nanoindentation tests were performed at 300 K using a MTS Nano Indenter, CSM/LFM Control Unit, with a calibrated Berkovich tip indenter. The depth of the indentation was constant ($h = 1 \, \mu m$) and the load was applied at a constant rate of 0.2 $\mu m/s$ for all measurements. The tests were carried out on the longitudinal and transversal section of the specimens and thirty indentation tests were performed for each section.
The elastic modulus and the hardness of the materials were obtained by nanoindentation at 300 K although the small size of the tip led to non-global measurements, as the defects of the material were not taken into account.

For the YBCO-2 and GdBCO/Ag samples the elastic modulus, $E$, was calculated using three different methods at 300K: i) nanoindentation, ii) vibrational resonance with a grindosonic (Belgium) device and iii) from the load-displacement curve of the three-point bending tests. For the latter, the elastic modulus was determined at both 300 and 77 K from the linear zone of the stress-strain curves of the strength tests.

The hardness of the single grains was also obtained by Vickers hardness measurements. During the test, the load is applied by a pyramidal diamond tip with dihedral angle of 136° which is pressed into the specimen. Then the hardness is defined as the ratio between the load and the projected area into the surface. For the Vickers tests the area, $A$, was obtained by measuring the diagonals of the pyramidal shaped mark by optical microscopy with lens resolution of 1 µm. The $H_V$ was computed by

$$H_V = \frac{2P \sin \left( \frac{\theta}{2} \right)}{L^2} = \frac{1.854P}{L^2}$$  \hspace{1cm} (2.7)

being $P$ the load, $L$ the length of the diagonals in mm and $\theta$ the dihedral angle of the tip.

The Vickers hardness at 300 and 77 K was measured using an AKASHI, MVK-EIII instrument for the two loading directions, like in the case of the three-point bending tests. To perform the study at service temperature a bespoke chamber was designed that was isolated by polyurethane and attached to the hardness tester as it can be observed in figure 2.12. The sample was adapted inside a metallic ring, to avoid any movement of the sample during the test, and then was placed inside the chamber. Two different load values were used, 0.98 N (100 g) and 9.80 N (1 kg), and were applied during 15 seconds. The test was repeated 10 times under each test condition in order to obtain statistically significant data.
2.5 Results and discussion

2.5.1 Flexural strength

Three-point bending tests were performed to obtain the flexural strength of each single grain at 77 and 300 K. The direction of loading during the tests was either parallel to the c-axis or parallel to the ab-plane (Tables 2.2 and 2.3, respectively). For the YBCO-1 and YBCO-3 single grains, five tests were performed for each loading direction and temperature. In all cases, linear elastic brittle fracture was observed both at room and service temperature. The obtained flexural strength for YBCO-1 and YBCO-3, fabricated in the University of Barcelona, is presented in figure 2.13. This figure shows that YBCO-1 samples tested with the crystallographic ab-plane perpendicular to the applied load direction presented a value of the strength, $\sigma_b$, 40% lower than the value obtained with the crystallographic ab-plane parallel to the applied load direction. YBCO-3 samples tested at 300 K exhibited the same flexural strength as the YBCO-1 with the loading direction parallel to the ab-plane.
Table 2.2 Results obtained of the flexural strength with the loading direction parallel to the c-axis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_F$ (MPa) at 300 K</th>
<th>$\sigma_F$ (MPa) at 77 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBCO-1</td>
<td>57 ± 5</td>
<td>81 ± 9</td>
</tr>
<tr>
<td>YBCO-2</td>
<td>54 ± 5</td>
<td>71 ± 6</td>
</tr>
<tr>
<td>GdBCO/Ag</td>
<td>91 ± 4</td>
<td>105 ± 7</td>
</tr>
</tbody>
</table>

Table 2.3 Results obtained of the flexural strength with the loading direction parallel to the $ab$-plane.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_F$ (MPa) at 300 K</th>
<th>$\sigma_F$ (MPa) at 77 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBCO-1</td>
<td>70 ± 10</td>
<td>80 ± 13</td>
</tr>
<tr>
<td>YBCO-2</td>
<td>60 ± 5</td>
<td>78 ± 4</td>
</tr>
<tr>
<td>YBCO-3</td>
<td>70 ± 9</td>
<td>135 ± 15</td>
</tr>
<tr>
<td>GdBCO/Ag</td>
<td>90 ± 5</td>
<td>108 ± 7</td>
</tr>
</tbody>
</table>

At 77 K the mean value of the flexural strength increased, achieving a value that was almost twice the value of YBCO-1 at the same temperature. When the test was carried out at 77 K, the flexural strength provided equal results for each direction. This effect, according to the literature (Planas J. et al., 1989; Rocco C. et al., 2001), takes place due to the formation of thin ice layers over the surface of the specimen during the cooling process, from pre-existing ambient humidity. These ice layers partially covered the surface of pre-existing defects on the specimen surface, hence decreasing the critical size of the flaw and rounding its initial superficial tip radius.
Fig. 2.13. Variation of the flexural strength in function of temperature, test direction and process technique. Each point represents the value of the mean of at least five tests and the bars indicate the quadratic mean error.

This effect is also observed in other porous materials like concrete; during cooling, water vapor from the atmosphere condensates and produces a gradual sealing of the pores or a reduction in their size (Pastor J. Y. et al., 1999; Salazar A. et al., 2003). Consequently, a smaller superficial flaw tip radius arises, that reduce significantly the local stress intensity factor, and as a result, higher flexural strength of the material is necessary for material failure.

This is a plausible explanation for the mechanical behavior of the YBCO-1 material at low temperature when the value of the flexural strength converges to the same result for both test directions. In the case of YBCO-3, the smaller pore, size and geometry, made this mechanism more effective, producing therefore a marked increase of the flexural strength.
For the YBCO-2 and GdBCO/Ag samples, processed in the University of Cambridge, ten tests were carried out for each loading direction and test temperature. Figures 2.14-2.15 show the obtained results.

![Graph showing variation of flexural strength in function of temperature and test direction.](image)

**Fig. 2.14.** Variation of the flexural strength in function of temperature and test direction. Each point represents the value of the mean of ten tests and the bars indicate the quadratic mean error.

