Solution-based synthesis and processing of Sn- and Bi-doped \( \text{Cu}_3\text{SbSe}_4 \) nanocrystals, nanomaterials and ring-shaped thermoelectric generators

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Copper-based chalcogenides that comprise abundant, low-cost, and environmental friendly elements are excellent materials for a number of energy conversion applications, including photovoltaics, photocatalysis, and thermoelectrics (TE). In such applications, the use of solution-processed nanocrystals (NCs) to produce thin films or bulk nanomaterials has associated several potential advantages, such as high material yield and throughput, and composition control with unmatched spatial resolution and cost. Here we report on the production of Cu\(_3\)SbSe\(_4\) (CSe) NCs with tuned amounts of Sn and Bi dopants. After proper ligand removal, as monitored by nuclear magnetic resonance and infrared spectroscopy, these NCs were used to produce dense CSe bulk nanomaterials for solid state TE energy conversion. By adjusting the amount of extrinsic dopants, dimensionless TE figures of merit (ZT) up to 1.26 at 673 K were reached. Such high ZT values are related to an optimized carrier concentration by Sn doping, a minimized lattice thermal conductivity due to efficient phonon scattering at point defects and grain boundaries, and to an increase of the Seebeck coefficient obtained by a modification of the electronic band structure with Bi doping. Nanomaterials were further employed to fabricate ring-shaped TE generators to be coupled to hot pipes, which provided 20 mV and 1 mW per TE element when exposed to a 160 °C temperature gradient. The simple design and good thermal contact associated with the ring geometry and the potential low cost of the material solution processing may allow the fabrication of TE generators with short payback times.

1. Introduction

Tetrahedrally coordinated copper-based chalcogenides have emerged as realistic alternative materials for a number of energy conversion applications, including photovoltaics, photocatalysis and thermoelectricity.\textsuperscript{17} Beyond the best studied ternary and quaternary Cu-Ga-In,\textsuperscript{8-10} Cu-Zn-Sn,\textsuperscript{11-15} and Cu-Zn-Ge\textsuperscript{16-17} compounds, some 1-VI tetrahedrally
coordinated semiconductors also offer excellent functional properties, but remain largely unexplored. In particular, Cu$_2$SbSe$_4$ (CAsE) is a semiconductor with a relatively small direct band gap of 0.3 eV and a defect-related carrier density on the order of $10^{18}$ cm$^{-3}$ at ambient temperature. It crystallizes in a zinc blende-type tetragonal superstructure that can be viewed as a three-dimensional Cu-Se framework of distorted [CuSe$_4$] tetrahedra with inserted one-dimensional array of [SbSe$_2$] tetrahedra. It features two Cu sites with different Cu-Se bond lengths. The valence band maximum (VBM) is mainly formed by a hybridization of Cu-3d and Se-4p states, while the conduction band minimum (CBM) has a strong contribution from the Sb-5s and Se-4p hybridization. In such a structure, the Cu-Se framework provides avenues for hole transport with relatively high mobility, up to 135 cm$^2$ V$^{-1}$ s$^{-1}$ for undoped and 49 cm$^2$ V$^{-1}$ s$^{-1}$ for highly doped materials. Furthermore, such a complex lattice structure is not effective for phonon propagation, resulting in low thermal conductivities. The high hole mobility and the low phonon mean free path combined with a suitable electronic band structure (including a large degeneracy at the VBM) render CAsE an excellent thermoelectric (TE) material. However, to maximize its TE performance, it is strictly necessary to optimize its charge carrier concentration either by adjusting the density of intrinsic defects that control hole concentration or by introducing an extrinsic p-type dopant, preferably in the non-conducting sub-lattice, i.e. by substituting Sb, to minimize the adverse effects on the hole mobility.

Nanoparticle-based bottom-up strategies offer several advantages to produce thin films and bulk nanostructured materials for a wide range of applications. From an engineering viewpoint, the unmatched compositional and interfacial control makes this route very robust and versatile, allowing the establishment of structure-property relationships and subsequently enabling the rational design of superior materials. From a commercial viewpoint, facile and inexpensive solution synthesis and processing allow for a low-cost and high throughput production with high material yields. However, two major challenges in this technology are the incorporation of controlled amounts of electronic dopants and the removal of organics. Both of them are critical to optimize transport properties within such nanomaterials.

Thus far, colloidal Cu$_2$Sb$_4$ and Cu$_{14}$Sb$_8$S$_4$ nanocrystals (NCs) have been primarily used for photoelectrochemical studies. Few reports have also detailed the production of bulk nanostructured CAsE. However, bottom-up strategies to cost-effectively produce efficient CAsE NCs, nanomaterials and CAsE-based devices remain to be demonstrated. Here, we report a solution-based scalable synthesis approach to produce several grams of monodispersed CAsE NCs doped with controlled amounts of Sn and Bi. We demonstrate their bottom-up processing into bulk nanostructured materials with high relative density and excellent TE performances. We further use this material to fabricate ring-shaped TE devices, which provide improved thermal contact for heat recovery from pipes.

2. Experimental section

2.1. Chemicals and solvents

Copper(i) chloride (CuCl, ≥99%), antimony(m) chloride (SbCl$_3$, 99%), bismuth(III) acetate (Bi(CH$_3$COO)$_3$, 99.99%), selenium powder (Se, 99.5%), ammonium thiocyanate (NH$_4$SCN, ≥99%), dodecanedioic acid (DDT, 98%), 1-octadecene (ODE, technical grade 99%), oleic acid (OA, technical grade 99%), decanoic acid (DAC, ≥98%), and oleyamine (OLA, technical grade 70%) were purchased from Sigma Aldrich. Tin(II) chloride (SnCl$_2$, 98%) was purchased from Strem. Analytical grade methanol, ethanol and chloroform were obtained from various sources. All chemicals were used as received without further purification.

