SnSe:K$_x$ intermetallic thermoelectric polycrystals prepared by arc-melting

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ABSTRACT

Neutron powder diffraction and thermoelectric characterization of SnSe:K$_x$ intermetallic alloys are presented. Nanostructured ingots were prepared by arc-melting elemental tin and selenium along with potassium hydride. Up to $x = 0.1$ of K can be incorporated into SnSe. Rietveld refinement of the diffractograms locates potassium on the Sn site in the high-temperature Cmcm structure. However, in the low-temperature Pnma structure, K cannot be localized by difference Fourier maps, indicating the incorporation of K in a disordered form in the interlayer space. STEM-EELS indicates the incorporation of K into the SnSe grains. The resistivity upon K-doping at intermediate temperatures decreases by 1–2 orders of magnitude, but at high temperature is higher than the undoped SnSe. The Seebeck coefficient of K-doped SnSe remains p-type and almost temperature independent (400 $\mu$V/K for $x = 0.1$). The ultralow thermal conductivity of undoped SnSe decreases further upon K-doping to below 0.3 W/m K.

Introduction

Thermoelectric materials hold the promise to help create a greener and eco-friendlier energy economy [1]. Thermoelectrics can convert temperature gradients into electrical voltage, or electric current to (negative) heat through the Seebeck or Peltier effect. Thermoelectrics are typically good semiconductors with large Seebeck coefficient ($S$), but they also need good electrical conductivity ($\sigma$), which requires a compromise by tuning the Fermi level with chemical doping. Furthermore, good thermoelectrics extract low thermal conductivity ($\kappa$), but since the
Wiedemann–Franz law connects the electrical conductivity to the electronic thermal conductivity \( (\kappa_{el}) \), only the lattice thermal conductivity \( (\kappa_{latt}) \) may be improved independently [2]. Nanostructuring is often the chosen strategy to decrease \( \kappa_{latt} \) and preserve the electronic transport properties \( S \) and \( \sigma \) [3–8]. In the realm of material science, these competing properties are evaluated in terms of the dimensionless thermoelectric figure of merit 
\[
zT = T \cdot S^2 \sigma / (\kappa_{el} + \kappa_{latt}).
\]

Thermoelectrics offer versatile ways for applications, such as devices for waste heat to electricity conversion in thermoelectric generators, or Peltier coolers for reliable systems with no gases or moving parts [9, 10]. The full design from the synthesis of materials to the fabrication of devices must be assessed [11, 12]. For many applications such as powering sensors or for Peltier coolers, good room temperature thermoelectrics are needed [13].

There are several successful families of thermoelectrics that can provide both the required p- and n-type semiconductors for thermoelectric modules [14, 15]. Thermoelectrics are often made of environmentally toxic or rare elements. Finding cost-effective synthesis of environmentally friendly nanostructured thermoelectrics has become a focus of recent research [16]. Nevertheless, some of the more successful types of thermoelectrics are based on tellurides [17], such as bismuth telluride \( (Bi_2Te_3) \) [4–7, 18–22], lead telluride \( (PbTe) \) [23–25] and germanium telluride \( (GeTe) \) [26–31]. Skutterudites are another attractive family of thermoelectrics, as they are high mobility semiconductors that chemically and structurally offer many ways of doping and property tuning [1, 32, 33]. They can be prepared by various methods in addition to conventional metallurgy, including high-pressure synthesis [34–36], melt spinning [37, 38], microwave synthesis [39], etc. As alternatives, oxides, such as \( SrTiO_3 \) have been considered recently [40, 41].

There are multiple strategies to improve some of the thermoelectric properties in addition to nanostructuring, such as band engineering [42–47], energy filtering [48–50], the phonon glass electron crystal approach [51, 52] or high entropy design [53].