The mechanical behavior of YBCO-2 and GdBCO/Ag single grains was similar for both directions tested. An increase in $\sigma_F$ of 30% is observed for YBCO-2 at 77 K, independent of the loading direction and between 15 and 20% (depending on the loading direction) for GdBCO/Ag. However, the values of $\sigma_F$ obtained for the GdBCO/Ag single grain are approximately 45% than those determined for YBCO-2 at 77 K, compared to a difference of around 55% at room temperature. The addition of silver particles is well known to improve both the superconducting properties, by acting as pinning centers, and also the mechanical behavior (Hull J. R. and Murakami M., 2004) of the samples. Flexural strength has been observed to depend
on the loading direction for all YBCO-1,2,3 samples. Additionally, YBCO-1 and YBCO-2 samples presented similar flexural strength, although the second single grain was characterized by a more isotropic mechanical behavior. SEM observation of the fracture surfaces of the samples following mechanical testing investigated the fracture mechanisms and the effect of the microstructural characteristics on the macroscopic mechanical properties of the samples.

![Graph showing variation of flexural strength in function of temperature and test direction.](image)

**Fig. 2.15.** Variation of the flexural strength in function of temperature and test direction. Each point represents the value of the mean of ten tests and the bars indicate the quadratic mean error.

As can be observed in figures 2.16-2.17, YBCO-1 and YBCO-3 materials exhibited an appreciable amount of porosity, with a considerable size. The main difference between them was the different size of pores, greater for YBCO-1 and significantly smaller, though in a larger amount, for YBCO-3. In addition, it was observed that materials obtained by both methods were not perfectly sintered. These poorly-

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sintered zones (cavity) (figure 2.18) could be responsible of the observed porosity in both materials.

The fracture surfaces of both materials were in all cases typically brittle, with macroscopically flat fracture surfaces and at the microscopically level fractures due to cleavage processes (figures 2.19-2.20). No dependence on the material, the temperature or test direction was found. In addition, it can be observed that in the case of YBCO-1 material with loading direction parallel to the c-axis the fracture surface was macroscopically flatter than in the other loading direction, where several discontinuities were observed in the fracture surface due to the relative orientation of the grain respect to the loading axis. Conversely, the fracture surface of the YBCO-3 (figures 2.21-2.22) was rough, more similar to that of the YBCO-1 when the loading direction was parallel to the ab-pane direction than that of the other loading direction. It can also be observed that during the three-point bending tests in YBCO-3, as well as in YBCO-1 (loading direction parallel to the ab-plane), several cracks propagated in the perpendicular direction to the plane of the main crack propagation (figure 2.23). This local ramification of the crack front resulted in an increase of the energy and the flexural strength of the material, as was observed.

Figure 2.24 shows the brittle fracture surface of YBCO-2 sample at 77 K. The loading direction was parallel to the c-axis, with the resulting direction of propagation of cracks being perpendicular to the orientation of the pre-existing microcracks. The fracture characteristics of the grain and decohesion can be seen in figure 2.24. The crack propagates initially perpendicular to the ab-plane (fracture of the grain) and then parallel to the ab-plane, resulting in decohesion. However, similar values of flexural strength were observed in both loading directions when the load was applied parallel to the ab-plane, resulting in propagation of cracks through the pre-existing microcracks, as shown in figures 2.25-2.26. This occurred at both test temperatures, where the single grains exhibit similar, abrupt fracture surfaces. The propagation of cracks through the pre-existing microcracks would be reasonably expected to lower the flexural strength in this loading direction. According to the visual appearance of the fracture surfaces, however, decohesion of the grain is observed when the loading direction is parallel to the c-axis. The fracture mechanics are controlled by the density of cracking when the loading direction is parallel to the ab-plane, whereas, for the other loading direction, the fracture depends on the crack density as well as on decohesion of the grain.
Figures 2.27-2.28 show the fracture surfaces of GdBCO/Ag grain tested at 77 K for a loading direction parallel to the c-axis. These surfaces are much smoother than those observed for the YBCO-2 single grain from the fractographic results. However, the presence of Ag particles reinforces the GdBCO single grain and leads to a higher fracture energy for the propagation of the cracks, which results in a narrowing of the area between the cracks.

The fracture mechanics of the bulk samples is determined predominantly by the crack density when the loading direction is parallel to the ab-plane (figure 11), with cracks propagating through the pre-existing cracks and around the silver particles. The similar behavior observed between the two directions tested for GdBCO/Ag is due to the presence of the Ag particles and their homogeneous distribution within the single grain. This results directly in the formation of smaller cracks and an associated higher energy being necessary to fracture the grain.

![Fracture surface of YBCO-1 single grain after the three-point bending test at 77K.](image)

**Fig. 2.16.** Fracture surface of YBCO-1 single grain after the three-point bending test at 77K. The density of voids and their larger size compared with YBCO-3 single grain are indicated.
Fig. 2.17. Fracture surface of YBCO-3 single grain after the three-point bending test at 77 K. Higher density of voids with smaller size compared with YBCO-1 single grain can be observed.

Fig. 2.18. The inside part of a cavity on the fracture surface of YBCO-1 single grain after the three-point bending test for the measurement of the flexural strength can be observed. The loading direction was parallel to the c-axis.
Fig. 2.19. Fracture surfaces of YBCO-1 single grain after the three-point bending tests for the measurement of the flexural strength at 77 K. The loading direction was parallel to the c-axis. The brittle fracture surface and macroscopically plane can be observed.

Fig. 2.20. Fracture surface of YBCO-1 single grain after the three-point bending test at 77 K. The loading direction was parallel to the ab-plane. The brittle and curved fracture surface can be observed.
Fig. 2.21. Fracture surface of YBCO-3 single grain after the three-point bending test. A perpendicular crack to the fracture surface, produced during the fracture process, can be observed.

Fig. 2.22. Fracture surface of YBCO-3 single grain after the three-point bending tests at 300 K. This figure presents the density of voids and its smaller size.
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Fig. 2.23. Fracture surface of YBCO-1 single grain after the three-point bending test for the measurement of the flexural strength at 300 K. The loading direction was parallel to the ab-plane. Propagation of the crack perpendicular to the ab-plane can be observed.

