

Low-Temperature Transport Properties of Bi-Substituted β -As₂Te₃ Compounds

J.-B. VANEY,^{1,2,6} J. CARREAUD,² G. DELAIZIR,² C. MORIN,³
J. MONNIER,³ E. ALLENO,³ A. PIARRISTEGUY,⁴ A. PRADEL,⁴
A.P. GONÇALVES,⁵ E.B. LOPES,⁵ C. CANDOLFI,¹ A. DAUSCHER,¹
and B. LENOIR¹

1.—Institut Jean Lamour (IJL), UMR 7198 CNRS, Université de Lorraine, Nancy, France. 2.—SPCTS, UMR CNRS 7315, Université de Limoges, Lyon, France. 3.—Institut de Chimie et des Matériaux de Paris Est (ICMPE), UMR 7182 CNRS, CMTR, Thiais, France. 4.—Institut Charles Gerhardt (ICG), UMR 5253 CNRS, Université Montpellier 2, Montpellier, France. 5.—C2TN Instituto Superior Técnico, Universidade Técnica de Lisboa, 2695-066 Bobadela LRS, Portugal. 6.—e-mail: jean-baptiste.vaney@univ-lorraine.fr

β -As₂Te₃ belongs to the family of Bi₂Te₃-based alloys, a well-known class of efficient thermoelectric materials around room temperature. As₂Te₃ exists in two allotropic configurations: α - and β -As₂Te₃, of which only the latter crystallizes in the same rhombohedral structure as Bi₂Te₃. Herein, we report on substitution of Bi for As in the As_{2-x}Bi_xTe₃ system with $x = 0.0, 0.015, 0.025,$ and 0.035 . These samples have been characterized by x-ray diffraction and scanning electron microscopy. The transport properties have been measured at low temperatures (5 K to 300 K) in both directions, parallel and perpendicular to the pressing direction. The results are compared with those obtained in previous study on samples substituted by Sn. Compared with Sn, Bi allows for a clear decrease in electrical resistivity while maintaining the thermal conductivity below 1 W/(m K) over the whole temperature range. As a result, a comparable peak ZT value near 0.2 was obtained at room temperature.

Key words: Thermoelectric materials, arsenic telluride, metastable thermoelectric phase

INTRODUCTION

In the current context of environmental concerns, energy harvesting has become a central focus in materials science research. Among all the technologies under scrutiny and development, thermoelectricity might play a role due to its numerous advantages such as absence of gaseous emission, vibration-free character, and versatility. However, for decades, the performance and efficiency of thermoelectric (TE) materials have been limited, confining them to niche applications and markets. Near room temperature, Peltier coolers are used as

solid-state heat pumps for electronic device cooling, for example.¹

The thermoelectric performance of TE materials is quantitatively described by the dimensionless figure of merit ZT defined as $ZT = \alpha^2 T / \rho \lambda$, where α is the Seebeck coefficient or thermopower, T is the absolute temperature, ρ is the electrical resistivity, and λ is the total thermal conductivity. Achieving high ZT over a broad temperature range still represents one of the most challenging aspects of thermoelectricity.^{2,3} Ternary or quaternary compounds based on A₂B₃^{VI} (A = Bi or Sb; B = Te or Se) compounds remain the most efficient thermoelectric materials to date, for applications close to room temperature. When properly optimized, both p -type and n -type compounds show ZT values close to unity near 300 K.

(Received June 2, 2015; accepted November 5, 2015; published online December 7, 2015)

