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# Thermoelectric properties of the $\alpha$ -As<sub>2</sub>Te<sub>3</sub> crystalline phase

## Authors

J-B. Vaney<sup>1,2</sup>, J. Carreaud<sup>2</sup>, G. Delaizir<sup>2</sup>, C. Morin<sup>3</sup>, J. Monnier<sup>3</sup>, E. Alleno<sup>3</sup>, A. Piarristeguy<sup>4</sup>, A. Pradel<sup>4</sup>, A.P. Gonçalves<sup>5</sup>, E.B. Lopes<sup>5</sup>, C. Candolfi<sup>1</sup>, A. Dauscher<sup>1</sup>, B. Lenoir<sup>1</sup>

## Affiliations

<sup>1</sup>*Institut Jean Lamour (IJL), UMR 7198 CNRS-Université de Lorraine, France*

<sup>2</sup>*SPCTS, Université de Limoges UMR CNRS 7315, France*

<sup>3</sup>*Institut de Chimie et des Matériaux de Paris Est (ICMPE), UMR 7182 CNRS, CMTR, Thiais, France*

<sup>4</sup>*Institut Charles Gerhardt (ICG), UMR 5253 CNRS-Université Montpellier 2, France*

<sup>5</sup>*C2TN Instituto Superior Técnico, Universidade de Lisboa, P-2695-066 Bobadela LRS, Portugal*

## Abstract

As<sub>2</sub>Te<sub>3</sub> exists in two allotropic configurations:  $\alpha$ - and  $\beta$ -As<sub>2</sub>Te<sub>3</sub>, of which only the latter crystallizes in the same rhombohedral structure-type as Bi<sub>2</sub>Te<sub>3</sub>. While  $\beta$ -As<sub>2</sub>Te<sub>3</sub> shows interesting thermoelectric properties that can be adjusted through alloying, the transport properties of the monoclinic phase  $\alpha$ -As<sub>2</sub>Te<sub>3</sub>, more thermodynamically stable than the  $\beta$ -phase at room temperature, has not yet been studied thoroughly. We report here on the preparation by powder metallurgy and on the microstructural characterization of polycrystalline  $\alpha$ -As<sub>2</sub>Te<sub>3</sub>. Preliminary results on the electrical and thermal properties measured between 5 and 523 K are also reported. Transport properties measurements were performed both along and perpendicular to the pressing direction indicating that the transport properties demonstrate some degree of anisotropy. Remarkably, low thermal conductivity values (below 1 W.m<sup>-1</sup>.K<sup>-1</sup> above 300 K) were measured suggesting that this compound may be an interesting platform to design novel thermoelectric materials with high efficiency.

## Introduction

Thermoelectric materials offer an effective way to convert thermal energy into electrical energy (Seebeck effect) and, reciprocally, electrical energy into thermal energy (Peltier effect). The performance of thermoelectric devices is directly related to the materials' dimensionless thermoelectric figure of merit  $ZT$  defined by

$$ZT = \frac{\alpha^2 T}{\rho \lambda} = \frac{PT}{\lambda}$$
 where  $T$  is the absolute temperature,  $\alpha$  is the Seebeck coefficient (or thermopower),

$P = \alpha^2 / \rho$  is the power factor,  $\rho$  is the electrical resistivity and  $\lambda$  is the total thermal conductivity. For decades, the performance of thermoelectric (TE) materials have been limited, confining them to niche applications and markets [1]. Owing to strong interdependence between the three transport properties, achieving high  $ZT$  on a broad temperature range still remains the most challenging aspect in thermoelectricity [2, 3].

Recently, the metastable  $\beta$ -As<sub>2</sub>Te<sub>3</sub> phase, isostructural to the state-of-the-art Bi<sub>2</sub>Te<sub>3</sub> based materials, showed interesting performance upon substitution of Sn for As, with peak  $ZT$  around 0.6 at 423 K [4]. As<sub>2</sub>Te<sub>3</sub> however exists in two allotropic forms: the rhombohedral  $\beta$ -As<sub>2</sub>Te<sub>3</sub>, firstly described at high pressure [5] and then obtained at room pressure by rapid quenching from the melt [6, 7], and the monoclinic  $\alpha$ -As<sub>2</sub>Te<sub>3</sub> [8], the former transforming into the latter upon heating above 410 K.  $\alpha$ -As<sub>2</sub>Te<sub>3</sub> has been scarcely studied from the thermoelectric point of view but may show interesting properties as early studies [9, 10] and first-principles calculations hint at [11]. Herein, we describe the crystalline structure of  $\alpha$ -As<sub>2</sub>Te<sub>3</sub> and its successful synthesis and shaping by Spark Plasma Sintering (SPS) technique. The thermoelectric properties of this binary compound are further probed between 5 and 523 K. Although the maximum  $ZT$  remains very low, our results suggest that there is still much room for further improvement upon alloying if the carrier concentration can be properly controlled.

