



# Article Structural Evolution from Neutron Powder Diffraction of Nanostructured SnTe Obtained by Arc Melting

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**Abstract:** Among chalcogenide thermoelectric materials, SnTe is an excellent candidate for intermediate temperature applications, in replacement of toxic PbTe. We have prepared pure polycrystalline SnTe by arc melting, and investigated the structural evolution by temperature-dependent neutron powder diffraction (NPD) from room temperature up to 973 K. In this temperature range, the sample is cubic (space group *Fm-3m*) and shows considerably larger displacement parameters for Te than for Sn. The structural analysis allowed the determination of the Debye model parameters and provided information on the Sn–Te chemical bonds. SEM images show a conspicuous nanostructuration in layers below 30 nm thick, which contributes to the reduction of the thermal conductivity down to  $2.5 \text{ W/m} \cdot \text{K}$  at 800 K. The SPS treatment seems to reduce the number of Sn vacancies, thus diminishing the carrier density and increasing the Seebeck coefficient, which reaches 60  $\mu$ V K<sup>-1</sup> at 700 K, as well as the weighted mobility, almost doubled compared with that of the as-grown sample.

Keywords: thermoelectrics; neutron powder diffraction; Ge deficiency; structural phase transition

# 1. Introduction

The recent revival of interest in thermoelectric materials (TEs) over the past two decades is motivated by the fact that around two-thirds of produced energy is lost as waste heat. TEs can recover part of this heat and convert it directly to useful electrical energy using thermal gradients via the Seebeck effect [1,2]. Advances in thermoelectricity are hindered by the fact that the relevant thermoelectric properties are strongly and antagonistically interrelated. TEs obviously require a large Seebeck coefficient (S), but also low electrical resistivity ( $\rho$ ) against Joule-heating losses and low thermal conductivity ( $\kappa$ ) against shorting the thermal gradients. However, S and  $\rho$  are coupled in the heavily doped semiconductors that yield the best TEs. Additionally, the Wiedemann–Franz law couples  $\rho$  and  $\kappa$  for electronic transport. To evaluate the thermoelectric properties, TEs are characterized by a dimensionless figure of merit ( $ZT = S^2T/\rho\kappa$ ); commercial TEs, typically made of chalcogenide semiconductors such as alloys of PbTe or Bi<sub>2</sub>Te<sub>3</sub> [3,4], have ZT~1, with state-of-the-art TEs reaching ZT~2–2.5, depending on temperature (T) [5–7].

In recent years, we studied in detail the structure and excellent thermoelectric properties of the revisited SnSe chalcogenide (Kanatzidis group at Northwestern University, published in *Nature* [8]) with various types of doping, using straightforward arc-melting procedures. We obtained highly nanostructured SnSe with exceptionally low thermal



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). conductivity [9] and followed its high temperature structural phase transition [10]. After improving the electrical grain-to-grain resistivity, we obtained n-type semiconducting SnSe at high temperature, according to an unreported midtemperature sign change of the Seebeck coefficient. It was associated with a pronounced increase in the electronic conductivity near the structural phase transition, yielding a high-performance thermoelectric ZT of ~1.8 in a polycrystalline sample [11]. SnSe prepared by arc melting is also an excellent platform for modifications. We doped or alloyed SnSe with Sb at Sn positions, stabilizing n-type thermoelectricity [12], and developed a novel technique to incorporate K as a potassium hydride precursor [13], opening the way for other air sensitive alkali and alkaline incorporations. Thermoelectric efficiency is often improved upon structural phase transitions to higher symmetry polymorphs, inducing band convergence criteria. We studied in detail the high-temperature structural changes in SnSe doped with Ge [14,15], and of GeTe [16–18] and PbTe [19], using neutron diffraction.

As an alternative to toxic PbTe, an appealing thermoelectric material is SnTe, since it also crystallizes in the rock-salt structure. Moreover, SnTe has been described as a paradigmatic example of a topological crystalline insulator, by identifying its nonzero topological index. It has been shown that SnTe has metallic surface states with an even number of Dirac cones on high-symmetry crystal surfaces, such as {001}, {110}, and {111} [20]. Threedimensional topological (crystalline) insulators are materials with an insulating bulk but conducting surface states that are topologically protected by time-reversal (or spatial) symmetries [21]. In fact, experimental evidence for the topological crystalline insulating (TCI) phase has been reported in tin telluride [22] from angle-resolved photoemission spectra. Nevertheless, pristine SnTe is a poor TE due to an intrinsically high hole concentration arising from Sn vacancies, on the one hand, as well as its excessive thermal conductivity [23,24]. Unfortunately, SnTe has a prominent band offset between its two valence bands and a high lattice thermal conductivity, both of which limit its peak thermoelectric figure of merit. Valence bands convergence or introducing resonant states is found to enhance the electronic properties [25], while nanostructuring or introducing interstitial defects is believed to reduce the lattice thermal conductivity [26]. Alternatively, it has been shown that the thermoelectric performance of SnTe can be improved by microstructure and band structure engineering, establishing that melt spinning is a controllable synthetic method to high-performance thermoelectrics [27].