Tin selenide, \( SnSe \), is a semiconductor with a quasi 2D laminar crystal structure resembling that of black phosphorous, also a potential thermoelectric [54]. In 2014, single crystals of \( SnSe \) were found to be the best thermoelectric up then with \( zT \sim 2.6 \) [55]. It has remarkable 3D charge but 2D phonon transport properties due to its crystal structure [56], anharmonicity, multiple valence band along with a continuous phase transition near maximum \( zT \) [57]. Polycrystalline \( SnSe \) can be prepared by several synthesis techniques [58], among them with co-doping and multi-nanoprecipitates [59], with aqueous synthesis [60], as well as arc-melting. \( SnSe \) films can also show good thermoelectric performance [61–63]. Successful thermoelectric generators have been made based on \( SnSe \) very recently [64]. The effects of vacancy on the thermoelectric properties have been studied in detail [65–68]. Applied pressure transforms \( SnSe \) into a semimetal [69]. \( SnSe \) can be doped with a wide variety of elements, including Ge [70–72], Sb [73], or alloyed with \( SnTe \) [8] and \( SnS \) [74].

Arc-melting produces highly nanostructured \( SnSe \) efficiently [3] and is a versatile synthesis procedure for various dopings [70, 75]. This synthesis produces material with elemental ratios or doping different from the nominal amount, as either dopant, tin or selenide is easily lost to the arc [73, 76]. The polycrystalline n-type \( SnSe \) pellets produced by arc-melting can reach high \( zT \) up to 1.8 [77].

High-performance p-type \( SnSe \) polycrystal may be stabilized by alkali doping (with Li, Na and K) [78–80], as well as Na-doped \( SnSe_{1-x}Te_x \) [81]. In alkali-doped \( SnSe \), the location of the dopant is crucial. As stated by Wei et al., “…actual occupancy (i.e., substitutional, interstitial, or intercalated type) of these dopants is an important concern” [78]. Alkali doping may be beneficial in removing or preventing the formation of the high-thermal conductivity intergrain tin oxide layers and forming coherent nanoprecipitates [82]. In conventional synthesis techniques, the handling and introduction of highly flammable and air-sensitive alkali metals poses a technical nuisance.

Here we report the synthesis of \( SnSe:K_x \) intermetallic alloys, using potassium hydride, and their high resolution neutron powder diffraction (NPD) investigation directed to characterize the position of the K dopant, along with the thermoelectric properties. The advantage of using KH as starting material to introduce K has to do with its easy handling, avoiding issues with ambient oxidation, with the expectation that \( H_2 \) is released and lost during synthesis. A similar method, using KH, was employed recently to produce K-filled \( CoSb_3 \) skutterudite under high pressure [32]. The synthesis may also help
avoiding the formation of tin oxide, which has been shown to be responsible for an undesired increase of effective thermal conductivity [83–85].

Materials and methods

SnSe:K\(_x\) intermetallic alloys were prepared in an Edmund Buhler MAM-1 mini-arc furnace. A mixture of stoichiometric amounts of Sn and Se powder metals, and KH as a source of K, was pelletized under N\(_2\) atmosphere in a glove box; the pellets were arc-molten under Ar atmosphere in a water-cooled Cu crucible, leading to compact ingots, which were ground to powder for structural characterization, or cold-pressed into regular disk-shaped specimens for transport measurements. Cold-pressing SnSe is sufficient for decent thermoelectric performance [77, 86]; it provides samples with about 90% of the crystallographic density thanks to its malleability. On the contrary, more typical consolidation techniques, such as hot pressing [87] or spark plasma sintering [21, 85], would yield higher densities but tend to deteriorate the electrical and thermal conductivities, mainly by causing intergrain oxide growth [88].

Neutron powder diffraction (NPD) data were taken in the D2B diffractometer at the Institut Laue-Langevin, Grenoble, in the high-resolution configuration, with a neutron wavelength of \(\lambda = 1.594\) Å. About 2 g of the sample were contained in a vanadium can and placed in the isothermal zone of a furnace with a vanadium resistor operating under vacuum (\(P_{\text{O}_2} \approx 10^{-6}\) Torr residual pressure). The measurements were carried out upon warming at 295, 523, 773, 873 and 973 K. The NPD patterns were collected for 2 h in the high-flux mode. The diffraction patterns were analyzed by the Rietveld method with the FULLPROF program [89]. The line shape of the diffraction peaks was generated by a pseudo-Voigt function. The following parameters were refined: background points, zero shift, half width, pseudo-Voigt, scale factor and unit-cell parameters. Positional and occupancy factors and isotropic displacement factors were also refined. The coherent scattering lengths for Sn, K and Se were, respectively, 6.225, 3.670 and 7.970 fm. A preferred orientation correction was applied, considering platelets perpendicular to the [100] direction.

