



Full paper

Direct observation of vast off-stoichiometric defects in single crystalline SnSe



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ABSTRACT

Single crystalline tin selenide (SnSe) recently emerged as a very promising thermoelectric material for waste heat harvesting and thermoelectric cooling, due to its record high figure of merit ZT in mediate temperature range. The most striking feature of SnSe lies in its extremely low lattice thermal conductivity as ascribed to the anisotropic and highly distorted Sn–Se bonds as well as the giant bond anharmonicity by previous studies, yet no theoretical models so far can give a quantitative explanation to such low a lattice thermal conductivity. In this work, we presented direct observation of an astonishingly vast number of off-stoichiometric Sn vacancies and Se interstitials, using sophisticated aberration corrected scanning transmission electron microscope; and credited the previously reported ultralow thermal conductivity of the SnSe single crystalline samples partly to their off-stoichiometric feature. To further validate the conclusion, we also synthesized stoichiometric SnSe single crystalline samples, and illustrated that the lattice thermal conductivity is deed much higher as compared with the off-stoichiometric single crystals. The scattering efficiency of individual point defect on heat-carrying phonons was then discussed in the state-of-art Debye–Callaway model.

1. Introduction

Thermoelectricity, a physical phenomenon that converts heat directly to electricity or *vice versa*, can provide added efficiencies to ameliorate the fierce conflict between rising energy consumption and exhausting fossil fuels [1,2]. The performance of a specific thermoelectric material is evaluated by a dimensionless figure of merit (ZT), which is defined as $ZT = (S^2 \sigma / \kappa) T$, where S , σ and κ are the Seebeck coefficient, electrical conductivity and thermal conductivity, respectively [3–5]. Among the various promising thermoelectric materials working in the mediate-temperature range, SnSe has attracted strong interest since few years ago, not only because a peak ZT value of 2.6 [6] at 923 K was reported in its pristine single crystalline form, but also a broad ZT plateau over 1 was achieved when the single crystal was properly hole doped [7,8]. SnSe has a layered orthorhombic crystal structure at room temperature (space group $Pnma$, #62) with two-atom-thick slabs (along b - c plane) of strong Sn–Se bonds stacking along a axis; as temperature increases to ~ 800 K, it converts to a more

symmetric crystallographic structure (space group $Cmcm$, #63), where superior thermoelectric performance was achieved.

One of the most striking features of single crystalline SnSe is the ultralow lattice thermal conductivity in a direction along which the Sn–Se slabs are stacked. It has been argued [6] that the highly distorted SnSe₇ polyhedral coordination and sterically accommodated Sn²⁺ lone-pairs cause giant bond anharmonicity, which was deemed the main reason for the extremely low lattice thermal conductivity. Further studies *via* inelastic neutron scattering (INS) and first-principles simulations by Delaire et al. [9] provided strong evidence that electronic structure instability of the SnSe lattice, associated with a transverse optical phonon mode softening and broadening, causes giant ionic-potential anharmonicity and intense phonon scattering. Despite these reasonable qualitative physical pictures and analysis, no quantitative account of the ultralow thermal conductivity in SnSe single crystals has been given so far. Theoretical simulations based on first-principles calculations and phonon Boltzmann Transport Equation (BTE) always showed significantly higher lattice thermal conductivities

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than experimental values [6,8,10,11], even with higher-order interatomic interactions and bond anharmonicity already included in these simulations. Another pending issue in SnSe is that the typical experimental thermal conductivity values of polycrystalline samples are larger than those of single crystals [12–14], which is beyond rule of thumb for phonon scattering considering the effect of grain boundary scattering. Although a recent neutron diffraction study demonstrated that an ultralow thermal conductivity value $< 0.2 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature could be obtained in off-stoichiometric polycrystalline SnSe [15,16], no further experimental or theoretical evidences have been given yet to support these conclusions. This potential controversy regarding the thermal conductivity of SnSe and its physical nature motivated us to investigate the underlying mechanisms in more details. As for the experimental lattice thermal conductivity values, one might argue that the strong tendency of the fragile SnSe crystals to cleave along the *bc* plane leaves micro-gaps in the specimens which can complicate specimen preparations and the accuracy of some thermal conductivity measurements; besides, oxidation was also reported to affect the exact value of lattice thermal conductivity significantly [17]. In this work, our recent findings *via* aberration corrected scanning transmission electron microscopy (STEM) revealed another possibility, since we have directly observed in our SnSe and $\text{Sn}_{0.985}\text{Na}_{0.015}\text{Se}$ single crystals [6,8] an astonishingly large number of point defects, *i.e.*, Se interstitials and Sn vacancies. Electron probe micro-analysis also validated severe off-stoichiometry in them. In contrast, in the almost stoichiometric single crystal synthesized by our collaborators (at NIMTE, using horizontal gradient freezing method), no such point defects were seen under STEM. The strong scattering of heat-carrying phonons by these defects can then be used to resolve the puzzles associated with the previously reported ultralow lattice thermal conductivity in single crystalline SnSe and $\text{Sn}_{0.985}\text{Na}_{0.015}\text{Se}$ samples.