Fig. 2.24. Fracture surface of YBCO-2 single grain after the three-point bending test for the measurement of the flexural strength at 77 K. The loading direction was parallel to the c-axis. Decohesion and fracture of the domain is shown in the figure.
Fig. 2.25. Fracture surface of YBCO-2 single grain after the three-point bending test for the measurement of the flexural strength at 77 K. The loading direction was parallel to the $ab$-plane. The propagation of the crack parallel to the $ab$-plane and the density of voids are indicated.

Fig. 2.26. Fracture surface of GdBCO/Ag single grain after the three-point bending test for the measurement of the flexural strength at 77 K. The loading direction and the propagation of the crack were parallel to the $ab$-plane. Cracks propagate through the pre-existing microcracks and around the Gd-211 secondary inclusions.
Fig. 2.27. Fracture surface of GdBCO/Ag single grain after the three-point bending test for the measurement of the flexural strength at 77 K. The loading direction was parallel to the c-axis. A smooth fracture surface and the propagation of cracks perpendicular to the ab-plane are observed.

Fig. 2.28. Fracture surface of GdBCO/Ag single grain after the three-point bending test for the measurement of the flexural strength at 77 K. The loading direction was parallel to the c-axis. The fracture of the grain and propagation of the crack parallel to the ab-plane are shown.
2.5.2 Fracture toughness

Three-point bending tests on notched, prismatic samples were performed to determine the fracture toughness of each single grain. The tests were performed for the two loading directions at temperatures of 300 and 77 K. The obtained results are shown in Tables 2.4 and 2.5. For YBCO-1 and YBCO-3 single grains, five tests were performed for each measurement condition, with the results of the fracture toughness, $K_{IC}$, shown in figure 2.29. As can be observed, YBCO-1 samples tested for a loading direction parallel to the c-axis presented the higher value of fracture toughness at 300 K.

**Table 2.4.** Results obtained of the fracture toughness with the loading direction parallel to the c-axis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$K_{IC}$ (MPa.m$^{1/2}$) at 300 K</th>
<th>$K_{IC}$ (MPa.m$^{1/2}$) at 77 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBCO-1</td>
<td>1.47 ± 0.15</td>
<td>1.35 ± 0.06</td>
</tr>
<tr>
<td>YBCO-2</td>
<td>1.24 ± 0.06</td>
<td>1.38 ± 0.08</td>
</tr>
<tr>
<td>GdBCO/Ag</td>
<td>1.72 ± 0.07</td>
<td>2.12 ± 0.08</td>
</tr>
</tbody>
</table>

**Table 2.5.** Results obtained of the fracture toughness with the loading direction parallel to the ab-plane.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$K_{IC}$ (MPa.m$^{1/2}$) at 300 K</th>
<th>$K_{IC}$ (MPa.m$^{1/2}$) at 77 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBCO-1</td>
<td>1.19 ± 0.05</td>
<td>1.31 ± 0.16</td>
</tr>
<tr>
<td>YBCO-2</td>
<td>1.26 ± 0.05</td>
<td>1.87 ± 0.09</td>
</tr>
<tr>
<td>YBCO-3</td>
<td>1.28 ± 0.09</td>
<td>1.35 ± 0.09</td>
</tr>
<tr>
<td>GdBCO/Ag</td>
<td>1.69 ± 0.07</td>
<td>2.06 ± 0.09</td>
</tr>
</tbody>
</table>
In contrast, the YBCO-3 at 300 K exhibited almost the same fracture toughness value as YBCO-1 when the load was applied parallel to the $ab$-plane and fracture toughness increased at 77 K. On the other hand, YBCO-1 with loading direction parallel to the $c$-axis presents a slight decrease of the toughness value at 77 K.

For YBCO-2 and GdBCO/Ag samples ten tests were carried for each loading direction and test temperature and the obtained results are shown in figures 2.30-2.31.

Both materials exhibit higher fracture toughness at 77 K, although the behavior of the GdBCO/Ag single grain is more isotropic than YBCO-2, with anisotropic behavior observed for the latter for the two loading directions employed. The fracture toughness of YBCO-2 is 35% higher for the different loading directions at room
temperature, whereas the observed differences in this parameter for both loading directions at 77 K and room temperature for GdBCO/Ag sample were negligible.

The fracture toughness of YBCO-2 and GdBBCO/Ag at 77 K is between 1.38-1.87 MPa.m$^{1/2}$ and 2.12-2.06 MPa.m$^{1/2}$, respectively. This significant difference is again due to the presence of Ag particles, which improves the mechanical properties and lead to more isotropic single grains with regard to their mechanical behavior.

![Graph showing fracture toughness vs temperature](image)

**Fig. 2.30.** Variation of the fracture toughness as a function of temperature and test direction. Each point represents the value of the mean of ten tests and the bars indicate the quadratic mean error.

YBCO-2 single grains exhibit similar behavior at 300 K for both loading directions but not at service temperature. The fracture toughness for YBCO-2 is much higher and closer to the values obtained for the GdBCO/Ag samples when the loading direction is parallel to the $ab$-plane.
Fig. 2.31. Variation of the fracture toughness as a function of temperature and test direction. Each point represents the value of the mean of ten tests and the bars indicate the quadratic mean error.

SEM characterization of the fracture surfaces has been carried out to identify the fracture mechanisms for each material. In the case of YBCO-3, more cavities and voids were found in the fracture path, which contributed in enhancing grain boundary decohesion (figure 2.32). Such an effect was probably responsible for the lower value of fracture toughness observed in the case of the material fabricated by the Bridgman technique. It was observed that in the case of YBCO-3 and YBCO-1 (loading direction parallel to the ab-plane), the fracture was mainly controlled by the density of cracking (figures 2.33-2.34). In the case of the material YBCO-1 with loading direction parallel to the c-axis (figure 2.35), the fracture was mainly controlled by the fracture of the areas between cracks (propagation of the crack perpendicular to the ab-plane). For this reason, and considering the small and narrow areas produced due to microcracking on YBCO-3 and YBCO-1 domain, the propagation of the crack happened more easily through the pre-existing microcracks.
than perpendicular to the \textit{ab}-plane. This result explained the lower value of the fracture toughness for YBCO-1 (loading direction parallel to the \textit{ab}-plane) and YBCO-3 at 300 K. However, the microstructural anisotropy of the YBCO-3 single grain, due to the tilt angle of the \textit{c}-axis, leads to slightly higher fracture toughness, compared to the YBCO-1 with loading direction parallel to the \textit{ab}-plane. Therefore and according to the fractographic study (figure 2.36), there are two fracture mechanisms for YBCO-3 samples: a) the density of cracking and b) the propagation of the crack following a direction with a certain angle with respect to the \textit{ab}-plane.