2.2. Se precursor solution

Se powder (23.69 g, 300 mmol) was dissolved in 300 ml OLA and 300 ml DDT at room temperature, cycled between vacuum and Ar to remove oxygen, and then stirred under an Ar atmosphere until Se powder was completely dissolved.

2.3. Synthesis of Cu$_2$Sb$_4$, NCs

In a typical synthesis, 10.0 mmol CuCl, 4.0 mmol SbCl$_3$, 15 ml OLA, 10 ml OA and 100 ml ODE were mixed in a 500 ml three-neck flask and stirred for 20 min at room temperature. The solution was kept at 130 °C under vacuum and vigorous stirring for 30 min, and then heated to 180 °C. The colour of the solution changed from light green to yellowish brown at ~170 °C. At 180 °C, 50 ml of the Se precursor solution was swiftly injected and the color of the solution changed immediately from brown to dark green, indicating the nucleation and subsequent growth of CAsE NCs. After injection, the temperature of the reaction mixture dropped to around 165 °C, but it was allowed to recover to 180 °C. The overall reaction time after recovering to 180 °C was 30 min. Then the sample was rapidly cooled to room temperature using a water bath. NCs were collected by precipitation with ethanol. The final product could be dispersed in relatively non-polar solvents such as toluene or chloroform, forming a stable, dark-green dispersion (inset of Fig. S1bf). For subsequent chemical, structural and functional characterization, NCs were purified by multiple precipitation (6000 rpm for 5 min) and redispersion steps using chloroform as a solvent and ethanol as a non-solvent. The resulting powder was redispersed in chloroform and stored for subsequent characterization and use. This synthesis protocol was optimized to produce more than 2.0 g of NCs per batch (Fig. S1af), which was the amount required for a complete characterization of the material at the laboratory scale, including the fabrication of a ring-shaped prototype device.

2.4. Synthesis of Cu$_2$Sb$_{1-x}$Sn$_x$Se$_4$, Cu$_3$Sb$_{1-x}$Bi$_x$Se$_4$, and Cu$_2$Sb$_{1-x}$Sn$_x$Bi$_x$Se$_4$ NCs

Cu$_2$Sb$_{1-x}$Sn$_x$Se$_4$, Cu$_3$Sb$_{1-x}$Bi$_x$Se$_4$ and Cu$_2$Sb$_{1-x}$Sn$_x$Bi$_x$Se$_4$ NCs were produced following the above procedure, but replacing the desired amount of SbCl$_3$ by SnCl$_2$ and/or Bi(CH$_3$COO)$_3$. 
2.5. Ligand displacement
Cu$_2$SB$_2$Se$_4$, Cu$_2$Bi$_2$Sn$_2$Se$_4$, Cu$_2$Sb$_2$Bi$_2$Se$_4$ and Cu$_2$Sb$_2$Se$_4$ NCs produced in one batch were divided into 6 centrifuge tubes. In each of the tubes, containing ~350 mg in 10 ml of chloroform, 2 ml of a 50 mM NH$_4$SCN solution in acetone was added. Then the solution was shaken during 1–2 min to displace the organic ligands attached to the NC surface, followed by precipitation of the NCs by centrifugation. This process was repeated several times, adding chloroform and NH$_4$SCN in each step. Finally, NCs were precipitated and dried under vacuum to obtain a fine powder.

2.6. Bulk nanomaterial consolidation
The dried NCs were loaded into a graphite die and compacted into pellets (Ø 10 mm x ~1.5 mm). The process was carried out in an Ar atmosphere, using a custom-made hot press to simultaneously apply a pressure of 70 MPa and a temperature of 370–380 °C for 30 min. In this system, the heat was provided by an induction coil operated at 30–80 kHz and it was applied directly to a graphite die acting as a susceptor. Fast heating ramps of 20 °C s$^{-1}$ were reached by this method with a 25 kW induction heater. The relative densities of all the pressed pellets were measured by the Archimedes’ method and found to be ~90% of the theoretical values.

2.7. Ring thermoelectric generators
TE rings with an overall internal diameter of 28 mm and an external diameter of 39 mm were fabricated by placing the dried NCs between two concentric copper rings with 2 mm in thickness and hot-pressing the material at a temperature of 370–380 °C for 30 min and 20 MPa of pressure using a custom-made die.

2.8. Structural and chemical characterization
Crystallographic phases were characterized by X-ray diffraction (XRD, 2θ angle: 20° to 80°; scanning rate: 1° min$^{-1}$) on a Bruker AXS D8 ADVANCE X-ray diffractometer with Cu-Kα radiation ($λ = 0.15406$ Å). X-ray photoelectron spectroscopy (XPS) was performed on a VG ESCA scientific theta probe spectrometer in constant analyser energy mode with a pass energy of 28 eV and Al Kα (1486.6 eV) radiation as the excitation source. The size and shape of initial NCs were examined by transmission electron microscopy (TEM) using a ZEISS LIBRA 120, operating at 120 kV. In depth TEM analyses were performed in a FEI Tecnai F20 microscope operated at 200 keV with a point to point resolution of 0.19 nm. High-resolution TEM (HRTEM) analyses were combined with high angle annular dark field (HAADF) scanning TEM (STEM). We also examined elemental composition using spectroscopy analyses with nanometer resolution by means of electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDX) with a Gatan Quantum EELS and an Oxford EDX detector, respectively, both coupled to the FEI TEM. The grain size and morphology of the hot-pressed materials were characterized using field-emission scanning electron microscopy (SEM, Auriga Zeiss) at 5.0 kV. The overall material composition was analyzed by using an Oxford energy dispersive X-ray spectrometer (EDX) attached to the Zeiss Auriga SEM and by optical emission spectroscopy by means of inductively coupled plasma (ICP) on a Perkin Elmer Optima 3200 RL system. Fourier transform infrared spectra (FTIR) were acquired using a Bruker FTIR spectrometer with the platinum attenuated total reflectance (ATR) single reflection module.