## Experimental details

The  $\alpha$ -As<sub>2</sub>Te<sub>3</sub> sample was prepared by direct reaction of stoichiometric amounts of pure elements (As (Goodfellow, 99.99%, shots) and Te (5N+, 99.999%, shots)) sealed under secondary vacuum (10<sup>-5</sup> mbar) in quartz tubes. The tubes were heated slowly up to 923 K at a rate of 10 K min<sup>-1</sup>, dwelt at this temperature for 2 hours and finally quenched in iced water. At this step the  $\beta$ -phase was obtained [4]. The ingot was subsequently

annealed at 613K for 3 days to finally obtain the pure  $\alpha$ -As<sub>2</sub>Te<sub>3</sub> phase. The resulting ingots were ground into micron-sized powders and consolidated by SPS (Spark Plasma Sintering) into 10 mm diameter cylindrical pellet under a pressure of 50 MPa at a temperature of 613K for 2 minutes. The obtained pellet showed a relative density close to 99% of the theoretical density.

The crystal structure was determined by powder X-ray diffraction (PXRD) at 300 K with a Bruker D8 Advance instrument using CuK $\alpha$ <sub>1</sub> radiation. The chemical homogeneity of the sample was checked by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDXS) using a Quanta FEG (FEI). Electron Probe Micro-Analysis (EPMA) was performed with a JEOL JXA 8530F equipped with wavelength-dispersive spectrometers. Backscattered electrons were used for imaging the surface of the samples. In order to minimize matrix effects, X-ray intensities of As and Te were compared with those of a calibrated  $\beta$ -As<sub>2</sub>Te<sub>3</sub> standard for quantitative analysis. The chemical compositions of the  $\alpha$ -As<sub>2</sub>Te<sub>3</sub> specimens were determined from analysis of a set of at least 90 different points for each sample. Bulk pieces of the densified sample were carefully polished down to 1  $\mu$ m alumina powder for EPMA analysis.

The thermoelectric properties were measured between 5 and 523 K on well-shaped samples cut with a diamond wire-saw (typical dimensions of 2 $\times$ 3 $\times$ 8 mm<sup>3</sup>). Owing to the anisotropic crystal structure of the present compound, the transport properties were measured on samples cut both parallel and perpendicular to the pressing direction.  $\alpha$  and  $\rho$  data were collected in the 300 – 523 K temperature range using a ZEM-3 apparatus (ULVAC-RIKO). Thermal diffusivity  $a$  was measured by a laser flash technique (Netzsch LFA 427) between 300 and 523 K. The specific heat  $C_p$  was measured by differential scanning calorimetry (DSC Netzsch Pegasus) above room temperature. The thermal conductivity was then calculated via  $\kappa = a \cdot C_p \cdot d$  where  $d$  is the density measured using the mass and the geometric dimensions of the densified pellet. The density was considered temperature-independent in the present case. The errors for each measured properties are estimated to be about 5% so that the combined uncertainty on the  $ZT$  values is about ~20%. To measure the thermoelectric properties between 5 and 300 K, we used the thermal transport option (TTO) of a physical property measurement system (PPMS, Quantum Design). These measurements were conducted by brazing four copper bars on the samples to ensure excellent electrical and thermal contacts. Specific heat was measured on a small prism-shaped sample (mass of ~ 15 mg) from 2 to 260 K using the He<sup>4</sup> option of the PPMS.

