

Synthesis and physical properties of single-crystalline InTe: Towards high thermoelectric performance

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1). Discussion of various structural models for the possible low-temperature phase transition of InTe

As shown in the main text, low-temperature PXRD measurements below 200 K evidence the developments of extra reflections, which may be straightforwardly ascribed to either a structural transition or a phase decomposition. Of note, measurements performed over several hours reveal that these additional reflections only appear after at least seven hours, which seems in par with a slow decomposition of the main phase, kinetically slowed down at low temperatures. While the appearance of additional reflections is consistent with the results reported by Back *et al.*¹, only two reflections have been observed in their study due to the problem of preferred orientation of the crystallites that also impacts the intensity of these additional reflections.

The two extra Bragg reflections observed in Ref. 1 were interpreted as a transition to an orthorhombic lattice distortion, with the *Ibam* space group proposed to describe the low-temperature crystal structure. In reducing the symmetry from *I4/mcm* to *Ibam*, the *8h* site of the Te atoms splits into *4a* and *4b* Wyckoff positions, which become equivalent to those of the In1 and In2 atoms. However, this orthorhombic space group does not index all of the six additional reflections we observe, unambiguously showing that the low-temperature PXRD pattern does not correspond to a weak lattice distortion described in the *Ibam* space group. Further attempts at indexing the entire pattern by considering a weak lattice distortion of the tetragonal unit cell were considered but remained unsuccessful. Intriguingly, no significant changes in the Bragg reflections associated with the room-temperature tetragonal structure of InTe are observed upon cooling, suggesting that the tetragonal phase only experiences a lattice contraction upon cooling without any obvious change in symmetry. Hence, we further tried to index the PXRD pattern by assuming the growth of a secondary phase out of the main tetragonal phase. Within this

approach, the low-temperature PXRD pattern at 115 K could be successfully indexed by considering a decomposition of InTe into a two-phase mixture consisting in the room-temperature tetragonal phase and a previously-unknown hexagonal phase with an estimated volume ratio of 85% – 15%, respectively, from Rietveld refinements. The different symmetry of the two phases indicates that such a decomposition would not correspond to an exsolution process, as observed for instance in tetrahedrites,²⁻⁴ that would yield two phases of distinct chemical compositions but with the same crystal structure. A possible origin of this decomposition might be related to an incomplete martensitic-like decomposition of the main InTe phase.

Assuming that InTe experiences a phase decomposition into a low-temperature hexagonal phase, two possible structural models were then considered. A first model, based on the ZnO structure type described in the $P6_3mc$ (or, equivalently, the non-centrosymmetric $P6_3/mcm$) space group with lattice parameters $a = 4.557 \text{ \AA}$ and $c = 7.416 \text{ \AA}$, accounts for all the additional reflections (see Figure S1 below). However, the mismatch between the experimental and theoretical relative intensities implies a strong preferred orientation of the crystallites that could possibly be due to their nucleation within the InTe matrix. An alternative model that also accounts for both the six extra reflections and their relative intensities is based on SiC polytypes, which correspond to structural variants of the ZnO structure type with a lattice parameter a practically unchanged but with a significantly higher c parameter that can reach $\sim 345 \text{ \AA}$.⁵⁻⁷ Both structure types are formed by infinite chains of In-Te tetrahedra stacked along the c axis that resemble the chain-like organization of these tetrahedra in the tetragonal phase of InTe. However, although appealing, this structural model would imply a significant distortion of the atomic environment of the In₂ atoms to become tetrahedral. For this reason, whether these models really account for the extra reflections remains an open question.

At this stage, although a phase decomposition provides a straightforward explanation, the crystallization of hexagonal ice during the PXRD measurements cannot be strictly ruled out. This extrinsic origin would account for all the six extra reflections observed, also explaining the time required to observe their appearance and the absence of obvious modifications of the reflections of the tetragonal phase of InTe upon cooling. Intriguingly, the above-mentioned lattice parameters inferred from the Rietveld refinements closely correspond to those reported for hexagonal ice, lending further credit to this scenario.