2.9. Nuclear magnetic resonance (NMR)
NMR measurements were recorded on a Bruker Advance III Spectrometer operating at a $^1$H frequency of 500.13 MHz and equipped with a BBI-Z probe. The sample temperature was set to 298.2 K. One dimensional (1D) $^1$H and 2D NOESY (Nuclear Overhauser Effect Spectroscopy) spectra were acquired using standard pulse sequences from the Bruker library; 2g and noesyppphpp respectively. For the quantitative 1D $^1$H measurements, 64k data points were sampled with the spectral width set to 10 ppm and a relaxation delay of 30 s. The NOESY mixing time was set to 300 ms, with 2048 data points sampled in the direct dimension for 512 data points in the indirect dimension, with the spectral width set to 11.5 ppm. For 2D processing, the spectra were zero filled to a 4096 x 2048 real data matrix, followed by multiplication with a squared cosine bell function in both dimensions prior to Fourier transformation. The 1D spectra were apodized with an exponential window function. Concentrations were obtained using the Digital ERETIC method. Diffusion measurements (2D DOSY) were performed using a double stimulated echo sequence (dstegp2s) for convolution compensation and with monopolar gradient pulses. Smoothed rectangle gradient pulse shapes were used throughout. The gradient strength was varied linearly from 2–95% of the probe’s maximum value (calibrated at 50.2 G cm$^{-1}$) in 64 steps, with the gradient pulse duration and diffusion delay optimized to ensure a final attenuation of the signal in the final increment of less than 10% relative to the first increment. The diffusion coefficients were obtained by fitting the Stejskal-Tanner (ST) equation to the signal intensity decay. For the pulse sequence at hand, the appropriate ST equation is:

$$J = J_0 e^{-\gamma^2 D g^2 \tau}$$

(1)

with the gyromagnetic ratio of the observed $^1$H nucleus $γ$, the gradient pulse length $δ$, the gradient strength $g$, the diffusion time $D$ and the diffusion coefficient $D$. The shape factor $ξ$ depends on the gradient shape but this is usually already corrected for in the gradient strength value by the Bruker software, TOPSPIN. The ST equation for other pulse programs is only slightly different and the impact on the diffusion coefficient is very small in the case of long diffusion times ($D > 250$ ms). In a real DOSY experiment, values of $D$ and $δ$ are set while varying $g$ to derive the decay curve.

2.10. Thermoelectric property measurements
Seebeck coefficients were measured using a static DC method. Electrical resistivity data were obtained by a standard four-probe method. Both the Seebeck coefficient and the electrical resistivity were measured simultaneously in a LSR-3 LINSEIS
system in the temperature range between room temperature and 673 K, under a helium atmosphere. At each temperature, 3 measurements were generally taken. Taking into account the system accuracy and the measurement precision, we estimate an error of ca. 4% in the measurement of the electrical conductivity and Seebeck coefficient. The thermal conductivity was calculated by \( \kappa = \lambda C_p \rho \), where \( \lambda \) is the thermal diffusivity, \( C_p \) is the heat capacity, and \( \rho \) is the mass density of the specimen. A XPA 600 Xenon Flash apparatus from Linseis was used to determine the thermal diffusivities of the samples with an estimated error of 5%. The specific heat \( (C_p) \) was measured by means of the differential scanning calorimeter method (DSC model T2000 TA Instruments) with an associated error of ca. 2%. The density \( (\rho) \) values used here were calculated using the Archimedes’ method with a measurement error of ca. 2%.

2.11. Hall measurement

Hall carrier concentrations and mobilities at room temperature were measured using a magnetic field of 2 T with a PPMS-9T (Quantum Design Inc., USA). Values reported correspond to the average of 5 consecutive measurements, from which an error of ca. 10% was estimated.

2.12. Device test

TE rings were tested in a custom-made test station. Temperature was monitored by two thermocouples attached at the copper electrodes and the open circuit voltage was measured by using a Keithley 2400. A heating cartridge within a cylindrical metal block was used to increase the temperature of the internal part of the ring, while the external part of the ring was kept at lower temperature by means of TE coolers. The maximum temperature reached at the hot side was 250 °C. At this point, the temperature at the cold side was 90 °C, which provided a maximum temperature gradient of 160 °C.