# Results and discussion

## Structural and chemical characterizations

The study of  $\alpha$ -As<sub>2</sub>Te<sub>3</sub> is to be put in perspective with its allotropic counterpart  $\beta$ -As<sub>2</sub>Te<sub>3</sub>. The metastable  $\beta$ -As<sub>2</sub>Te<sub>3</sub> (space group  $R\bar{3}m$ ), produced by rapid quenching [6] or under high pressures [7], transforms into the  $\alpha$  structure (space group  $C2/m$ ) upon heating above 410K [12]. The perspective views of the unit cell of both structures (the hexagonal cell of  $\beta$ -As<sub>2</sub>Te<sub>3</sub> is displayed rather than the rhomboedric cell) are represented on Figure 1. It could be expected that both are very close and that the  $\alpha$  form would appear as a distorted version of the more ordered  $\beta$ -structure. Projections of the atomic arrangements of the  $\alpha$ - and  $\beta$ -phases along their  $a$ -axis are displayed on Figure 2. It can be clearly observed that both show layered arrangements with alternating As-planes and Te-planes. However, upon closer examination, these projections reveal different sequences separated by van der Waals bonding with a quintet sequence Te<sub>1</sub>-As-Te<sub>2</sub>-As-Te<sub>1</sub> for  $\beta$ -As<sub>2</sub>Te<sub>3</sub> in the  $c$ -direction and a zigzag stacking for the  $\alpha$ -As<sub>2</sub>Te<sub>3</sub> structure [13].

Figure 3 presents the powder X-ray diffraction (PXRD) pattern collected on the binary sample  $\alpha$ -As<sub>2</sub>Te<sub>3</sub>. All reflections can be indexed to the  $C2/m$  space group without any additional peak that would reveal a secondary phase. Due to the anisotropy of the structure, the sample show a slight preferred orientation resulting in a very shallow renormalization of the relative intensities of the Bragg peaks. The Rietveld refinement of this pattern leads to good fits allowing determining precisely the lattice parameters, in good agreement with literature data [7]. All refined parameters are described in Table 1. Scanning electron microscopy (SEM) and X-Ray mapping further revealed an overall homogeneous distribution of the different elements as displayed in Figure 4. EPMA gave an average composition of As<sub>1.99</sub>Te<sub>3.01</sub> for the compound, which is close to the nominal one.

**Table 1: Parameters of the power X-Ray diffraction of the  $\alpha$ -As<sub>2</sub>Te<sub>3</sub> phase obtained by Rietveld refinement.**

a (Å)	b (Å)	c (Å)	$\beta$ (°)
14.3392	4.0147	9.8859	95.046
Atomic position	x	y	z
As <sub>1</sub>	0.6135	0.0000	0.4406
As <sub>2</sub>	0.2014	0.0000	0.1413

Te <sub>1</sub>	0.2906	0.0000	0.2887
Te <sub>2</sub>	0.7779	0.0000	0.3401
Te <sub>3</sub>	0.3753	0.0000	0.0360
Reliability factors	R <sub>WP</sub>	R <sub>Bragg</sub>	$\chi^2$
	11.41	4.024	8.04

### Thermoelectric properties of the binary phase $\alpha$ -As<sub>2</sub>Te<sub>3</sub>

The temperature dependences of  $\rho$  and  $\alpha$  measured parallel and perpendicular to the pressing direction are displayed on Figures 5-A and 5-B respectively. Both properties exhibit a slight anisotropy, clearly observed below 200 and above 150 K in the  $\rho(T)$  and in the  $\alpha(T)$ , respectively. Over the entire temperature range, the electrical resistivity in both direction displays an activated behavior with values ranging from around 1  $\Omega\cdot\text{m}$  at 5 K to less than 600  $\mu\Omega\cdot\text{m}$  at 500 K. The high-temperature region can be described by an Arrhenius law  $\rho = \rho_0 \cdot \exp[E_a/k_B T]$  (shown by the solid line in the inset of Fig. V5-A), where the activation energy  $E_a = 65$  meV,  $k_B$  the Boltzmann's constant and  $\rho_0$  is a constant. This activation energy could imply an intrinsic semiconducting gap of  $\sim 130$  meV. This result is however different from that of Sharma et al. [11] deduced from ab-initio band structure calculations where a value of 0.4 eV was obtained. Below 17 K,  $\rho$  has a nearly exponential temperature dependence with much lower activation energy. The best fit to the data in this temperature region was of the form  $\rho = \rho_0 \exp[T_0/T]^{1/4}$  (where  $\rho_0$  is a constant and  $T_0$  is the characteristic temperature of the system) indicative of Mott variable range hopping.