In this study, we demonstrate that SnTe can be prepared as a nanostructured material by arc-melting procedures, yielding a reduced thermal conductivity at high temperature with respect to some reports elsewhere [25,28–31]. Moreover, a neutron powder diffraction study unveils that the Sn vacancies, of 20% at RT, decrease at moderate temperatures, below 4%, in the range of application of this thermoelectric material. An SPS process applied to the sample seems to reduce the number of these vacancies, in agreement with the neutron powder diffraction data.

#### 2. Materials and Methods

SnTe alloys were obtained as compact pellets directly from an Edmund Buhler miniarc furnace. Mixtures of nominal 1:1 stoichiometric amounts of analytical-grade Sn (Alfa Aesar, 99.8%) and Te (Alfa Aesar, 99.99%) were ground, pelletized, and molten under Ar atmosphere in a water-cooled Cu crucible, leading to intermetallic ingots. The as-grown ingots were uniaxially pressed (~1 ton) for transport characterization, or ground to powder for structural analysis. Alternatively, some ingots were ground to powder and then sintered by spark plasma sintering (SPS) at 773 K for 8 min under an axial pressure of 40 MPa (Dr. Sinter Lab Jr. SPS-212Lx) for transport characterization.

A laboratory XRD pattern was collected on a Bruker D8 diffractometer with Cu K $\alpha$  ( $\lambda$  = 1.5418 Å) radiation. To study the crystallographic structure evolution, NPD patterns were collected in the D2B instrument (Institut Laue–Langevin, Grenoble, France) with a wavelength of 1.594 Å, at room temperature (298 K, RT) and at 523, 673, 773, 873, and 973 K. The sample (about 2 g), contained in a V cylinder, was introduced in a vanadium furnace

working under vacuum  $(10^{-5} \text{ mbar})$ . The measurement of each pattern lasted 2 h in the high-flux mode. The refinement of the structure was performed by the Rietveld method using the FullProf software (April 2019) [32,33]. A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. The background was interpolated between regions devoid of reflections. The following parameters were refined in the final run: scale factor, background coefficients, zero-point error, pseudo-Voigt corrected for asymmetry parameters, positional coordinates, anisotropic displacement factors, and occupancy factors. For the neutron refinements, the coherent scattering lengths for Sn and Te were 6.225 and 5.80 fm, respectively.

The high-temperature Seebeck coefficient was measured using an MMR technologies instrument under vacuum ( $10^3$  mbar) from room temperature up to ~800 K. Conventional van der Pauw geometry was employed to determine the electrical resistivity. The measurements have always been made perpendicular to the pressing direction. The total thermal conductivity was calculated from the thermal diffusivity ( $\alpha$ ) using a Linseis LFA 1000 equipment by the laser flash technique. The thermal conductivity ( $\kappa$ ) is determined from  $\kappa = \alpha \cdot c_p \cdot d$ , where  $c_p$  is the specific heat, calculated using the Dulong–Petit equation, and *d* is the sample density. Scanning electron microscopy (SEM) images of an as-grown pellet were collected with a FEI Nova NanoSEM 230 microscope. The results are reproducible; and the synthesis procedure, by arc melting, has been repeated a sufficient number of times, as well as the measurements, yielding similar results in 4–5 samples.

The experimental study was also supported by theoretical models based on density functional theory (DFT) with the CRYSTAL17 package [34]. Based on a previous evaluation of functionals for this system, the WC1LYP [35] functional was chosen for the elaboration of the theoretical study. The Te and Sn basis set used in the calculations were triple-zeta valence with polarization Gaussian basis sets developed by Laun and Bredow [36].

The coulomb and exchange series thresholds (overlap and penetration for coulomb integrals, overlap for HF exchange integrals, and pseudo-overlap) used in the CRYSTAL17 package were defined as 8, 8, 8, 8, 16 ( $10^{-8}$ ,  $10^{-8}$ ,  $10^{-8}$ ,  $10^{-8}$ ,  $and 10^{-16}$ ). The shirking factors (Pack–Monkhorst method Gilat net) were set as 8 and 8, respectively. The gradient components and nuclear displacement tolerance on their root mean square were 0.0003 and 0.0012 a.u., respectively. The topochemistry evaluation was performed according the "Quantum Theory: Atoms in Molecules" (QTAIM) method implemented in the TOPOND, program that is part of the crystal package [37].

## 3. Results and Discussion

#### 3.1. Crystal Structure Evolution

Polycrystalline SnTe powder was obtained by carefully grinding the as-grown ingot from the arc furnace. The X-ray diffraction pattern collected with Cu K $\alpha$  radiation (Figure 1) corresponds to the well-known cubic structure, as identified via Rietveld refinement; no impurities or unreacted products were detected.



Figure 1. XRD pattern of SnTe from laboratory equipment, with Cu Kα radiation.