All the thermoelectric properties were measured along the pressing direction, where previous reports show a higher \(ZT\) [90–92]. Seebeck coefficient and four-probe resistivity measurements were carried out in high vacuum (10\(^{-6}\) mbar) in a commercial MMR instrument. Thermal conductivity was determined from the thermal diffusivity (\(\kappa\)) using a Linseis LFA 1000 instrument by a laser-flash technique, as \(\kappa = \alpha C_p d\), where \(C_p = 252–263\) J/kg K is the specific heat calculated using the Dulong–Petit equation, and \(d = 5.5–6.0\) g/cm\(^3\) is the sample density (90–96% of the crystallographic value), for the various compositions between \(x = 0–0.1\).

Scanning transmission electron microscopy (STEM) is carried out in a JEOL ARM 200 electron microscope operated at 200 kV. The microscope is equipped with a Gatan Quantum electron energy loss spectrometer (EELS). Transmission electron microscopy (TEM) image S7 is done in JEOL 3000F electron microscope operated at 300 kV.

Results

X-ray diffraction

SnSe:K\(_x\) specimens were obtained by arc-melting as robust ingots, ground into black, well-crystallized powders in order to perform the structural characterization. Typical diffraction patterns are affected by a certain preferred orientation [3, 93]. Figure 1 shows the XRD patterns of SnSe:K\(_x\) samples (\(x = 0, 0.0.25, 0.05, 0.075, 0.1\)) including that of the parent SnSe compound. All the diagrams correspond to well-crystallized GeSe-like structures with orthorhombic geometry defined in the space group \(Pnma\). The crystal structures were initially refined from XRD data in order to follow the evolution of the lattice parameters upon K doping. Figure 2 displays the mentioned variation with \(x\) (nominal amount of K). The unit-cell sizes substantially differ from that of the parent SnSe compound (with unit-cell parameters: \(a = 11.5067(1), b = 4.1551(1)\) and \(c = 4.4475(2)\) Å), showing an overall increment of \(a, b\) and \(c\) parameters and unit-cell volume, \(V\), as K is introduced into the crystal structure up to a maximum of \(x = 0.1\). This expansion of the lattice happens because the atomic size of K\(^+\) is bigger than that of Sn\(^{2+}\). Beyond this doping level (nominal \(x = 0.15, 0.2\)), the size of the cell decreases again. Figure S6 (in the Supplementary
Information) displays the XRD pattern of the $x = 0.2$ material, showing the appearance of some impurities (unidentified) in the low Bragg-angle region. Therefore, we consider that $x = 0.1$ is the maximum K content the system is able to accept under the current preparation conditions and, thus, the $x = 0.15$ and 0.2 specimens were excluded from this study.

**In-situ NPD study**

The investigation of the crystal structure evolution by neutron powder diffraction (NPD) of the sample with the maximum K doping level ($x = 0.1$) was essential since the bulk analysis provided by neutrons is exceptionally good to minimize the preferred orientation effect, given the packing of the ground crystals in vanadium cylinders. Furthermore, neutrons allow us to explore a much wider range of the reciprocal space, whereas the lack of form factor permits the precise determination of the site occupancy and anisotropic displacement factors, since the neutron scattering lengths do not decrease with the scattering angle. Figure 3a, b show the NPD patterns collected at 295 K and 873 K, respectively; a symmetry increase is observed, since a structural phase transition from
Pnma to Cmcm space groups occurs between the 673 K and the 773 K patterns (represented in the SI).