$\alpha(T)$  does not evolve monotonously but increases with temperature up to 160  $\mu\text{V}\cdot\text{K}^{-1}$  at 250 K, followed by a two-step decrease and a transition from p- to n-type transport above 400 K in the perpendicular direction only. This behavior is likely due to the manifestation of minority carrier effect (electrons in the present case). The fact that the p- to n-type transition is only seen in the perpendicular direction may point to some degree of anisotropy in the carrier mobility as well. Doping heavily this compound would result in pushing this transition towards higher temperatures and would likely enhance the power factor  $\alpha^2/\rho$ . Comparisons between our results and the electronic transport properties predicted by band structure calculations show important deviations [11]. Among the possible reasons explaining these discrepancies, we speculate that the influence of native defects, not taken into account in the modeling, could play a major role. Actually, it is well-established that native defects such as anti-structure defects or vacancies can strongly affect the electronic transport properties in thermoelectric

materials such as bismuth telluride [14]. It is worth to note that early studies showed n-type properties for the  $\alpha$ -As<sub>2</sub>Te<sub>3</sub> binary compound [9, 10]. According to the EPMA measurement, the excess Te in our material would corroborate a transition to p-type, likely due to Te-doping on As sites as obtained by Harman for  $\alpha$ -As<sub>2</sub>Te<sub>3</sub> single crystals with excess Te.

Figure 6 displays the temperature dependence of the specific heat. Extrapolation of the low temperature data is in very good agreement with the measurements above room temperature. It is seen that the specific heat deviates slightly from the calculated Dulong-Petit value of 0.234 J/g.K between 300 and 500 K. Figure 7-A presents the temperature dependence of the thermal conductivity of  $\alpha$ -As<sub>2</sub>Te<sub>3</sub>.  $\lambda$  shows a marked dielectric peak at low temperatures centered at 25K, attaining the value of 6.5 W/m.K in the perpendicular direction and 5.1 W/m.K in the parallel direction, before decreasing to the very low value of 0.7 W.m<sup>-1</sup>.K<sup>-1</sup> at 523K. Above 300 K, the anisotropy is no longer visible to within experimental uncertainty. In this particular case where the electrical resistivity is high, the electronic contribution to thermal conductivity is negligible, so that  $\lambda$  reflects exclusively the lattice contribution. Noteworthy, the thermal conductivity of  $\beta$ -As<sub>2</sub>Te<sub>3</sub> is even lower reaching values below 0.6 W.m<sup>-1</sup>.K<sup>-1</sup> at 423K [4] with a non-negligible electronic contribution. In terms of ZT values, presented on Figure 7-B, the large electrical resistivity and the low thermopower values result in only very low ZT values around 0.001. Further studies aiming at probing the influence of different dopants are worthwhile to determine the potential of this compound for thermoelectric applications.

## Conclusion

We presented results on the thermoelectric characterization of the compound  $\alpha$ -As<sub>2</sub>Te<sub>3</sub> between 5 and 523 K. Owing to presumably low carrier concentration, the influence of minority carriers above 250 K strongly undermines the Seebeck coefficient, even leading to a sign change near 500K. Even though displaying an interesting thermal conductivity lower than 1 W.m<sup>-1</sup>.K<sup>-1</sup> above 300 K, the very low power factors (< 5.10<sup>6</sup> W.m<sup>-1</sup>.K<sup>-2</sup>) therefore do not allow achieving high ZT values. However, this is not to say that this phase does not deserve further attention. Appropriated substitutions to tune the carrier concentration may be beneficial in optimizing the ZT values.

## Figure captions

Fig 1: Perspective view of the hexagonal crystal structure  $\beta$ -As<sub>2</sub>Te<sub>3</sub> (rhombohedral of space group  $R\bar{3}m$ ,  $a = 4.0473 \text{ \AA}$  and  $c = 29.5018 \text{ \AA}$ ) (A) and  $\alpha$ -As<sub>2</sub>Te<sub>3</sub> (monoclinic of space group C2/m,  $a = 14.339$ ,  $b = 4.0114$ ,  $c = 9.8859$ ,  $\beta = 95.046$ )(B). The As atoms are represented as small red balls and the Te atoms by large blue balls.

Fig 2: Projections onto the a axis of supercells of  $\beta$ -As<sub>2</sub>Te<sub>3</sub> (A) and  $\alpha$ -As<sub>2</sub>Te<sub>3</sub> (B). The unit cells are represented by black lines, the As atoms are represented as small red balls and the Te atoms by large blue balls. The atomic plans alternation is in fact very different between the two structures. Van der waals bonding is represented by the broken green lines.