2.13. Density functional theory (DFT)

It is well known that common DFT methods fail to correctly predict the bandgap. Unfortunately, accurate methods such as screened hybrid functional or quasi particle energy calculations are extremely time-consuming and computationally expensive. D. Do et al. carried out electronic structure calculations for Cu$_3$SbSe$_4$, using GGA, GGA+U, m-BJ exchange potential and HSE06 exchange-correlation potential. Only bandgap values calculated by using HSE06 and GGA+U were in agreement with experimental values (0.1-0.4 eV), and a large effective value of \( U (U_{\text{eff}} = 15 \text{ eV}) \) was necessary to get an accurate bandgap. Based on these results and to minimize computational cost, total energy calculations were carried out using the GGA+U approach. The PBE exchange correlation functional along with the formalism proposed by Dudarev et al. was applied. We use \( U_{\text{eff}} = 15 \text{ eV} \) for the Cu-3d states. Total energy calculations were carried out with the plane-wave based Vienna \textit{ab initio} simulation package (VASP), along with projector augmented wave (PAW) potentials to represent the inert core electrons. We used a plane-wave energy cutoff of 400 eV, an energy convergence criterion of \( 10^{-4} \text{ eV} \), and a Methfessel–Paxton first-order scheme with 0.1 eV of smearing to extract the occupations of Kohn–Sham eigenvalues. For the Brillouin zone integration, we used a \( 12 \times 12 \times 12 \) Monkhorst-Pack scheme \( k \)-point mesh. All the calculations were performed with the experimental lattice parameters of the native compound. The model system Cu$_3$SbSe$_4$ was studied through a tetragonal unit cell with 64 atoms (Cu$_{34}$Sb$_{32}$Se$_{64}$). Structures derived from Cu$_3$SbSe$_4$ due to the substitution with Bi or Sn were obtained by replacing one Sb atom by one Bi or Sn atom. In this way, the doping concentration was equal to \( x = 0.125 \), which is similar to the largest values experimentally produced and measured \( (x = 0.10) \). The transport properties were calculated using a semi-classical solution based on Boltzmann’s transport theory within the constant scattering time and the rigid band approximations using the BoltzTraP code.

3. Results and discussion

GaSe NCs were produced from copper chloride, antimony chloride and selenium powder dissolved in OLA and DDT, as detailed in the experimental part. This synthesis protocol enabled a high batch-to-batch reproducibility and a 94% material yield. Fig. 1 and S2† show representative TEM and HRTEM micrographs with the respective indexed power spectrum of the 18 ± 2 nm GaSe NCs produced following this procedure. From HRTEM analysis, the NC crystallographic phase was identified as tetragonal GaSe (space group I4/mmm (121), Table S1†) with lattice constants \( a = b = 0.566 \text{ nm} \) and \( c = 1.288 \text{ nm} \), which is in agreement with XRD data [Fig. 2a, JCPDS card no. 85-0003]. No secondary phases were detected by HRTEM and XRD analysis, except for a minor peak at 2\( \theta \sim 34^\circ \) in the XRD pattern, which could correspond to Cu$_3$SbSe$_4$ (JCPDS card no. 1-86-1751, Fig. S3†).

Within its experimental error, SEM-EDX analysis showed the metal and chalcogen ratios to match those of stoichiometric GaSe (Cu$_3$SbSe$_4$, Fig. S4†). EELS was used for compositional

![Fig. 1](image-url) (a) Representative TEM micrograph of GaSe NCs. The inset shows the histogram for the measured particle size distribution (10 ± 2 nm) (b) Higher-magnification TEM micrograph, (c) HRTEM image of a single GaSe NC, (d) Its respective power spectrum fitting with the GaSe tetragonal phase, (e) Detail of the squared regions of the single GaSe NCs, (f) Annular dark field scanning TEM (ADF-STEM) image of some GaSe NCs and (g)–(i) areal density of each of the elements extracted from the EELS spectrum image.
NMR analysis was performed. Fig. 3a shows a $^1$H NMR spectrum of the as-synthesized NCs (unpurified) and the $^1$H NMR spectrum of NCs purified four times by precipitation/redispersion with acetonitrile as a non-solvent and toluene as a solvent. In the spectrum of unpurified NCs we observe the characteristic resonances of a terminal alkene at 5.0 and 5.8 ppm, associated with ODE. The resonance around 5.5 ppm is associated with an internal alkene, from OLA and/or OA. The ODE resonances possess a fine structure, indicating the unbound nature of ODE. In contrast, the alkene resonance is a superposition of sharp and broad resonances, associated with free and bound ligands respectively. After purification, the ODE features disappear completely together with the majority of the sharp resonance corresponding to the free molecules OLA or OA, indicating a successful purification of the NC solution. Further purification to remove the remaining free ligands in solution render the NCs completely insoluble in any solvent. The NOESY spectrum (Fig. S13f) contains negative (black) NOE cross peaks confirming the interaction of OLA/OA with the surface. To discriminate whether OLA or OA (or both) is stabilizing the NC surface, we reproduced the exact same synthesis described above but instead of OA we used DAc. Although DAc and OA are both fatty acids and are expected to interact identically with NC surfaces, DAc has no alkene group and this allows us to distinguish OLA from OA. Fig. 3b shows the NMR spectra of CASe NPs synthesized with DAc. Since the $^1$H NMR spectra are almost identical to spectra of the dispersions prepared with OA and because OLA is now the only molecule with an alkene resonance, we identify OLA as a ligand. Additionally, the intensity of the alkene resonance and CH3 resonance features a 2 : 3 ratio. This excludes any other (fully saturated) ligands such as DDT or DAc, proving that OLA is the only ligand present. Since OLA is an L-type ligand and the NCs were found to be stoichiometric that OLA is the only ligand present. Since OLA is an L-type ligand and the NCs were found to be stoichiometric (vide supra), this NC system belongs to the earlier established class of binding motifs; NC (L). To assess the dynamics of interaction, DOSY experiments were performed. A good fitting of the CH3 signal decay was only obtained with two exponentials, indicating two populations (Fig. S14f). The small fraction with a high diffusion coefficient (552 um$^2$s$^{-1}$) is attributed to free OLA while the fraction with a low diffusion coefficient (45 um$^2$s$^{-1}$) is associated with bound OLA. Using the Stokes–Einstein equation, a solvodynamic diameter of 16.5 nm is calculated from the diffusion coefficient. Since this is close to the diameter from TEM (16–20 nm), we conclude that OLA is firmly attached to the NC surface and diffuses together with the NC. Considering the L-type nature of OLA, it is usually involved in a more dynamic stabilization of the NC surface. However, it was repeatedly reported that Cu-based NCs typically have tightly bound amines bound to the surface. It should however be noted that OLA is quite easily desorbed during purification suggesting only a moderate binding affinity for the NC surface, in line with L-type ligand behaviour.