In fact, Pnma is a subgroup of Cmcm, retaining half of the space group symmetry elements. For the room-temperature pattern (T = 295 K), the crystal structure was Rietveld-refined in the Pnma space group (No. 62) with a = 11.5132 (8) Å, b = 4.1538 (3) Å, c = 4.4438 (3) Å and V = 212.52 (2) Å³. Both Sn and Se atoms are located at 4c (x, 1/4, z) positions. Figure 4 shows a sketch with the crystal structures defined in the Pnma (low-temperature) and Cmcm (high-temperature).

Despite the net expansion observed with respect to pristine SnSe at RT, the localization of K atoms was not possible from NPD data: trial refinements with K at the Sn sites led to slightly negative occupancy factors for K. Difference Fourier maps did not show a clear location of the additional atoms, and therefore we assume that the expansion affecting mainly the a parameter (perpendicular to the corrugated layers of SnSe) is due to the incorporation of K in a disordered form in the interlayer space. This configuration is suggested in Fig. 4. Table S1 (Supporting information) includes the atomic parameters and displacements factors at 295 K.

The refinement of the 573 K and 673 K structures was also carried out in the Pnma space group; the patterns did not show symptoms of deviations from that symmetry and space group. The results of those refinements are included in Tables S2 and S3; the quality of the Rietveld plots is shown in Figs. S1 and S2, also corresponding to excellent agreement factors.

The left panel of Fig. 4 depicts the orthorhombic Pnma low-temperature phase, consisting of puckered layers of corner sharing SnSe3 polyhedra, perpendicular to the a unit-cell parameter. Selenium atoms also form SeSn3 trigonal pyramids. As indicated above, the K atoms could not be identified at Sn sites, so it is inferred that they occupy the interlayer space, driving the observed expansion of the a unit-cell parameter.

The 773 K, the NPD pattern already shows a mixture of the low-temperature Pnma and high-temperature Cmcm phases, described below (Fig. S3). The full refinement was performed with both structural models; from the scale factors we could determine 66% of Pnma phase and 33% of Cmcm coexisting in equilibrium during the two hours of data acquisition at 773 K. The 873 K pattern (Fig. S4) already corresponds to a pure Cmcm phase, as well as the 973 K diagram (Fig. S5); the crystal structure was modeled as belonging to the TlI family [94] with both Sn and Se atoms at 4c (0, 1/4, z) positions. Table S4 includes the results of the simultaneous refinement of both Pnma and Cmcm phases identified at 773 K, and Tables S5 and S6 contain the structural details for the high-temperature phase at 873 K and 973 K, with unit-cell parameters a = 4.3132 (12) Å, b = 11.750 (3) Å, c = 4.3297 (13) Å, V = 219.42 (11) Å³.

Figure 4 (right panel) displays a view of the Cmcm crystal structure at 873 K. It is also a layered structure showing a more regular arrangement of Sn and Se atoms, this time exhibiting SnSe5 polyhedra confined within each layer (perpendicular to the b axis). Very interestingly, in the case of the high-temperature phase defined in the Cmcm space group,
the mixed refinement of the Sn,K positions led to positive occupancy factors for K, suggesting that this element stored in the interlayer space in the low-temperature phase is assimilated into the Sn positions in the high-temperature phase, probably because of the superior coordination number of this crystal structure. Both phases coexist at the same temperature of 773 K, indicating the sudden formation of strongly intra-layer covalent bonds between Sn and Se, therefore weakening the Van-der-Waals bonds between layers.

Figure 5 depicts the phase diagram displaying the thermal evolution of the unit-cell parameters of both orthorhombic phases. Upon heating, the \(b\) and \(c\) unit cell parameters of the \(Pnma\) space group tend to become identical, giving rise to similar values of \(c\) and \(a\) parameters in the \(Cmcm\) setting. The \(a\) parameter in \(Pnma\), perpendicular to the puckered layers of \(SnSe_3\) pyramids, regularly increases upon heating, even across the phase transition, yielding a correspondingly higher \(b\) parameter in \(Cmcm\).