Fig 3: Powder X-Ray diffraction pattern of  $\alpha$ -As<sub>2</sub>Te<sub>3</sub>. The observed data are marked as open red circles. The calculated profile is represented by a solid black line while the difference between experimental and numerical patterns is shown by the solid blue line (RF = 4.024,  $\chi^2 = 8.04$ ). The positions of the Bragg reflections are indicated as green bars.

Fig 4: Scanning Electron Microscope (SEM) elemental contrast picture of the sample  $\alpha$ -As<sub>2</sub>Te<sub>3</sub> in Secondary electron (SE) and Back Scattering Electrons (BSE) mode, together with the corresponding element mapping of As and Te. The distribution of the elements is overall homogeneous.

Fig 5: Temperature dependence of the electrical resistivity  $\rho$  (A) and the Seebeck coefficient  $\alpha$  (B) of the polycrystalline  $\alpha$ -As<sub>2</sub>Te<sub>3</sub> sample. The measurements performed parallel and perpendicular to the pressing direction are represented by filled and open symbols respectively. Measurements at low (5-300K) and high (300-523K) temperature show great agreement at 300K. The inset in Fig 5-A represents the evolution of  $\rho$  at low temperature in  $T^{-1/4}$ .

Fig 6: Specific heat of the compound  $\alpha$ -As<sub>2</sub>Te<sub>3</sub> measured between 2 and 260 K and between 360 and 523 K. Between 260 and 300K, the influence of the addenda on the low temperature measurement does not allow to



display reliable data. In the same fashion measurement artifacts do not allow to show reliable data between 300 and 360K.

Fig 7: Temperature dependence of the thermal conductivity  $\lambda$  (A) and the figure of merit ZT (B) of the polycrystalline  $\alpha$ -As<sub>2</sub>Te<sub>3</sub> sample. The measurements performed parallel and perpendicular to the pressing direction are represented by filled and open symbols respectively. The measurements of  $\lambda$  at low (5-300K) and high (300-523K) temperature show a slight discrepancy at 300K due to issues in correcting the radiation heat loss over 200K with the TTO option of the PPMS.

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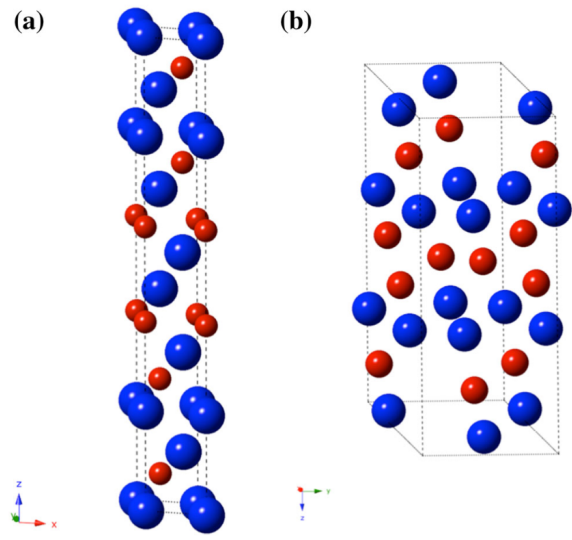