2. Results and discussions

2.1. Discrepancy between experimental and simulated lattice thermal conductivity in SnSe single crystal

First, we present the calculated thermal conductivity of perfect SnSe single crystal along *a*, *b* and *c* directions, respectively, as shown in Fig. 1(a), where the mass density has already been corrected according to a recent comment by Wei et al. [18]. The calculations were obtained *via* feeding the second-order and third-order interatomic force constant (IFC) derived from density functional theory (DFT) into the Boltzmann transport equation (BTE), where the contributions of all phonon modes are well taken into account (details in Supplementary information). Our simulations are in decent agreement with a previously published work by Huang et al. [11]. It is also remarkable that the cut-off radius for third-order IFC used in our anharmonic calculations is as large as 6.5 Å, to allow adequate atomic interaction range as suggested by Delaire et al. [9]. To avoid any unnecessary complications related to the phase transition, our simulations and discussion are limited to the low-temperature *Pnma* phase (below 750 K). Hereafter, we denote these calculated results as κ_{BTE} , to distinguish them from a later simulation using the Callaway model (κ_{CM}). Indeed, obvious discrepancies are found between the calculated and experimental values, Fig. 1(b), under perfect SnSe single crystal presumption; specifically, even though the simulated results do indicate a very low thermal conductivity they are still more than two times as large as the experimental ones, along all the three principle directions. We also present the extremely low lattice thermal conductivity values of hole doped $\text{Sn}_{0.985}\text{Na}_{0.015}\text{Se}$ [8] single crystal in this figure. We credit the small difference in lattice thermal conductivity values between pristine and hole doped samples to the Na_{Sn} substitutional point defects.

To explore what caused the discrepancies between BTE calculations and experiments, we conducted chemical composition analysis in single crystalline samples with nominal composition SnSe and

$\text{Sn}_{0.985}\text{Na}_{0.015}\text{Se}$ using the electron probe micro-analysis (EPMA), which works similarly to a scanning electron microprobe but with a significantly higher resolution for chemical composition determination (~100 ppm). EPMA results indicate the Sn:Se atomic ratio is severely off-stoichiometric, and that the numbers are almost unchanged regardless of probing spots on the same sample or from sample to sample, revealing a consistent off-stoichiometric feature (Table 1). This very interesting off-stoichiometric feature might come from the segregation of Sn^{2+} and Se^{2-} at the melting state due to gravity during the crystal growing process with vertical Bridgman method. Besides, solidified Sn drops were found adhering to the inner surface of the evacuated quartz tubes at the end of synthesis process. A further study under scanning transmission electron microscope (STEM) disclosed that a large amount of Se atoms exist at the interlayer interstitial positions, and that a number of Sn vacancies are also present to accommodate the off-stoichiometric Sn-Se ratio in both SnSe and $\text{Sn}_{0.985}\text{Na}_{0.015}\text{Se}$ single crystals. The existence of interstitial point defects is schematically shown in Fig. 1(c) and to be discussed in the follow-up section. Density functional theory (DFT) calculations suggest that Se interstitials and Sn vacancies are energetically favorable, Fig. S6. Considering Se interstitials and Sn vacancies are strong phonon scattering sources for phonons with small mean free paths (MFPs) such as in SnSe, they are thus implemented into a modified Debye-Callaway model to explain the experimentally observed ultralow lattice thermal conductivity in SnSe single crystals, Fig. 1(d). The simulated lattice thermal conductivity of SnSe involving off-stoichiometry, $\kappa_{\text{CM_os}}$, is way lower than that of stoichiometric SnSe ($\kappa_{\text{CM_s}}$). Similar simulated results for $\text{Sn}_{0.985}\text{Na}_{0.015}\text{Se}$ single crystal are given in Fig. S7(b), with extra scattering from Na_{Sn} point defects taken into account.

2.2. TEM discovery of vast interstitial and vacancy point defects

In this section, we present in details the aberration corrected atomic TEM imaging of the lattice structure of SnSe. Considering the similarity in lattice structure between pristine and hole doped SnSe single crystals, the discussion associated with TEM images in the main text will be restricted to hole doped $\text{Sn}_{0.985}\text{Na}_{0.015}\text{Se}$; extra TEM images for pristine SnSe can be found in SI. Fig. 2(a)–(c) show the high angle annular dark field-scanning transmission electron microscope (HAADF-STEM) images of single crystalline $\text{Sn}_{0.985}\text{Na}_{0.015}\text{Se}$ viewed along *a*, *b* and *c* axes, respectively; multi-slice simulations, atomic models and corresponding diffraction patterns are displayed alongside. Due to the *Z* contrast, Sn and Se atomic columns can be directly distinguished by their brightness, as can be seen along *b* and *c* directions that two-atom-thick Sn-Se slabs are stacked in staggered fashion. As for *a* direction, Sn and Se columns are overlapped so that they are not distinguishable by the electron microscope. The observed atomic array is exactly the same as the reported room temperature crystallographic space group *Pnma*, confirming a layered orthorhombic crystal structure in $\text{Sn}_{0.985}\text{Na}_{0.015}\text{Se}$. Moreover, simultaneously acquired annular bright field-transmission electron microscope (ABF-STEM) images along *c* direction not only confirm the alternatively stacking of Sn-Se slabs, but also unexpectedly reveal a vast number of interstitial atoms, Fig. 2(d). Dissimilar with HAADF which has a strong *Z*-contrast, ABF has been demonstrated extremely useful in identifying atoms with weak scattering power [19,20]. That explains why interstitial atoms can be seen clearly in ABF mode rather than HAADF mode. Interstitial atoms were also observed in pristine SnSe single crystals, Fig. S1.

2.3. No interstitial and vacancy point defects & higher lattice thermal conductivity in stoichiometric SnSe samples

As we mentioned earlier, a variety of reported lattice thermal conductivity of our SnSe single crystals [6,8] might have caused potential controversies in the field of thermoelectrics. Therefore, we

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