The NPD pattern collected at RT was essential to evaluate the microscopic composition of our specimen, elaborated by arc melting. Neutrons take advantage of the access to a large region of the reciprocal space with no form factors, enabling us to decouple the displacement factors and occupancy factors during the structural refinement. The penetration of neutrons enables probing the bulk and minimizes preferred orientation and absorption issues. The cubic crystal structure was defined in the *Fm-3m* space group (No. 225), Z = 4, with unit-cell parameter a = 6.3212(1) Å, V = 252.579(7) Å<sup>3</sup> at 298 K. The starting model was taken from Bauer-Pereira et al. [38]. Sn atoms were located at 4a (0,0,0) positions, while Te was placed at 4b ( $\frac{1}{2}$ ,  $\frac{1}{2}$ ,  $\frac{1}{2}$ ). Given the high-symmetry positions, the displacement factors were isotropic (spherical); the occupancy factors of Sn (with respect to Te fixed to unity) gave a Sn-defective stoichiometry, as Sn<sub>0.803(13)</sub>Te. Table 1 condenses the most important parameters after the Rietveld refinement from NPD data at RT, and Figure 2a displays the goodness of the fit.

**Table 1.** Main structural parameters after the Rietveld refinement from NPD data at RT for SnTe in the cubic (*Fm*-3*m*) phase; a = 6.3212(1) Å.

Atom	Site	x	у	z	B (Å <sup>2</sup> )	f <sub>occ</sub>
Sn	4a	0.0	0.0	0.0	0.79(8)	0.803(13)
Te	4b	0.5	0.5	0.5	1.60(9)	1.0
D' ( )	D 0 700/	D 2.740/ D	1 200/ 2	2.25		

Discrepancy factors:  $R_p = 2.78\%$ ,  $R_{wp} = 3.74\%$ ,  $R_{Bragg} = 1.30\%$ ;  $\chi^2 = 3.35$ .



**Figure 2.** NPD profiles after the Rietveld refinement of the cubic crystal structure at (**a**) 298 K and (**b**) 973 K. Stars indicate unidentified impurities.

A temperature-dependent NPD study was also essential to investigate the thermal evolution of the crystal structure above room temperature. Besides, an increase in density in nanoprecipitates and an induced Te deficiency due to neutron irradiation in some tellurides have been reported [39], so this neutron study becomes even more relevant. NPD data were collected at 523, 673, 773, 873, and 973 K. The same cubic model was utilized to refine the crystal structures in all the temperature range; no phase transition was detected. A progressive segregation of an unidentified phase was observed at high temperatures, which agrees with the similar case of segregation of Ga<sub>2</sub>Te<sub>3</sub> reported for an irradiated Pb<sub>0.975</sub>Ga<sub>0.025</sub>Te-0.25% ZnTe compound inserted in a nuclear reactor [39]. This is illustrated in the Rietveld plots included in Figure 2a, at 298 K, and Figure 2b, at 973 K. The plots corresponding to the remaining temperatures are included as Figure S1 in the Supplementary Information (S.I.).

Table S1 at the S.I. includes the structural parameters at 973 K. The displacement parameters and full coordination at RT are shown in the representation of the crystal structure of Figure 3. Whereas at RT, the Sn isotropic factors are conspicuously smaller than the Te ones, at 973 K, they become virtually similar. It is also noteworthy that the occupancy factors become virtually stoichiometric at high temperatures, for example, at 973 K, the

crystallographic formula is  $Sn_{0.97(53)}$ Te (see Table S1). The unit cell monotonically expands in this temperature range, as shown in Figure 3c.



**Figure 3.** Views of the cubic crystal structure, highlighting the evolution of the displacement parameters with temperature, from NPD data, at (**a**) 298 K and (**b**) 973 K. (**c**) Thermal variation of the *a* unit-cell parameter.

Taken into account that we start from a stoichiometric 1:1 Sn/Te relationship, the fact that we conspicuously observe a significant Sn deficiency implies that some Sn is segregated from the main phase during the synthesis process, as either tiny particles or superficial coating of each individual microcrystals, where it is not visible by diffraction methods. Upon warming, the segregated Sn is progressively incorporated into the crystal structure, which is detected by neutron diffraction and as an increase in the Sn occupancy factor.

#### 3.2. Debye Model Fittings and DFT Calculation

From the Rietveld refinements, we have extracted the temperature-dependent meansquare relative displacements, abbreviated as MSDs or  $U_{eq}$  in units of Å<sup>2</sup>. From those data, we can estimate the Debye temperature ( $\theta_D$ ) and the bonding stiffness. In solid-state physics, the Debye theory describes the temperature evolution of the MSDs according to the next formula [40,41],

$$U_{eq} = d_s^2 + \frac{3\hbar^2 T}{mk_B \theta_D^2} \left[ \frac{T}{\theta_D} \int_0^{\theta_D/T} \frac{x}{e^x - 1} dx + \frac{\theta_D}{4T} \right]$$
(1)

where  $d_s^2$  is the static disorder and m,  $k_B$ ,  $\hbar$ , and T keep their usual meaning in physics. In Figure 4, the experimental MSDs are compared with the fitting using Equation (1). We have fixed  $d_s^2 = 0$ , since we recorded only high-temperature NPD data, being mandatory low-temperature points to provide reliable static disorder values. Therefore, the Debye analysis for individual MSDs for Sn and Te revealed Debye temperatures of 145(2) K and 128(2) K, respectively. Those values provided a Debye temperature for SnTe of 136(2) K, which fully agrees with specific heat measurements yielding  $\theta_D$  of 135(3) K [42]. Indeed, the local bonding Sn–Te properties can be estimated using the harmonic potential, from which a force constant can be determined as  $K = mk_B\theta_D^2/3\hbar^2$ . For an average <Sn–Te> interaction, we have a *K* of 1.36(3) eV/Å<sup>2</sup>. Those values can be used as starting point to better constrain the bond anharmonicity in SnTe in future investigations.