To facilitate charge transport/transfer, CASe NCs were thoroughly purified by multiple precipitation/re-dispersion steps and subsequently treated with NH4SCN, which could efficiently displace remaining OLA. Fig. S15f shows FTIR spectra of dried analysis within each particle using Sb M4.5, Cu L2,3 and Se L2,3 edges (Fig. 1f–i and S5†). In the central region of the NC, elemental quantification (in at%) showed the presence of around 12% Sb, 30% Cu and 48% Se, which is compatible with the CASe stoichiometry. In the outer part of the NCs, the relative composition of Sb and Cu were found to be slightly higher than that in the core and that of Se was slightly lower: 17% Sb, 40% Cu and 43% Se (Fig. S5†). CASe NCs were synthesized in the presence of OLA, OA and DDT. In order to identify which surfactants were finally present on the NC surface and establish their bonding nature, NMR analysis was performed. Fig. 3a shows a $^1$H NMR spectrum of the as-synthesized NCs (unpurified) and the $^1$H NMR spectrum of NCs purified four times by precipitation/redispersion with acetonitrile as a non-solvent and toluene as a solvent. In the spectrum of unpurified NCs we observe the characteristic resonances of a terminal alkene at 5.0 and 5.8 ppm, associated with ODE. The resonance around 5.5 ppm is associated with an internal alkene, from OLA and/or OA. The ODE resonances possess a fine structure, indicating the unbound nature of ODE. In contrast, the alkene resonance is a superposition of sharp and broad resonances, associated with free and bound ligands respectively. After purification, the ODE features disappear completely together with the majority of the sharp resonance corresponding to the free molecules OLA or OA, indicating a successful purification of the NC solution. Further purification to remove the remaining free ligands in solution render the NCs completely insoluble in any solvent. The NOESY spectrum (Fig. S13f) contains negative (black) NOE cross peaks confirming the interaction of OLA/OA with the surface. To discriminate whether OLA or OA (or both) is stabilizing the NC surface, we reproduced the exact same synthesis described above but instead of OA we used DAc. Although DAc and OA are both fatty acids and are expected to interact identically with NC surfaces, DAc has no alkene group and this allows us to distinguish OLA from OA. Fig. 3b shows the NMR spectra of CASe NPs synthesized with DAc. Since the $^1$H NMR spectra are almost identical to spectra of the dispersions prepared with OA and because OLA is now the only molecule with an alkene resonance, we identify OLA as a ligand. Additionally, the intensity of the alkene resonance and CH3 resonance features a 2 : 3 ratio. This excludes any other (fully saturated) ligands such as DDT or DAc, proving that OLA is the only ligand present. Since OLA is an L-type ligand and the NCs were found to be stoichiometric (vide supra), this NC system belongs to the earlier established class of binding motifs; NC (L). To assess the dynamics of interaction, DOSY experiments were performed. A good fitting of the CH3 signal decay was only obtained with two exponentials, indicating two populations (Fig. S14f). The small fraction with a high diffusion coefficient (552 um$^2$s$^{-1}$) is attributed to free OLA while the fraction with a low diffusion coefficient (45 um$^2$s$^{-1}$) is associated with bound OLA. Using the Stokes–Einstein equation, a solvodynamic diameter of 16.5 nm is calculated from the diffusion coefficient. Since this is close to the diameter from TEM (16–20 nm), we conclude that OLA is firmly attached to the NC surface and diffuses together with the NC. Considering the L-type nature of OLA, it is usually involved in a more dynamic stabilization of the NC surface. However, it was repeatedly reported that Cu-based NCs typically have tightly bound amines bound to the surface. It should however be noted that OLA is quite easily desorbed during purification suggesting only a moderate binding affinity for the NC surface, in line with L-type ligand behaviour.

To facilitate charge transport/transfer, CASe NCs were thoroughly purified by multiple precipitation/re-dispersion steps and subsequently treated with NH4SCN, which could efficiently displace remaining OLA. Fig. S15f shows FTIR spectra of dried
CASe NCs before (CASe-OL) and after (CASe-LD) organic ligand displacement with a 50 mM NH₄SCN solution. The CASe-OL spectrum showed the characteristic features of OLA: C-H vibration modes have a strong band in the high-frequency region (2850–3000 cm⁻¹) and various peaks in the lower frequency region, between 700 cm⁻¹ and 1650 cm⁻¹. These features completely disappeared from the CASe-LD spectrum, proving the effective organic ligand displacement.