However, with the reduction of the temperature at 77 K, the slight decrease of the fracture toughness for YBCO-1 with loading direction parallel to the \textit{c}-axis could occur due to the embrittlement of the superconducting domain as the testing temperature decreased. This small effect is not relevant for the other conditions, where the microcracks control the fracture process. In fact, the size of the microcracks can improve at low temperature due to the increase of thermal stresses.

Observing the fracture surfaces of YBCO-2 and GdBCO/Ag samples (figures 2.37-2.38), it can be concluded that, although the cracks are propagate perpendicular to that of the main crack propagation plane, the presence of voids leads to decohesion of the grain.

Narrow regions between cracks can be observed that are similar in appearance to the fracture surfaces of the GdBCO/Ag samples for the \textit{c}-axis loading direction (figure 2.39). A fractographic study of the fracture surfaces of the GdBCO/Ag single grains is shown in figures 2.40-2.41. In both cases, examination of the surfaces indicates that brittle fracture has occurred. It can be concluded from the experimental results that the propagation of cracks perpendicular to the \textit{ab}-plane requires a similar order of magnitude of fracture energy as that for crack propagation in the direction parallel to the \textit{ab}-plane. The silver particles act as barrier to the propagation of the cracks, which consequently improves the flexural strength of the samples and homogenizes their mechanical behavior.
Fig. 2.32. Fracture surface of YBCO-3 single grain after three-point bending test for the measurement of the fracture toughness at 300 K. Decohesion of the superconducting domain was observed.

Fig. 2.33. Fracture surface of YBCO-1 single grain after the three-point bending test for the measurement of the fracture toughness at 300 K. The loading direction was parallel to the \( \alpha\beta \)-plane. The propagation of the crack parallel to the \( \alpha\beta \)-plane through the pre-existing cracking and finally the fracture of the superconducting domain are shown.
Fig. 2.34. Fracture surface of YBCO-3 single grain after the three-point bending tests for the measurement of the fracture toughness at 77 K. The loading direction was parallel to the \( ab \)-plane. The propagation of the crack was through the pre-existing cracking.

Fig. 2.35. Fracture surface of YBCO-1 single grain after the three-point bending test for the measurement of the fracture toughness at 77 K. The loading direction was parallel to the \( c \)-axis. The propagation of the crack happened perpendicular to the \( ab \)-plane through the superconducting domain.
Fig. 2.36. Fracture surface of YBCO-3 single grain after the three-point bending test for the measurement of the fracture toughness at 77 K. The crack was propagated following a direction with a certain angle with respect of the $ab$-plane due to microstructural anisotropy.

Fig. 2.37. Fracture surface of YBCO-2 single grain after the three-point bending test for the measurement of the fracture toughness at 77 K. The loading direction was parallel to the $c$-axis.
Fig. 2.38. Fracture surface of YBCO-2 single grain after the three-point bending test for the measurement of the fracture toughness at 77 K. The loading direction was parallel to the $c$-axis. a) Propagation of the crack perpendicular to the $ab$-plane and b) Decohesion of the grain.
Fig. 2.39. Fracture surface of YBCO-2 single grain after the three-point bending test for the measurement of the fracture toughness at 77 K. The loading direction was parallel to the $ab$-plane. Brittle fracture and curved fracture surface are observed.

Fig. 2.40. Fracture surface of GdBCO/Ag single grain after the three-point bending test for the measurement of the fracture toughness at 77 K. The loading direction was parallel to the $c$-axis. A change in the direction of the propagation of the main crack is observed.
**Fig. 2.41.** Fracture surface of GdBCO/Ag single grain after the three-point bending test for the measurement of the fracture toughness at 77 K. The loading direction was parallel to the $ab$-plane. Brittle fracture and abrupt fracture surface is observed.

### 2.5.3 Analysis of semielliptical surface cracks

The precise study of surface cracks on the specimens and the accurate stress analysis are essential for a certain prediction of the fracture strengths. Newman and Raju (1981) proposed an empirical stress-intensity factor equation for semielliptical surface cracks in finite elastic plates subjected in tension or bending loads (figure 2.42). The stress-intensity factor is given by

$$K_i = (S_t + HS_b) \sqrt{\frac{a}{Q} F \left( \frac{a}{t}, \frac{c}{b}, \theta, \varphi \right)}$$

(2.8)

For $0 \leq a/c \leq 1.0$, $0 \leq a/t < 1.0$, $c/b < 0.5$ and $0 \leq \varphi \leq \pi$. The functions $F$ and $H$ are defined so that the boundary-correction factor for bending is equal to the product of $F$ and
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\( H, S_b \) is the bending stress, \( St \) is the tension stress, \( a \) is the depth of the surface crack, \( b \) is the half-width of the cracked plate, \( c \) is the half-length of the surface crack, \( t \) is the plate thickness, \( \varphi \) is the parametric angle of the ellipse and \( Q \) is a shape factor for elliptical crack (Merkle J. G., 1973)

\[
Q = 1 + 1.464 \left( \frac{a}{c} \right)^{1.65} \quad \left( \frac{a}{c} \leq 1 \right)
\]  

(2.9)

Once the characterization by three-point bending tests was performed, the stress-intensity factor for a semielliptical surface crack was calculated as a function of parametric angle, crack depth, crack length, thickness and width of the specimen. As the four materials were tested under three-point bending tests, only the bending loads were taken into account for the determination of the stress-intensity factor:

\[
K_I = HS_b \sqrt{\pi a} F \left( \frac{a}{t}, \frac{a}{c}, \frac{c}{b}, \varphi \right)
\]  

(2.10)