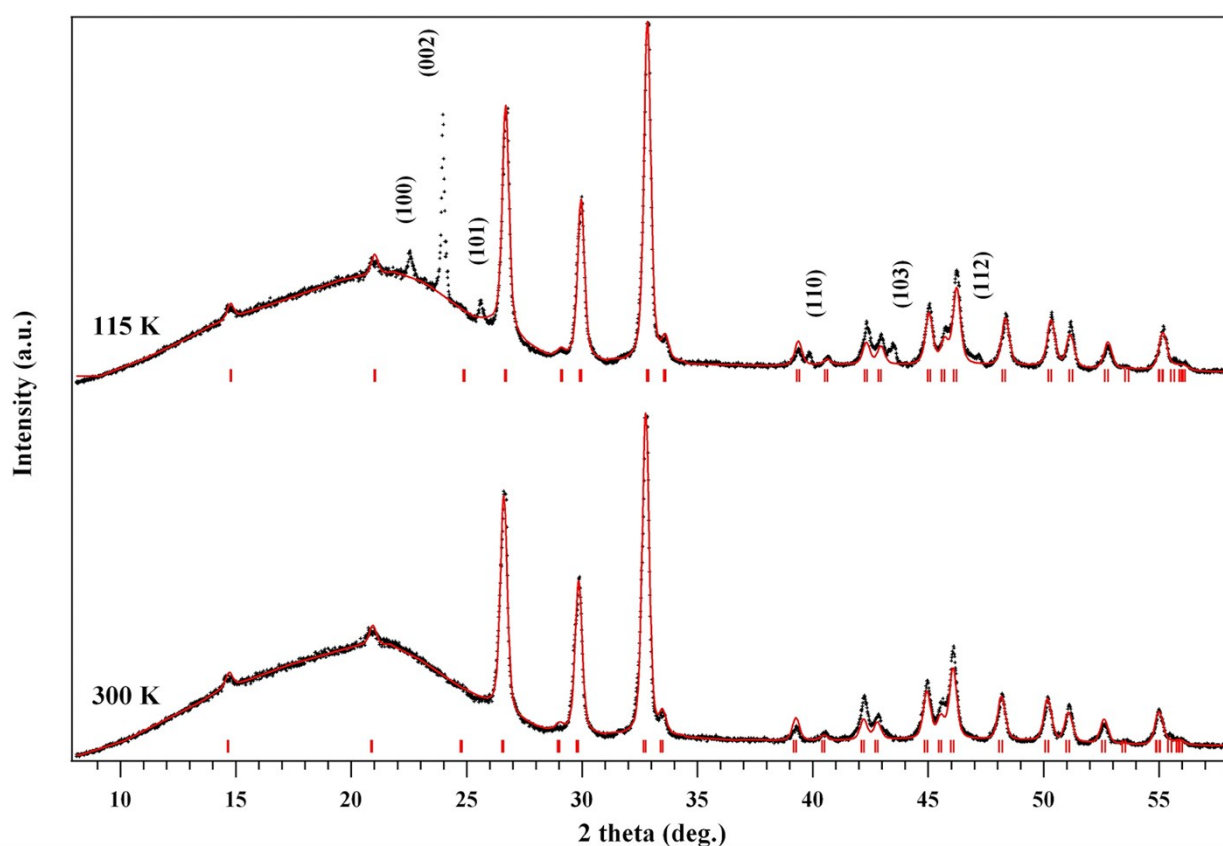


Figure S1. PXRD patterns measured at 300 (upper pattern) and 115 K (lower pattern) with the theoretical reflections of tetragonal InTe superimposed in red, showing the position of the six extra reflections on the 115 K pattern. The Rietveld refinement of the PXRD pattern collected at 115 K shows that all the extra reflections can be indexed by considering a hexagonal unit cell described in the $P6_3mc$ space group.