Nanocrystalline disk-shaped CASe pellets (Ø 10 mm × ~1.5 mm) were prepared under an Ar atmosphere by hot-pressing ~700 mg of ligand-displaced NCs at ~380 °C, 70 MPa and for 30 min. The pellets had a metallic luster and were mechanically robust enough to endure polishing. Relative densities ~90% of the theoretical value were measured for all samples. XRD analysis of the CASe pellets showed no crystallographic or related compositional change after the hot-press process (Fig. S3 and S16f). However, during this process, CASe NCs coalesced to form larger crystalline domains with sizes ranging from tens to few hundred nanometers (Fig. S17f).

The electrical conductivity (σ), Seebeck coefficient (S), thermal conductivity (κ), and the dimensionless TE figure of merit (ZT = σS²T/κ) of undoped and Sn- and Bi-doped CASe pellets are displayed in Fig. 4 and 5. Undoped CASe nanomaterials were characterized by relatively low σ, which increased with temperature up to 6.2 × 10⁴ S m⁻¹, and positive S in the whole temperature range measured. Significantly higher σ, up to 9.0 × 10⁴ S m⁻¹ at room temperature, was obtained for Sn-CASe (Fig. 4a), which showed a degenerated semiconductor behavior with a decrease of σ with temperature. In contrast, S decreased with the Sn introduction (Fig. 4b). The observed increase of σ and decrease of S with the amount of Sn indicated Sn ions to act as a p-type dopant within CASe. This electronic role was confirmed by a one order of magnitude increase in the Hall charge carrier concentration with the Sn introduction, from p = 5 × 10¹⁴ cm⁻³ in CASe to p = 9 × 10¹⁹ cm⁻³ in Cu₃Sb₀.₉Sn₀.₁Se₄ (Table S7f). Overall, higher power factors (PF = σS²) were obtained for the Sn-doped samples, with a maximum PF of 1.14 mW m⁻¹ K⁻² at 673 K for the sample containing a 2% replacement of Sb by Sn, Cu₃Sb₀.₉Sn₀.₁Se₄ (Fig. S18a†).

Fig. 3 ¹H NMR spectrum of CASe 18 ± 2 nm NPs synthesized with (a) OA and (b) DAc shown before (bottom) and after (top) purification.

Fig. 4 (a–d) Temperature dependence of (a) electric conductivity (σ), (b) Seebeck coefficient (S), (c) thermal conductivity (κ), and (d) TE figure of merit (ZT) of Cu₃Sb₁ₓSnₓSe₄ (x = 0.01, 0.02, 0.05 and 0.10). (e) Time evolution of the electrical conductivity (σ, ▪), Seebeck coefficient (S, □) and temperature (T, ▲) of Cu₃Sb₀.₉Sn₀.₁Se₄ during a 55 h test.
was surprising experimental evidence if assuming Sb$^{5+}$ replaced by Bi$^{3+}$ as it have to be the case taking into account the Hall hole concentrations cm$^{-3}$, Table S7$f$). This obtained (Fig. 5a), which correlated with a small decrease in the conductivity and Seebeck coefficient changed by around 1% to 653 K. These are lower $\kappa$ values than those previously reported for bulk CASE, but slightly higher than those reported for nanostructured CASE produced by co-precipitation, and much higher than the estimated minimum $\kappa$ of this material (0.26 W m$^{-1}$ K$^{-1}$). Lower lattice thermal conductivities ($\kappa_l$) were obtained with the incorporation of Sn due to the introduced lattice distortion and the increased density of point defects (Fig. S18$d$). However, the associated increase of the electronic contribution to the thermal conductivity ($\kappa_e$) resulted in an overall increase of $\kappa$ for most of the Sn-CASE pellets. Overall, ZT significantly increased with the introduction of relatively small amounts of Sn, reaching $ZT = 0.97$ at 673 K for Cu$_3$Sb$_{0.96}$Sn$_{0.04}$Se$_4$, which represents more than a 2-fold increase over undoped CASE (Fig. 4$d$).

Nanocrystalline CASE showed good stability even when maintained at relatively high temperatures for long periods of time. Fig. S21$^f$ shows the results obtained from 5 consecutive heating-cooling cycles. Minor differences were observed from cycle to cycle and mainly from the first cycle to the following ones. To account for the minor variations obtained from the first to the following cycles, all samples were measured at least 3 consecutive times and results from the first cycle were discarded. Fig. 4$e$ shows the results obtained from Cu$_{0.6}$Sb$_{0.4}$Sn$_{0.4}$Se$_4$ during a 55 h test involving the heating of the sample from 323 to 626 K at a rate of 10 K min$^{-1}$ and then maintaining the sample at 656 K for 54 h. During this time, the electrical conductivity and Seebeck coefficient changed by around 1% and 3%, respectively.

When replacing part of Sb by Bi, slightly lower $\sigma$ was obtained (Fig. 5$a$), which correlated with a small decrease in the Hall hole concentrations ($p = 2 \times 10^{18}$ cm$^{-3}$, Table S7$f$). This was surprising experimental evidence if assuming Sb$^{5+}$ to be replaced by Bi$^{3+}$ as it have to be the case taking into account the very high energy required to oxidize Bi$^{3+}$ to Bi$^{5+}$. As no increase of the hole concentration was observed, the difference in the oxidation state between Sb and Bi is probably compensated with the creation of an equivalent amount of Se$^{2-}$ vacancies. The slight decrease in the measured charge carrier concentration could be further associated with an indirect diminution of the concentration of intrinsic defects acting as p-type dopants, e.g. the presence of Cu$^+$ at Sb$^{5+}$ sites or Cu or Se vacancies.