Scanning transmission electron microscopy (STEM) confirms that potassium intercalates into the \(SnSe\) crystal in the form of random defects. The K-\(SnSe\) polycrystalline grains are observed to be a few micrometers in size. We have investigated more than a dozen grains by the means of electron energy loss spectroscopy (EELS). Figure 6 shows a chemical composition of a nanometric part of one K-\(SnSe\) grain. Panel (a) shows the region of the grain where EELS spectra are taken. The EELS spectra shown here cover just the energy range for potassium and tin edge: selenium L2,3 edge at 1436 eV has been detected in different EELS spectra (not shown). The grains are of high purity and contain only potassium (K—
L2,3 edge) and tin (Sn—M4,5 edge), as shown in a typical EELS spectrum—panel b. Panels (c) and (d) show the relative composition of K and Sn. Note that the maximum K/Sn ratio of 15/85 in this two-elements quantification yields the potassium concentration of 8.1% when all three elements are taken into the account. In conclusion, potassium is distributed inhomogeneously in the crystal matrix of SnSe with the concentrations between 0 and 9%.

The K–SnSe grain grains are highly polycrystalline and difficult to orient for the atomic resolution imaging. Figure S7 shows the high-resolution transmission electron microscopy (HR-TEM) image of a small part (20 × 22 nm) of the K–SnSe grain. The lattice parameters deduced from this image are in agreement with the values found from the neutron powder diffraction. From the contrast patterns in Fig. S7, one can see that the left part of the image is oriented nearly on the zone axis, while the right part is of different crystal orientation. Additionally, the wavelike patterns on the upper left side are the same as the “Moiré pattern” in the SnSe undulated crystal, as reported in Gainza et al. [73]. In general, Fig. S7 indicates that the title material has the same Pnma crystal structure, and the nanostructuring is similar as in as other weakly doped SnSe crystals.

Thermoelectric transport properties

The thermoelectric transport properties of the SnSe:Kx series are plotted in Fig. 7. The resistivity near room temperature is about one order of magnitude lower than the resistivity of pristine SnSe; however, at high temperature, the undoped compound shows a dramatic decrease that is not mirrored by the samples doped with potassium. Among them, SnSe:K0.05 shows the lowest resistivity, reaching 10−3 Ωm at 780 K, whereas the Seebeck coefficient of the undoped SnSe made by arc-melting shows a change of sign reflecting a p-ton-type transition [77], it does not happen in any of the K-doped compounds, as they remain firmly p-type. The Seebeck coefficient of the SnSe:Kx samples remains at around ~200 μV/K until it drops above ~700 K, indicating the start of bipolar conduction. However, the SnSe:K0.1 compound has a higher Seebeck coefficient growing above 400 μV/K, with no sign of bipolar transport. Even this is low though compared to the K-doped SnSe prepared by ball-milling, which shows a Seebeck coefficient of 500–600 μV/K for the 8–12-h milled samples [82]. However, both resistivity and Seebeck coefficient behave very similar to that reported for Sn0.99K0.01Se prepared by melting in quartz tubes [78]. The maximum power factor, S^2/σ = 0.07 mW/m K^2, is obtained in the SnSe:K0.05
composition at 700 K, comparable to that measured in the undoped sample at the same temperature.

The thermal conductivity of each SnSe:K\text{\textsubscript{x}} sample is very similar, as shown in Fig. 8. There are no significant differences between the total thermal conductivity of all the prepared compositions. In every case, the thermal conductivity of the K-doped samples is lower than that of undoped SnSe, but they all follow the same behavior corresponding to Umklapp process dominated phonon scattering [95], \( \sim \alpha T^{-1} \). The lattice thermal conductivity is almost entirely the total thermal conductivity, since the electronic thermal conductivity is irrelevant below \( \sim 800 \) K in these arc-melted tin selenides [77]. For all the samples, we obtain an ultra-low thermal conductivity [57] (< 0.4–0.5 W/m K) at high temperature, an important feature for high-performance thermoelectric materials, probably due to the absence of tin oxides at the grain boundaries, promoted by the potassium doping [82], as well as the strong and multifaceted nanostructuring (see Fig. S7), already seen in the undoped compound [73].