Figure 1

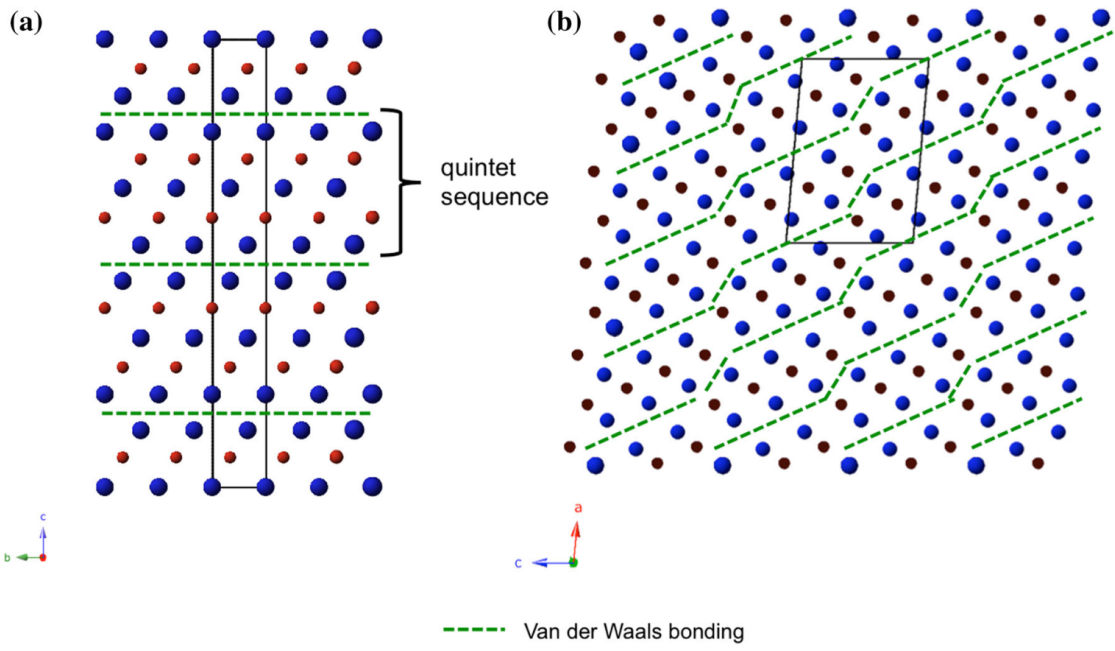


Figure 2

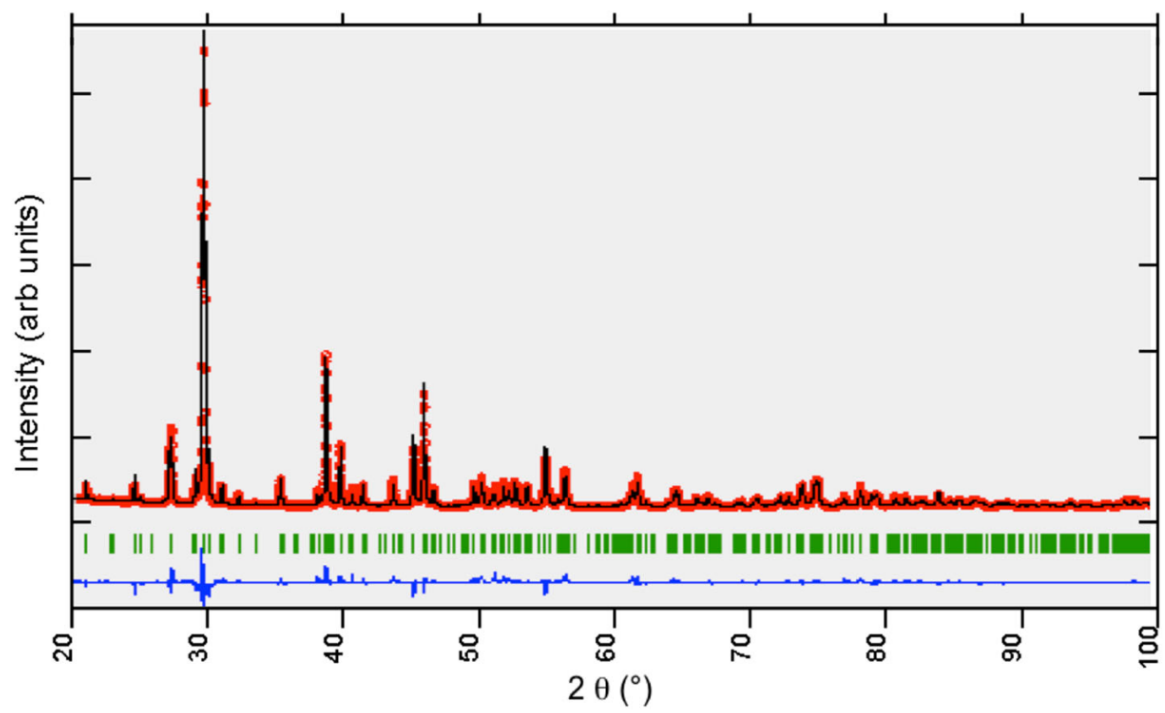