Significantly larger $S$ values were measured for all Bi-CASE samples (Fig. 5$b$) when compared with CASE, which did not correlate well with the small decrease in electrical conductivity when just taking into account a slight modification of the charge carrier concentration (Table S7$f$). Combining $\sigma$ with $S$, the highest PF values for Bi-CASE were obtained with a composition Cu$_3$Sb$_{0.98}$Bi$_{0.02}$Se$_4$ ($\sim 0.77$ mW m$^{-1}$ K$^{-1}$) at 608 K, Fig. S19$af$). Additionally, Bi-doped CASE was characterized by lower $\kappa$ than CASE due to slightly lower $\kappa_e$ and $\kappa_l$ contributions (Fig. 5$c$ and S19$d$). Overall, higher ZT values, up to 0.81 for Cu$_3$Sb$_{0.98}$Bi$_{0.02}$Se$_4$ at 648 K, were obtained for Bi-CASE when compared with CASE (Fig. 5$d$).

To further determine the influence of Sn and Bi on the electronic band structure of CASE, DFT calculations were carried out. Fig. 6 shows the band structure of pure CASE, Cu$_3$Sb$_{0.875}$Sn$_{0.125}$Se$_4$ and Cu$_3$Sb$_{0.875}$Bi$_{0.125}$Se$_4$. Results indicate that pure CASE is a semiconductor with a direct band gap of 0.27 eV measured at $\Gamma$ point, which is consistent with experimental values ($0.1$--$0.4$ eV). The calculated bandgap was also in agreement with theoretical results from Do et al., using the non-local exchange HS06 model (0.26 eV). As expected, the VBM in CASE is mainly composed of Cu-3d and Se-4p states and the CBM is mainly formed by Sb-5s and Se-4p states (Fig. 6$a$).

Fig. 7 shows the temperature dependence of the DFT-derived $S$ for different concentrations of the majority charge carrier. For pure CASE, at moderate $p$ levels ($p < 5 \times 10^{19}$ cm$^{-3}$) the Seebeck coefficient increases with temperature up to a maximum and then rapidly decreases. At higher hole concentrations ($p > 5 \times 10^{19}$ cm$^{-3}$), $S$ monotonously increases with temperature in the analysed range ($T \leq 700$ K). Calculated values matched relatively well with experimental results and qualitatively predicted the measured temperature evolution.

The introduction of small amounts of Sn at the Sb sites significantly reduced the band gap, to 0.16 eV, and shifted the Fermi level to within the valence band due to the p-type doping character of Sn$^{4+}$ ions (Fig. 6$b$). Thus, only Seebeck coefficients for relatively high carrier concentrations $p \geq 5 \times 10^{19}$ cm$^{-3}$ were reliably calculated. In agreement with experimental measurements, such large charge carrier concentrations resulted in an important diminution of $S$. A hole carrier concentration $p \approx 1 \times 10^{20}$ cm$^{-3}$ was needed to match the experimental $S$ values, which is consistent with the Hall charge carrier concentrations measured for the Sn-doped materials.

The partial substitution of Sb by Bi had little effect on the band structure at the VBM, but it significantly affected the CBM, decreasing the band gap and resulting in a divergence of the multi-valleys (Fig. 6$c$). Taking into account only the contribution of majority carriers, the DFT-derived $S$ just slightly changed with the Bi introduction (Fig. 7) mainly due to the bandgap...
Fig. 6 Electronic band structure of (a) CASe, (b) Cu$_3$Sb$_{0.875}$Sn$_{0.125}$Se$_4$ and (c) Cu$_3$Sb$_{0.875}$Bi$_{0.125}$Se$_4$. The symbols stand for the main atomic contributions of the bands. Band energies were plotted with respect to the Fermi level.

reduction. However, the perturbation of the CBM associated with the Bi presence certainly had a strong influence on the contribution of the conduction electrons to the transport properties. In this regard, the splitting of the degenerated multi-valleys at the CBM should translate in a reduction of a bipolar effect on $S$, thus resulting in overall higher $S$ values. In this direction, our DFT analysis clearly showed a significant diminution of the effective mass of electrons with the introduction of Bi (Table S8, Fig. S22f). While the calculation of this effect is beyond the present work, we qualitatively analyzed the bipolar impact to $S$ by calculating the contribution of thermally generated charge carriers (Fig. S23 and S24f).

Fig. 7 Temperature dependence of DFT-calculated Seebeck coefficients ($S$) of pure CASe, Cu$_3$Sb$_{0.875}$Bi$_{0.125}$Se$_4$ and Cu$_3$Sb$_{0.875}$Sn$_{0.125}$Se$_4$ at different hole concentrations (colored lines and symbols). Experimental values for pure CASe, Cu$_3$Sb$_{0.875}$Bi$_{0.125}$Se$_4$ and Cu$_3$Sb$_{0.875}$Sn$_{0.125}$Se$_4$ are also plotted (in black).

The introduction of Sn also translated into large differences in the effective masses of holes and electrons which in spite of the strong band gap decrease in this material also resulted in higher $S$ values at moderate doping levels. However, the modification of the electronic band structure by means of sufficient amounts of Sn injected very large amounts of charge carrier, which inevitably resulted in overall lower $S$. Thus the introduction of both dopants, a small amount of Sn to control charge carrier concentration and Bi to modify the band structure, was necessary to optimize performance.