The optimized unit cell of the theoretical model presented a lattice parameter of 6.30 Å, a value in accordance with the experimental result at room temperature (6.3212(1) Å, as listed in Table 1). In addition, the evaluation of the electronic structure showed a direct band gap (K $\rightarrow$ K) of 0.42 eV (see Figures S2 and S3). The topochemical analysis of the bond critical point (BCP) of the Sn–Te bond was performed. The electron density ( $\rho$ ), Laplacian of electron density ( $\nabla^2 \rho$ ), virial field density (V), Lagrangian kinetic energy density (G), and total energy (H) (all in atomic units) of the BCP are 0.0321, 0.0247, -0.0166, 0.0114, and -0.0052, respectively. The  $\nabla^2 \rho > 0$ , H < 0, and  $1 < \frac{|V|}{G} < 2$  (1.46) indicate a transit bond (transit region between closed-shell and shared-shell bond) [43]. Such a behavior was expected, since it is a material composed by Sn and Te, as estimated from the Debye model.

Figure 5 shows the Laplacian of electronic density map of the <100> planes, which brings some combined isolines between the atomic centers.



**Figure 4.** Temperature dependence of the mean-square relative displacements (spheres, MSDs in units of  $Å^2$ ) fitted according to the Debye model (dotted lines).



Figure 5. (a) Laplacian of the electronic density map of (b) the <100> planes of the SnTe structural model.

## 3.3. SEM Investigation

The texture of the as-grown SnTe pellets can be appreciated in the high-resolution FE-SEM images shown in Figure 6. The material consists of a stacking of sheets, each of them presumably single crystalline, with the large surfaces perpendicular to *a* crystallographic axis. The thickness of the individual sheets, better evaluated in Figure 6b, is below 0.03  $\mu$ m; Figure S4 at the Supplementary Material assesses layer thicknesses in the 15–30 nm range. This strong nanostructuration is also responsible for its potential as thermoelectric material, as described below.



**Figure 6.** SEM micrographs with (a)  $60,000 \times$  and (b)  $55,020 \times$  magnification, illustrating the nanostructuration in layers observed in this material, grown from arc melting.

## 3.4. Thermoelectric Properties

The thermoelectric transport properties of arc-melted SnTe are shown in Figure 7. Additionally, we can see the transport properties of an arc-melted SnTe with an SPS treatment applied afterwards, for the sake of comparison.



**Figure 7.** Temperature dependence of the three main thermoelectric properties: (**a**) resistivity, (**b**) Seebeck coefficient, and (**c**) power factor.

The electrical resistivity (Figure 7a) is quite similar in both cases, starting with  $2 \times 10^{-6} \Omega \cdot m$  at room temperature and increasing with temperature till reaching  $10^{-5} \Omega \cdot m$  at 780 K, which is a metal-like behavior reported before elsewhere [25,28–30]. The resistivity of the sintered sample seems to be slightly lower than the other one, which may be caused by the increased density achieved, thanks to the thermal and pressure treatment. This result agrees with some reports on other tellurides, which show that some samples of relatively low density, or even with pores within, have an increased electrical resistivity [44]. This low resistivity shown by the undoped SnTe is reflected in the very low Seebeck coefficient shown at room temperature (Figure 7b), around 15–20  $\mu$ V/K. This low value agrees with

the usually reported data for pristine SnTe, which shows a low thermopower associated with the relatively high carrier density intrinsic to this compound [23–25,30,31,45]. Finally, with the measured resistivity and Seebeck coefficient, we can calculate the power factor, displayed in Figure 7c. The sample measured after the SPS treatment shows a higher power factor than the just arc-melted one, so we can say that the sintering process seems to be beneficial for the thermoelectric performance of the SnTe compound, unlike in other chalcogenides [46]. It is worth remarking that the XRD pattern after the SPS treatment is exactly comparable to that of the pristine sample.

The weighted mobility [47] of both samples is shown in Figure 8. This calculated parameter gives nearly the same information about carrier transport compared with that offered by the Hall mobility data. Their dependence on temperature is very similar in both cases, showing that the electronic transport is hindered by the acoustic phonon scattering  $(\alpha T^{-3/2})$ , a feature commonly found in most good thermoelectric materials [47]. The higher weighted mobility shown by the sintered composition comes from the increased Seebeck coefficient measured in the compound after the thermal and pressure treatment.



**Figure 8.** Temperature dependence of the weighted mobility calculated for the arc-melted SnTe and the arc-melted and sintered (SPS) SnTe.