Figure 3

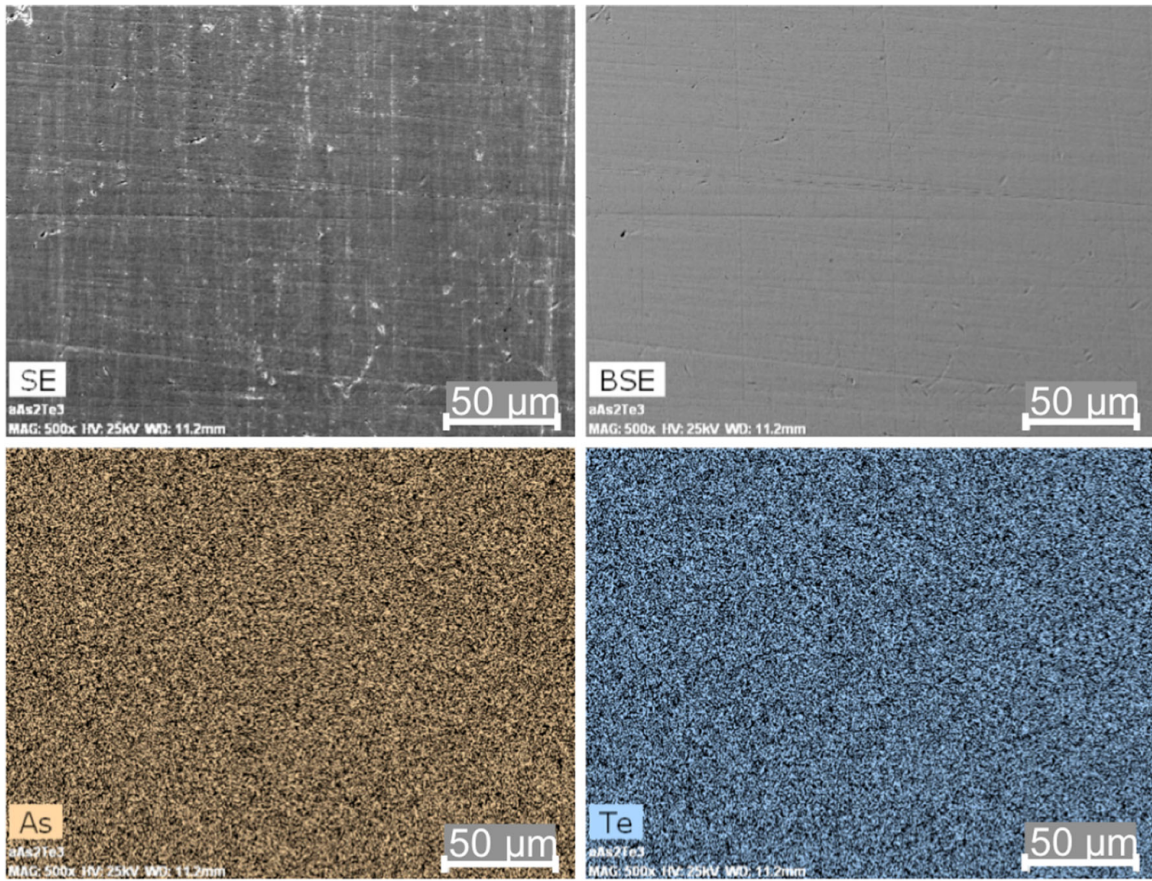


Figure 4

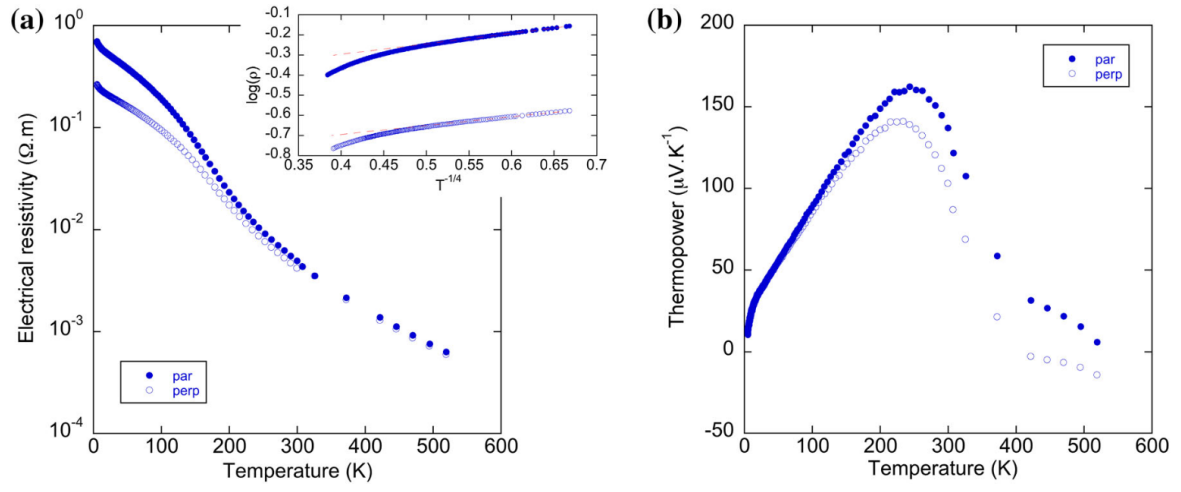


Figure 5