To take advantage of the carrier concentration control provided by Sn doping and the relative increase of $S$ with the inclusion of Bi, we prepared a series of Sn,Bi-doped CASe samples. Fig. 8 shows the temperature dependence of the electrical and thermal transport properties of Cu$_3$Sb$_{0.9-x}$Sn$_x$Bi$_{0.05}$Se$_4$. These samples showed a degenerated electrical conductivity behavior, associated with a large level of doping, $\sigma$ increased with the Sn content as in the Sn-CASe series. Surprisingly, $\sigma$ of co-doped Sn,Bi-CASe was systematically larger than that of Sn-CASe samples with the same amount of Sn. Hall measurements showed the presence of high charge carrier concentrations, up to $p = 1 \times 10^{20}$ cm$^{-3}$ for Cu$_3$Sb$_{0.98}$Sn$_{0.02}$Bi$_{0.05}$Se$_4$ (Table S7f). On the other hand, $S$ decreased for all Sn,Bi-CASe samples when compared with plain CASe due to the large increase of charge carrier concentration. However, $S$ values of co-doped materials slightly increased when compared with Sn-CASe with equivalent electrical conductivities, proving the positive effect of the Bi addition.

Overall, the PFs of co-doped Sn,Bi-CASe were significantly higher than those of Sn- or Bi-CASe, and reached up to around

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\text{PFs} \uparrow \text{Sn,Bi-CASe} > \text{Sn-CASe} > \text{Bi-CASe} \]

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\text{Fig. 8 Electrical and thermal transport properties of Cu$_3$Sb$_{0.9-x}$Sn$_x$Bi$_{0.05}$Se$_4$.}
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compared with conventional flat devices, the ring design optimizes the thermal contact between the TE generator and the walls of a hot or cold pipe, and at the same time minimizes the module form factor and provides improved mechanical stability. In a ring-based module, rings with n and p type materials could be placed thermally in parallel and electrically in series to harvest radial heat fluxes (Fig. 9a). Alternatively, multiple n and p elements could be integrated within each ring (Fig. 9d). The module, containing multiple n- and p-type rings or several multi-element rings, makes use of thin thermal and electrical insulators between rings to alternatively contact the outer and inner rings as shown in Fig. 9a.

Single p-type \( \text{Cu}_3\text{Sb}_{0.88}\text{Sn}_{0.10}\text{Bi}_{0.02}\text{Se}_{4} \) rings, with inner and outer diameter of 28 mm and 39 mm, respectively, and with copper ring thicknesses of 2 mm and thus a CASe thickness of 1.5 mm were assembled and tested in a custom made set-up as detailed in the experimental part (Fig. 9b). The inner ring temperature was increased up to 250 °C using a heat cartridge within a cylindrical metal block, while maintaining the outside ring at lower temperature using a metal block cooled using commercial thermoelectric devices. Fig. 9c shows the voltage obtained from a single p-type ring as a function of the temperature gradient. Open circuit voltages close to 20 mV were obtained for a single TE element exposed to a temperature gradient of 160 °C. Being the electrical resistance of the ring \(<0.4 \Omega\), this voltage translates into a \(>1\) mW of generated electric power for each single TE element. The combination of several TE p-n pairs in each ring (Fig. 9d) and of several rings into a module (Fig. 9e) could provide electric powers on the order of 100 W for 200-300 °C temperature gradients as those available among other in exhaust gas pipes of vehicles with combustion engines. Such power could suffice to supply all the electric energy spent by the vehicle, allowing the alternator replacement and thus improving the vehicle fuel efficiency.

These materials were further employed to fabricate simple TE generator prototypes with ring geometry (Fig. 9). When
4. Conclusions

In summary, a novel solution-based strategy to produce monodisperse CASe NCs and Sn- and Bi-doped CASe NCs at the gram scale was presented. The effect of Sn and Bi doping on the TE performance of CASe nanomaterials obtained via hot press was discussed. Sn was demonstrated to be a p-type dopant which effectively helped to control charge carrier concentration. On the other hand, the introduction of Bi conveniently modified the electronic band structure of the compound resulting in higher $S$ values. We tentatively associated the Bi effect to a reduction of the negative contribution of conduction electrons on the Seebeck coefficient, but further theoretical calculations and detailed experimental results are required to clarify the exact Bi role in such a complex system. Besides, the introduction of these impurities helped to reduce the material lattice thermal conductivity. By optimizing the amount of Sn in a Bi-doped material, $ZT$ values up to 1.26 at 673 K were obtained for Cu$_2$Sb$_{2-3}$Sn$_{1.4}$Bi$_{0.2}$Se$_{4}$, which is among the best $ZT$ values obtained with a Pb- and Te-free material in this middle temperature range, with the additional advantage of the high versatility and low cost associated with solution processing technologies. Taking advantage of this processability, we fabricated innovative ring-shaped TE generators, which provided 1 mW of electric power per TE element with a 160 °C temperature gradient.

Author contributions

The manuscript was prepared through the contribution of all authors. J. S., D. C. and A. C. conceived and guided the project, and supervised the work. Y. L. and D. C. designed the experiments, produced the nanomaterials, performed the thermoelectric characterization and wrote the manuscript. O. D. and Z. L. measured and discussed preliminary DFT calculations. G. M., P. P., J. L. and D. L. C. performed and discussed detailed DFT calculations including related transport properties. C. D. and D. L. C. performed the C$_p$ characterization. O. D. and Z. L. measured and discussed XPS data. The manuscript was corrected and improved by all authors.

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Notes and references