The stress-intensity factor equation was useful in order to estimate the fracture toughness of the four tested materials and compare the results with the other obtained experimentally. Fracture toughness is related with the flexural strength and the crack length for a prismatic beam tested under three-point bending tests by the expression (Anderson T. L., 1995):

\[
K_{IC} = Y \sigma_f \sqrt{\pi a}
\]  

(2.11)

where \( a \) is the length of the surface-crack and \( Y \) is a geometrical factor depending on the flaw and specimen shape. In the case of the four tested materials, \( Y \) is given by the equation:

\[
Y = \sqrt{\frac{1}{Q} F \left( \frac{a}{t}, \frac{a}{c}, \frac{c}{b}, \varphi \right)}
\]  

(2.12)

The analytical value of the fracture toughness was finally computed by the eq. 2.11 and in the Tables 2.6, and 2.7 the obtained results are compared with the experimental data. It is important to mention, that although in all fractured specimens a semielliptical crack was observed that was indicating the crack growth, there were
two cases that was not possible two define the semielliptical defect on the fracture surface: YBCO-1 at 300 K with the loading direction parallel to the c-axis and YBCO-2 at 77 K with the loading direction parallel to the ab-plane.

![Schematic of a surface crack in a finite plate.](image)

At service temperature as well as at 300 K, the analytical values are slightly lower than the experimental ones. This small difference between the experimental and analytical results could be due to the approximated measurement of the length of the surface crack by SEM. However, the obtained results indicate that the fracture toughness of the materials depends on the semielliptical flaw size and the microstructural anisotropy. When the loading direction is parallel to the c-axis, the microcracking perpendicular to the loading direction leads to the propagation of the crack in the perpendicular direction to the plane of the main crack propagation.

When the loading direction is parallel to the ab-plane the propagation of the crack is mainly controlled by the density of cracking that appears parallel to the loading direction. The pre-existing cracking acts as an “easy” path for the propagation of the crack. Due to this, the fracture toughness is slightly higher when the loading direction is parallel to the c-axis at 300 and 77 K.
The behavior of the materials under bending was different than for the fracture toughness. The results show that the fracture mechanisms and the behavior of the superficial defects change and decohesion of the grain is now the main fracture mechanism when the loading direction is parallel to the c-axis. Figures 2.43-2.44 show the measured semieliptical defects on the fracture surfaces of the tested specimens with loading direction parallel to the \( ab \)-plane and parallel to the c-axis, respectively. These results corroborate the crucial role of the critical defects size on the toughness and flexural strength of both materials and allow an enhanced understanding of the relationship between microstructural defects and macroscopic properties.

**Table 2.6.** Fracture toughness (MPa.m\(^{1/2}\)) obtained analytically and experimentally when the loading direction was parallel to the c-axis.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>300</th>
<th>77</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( K_{IC} )</td>
<td>( K_{IC} )</td>
</tr>
<tr>
<td>F // c-axis</td>
<td>analytical</td>
<td>experimental</td>
</tr>
<tr>
<td>YBCO-1</td>
<td>-</td>
<td>1.47 ± 0.15</td>
</tr>
<tr>
<td>YBCO-2</td>
<td>0.57</td>
<td>1.24 ± 0.06</td>
</tr>
<tr>
<td>GdBBCO/Ag</td>
<td>1.54</td>
<td>1.72 ± 0.07</td>
</tr>
</tbody>
</table>

**Table 2.7.** Fracture toughness (MPa.m\(^{1/2}\)) obtained analytically and experimentally when the loading direction was parallel to the \( ab \)-plane.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>300</th>
<th>77</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( K_{IC} )</td>
<td>( K_{IC} )</td>
</tr>
<tr>
<td>F // ( ab )-plane</td>
<td>analytical</td>
<td>experimental</td>
</tr>
<tr>
<td>YBCO-1</td>
<td>1.02</td>
<td>1.19 ± 0.05</td>
</tr>
<tr>
<td>YBCO-2</td>
<td>1.11</td>
<td>1.26 ± 0.05</td>
</tr>
<tr>
<td>YBCO-3</td>
<td>1.15</td>
<td>1.28 ± 0.09</td>
</tr>
<tr>
<td>GdBBCO/Ag</td>
<td>1.48</td>
<td>1.69 ± 0.07</td>
</tr>
</tbody>
</table>
Fig. 2.43. Semielliptical defects on the fracture surface of the samples after bending tests. The loading direction was parallel to the \textit{ab}-plane.
Fig. 2.44. Semielliptical defects on the fracture surface of the samples after bending tests. The loading direction was parallel to the c-axis.
2.5.4 Splitting tensile strength

Four splitting tests were performed at 77 K for each single grain. The loading direction was parallel to the growth facet lines in order to measure the tensile strength of the grain at its weakest position, which is the limiting condition for the practical application of these materials. The results of this measurement are shown in Table 2.8.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_T$ (MPa) F // facet lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBCO-2</td>
<td>31 ± 3</td>
</tr>
<tr>
<td>GdBCO/Ag</td>
<td>34 ± 3</td>
</tr>
</tbody>
</table>

It has been observed that both grains exhibit a similar tensile strength at 77 K, with the measured value for GdBCO/Ag being slightly higher than that for YBCO. The resulting observed tensile strength suggests that these tests are less sensitive to the presence of Ag than flexural strength and fracture toughness measurements. The fracture, in this case, is controlled mainly by the presence of pre-existing cracks, with crack propagation occurring predominantly parallel to the ab-plane. The similarity of results observed for the two materials can be also explained by taking into account their behavior during the fracture toughness measurements. $K_{IC}$ for YBCO-2 is 1.87 MPa m$^{1/2}$ at 77 K when the loading direction is parallel to the ab-plane, which is very close to the corresponding value for GdBCO/Ag (2.06 MPa m$^{1/2}$).

Figures 2.45-2.46 show the fracture surfaces of the YBCO-2 samples after the splitting tests, which tend to be flatter than the fracture surfaces of the GdBCO/Ag single grains. Additionally, a wider region between cracks is observed, although the fracture mechanism for both samples is the same. The slightly different size of the voids between the YBCO and GdBCO/Ag samples is also apparent from these figures.