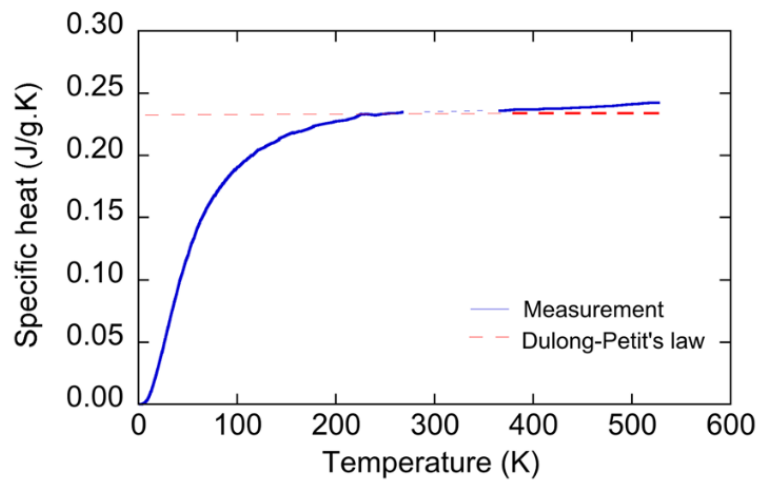


Figure 6

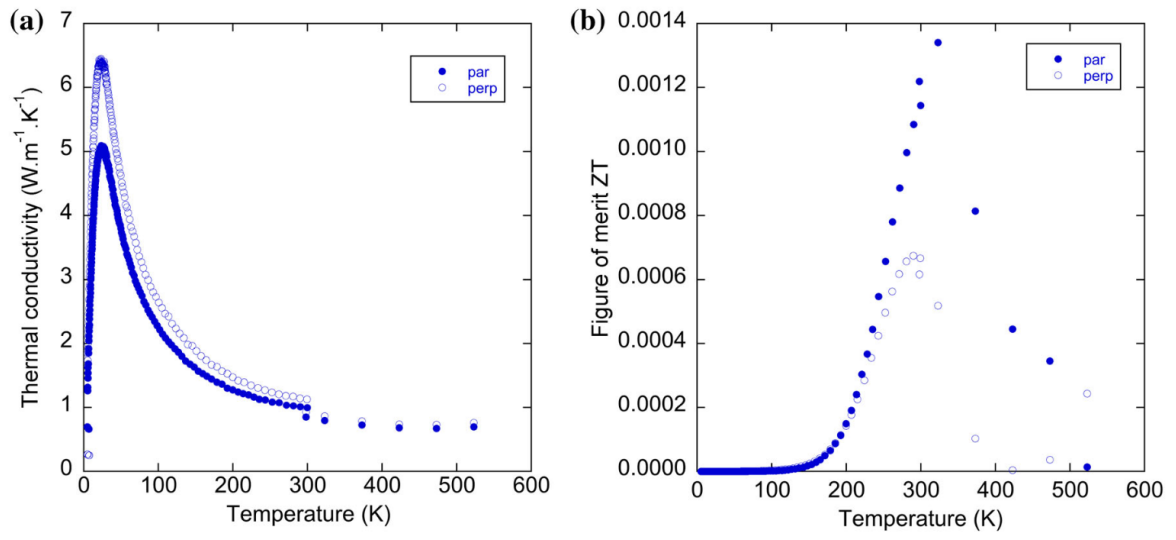


Figure 7