The figure of merit of SnSe:K\text{\textsubscript{x}} compounds is displayed in Fig. 9. The ZT peak is reached at \( \sim 700 \) K, with a maximum value of \( \sim 0.15 \) for the Sn\textsubscript{0.95}K\textsubscript{0.05}Se compound. This ZT shown by our non-optimized samples is similar to other values reported for SnSe doped with different alkali elements, with figures of merit around 0.2–0.4 at 700 K [78].

A single parabolic band (SPB) analysis of the measured results is summarized in Figs. 10 and 11. Figure 10a shows the Figure of Merit as a function of the reduced chemical potential, \( \eta \). This relation, determined by the thermoelectric quality factor B [96, 97], is a very useful tool to assess the potential...
performance of a thermoelectric material regardless of doping. The chemical potential is a magnitude that we can modify, in some measure, with proper doping. According to the analysis, for SnSe:K0.1 the Fermi-level lies far from the optimum position. This simple model predicts a $ZT$ of 0.2 for the SnSe:K0.1 and SnSe:K0.05 compounds at 723 K with properly modified chemical potential. This maximum value is in line with some data reported for SnSe doped with 1% K, which shows a figure of merit of $\sim 0.4$ at 700 K [78, 82].

The weighted mobility is below 5 cm$^2$/V s in all the compositions up to 800 K. This value is quite lower than that reported for PbTe or Mg$_3$Sb$_1$Bi$_{1.5}$ (above 100 cm$^2$/V s) [98]. The variations observed for the SnSe:K0.1 come from the slight variations of the resistivity with temperature, that can be observed in Fig. 7a. However, the net weighted mobility is very low at all temperatures, so these variations do not affect the transport analysis.

The electronic quality factor [99] for the compositions with potassium reaches a higher value than that of the undoped compound, as shown in Fig. 11b. The electronic quality factor for the SnSe:K0.025 remains almost the same, making clear that a certain minimum quantity of potassium doping is needed in order to observe significant changes in the carrier transport.
Conclusions

Summarizing, we have demonstrated that K doping has important repercussions on the transport properties of SnSe, which may be articulated as a function of some of the structural properties unveiled from neutron diffraction data. We observed that below the $Pnma$-to-$Cmcm$ structural phase transition, K ions cannot be located by diffraction methods, but the conspicuous expansion along the $a$ axis suggests that they are present in the interlayer space, also confirmed by STEM-EELS spectroscopic images. The transition to the more symmetric $Cmcm$ structure, where the coordination index increases from 3 to 5, facilitates the incorporation of large K$^+$ ions into the Sn positions, where they can indeed be located from NPD data. This incorporation drives important consequences concerning the electronic transport, accounting for the comparatively much higher resistivity above 700 K, where the K migration from the interlayer space to the Sn positions is triggered by the phase transition. Indeed, the electronic resistivity of pristine SnSe reaches values inferior by two orders of magnitude to the doped specimen at 800 K, which explains the poor Figure of Merit reached by K-doped specimens. At the same time, the characteristic change of sign of the Seebeck coefficient is also altered by the partial occupancy of Sn sites by K atoms. Finally, the K doping results in an additional decrease of the thermal conductivity, probably as a consequence of the structural disordering induced by the substitutional incorporation of K.

Supplemental information

Supplemental Information includes Supplemental Experimental Data on crystal structure, and calculations based on the single parabolic band model (SPB) of the predicted maximum ZT figure of merit, weighted mobility and electronic quality factor in 3 Figures and 1 Table can be found with this article online at [link inserted by JMS].

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Author contributions

JG, JAA and NNM conceived and designed the study. JG and SM synthesized the samples. JG, JLM, NNM and OJD characterized the thermoelectric performance. JG, FS, JAA and MTFD carried out and analyzed the NPD data. NB carried and analyzed STEM/EELS measurements. JG and NNM coordinated the writing of the manuscript with discussion and input from all authors.

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Data and code availability

The authors declare that data supporting the findings of this work are available within the article and the Supplemental Information. Any other data are available from the Lead Contact upon request.

Materials availability

This study did not generate new unique reagents. K-doped SnSe may be available upon request.

Declarations

Conflict of interest The authors declare no competing interests.

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