On the other hand, figures 2.47-2.48 show the propagation of the cracks parallel to the ab-plane for a loading direction parallel to the growth facet lines for GdBCO/Ag.
single grain. An increase in density of cracks can be observed following fracture. The fracture mechanism is dominated by the presence and density of the pre-existing microcracks for both grains, which act as path for the propagation of the crack during the tests. However, the tensile strength of the grains is relatively high (~ 30 MPa) taking into account the brittle nature of these compounds and the fact that they contain a variety of microstructural defects, such as voids and microcracks.

![Fracture surface of the YBCO-2 single grain after the splitting test at 77 K. The propagation of cracks parallel to the $ab$-plane and the density of voids can be seen.](image1)

**Fig. 2.45.** Fracture surface of the YBCO-2 single grain after the splitting test at 77 K. The propagation of cracks parallel to the $ab$-plane and the density of voids can be seen.

![Fracture surface of the YBCO-2 single grain after the splitting test at 77 K. Cracks propagate mainly parallel to the $ab$-plane, although small perpendicular cracks can be observed.](image2)

**Fig. 2.46.** Fracture surface of the YBCO-2 single grain after the splitting test at 77 K. Cracks propagate mainly parallel to the $ab$-plane, although small perpendicular cracks can be observed.

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**Fig. 2.47.** Fracture surface of the GdBCO/Ag single grain after the splitting test at 77 K. The propagation of the cracks is parallel to the $ab$-plane and the density of cracking produced narrow superconducting areas within the sample.

**Fig. 2.48.** Fracture surface of the GdBCO/Ag single grain after the splitting test at 77 K. The propagation of the cracks is parallel to the $ab$-plane and the fracture is more abrupt than in the case of YBCO-2.
2.5.5 Hardness evaluation

The hardness on the nano- and micro-scale was studied via nanoindentation and Vickers tests, respectively. Table 2.9 shows the load and microstructural orientation effect of YBCO-1 and YBCO-3 single grains. In the case of YBCO-1 at 300 K the Vickers hardness presented an almost constant value for the transversal section, as well as for the longitudinal one, regardless of the applied load. In contrast, YBCO-3 exhibited a higher hardness in the transversal section than in the longitudinal one.

In addition, the difference between the hardness of the two sections was maintained with an increasing applied load. The value of the Vickers hardness of YBCO-1 was higher than that of the YBCO-3 in all cases at 300 K, probably due to a lower porosity level and the narrower cracks of its microstructure. On the contrary, the value of the nanohardness was higher for the material YBCO-3 and for both materials it could be observed an increase of the nano hardness for the transversal sections. At this point it should be noted that in the case of the Vickers hardness test, the load was applied on an extended zone of the surface of the material and consequently, the hardness corresponded to a large area of the superconducting domain. Conversely, in the case of the nano hardness test, the load was extremely small and as a result the size of the mark of the Berkovich tip was one order of magnitude smaller than the distance between the microcracks. Hence nanoindentation allowed the hardness of individual regions of the compound YBaCuO to be determined, while in the case of Vickers hardness the global microstructure of the material was characterized (defects, porosity, microcracks, amongst others). For this reason, it could be inferred that in the case of YBCO-1 narrower cracks parallel to the ab-plane have been observed than in the case of the YBCO-3, although the second presented more compact areas between cracking in the structure of the superconducting domain. This offered a significant degree of agreement with the results shown in previous sections. Thus, in spite of the fact that the results of both tests were different, they do provide complementary information about these materials.
Table 2.9. Mean values of hardness and quadratic errors for the nanoindentation measurements and Vickers hardness tests at 300 K.

<table>
<thead>
<tr>
<th>Material Section</th>
<th>Nano H (GPa) F = 130-160 mN</th>
<th>H\textsubscript{V} (GPa) F = 0.98 N</th>
<th>H\textsubscript{V} (GPa) F = 9.8 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBCO-1 (longitudinal)</td>
<td>8.2 ± 0.2</td>
<td>7.5 ± 0.2</td>
<td>5.7 ± 0.2</td>
</tr>
<tr>
<td>YBCO-3 (longitudinal)</td>
<td>8.8 ± 0.2</td>
<td>5.4 ± 0.2</td>
<td>4.4 ± 0.2</td>
</tr>
<tr>
<td>YBCO-1 (transversal)</td>
<td>8.0 ± 0.1</td>
<td>7.1 ± 0.2</td>
<td>6.1 ± 0.1</td>
</tr>
<tr>
<td>YBCO-3 (transversal)</td>
<td>9.3 ± 0.1</td>
<td>6.4 ± 0.2</td>
<td>5.5 ± 0.1</td>
</tr>
</tbody>
</table>

Hardness tests at 77 K (Table 2.10) showed that the value of the hardness increased at low temperature for both materials in a highly relevant proportion (around 50%). However, in this case the value of the Vickers hardness of YBCO-1 was smaller than that of the YBCO-3, inverting the situation from room temperature. This effect could be explained again by the formation of superficial ice layers during cooling. As this effect became more intense as the pore size decreased, it contributed to a greater extent to increase the low temperature hardness of YBCO-3.
Table 2.10. Mean values of hardness and quadratic mean errors for the Vickers hardness tests at 77 K for different applied loads.

<table>
<thead>
<tr>
<th>Material Section</th>
<th>H_v (GPa) F= 0.98 N</th>
<th>H_v (GPa) F= 9.8 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBCO-1 (longitudinal)</td>
<td>9.6 ± 1.0</td>
<td>8.1 ± 0.5</td>
</tr>
<tr>
<td>YBCO-3 (longitudinal)</td>
<td>14.1 ± 2.0</td>
<td>12.7 ± 0.7</td>
</tr>
<tr>
<td>YBCO-1 (transversal)</td>
<td>10.2 ± 0.4</td>
<td>7.5 ± 0.1</td>
</tr>
<tr>
<td>YBCO-3 (transversal)</td>
<td>14.9 ± 0.5</td>
<td>9.5 ± 0.2</td>
</tr>
</tbody>
</table>

Tables 2.11 and 2.12 shows the changes in hardness for the different sections and temperatures of YBCO-2 and GdBCO/Ag single grains. An increase in hardness at 77 K and isotropic behavior are observed for both single grains. In all cases, the values for GdBCO/Ag are lower than those of YBCO due to the presence of the relatively soft silver particles. On the other hand, the nanoindentation measurements enabled the hardness of the Ag particles and the Y-123/Gd-123 phases to be determined directly (Table 2.13). The much higher values are due to the smaller tip indenter that provides an opportunity to test the different phases (Y- or Gd-123, Y- or Gd-211, Ag) separately, in regions far from defects such as cracks and voids (figure 2.49).