This result suggests that the use of the SPS process reduces the Sn vacancies present in the structure of the arc-melted SnTe, as it was suggested from the analysis of the NPD data, yielding almost stoichiometric samples at high temperatures. Indeed, the Sn occupancy at 773 K, refined from NPD data, is 0.95(5), virtually stoichiometric within the standard deviation. Therefore, the reduction of the Sn vacancies also leads to a reduction of the carrier density, thus explaining the higher Seebeck coefficient observed in the sintered sample. Besides, the effect of the sintering process is noteworthy in the weighted mobility, which is doubled in the sintered SnTe compared with the weighted mobility of the arc-melted sample. This parameter does not depend on the carrier density [47], so the increase in the weighted mobility comes from the improved conductivity between the grains in this polycrystalline sample, which is promoted by the sintering process [48].

This enhancement of the electronic properties is represented in the power factor (Figure 7c), but also in the quality factor, B, and the electronic counterpart,  $B_E$ , in Figure S5, suggesting an overall improvement of the thermoelectric transport due to the SPS process. The chemical potential is also shifted closer to the optimal region due to the reduction of the Sn vacancies (Figure S6).

Regarding the thermal conductivity (Figure 9a), it seems to be very similar in both cases, with no appreciable differences between the sintered and nonsintered sample. At room temperature, the total thermal conductivity is  $\sim 7 \text{ W/m} \cdot \text{K}$ . This value agrees very well

with previously reported data for SnTe, which ranges between 6 and 8 W/m·K [25,28–31]. In this case, the two contributions to the total thermal conductivity, lattice and electronic (Figure 9b), are really close to each other, owing to the high carrier density usually present in this compound that we already mentioned before. This effect has been reported before in pristine SnTe with similar results [24,25,30].



**Figure 9.** Temperature dependence of the (**a**) total thermal conductivity and (**b**) lattice and electronic contributions.

In Figure 10, we can see the calculated figure of merit for both compounds, the arcmelted and the arc-melted and sintered SnTe. The figure of merit for the sintered compound is clearly higher at all temperatures, thus demonstrating that, for this compound, the effect of sintering and, more precisely, the reduction of the Sn vacancies, is beneficial for the thermoelectric performance of SnTe. The maximum *ZT* is achieved at 723 K, reaching a value of ~0.11. Compared with the calculated *ZT* (Figure S5) using the quality factor, we observe that these samples remain in the highly doped reduced chemical potential range, indicating the detrimental effect of Sn vacancies in the crystalline structure. This figure of merit is low if we compare it with other state-of-the-art thermoelectric materials [6–8,11,49], but it is similar to previously reported data of pristine SnTe, which barely reaches a *ZT* of ~0.3 at high temperature [23,25,30,31].



Figure 10. Temperature dependence of the thermoelectric figure of merit, ZT.

#### 4. Conclusions

We have prepared pure polycrystalline SnTe by arc-melting, and investigated the structural evolution by temperature-dependent neutron powder diffraction (NPD) up to 973 K. We find that, at all analyzed temperatures, the sample is cubic (space group *Fm-3m*), and it shows considerably larger displacement parameters for Te than for Sn. The structural analysis allowed us to obtain the Debye model parameters and provided information on the Sn–Te chemical bonds. We can see a conspicuous nanostructuration in layers below 30 nm thickness in the SEM images, which contributes to the reduction of the thermal conductivity down to 2.5 W/mK at 800 K. The Seebeck coefficient, reaching 60  $\mu$ V/K at 700 K, is considerably improved after an SPS treatment, as do the weighted mobility and the figure of merit. We can conclude that the reduction of the vacancies associated with the SPS treatment applied to the arc-melted SnTe is an effective way to enhance the overall thermoelectric performance.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cryst13010049/s1. Table S1: Structural parameters at 927 K; Figure S1: Additional refined NPD plots; Figure S2: Calculated band structure; Figure S3: Calculated density of states; Figure S4: Additional SEM images; Figure S5: Material's quality factors; Figure S6: *ZT* vs. *η* relation.

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**Data Availability Statement:** Original data are available from the corresponding authors upon reasonable request.