2). Possible scenarios explaining the anomaly observed in the $R_H(T)$ data

Hall effect measurements revealed a clear anomaly in the $R_H(T)$ data below 200 K, a temperature that closely corresponds to that below which extra reflections appear in the PXRD patterns. We note that this anomaly cannot be related to a possible anomalous Hall effect due to the non-magnetic character of InTe down to 5 K demonstrated by magnetization curves (see Figure S2 below). Both characteristics make a close connection between this anomaly and a phase decomposition plausible. In such a case, the resulting low-temperature microstructure of the sample, equivalent to a two-phase mixture, might result in the observed anomaly in $R_H(T)$, depending on the transport properties of both phases.

Alternatively, should the extra reflections proved to be due to ice, two other scenarios might explain the observed characteristics of this anomaly. A first possibility is related to temperature effects inducing slight modifications of the electronic band structure near the chemical potential. Electronic band structure calculations have shown that the Fermi level crosses two valence bands near the M and Z points of the Brillouin zone.^{1,8-10} The very low ν value, close to that measured in elemental Bi, indicates that the chemical potential nears the edge of the valence bands. Upon cooling, one of these two valence band maxima might slightly shift away from the chemical potential, giving rise to the increased R_H values observed below 200 K. The disappearance of this anomaly below 150 K might be due to a further shift in the relative position of these two maxima, recovering an electronic scheme equivalent to that existing near room temperature. Because the very low density of states at the Fermi level would remain weakly impacted by the energy shift of one of these bands, this temperature-induced mechanism may explain the absence of concomitant signature in the thermopower.

Alternatively, a second possibility might be related to the Umkehr effect, that is, an asymmetry in the magnetotransport tensors under sign reversal of the magnetic field.¹¹⁻¹³ This effect, demonstrated in elemental Bi, strongly depends on the crystalline direction along which the magnetic field is applied, which would explain the difference in the anomaly observed in InTe along the two crystalline directions probed and its sole presence in transport data collected under magnetic field. This second scenario may be confirmed or invalidated by further measurements of the magneto-thermopower under magnetic fields higher than those probed herein for which a stronger asymmetry may be observed.

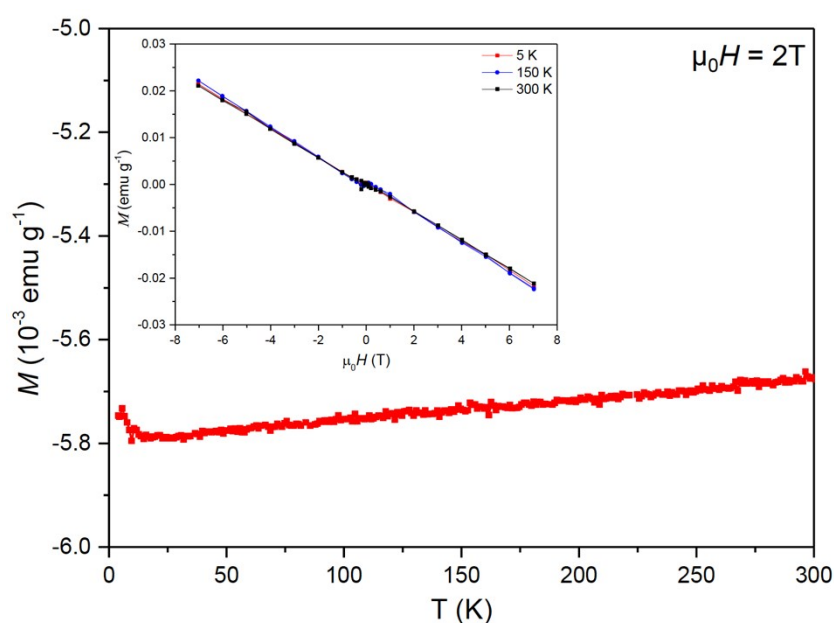


Figure S2. Temperature dependence of the magnetization M measured under an applied magnetic field of 2 T for single-crystalline InTe. Inset: Magnetization curves as a function of the magnetic field collected at 5, 150 and 300 K.

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