

## MEM electron density and 3D- $\Delta$ PDF study of disorder in thermoelectric InTe

Thermoelectric materials can interconvert heat and electricity, and thus they can harvest waste heat as a contribution to the green transition. The thermoelectric figure of merit is defined as  $zT = \alpha^2 \sigma T / \kappa$ , where  $\alpha$ ,  $\sigma$ ,  $T$ , and  $\kappa$  are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively. Recently, significant progress in  $zT$  values has been achieved, but it is noteworthy that no new materials have reached the market due to problems with materials stability under the harsh operating conditions of a thermoelectric module [1]. A main challenge for developing a high  $zT$  is that the physical properties  $\alpha$ ,  $\sigma$  and  $\kappa$  are inter-connected and many materials design strategies have been introduced over the years to tackle this challenge. The thermal conductivity should be as low as possible and it has two contributions; one from the charge carriers and the other from the crystal lattice. The latter can be lowered through structural disorder due to interstitial, disordered, and diffusive atoms. Disorder is well known in complex thermoelectric materials such as  $Zn_4Sb_3$  [2] but it is rarely seen in simple crystal structures. We have combined single-crystal synchrotron X-ray diffraction, diffuse scattering, the maximum entropy method, the 3D- $\Delta$ PDF method, physical property measurements and theoretical calculations, to observe and characterize one-dimensional disordered  $In^{1+}$  chains in InTe [3]. The crystal structure contains a significant  $In^{1+}$  vacancy along with interstitial indium sites. Intriguingly, the disordered  $In^{1+}$  chains undergo a static-dynamic transition with increasing temperature to form a one-dimensional diffusion channel. The present work provides an experimental basis for understanding ultralow thermal conductivity in a broad range of thermoelectric materials.

InTe has ultralow thermal conductivity [3], which

is much lower than for famous thermoelectric binary tellurides such as PbTe and  $Bi_2Te_3$ . It crystallizes in the TlSe-type structure and it can be described by the formula  $In^{1+}In^{3+}Te_2^-$ . The  $In^{3+}$  ions are tetrahedrally coordinated to  $Te^{2-}$  ions forming  $(InTe_2)^-$  chains along the  $c$  axis while the  $In^{1+}$  ions with  $5s^2$  lone pair electrons are weakly bound to a cage-like system of eight Te atoms with the square anti-prismatic arrangement (Fig. 1). Using the Bridgman method, we synthesized high quality single crystals and measured accurate single crystal X-ray scattering data at SPRING-8 BL02B1 using a high photon energy of 50.00 keV. X-ray diffraction data at 25 K had a resolution of  $\sin\theta/\lambda < 1.67 \text{ \AA}^{-1}$  and structure factors were used for Maximum Entropy Method (MEM) calculations to reconstruct the average electron density in the unit cell of the crystal [4].

The MEM electron density reveals two interstitial sites with low occupancy along the  $c$  direction, Fig. 1. Since the additional sites are close to the main  $In^{1+}$  site, vacancies must also be present on the main site. Structural refinement of a model with  $In^{1+}$  vacancies and two interstitial sites lead to an overall composition of  $In_{0.98}Te$  in perfect agreement with ICP-OES data. The new structural model leads to a drop in  $R_F$  from 2.54% to 1.33%. The observed  $In^{1+}$  vacancy agrees with formation energy calculations of native defects in InTe using density functional theory, and it explains the persistent p-type behavior of InTe.

We further conducted MEM calculations based on the single crystals data at 100–700 K, Fig. 2. With increasing temperature, the  $In^{1+}$  and interstitial In sites become delocalized and eventually form a continuous 1D channel along the  $c$  directions. At 25 and 100 K, two well separated interstitial sites are seen, but at 200 K the  $In^{1+}$  density merges with one interstitial.

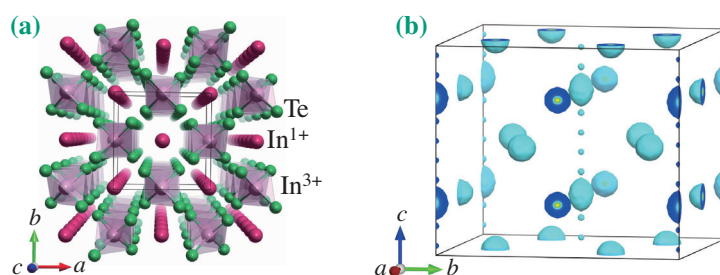


Fig. 1. (a) The ideal crystal structure of InTe along the  $c$  axis. (b) Reconstructed 3D electron density distribution of InTe by the MEM based on the high-resolution single-crystal synchrotron X-ray diffraction data at 25 K. The isosurface value is  $15 e \text{ \AA}^{-3}$ .