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## References

- Li, J.-F.; Liu, W.-S.; Zhao, L.-D.; Zhou, M. High-Performance Nanostructured Thermoelectric Materials. NPG Asia Mater. 2010, 2, 152–158. [CrossRef]
- 2. Snyder, G.J.; Toberer, E.S. Complex Thermoelectric Materials. Nat. Mater. 2008, 7, 105–114. [CrossRef] [PubMed]
- 3. Mao, J.; Chen, G.; Ren, Z. Thermoelectric Cooling Materials. Nat. Mater. 2021, 20, 454–461. [CrossRef] [PubMed]
- 4. Freer, R.; Powell, A. V Realising the Potential of Thermoelectric Technology: A Roadmap. J. Mater. Chem. C 2020, 8, 441–463. [CrossRef]
- 5. Biswas, K.; He, J.; Zhang, Q.; Wang, G.; Uher, C.; Dravid, V.P.; Kanatzidis, M.G. Strained Endotaxial Nanostructures with High Thermoelectric Figure of Merit. *Nat. Chem.* **2011**, *3*, 160–166. [CrossRef]
- 6. Zhou, C.; Lee, Y.K.; Yu, Y.; Byun, S.; Luo, Z.-Z.; Lee, H.; Ge, B.; Lee, Y.-L.; Chen, X.; Lee, J.Y.; et al. Polycrystalline SnSe with a Thermoelectric Figure of Merit Greater than the Single Crystal. *Nat. Mater.* **2021**, *20*, 1378–1384. [CrossRef]
- 7. Zhu, Y.; Hu, L.; Zhan, S.; Ina, T.; Gao, X.; Hong, T.; Zhao, L.-D. Breaking the Sodium Solubility Limit for Extraordinary Thermoelectric Performance in P-Type PbTe. *Energy Environ. Sci.* **2022**, *15*, 3958–3967. [CrossRef]
- 8. Zhao, L.-D.; Lo, S.-H.; Zhang, Y.; Sun, H.; Tan, G.; Uher, C.; Wolverton, C.; Dravid, V.P.; Kanatzidis, M.G. Ultralow Thermal Conductivity and High Thermoelectric Figure of Merit in SnSe Crystals. *Nature* **2014**, *508*, 373–377. [CrossRef]
- 9. Serrano-Sánchez, F.; Gharsallah, M.; Nemes, N.M.; Mompean, F.J.; Martínez, J.L.; Alonso, J.A. Record Seebeck Coefficient and Extremely Low Thermal Conductivity in Nanostructured SnSe. *Appl. Phys. Lett.* **2015**, *106*, 083902. [CrossRef]
- Serrano-Sánchez, F.; Nemes, N.M.; Dura, O.J.; Fernandez-Diaz, M.T.; Martínez, J.L.; Alonso, J.A. Structural Phase Transition in Polycrystalline SnSe: A Neutron Diffraction Study in Correlation with Thermoelectric Properties. J. Appl. Crystallogr. 2016, 49, 2138–2144. [CrossRef]
- Gainza, J.; Serrano-Sánchez, F.; Rodrigues, J.E.F.S.; Huttel, Y.; Dura, O.J.; Koza, M.M.; Fernández-Díaz, M.T.; Meléndez, J.J.; Márkus, B.G.; Simon, F.; et al. High-Performance n-Type SnSe Thermoelectric Polycrystal Prepared by Arc-Melting. *Cell Rep. Phys. Sci.* 2020, *1*, 100263. [CrossRef]
- Gainza, J.; Serrano-Sánchez, F.; Gharsallah, M.; Carrascoso, F.; Bermúdez, J.; Dura, O.J.; Mompean, F.J.; Biskup, N.; Meléndez, J.J.; Martínez, J.L.; et al. Evidence of Nanostructuring and Reduced Thermal Conductivity in N-Type Sb-Alloyed SnSe Thermoelectric Polycrystals. J. Appl. Phys. 2019, 126, 045105. [CrossRef]