Table 2.11. Mean values for hardness and quadratic errors for Vickers hardness tests at 300 K for different applied loads.

<table>
<thead>
<tr>
<th>Section</th>
<th>Material</th>
<th>H_v (GPa) F= 0.98 N</th>
<th>H_v (GPa) F= 9.8 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>longitudinal</td>
<td>YBCO-2</td>
<td>8.1 ± 0.2</td>
<td>6.7 ± 0.2</td>
</tr>
<tr>
<td>transversal</td>
<td>YBCO-2</td>
<td>7.3 ± 0.2</td>
<td>6.1 ± 0.2</td>
</tr>
<tr>
<td>longitudinal</td>
<td>GdBCO/Ag</td>
<td>7.1 ± 0.2</td>
<td>-</td>
</tr>
<tr>
<td>transversal</td>
<td>GdBCO/Ag</td>
<td>6.7 ± 0.2</td>
<td>4.5 ± 0.2</td>
</tr>
</tbody>
</table>
Table 2.12. Mean values of hardness and quadratic errors for the Vickers hardness tests at 77 K for different applied loads.

<table>
<thead>
<tr>
<th>Section</th>
<th>Material</th>
<th>( H_v ) (GPa) ( F= 0.98 ) N</th>
<th>( H_v ) (GPa) ( F= 9.8 ) N</th>
</tr>
</thead>
<tbody>
<tr>
<td>longitudinal</td>
<td>YBCO-2</td>
<td>13.6 ± 0.3</td>
<td>9.9 ± 0.1</td>
</tr>
<tr>
<td>transversal</td>
<td>YBCO-2</td>
<td>12.7 ± 0.4</td>
<td>7.9 ± 0.1</td>
</tr>
<tr>
<td>longitudinal</td>
<td>GdBCO/Ag</td>
<td>13 ± 1</td>
<td>7.5 ± 0.6</td>
</tr>
<tr>
<td>transversal</td>
<td>GdBCO/Ag</td>
<td>10.7 ± 0.5</td>
<td>7.1 ± 0.2</td>
</tr>
</tbody>
</table>

Table 2.13. Hardness obtained by nanoindentation measurements at 300 K. The mean value and the quadratic mean errors are as indicated.

<table>
<thead>
<tr>
<th>Section</th>
<th>Material</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>longitudinal</td>
<td>YBCO-2</td>
<td>11.3 ± 0.2</td>
</tr>
<tr>
<td>transversal</td>
<td>YBCO-2</td>
<td>10.9 ± 0.2</td>
</tr>
<tr>
<td>longitudinal</td>
<td>GdBCO/Ag</td>
<td>8.8 ± 0.3</td>
</tr>
<tr>
<td>transversal</td>
<td>GdBCO/Ag</td>
<td>9.3 ± 0.1</td>
</tr>
<tr>
<td>longitudinal/transversal</td>
<td>Ag</td>
<td>1 ± 0.1</td>
</tr>
</tbody>
</table>

Fig. 2.49. Nanoindentation on the transversal section of YBCO-2 single grain at 300 K. The measurement corresponds to the Y-123 phase.
The postmortem surface of each material was studied by means of scanning electron and optical microscopy. Figures 2.50-2.55 show the typical propagation of the cracks on the material surface. It could be observed how the cracks were preferentially propagated parallel to the \(ab\)-plane and just in the interface between them. Furthermore, when a crack was forced to grow perpendicularly to the \(ab\)-plane, it was quickly impelled by the microstructure to turn towards a direction parallel to the \(ab\)-plane. Due to the irregular pattern of cracks (consequence of the anisotropic microstructure) it was not possible to determine the fracture toughness by this method. Additionally, those regions with a greater proportion of Y-211, Gd-211 and Ag particles (secondary phases) presented crack deflections, because the propagation of the cracks occurred preferentially around and not through the secondary phases that are tougher than the Y-123 and Gd-123 phases. (Roa J. J. et al., 2007).

![Image](image_url)

**Fig. 2.50.** Indentation on the transversal section of YBCO-1 single grain at 300 K applying load of 9.8 N.
Fig. 2.51. Indentation on the transversal section of YBCO-2 single grain at 300 K applying load of 9.8 N.

Fig. 2.52. Indentation on the transversal section of YBCO-2 single grain at 77 K applying load of 9.8 N.
Fig. 2.53. Indentation on the transversal section of YBCO-3 single grain at 300 K applying load of 0.98 N.

Fig. 2.54. Indentation on the transversal section of GdBCO/Ag single grain at 300 K applying load of 9.8 N.
Fig. 2.55. Indentation on the transversal section of GdBCO/Ag single grain at 77 K applying load of 9.8 N.

Additionally, for all compounds, Vickers hardness decreases when higher loads were applied. This effect was a consequence of the increase in the damage introduced in the material with the higher loads; when force was increased, irreversible deformation grew in a linear way due to the delamination and fracture of the grain. Particularly when the longitudinal sections of the samples were tested, the fracture of the grain happened due to the delamination of part of the material around the indentation (figures 2.56-2.57). However, this fracture mechanism was observed more when the samples were tested at 300 K than at 77 K (figure 2.58).
Fig. 2.56. Indentation on the longitudinal section of YBCO-2 single grain at 300 K applying load of 9.8 N.