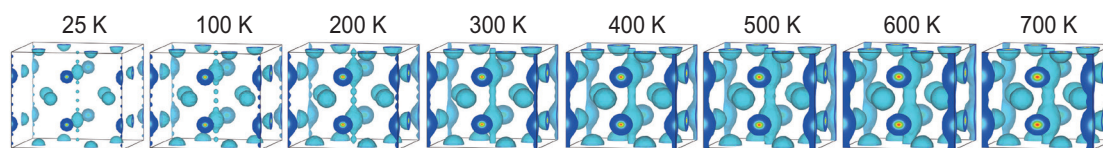


Fig. 2. Temperature-dependent 3D MEM electron density maps of InTe at 25–700 K.

As the temperature increases further a continuous 1D density channel forms along the  $c$  direction. From the time-space averaged MEM density, we cannot determine whether this dynamic behavior is induced by thermal disorder or dynamic positional disorder. However, the continuous 1D MEM density reveals that  $\text{In}^{1+}$  can diffuse or hop between sites. The diffusion/hopping increases with increasing temperatures, but it is not very high as the density value at 700 K is only  $\sim 5.3\%$  of the maximum  $\text{In}^{1+}$  peak value.

The local structural order was investigated through diffuse X-ray scattering and 3D- $\Delta$ PDF analysis [5]. The 3D- $\Delta$ PDF shows which interatomic vectors are more or less present in the real structure compared to the average crystal structure. At 25 K there are strong correlations along  $z$ , but they become weaker at 300 K. Thus, the defects are strongly correlated along the 1D chains at low temperatures, but less

so at higher temperatures, Fig. 3. At 25 K a positive peak observed at  $5.8 \text{ \AA}$  corresponding to the  $\text{In}_i(1)$  and an  $\text{In}_i(2)$  separation, which suggests the Frenkel pairs tend to be separated by this distance at low temperature.

The disordered  $\text{In}^{1+}$  ions contribute to the ultralow lattice thermal conductivity in InTe. The nearly temperature-independent behavior ( $\sim T^{-0.1}$ ) in thermal conductivity at  $\sim 25\text{--}80 \text{ K}$  may be attributed to the disorder revealed by the MEM density and 3D- $\Delta$ PDF. With increasing temperature the intrinsic phonon-phonon scattering becomes dominant, but the thermal conductivity has a weaker temperature dependence than expected probably due to the tunneling contribution from interstitial, disordered, diffusive  $\text{In}^{1+}$  ions. The detailed description of structural disorder in InTe is helpful for developing models to understand ultralow thermal conductivity.

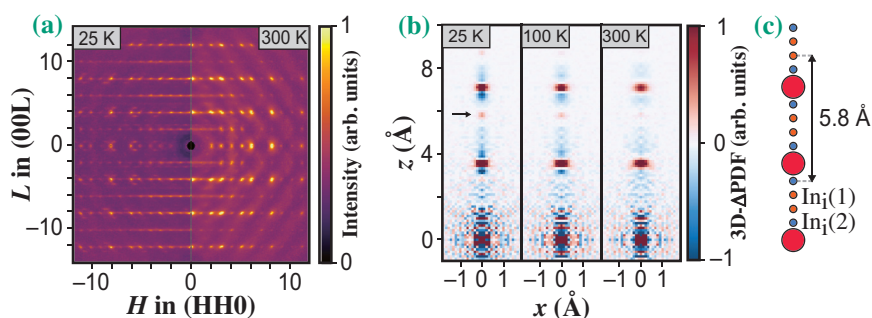


Fig. 3. (a) Measured diffuse X-ray scattering of InTe in the  $HHL$  plane at 25 and 300 K. (b) The 3D- $\Delta$ PDF along  $z$  at 25, 100 and 300 K. (c) Illustration of the 1D  $\text{In}^{1+}$  chain with the characteristic distance between interstitial sites marked, corresponding to the positive peak marked in (b) by a black arrow.

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