- 13. Gainza, J.; Moltó, S.; Serrano-Sánchez, F.; Dura, O.J.; Fernández-Díaz, M.T.; Biškup, N.; Martínez, J.L.; Alonso, J.A.; Nemes, N.M. SnSe:Kx Intermetallic Thermoelectric Polycrystals Prepared by Arc-Melting. *J. Mater. Sci.* **2022**, *57*, 8489–8503. [CrossRef]
- 14. Gharsallah, M.; Serrano-Sánchez, F.; Nemes, N.M.; Mompeán, F.J.; Martínez, J.L.; Fernández-Díaz, M.T.; Elhalouani, F.; Alonso, J.A. Giant Seebeck Effect in Ge-Doped SnSe. *Sci. Rep.* **2016**, *6*, 26774. [CrossRef]
- Serrano-Sánchez, F.; Nemes, N.M.; Martínez, J.L.; Juan-Dura, O.; de la Torre, M.A.; Fernández-Díaz, M.T.; Alonso, J.A. Structural Evolution of a Ge-Substituted SnSe Thermoelectric Material with Low Thermal Conductivity. *J. Appl. Crystallogr.* 2018, 51, 337–343. [CrossRef]
- 16. Serrano-Sánchez, F.; Funes, M.; Nemes, N.M.; Dura, O.J.; Martínez, J.L.; Prado-Gonjal, J.; Fernández-Díaz, M.T.; Alonso, J.A. Low Lattice Thermal Conductivity in Arc-Melted GeTe with Ge-Deficient Crystal Structure. *Appl. Phys. Lett.* **2018**, *113*, 083902. [CrossRef]
- 17. Gainza, J.; Serrano-Sánchez, F.; Nemes, N.M.; Martínez, J.L.; Fernández-Díaz, M.T.; Alonso, J.A. Features of the High-Temperature Structural Evolution of GeTe Thermoelectric Probed by Neutron and Synchrotron Powder Diffraction. *Metals* 2019, 10, 48. [CrossRef]
- 18. Gainza, J.; Serrano-Sánchez, F.; Nemes, N.M.; Dura, O.J.; Martínez, J.L.; Alonso, J.A. Lower Temperature of the Structural Transition, and Thermoelectric Properties in Sn-Substituted GeTe. *Mater. Today Proc.* **2021**, *44*, 3450–3457. [CrossRef]
- 19. Gainza, J.; Serrano-Sánchez, F.; Biskup, N.; Nemes, N.M.; Martínez, J.L.; Fernández-Díaz, M.T.; Alonso, J.A. Influence of Nanostructuration on PbTe Alloys Synthesized by Arc-Melting. *Materials* **2019**, *12*, 3783. [CrossRef]
- Hsieh, T.H.; Lin, H.; Liu, J.; Duan, W.; Bansil, A.; Fu, L. Topological Crystalline Insulators in the SnTe Material Class. *Nat. Commun.* 2012, *3*, 982. [CrossRef]
- Schindler, F.; Cook, A.M.; Vergniory, M.G.; Wang, Z.; Parkin, S.S.P.; Bernevig, B.A.; Neupert, T. Higher-Order Topological Insulators. Sci. Adv. 2018, 4, eaat0346. [CrossRef] [PubMed]
- 22. Tanaka, Y.; Ren, Z.; Sato, T.; Nakayama, K.; Souma, S.; Takahashi, T.; Segawa, K.; Ando, Y. Experimental Realization of a Topological Crystalline Insulator in SnTe. *Nat. Phys.* **2012**, *8*, 800–803. [CrossRef]
- Tan, G.; Zhao, L.-D.; Shi, F.; Doak, J.W.; Lo, S.-H.; Sun, H.; Wolverton, C.; Dravid, V.P.; Uher, C.; Kanatzidis, M.G. High Thermoelectric Performance of P-Type SnTe via a Synergistic Band Engineering and Nanostructuring Approach. J. Am. Chem. Soc. 2014, 136, 7006–7017. [CrossRef] [PubMed]
- 24. Moshwan, R.; Yang, L.; Zou, J.; Chen, Z.-G. Eco-Friendly SnTe Thermoelectric Materials: Progress and Future Challenges. *Adv. Funct. Mater.* **2017**, *27*, 1703278. [CrossRef]