Fig. 2.57. Indentation on the longitudinal section of GdBSCO/Ag single grain at 300 K applying load of 0.98 N.
2.5.6 Elastic modulus

The elastic modulus, $E$, of the samples was studied by three different methods. Nanoindentation, grindosonic and three-point bending tests were performed at 300 K, with the normalized stress-strain curves used to determine $E$ at 77 and 300 K. According to the literature, the most common method to obtain the elastic modulus of (RE)BCO samples is the nanoindentation (Y. Yoshimo et al., 2001; Hull J. R. and Murakami M., 2004). However, this method is generally independent of the sample microstructure due to the fact that the microstructure and the nanoindentation footprint are of a similar size. As a result, the values obtained by this measurement technique usually overestimate the actual macroscopic properties of the samples. Therefore, grindosonic measurements and calculation of $E$ from the linear part of the load-displacement curves of the specimens were performed preferentially. Table 2.14 shows the mean values of $E$ and the corresponding quadratic error in the measurement for each material, temperature and direction of applied load. It can be
observed that the values obtained by grindosonic and three-point bending tests are quite similar, whereas measurements by nanoindentation tend to be slightly higher. This result is in good agreement with the observed macroscopic behavior of the grain, since the former methods include the defects of the material, whereas the latter depends predominantly on the behavior of the constituent phases. However, a difference between the values obtained by grindosonic and three-point bending tests at 300 K can be observed that is more significant in the case of YBCO samples. The origin of this difference is due to the fact that during the three-point bending tests all the defects (cracks and porosity) are taken into account whereas in the case of the grindosonic method only the porosity is taken into account. Therefore, lower values are expected by means of three-point bending tests than by means of grindosonic. Moreover, this difference is less clear for the GdBCO/Ag samples where shorter cracks and smaller voids are observed due to the presence of the Ag particles.

Table 2.14. Young's modulus, E, measured by different methods. The values for E have been obtained by three-point bending tests at 7 K.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Test direction</th>
<th>Material</th>
<th>Nanoindentation E (GPa)</th>
<th>Grindosonic E (GPa)</th>
<th>TPB tests E (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>// c-axis</td>
<td>YBCO-2</td>
<td>155± 1</td>
<td>120 ± 2</td>
<td>94 ± 7</td>
</tr>
<tr>
<td></td>
<td>// ab-plane</td>
<td>YBCO-2</td>
<td>191 ± 1</td>
<td>126 ± 2</td>
<td>90 ± 6</td>
</tr>
<tr>
<td></td>
<td>// c-axis</td>
<td>GdBCO/Ag</td>
<td>146 ± 3</td>
<td>115 ± 2</td>
<td>100 ± 9</td>
</tr>
<tr>
<td></td>
<td>// ab-plane</td>
<td>GdBCO/Ag</td>
<td>173 ± 1</td>
<td>99 ± 2</td>
<td>105 ± 6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ag</td>
<td>85 ± 1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>77</td>
<td>// c-axis</td>
<td>YBCO-2</td>
<td>-</td>
<td>-</td>
<td>157 ± 13</td>
</tr>
<tr>
<td></td>
<td>// ab-plane</td>
<td>YBCO-2</td>
<td>-</td>
<td>-</td>
<td>145 ± 16</td>
</tr>
<tr>
<td></td>
<td>// c-axis</td>
<td>GdBCO/Ag</td>
<td>-</td>
<td>-</td>
<td>119 ± 11</td>
</tr>
<tr>
<td></td>
<td>// ab-plane</td>
<td>GdBCO/Ag</td>
<td>-</td>
<td>-</td>
<td>103 ± 15</td>
</tr>
</tbody>
</table>
2.6 Concluding remarks

The mechanical behavior of three second generation YBCO and one GdBCO/Ag single superconducting grains, processed by the TSMG and the Bridgman techniques, were studied. Strong correlation between the processing method, microstructure, and microscopic and macroscopic mechanical properties, at 300 and 77 K, has been found and discussed.

In the case of the YBCO-1 samples, the microstructure was transversely anisotropic, while for the YBCO-3 compound, a different microstructural anisotropy was observed, due to the tilt angle of the c-axis. It has been shown that this anisotropy determines the mechanical properties of both materials. Additional to the microstructural anisotropy (YBCO-1 was tested in two loading directions while YBCO-3 only in one), another important point to explain the mechanical behavior is the presence of porosity. In the case of the YBCO-1 single grain, the greater size of the pores determined its poorer mechanical strength.

The properties of YBCO-1 were anisotropic, because of the microstructural anisotropy of the crystal, while the material YBCO-3 did not show such characteristic. The fracture toughness of the YBCO-1 (loading direction parallel to the \(ab\)-plane) and YBCO-3 increased at 77 K, because the fracture was controlled by the density of cracking. On the other hand, the fracture toughness of the YBCO-1 grain (loading direction parallel to the \(c\)-axis) slightly decreased at 77 K, given the fact that the macroscopically fracture was controlled by the fracture of the superconducting domain that became brittler. For both materials, it was observed that the strength improved with the decrease of temperature due to formation of superficial ice layers that reduce the critical size and tip radius of superficial flaws. Additionally, YBCO-1 showed greater hardness at macroscopic level at 300 K than YBCO-3 due to the narrower areas in the structure of the superconducting domain. On the contrary, YBCO-3 presented greater hardness both at macroscopic level at 77 K and at nanoscale than YBCO-1, because the areas between cracks were more compact and also because of the higher number of microcracks in the case of YBCO-1.

The mechanical behavior of YBCO-2 and GdBCO/Ag 15 wt% has been studied for two directions of applied load at 77 and 300 K. The flexural strength and fracture toughness have been determined through three-point bending tests. The splitting
tensile strength of the samples has been evaluated at 77 K by Brazilian tests and the hardness and elastic modulus have been measured.

The results show that both single grains exhibit very good mechanical properties at 77 and 300 K. However, the intrinsic microstructural anisotropy within YBCO-2 influences significantly the measured macroscopic properties of the bulk material, whereas the mechanical behavior of GdBCO/Ag is more homogeneous.

The fracture mechanisms of both YBCO-2 and GdBCO/Ag single grains have been studied by SEM. This indicates that the presence of Ag particles for GdBCO/Ag samples not only improves the mechanical properties but also provides more homogeneous behavior, independent of the loading direction. Decohesion of the grain, on the other hand, was the main fracture mechanism observed for YBCO-2.

Finally, it can be concluded that the high quality of the YBCO-2 and GdBCO/Ag single grains and their improved mechanical performance at 77 K makes them potentially suitable for applications where the field-trapping capability need to be enhanced.