- 25. Li, W.; Zheng, L.; Ge, B.; Lin, S.; Zhang, X.; Chen, Z.; Chang, Y.; Pei, Y. Promoting SnTe as an Eco-Friendly Solution for p-PbTe Thermoelectric via Band Convergence and Interstitial Defects. *Adv. Mater.* **2017**, *29*, 1605887. [CrossRef]
- Li, W.; Wu, Y.; Lin, S.; Chen, Z.; Li, J.; Zhang, X.; Zheng, L.; Pei, Y. Advances in Environment-Friendly SnTe Thermoelectrics. ACS Energy Lett. 2017, 2, 2349–2355. [CrossRef]
- Yan, X.; Zheng, S.; Zhou, Z.; Wu, H.; Zhang, B.; Huang, Y.; Lu, X.; Han, G.; Wang, G.; Zhou, X. Melt-Spun Sn1-x-ySbxMnyTe with Unique Multiscale Microstructures Approaching Exceptional Average Thermoelectric ZT. *Nano Energy* 2021, 84, 105879. [CrossRef]
- 28. Shenoy, U.S.; Bhat, D.K. Bi and Zn Co-Doped SnTe Thermoelectrics: Interplay of Resonance Levels and Heavy Hole Band Dominance Leading to Enhanced Performance and a Record High Room Temperature ZT. J. Mater. Chem. C 2020, 8, 2036–2042. [CrossRef]
- 29. Ma, Z.; Wang, C.; Chen, Y.; Li, L.; Li, S.; Wang, J.; Zhao, H. Ultra-High Thermoelectric Performance in SnTe by the Integration of Several Optimization Strategies. *Mater. Today Phys.* **2021**, *17*, 100350. [CrossRef]
- Wang, L.; Hong, M.; Sun, Q.; Wang, Y.; Yue, L.; Zheng, S.; Zou, J.; Chen, Z.-G. Hierarchical Structuring to Break the Amorphous Limit of Lattice Thermal Conductivity in High-Performance SnTe-Based Thermoelectrics. ACS Appl. Mater. Interfaces 2020, 12, 36370–36379. [CrossRef]
- Moshwan, R.; Liu, W.-D.; Shi, X.-L.; Wang, Y.-P.; Zou, J.; Chen, Z.-G. Realizing High Thermoelectric Properties of SnTe via Synergistic Band Engineering and Structure Engineering. *Nano Energy* 2019, 65, 104056. [CrossRef]
- Rietveld, H.M. A Profile Refinement Method for Nuclear and Magnetic Structures. *J. Appl. Crystallogr.* 1969, 2, 65–71. [CrossRef]
   Rodríguez-Carvajal, J. Recent Advances in Magnetic Structure Determination by Neutron Powder Diffraction. *Phys. B Phys.*
- *Condens. Matter* 1993, 192, 55–69. [CrossRef]
  34. Dovesi, R.; Erba, A.; Orlando, R.; Zicovich-Wilson, C.M.; Civalleri, B.; Maschio, L.; Rérat, M.; Casassa, S.; Baima, J.; Salustro, S.; et al. Quantum-mechanical Condensed Matter Simulations with CRYSTAL. WIREs Comput. Mol. Sci. 2018, *8*, e1360. [CrossRef]
- 35. Demichelis, R.; Civalleri, B.; Ferrabone, M.; Dovesi, R. On the Performance of Eleven DFT Functionals in the Description of the Vibrational Properties of Aluminosilicates. *Int. J. Quantum Chem.* **2010**, *110*, 406–415. [CrossRef]
- 36. Laun, J.; Bredow, T. BSSE-Corrected Consistent Gaussian Basis Sets of Triple-Zeta Valence with Polarization Quality of the Fifth Period for Solid-State Calculations. J. Comput. Chem. 2022, 43, 839–846. [CrossRef]
- 37. Casassa, S.; Erba, A.; Baima, J.; Orlando, R. Electron Density Analysis of Large (Molecular and Periodic) Systems: A Parallel Implementation. *J. Comput. Chem.* **2015**, *36*, 1940–1946. [CrossRef]
- 38. Perlt, S.; Höche, T.; Dadda, J.; Müller, E.; Bauer Pereira, P.; Hermann, R.; Sarahan, M.; Pippel, E.; Brydson, R. Microstructure Analyses and Thermoelectric Properties of Ag1-XPb18Sb1+yTe20. *J. Solid State Chem.* **2012**, *193*, 58–63. [CrossRef]
- 39. Kempf, N.; Luo, Z.-Z.; Xie, H.; Daw, J.; Kanatzidis, M.G.; Zhang, Y. Thermoelectric Properties of High-Performance n-Type Lead Telluride Measured in Situ in a Nuclear Reactor Core. *J. Mater. Chem. A* 2022, *10*, 21266–21272. [CrossRef]
- Rodrigues, J.E.F.S.; Escanhoela, C.A.; Fragoso, B.; Sombrio, G.; Ferrer, M.M.; Álvarez-Galván, C.; Fernández-Díaz, M.T.; Souza, J.A.; Ferreira, F.F.; Pecharromán, C.; et al. Experimental and Theoretical Investigations on the Structural, Electronic, and Vibrational Properties of Cs 2 AgSbCl 6 Double Perovskite. *Ind. Eng. Chem. Res.* 2021, 60, 18918–18928. [CrossRef]
- 41. Mi, J.-L.; Christensen, M.; Nishibori, E.; Iversen, B.B. Multitemperature Crystal Structures and Physical Properties of the Partially Filled Thermoelectric Skutterudites M<sub>0.1</sub>Co<sub>4</sub>Sb<sub>12</sub> (M = La, Ce, Nd, Sm, Yb and Eu). *Phys. Rev. B* **2011**, *84*, 064114. [CrossRef]
- 42. Bukshpan, S. Determination of the Debye Temperature of SnTe Using the Mössbauer Effect in 119Sn and 125Te. *Solid State Commun.* **1968**, *6*, 477–478. [CrossRef]
- 43. Gatti, C.; Saunders, V.R.; Roetti, C. Crystal Field Effects on the Topological Properties of the Electron Density in Molecular Crystals: The Case of Urea. *J. Chem. Phys.* **1994**, *101*, 10686–10696. [CrossRef]
- 44. Zhang, Y.; Day, T.; Snedaker, M.L.; Wang, H.; Krämer, S.; Birkel, C.S.; Ji, X.; Liu, D.; Snyder, G.J.; Stucky, G.D. A Mesoporous Anisotropic N-Type Bi2Te3 Monolith with Low Thermal Conductivity as an Efficient Thermoelectric Material. *Adv. Mater.* **2012**, 24, 5065–5070. [CrossRef]
- 45. Sarkar, D.; Ghosh, T.; Banik, A.; Roychowdhury, S.; Sanyal, D.; Biswas, K. Highly Converged Valence Bands and Ultralow Lattice Thermal Conductivity for High-Performance SnTe Thermoelectrics. *Angew. Chem. Int. Ed.* **2020**, *59*, 11115–11122. [CrossRef]
- Lee, Y.K.; Luo, Z.; Cho, S.P.; Kanatzidis, M.G.; Chung, I. Surface Oxide Removal for Polycrystalline SnSe Reveals Near-Single-Crystal Thermoelectric Performance. *Joule* 2019, *3*, 719–731. [CrossRef]
- 47. Snyder, G.J.; Snyder, A.H.; Wood, M.; Gurunathan, R.; Snyder, B.H.; Niu, C. Weighted Mobility. Adv. Mater. 2020, 32, 2001537. [CrossRef]
- 48. Munir, Z.A.; Ohyanagi, M. Perspectives on the Spark Plasma Sintering Process. J. Mater. Sci. 2021, 56, 1–15. [CrossRef]
- 49. Wu, Y.; Chen, Z.; Nan, P.; Xiong, F.; Lin, S.; Zhang, X.; Chen, Y.; Chen, L.; Ge, B.; Pei, Y. Lattice Strain Advances Thermoelectrics. *Joule* 2019, *3*, 1276–1288. [CrossRef]

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