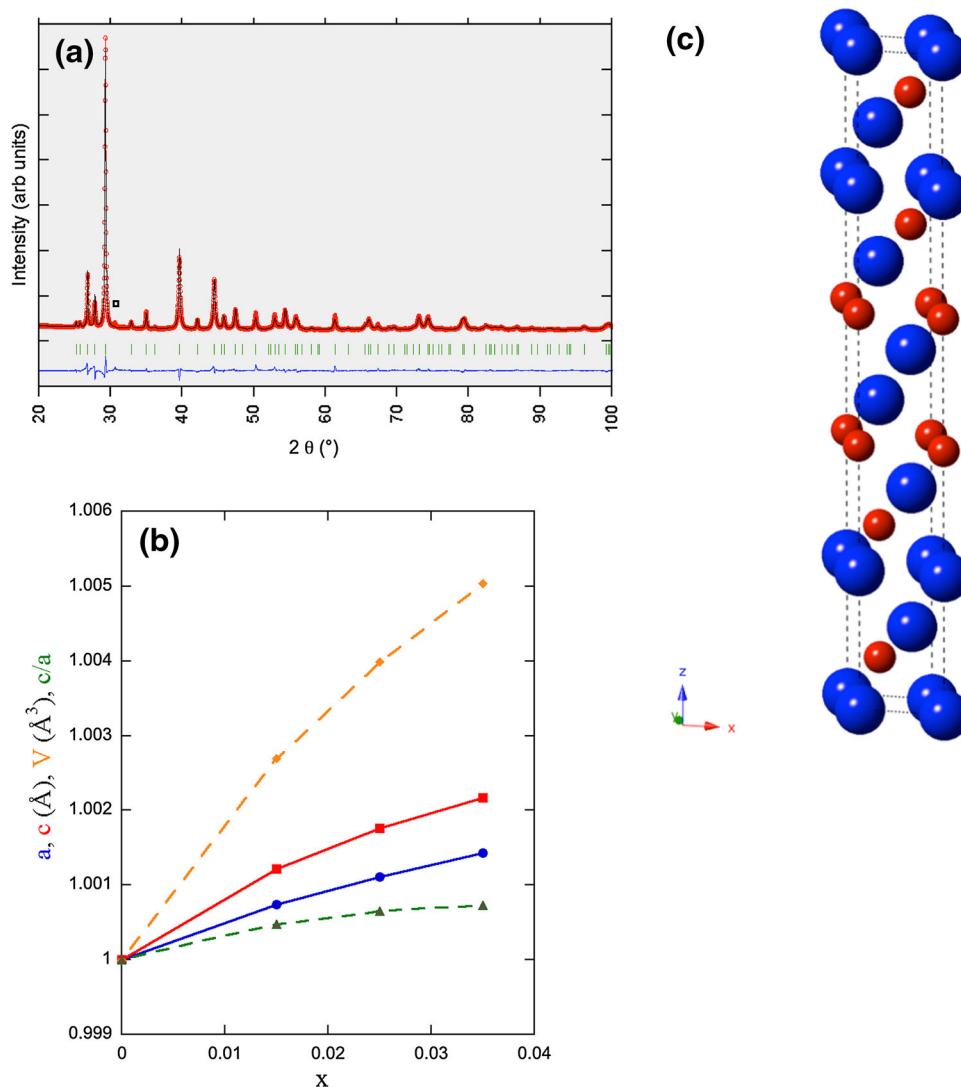


Fig. 1. (a) Powder x-ray diffraction pattern of β -As_{1.975}Bi_{0.025}Te₃. The observed data are marked as open red circles. The calculated profile is represented by a solid black line, while the difference between experimental and numerical patterns is shown by the solid blue line (RF = 4.024, $\chi^2 = 8.04$). The positions of the Bragg reflections are indicated by green bars. The peak ascribed to AsTe impurity is marked by an open black square. (b) Evolution of the hexagonal lattice parameters a and c (blue circles and red squares, respectively) as a function of Bi content. For information, the cell volume (orange diamonds) and c/a ratio (green triangles) are also presented. (c) Perspective view of the hexagonal crystal structure of β -As₂Te₃ (As atoms represented by small red balls, Te atoms by large blue balls) (Color figure online).

β -As₂Te₃ is one of the two allotropic forms of As₂Te₃ (together with α -As₂Te₃, monoclinic, space group $C2/m$) and, like Bi₂Te₃, belongs to the family of compounds crystallizing in the rhombohedral space group $R\bar{3}m$. β -As₂Te₃ has been reported to be a high-pressure phase, with a transition from α - to β -As₂Te₃ near 7 GPa.⁴ Further studies revealed that quenching could be an efficient method to produce these phases at ambient pressure,^{5,6} although they have not been extensively studied from the thermoelectric point of view so far. Recently, we demonstrated that β -As₂Te₃ could be stabilized under ambient conditions by crystallization of glassy Cu-As-Te.⁷ Further investigations led us to its direct synthesis, and we showed that the carrier concentration could be tuned by alloying

with Sn, leading to enhanced thermoelectric performance ($ZT \approx 0.6$ at 423 K).⁸

Herein, we report on the effect of substitution of Bi for As on the thermoelectric properties of β -As₂Te₃ at low temperatures (5 K to 300 K). We evidence that Bi is another element that might lead to interesting thermoelectric properties in p -type β -As_{2-x}Bi_xTe₃ (up to $x = 0.035$) above room temperature.

EXPERIMENTAL PROCEDURES

All β -As_{2-x}Bi_xTe₃ ($x = 0.0, 0.015, 0.025, 0.035$) samples were prepared by direct reaction of stoichiometric amounts of pure elements As (Goodfellow, 99.99%, shot), Te (5 N PLUS, 99.999%, shot), and Bi (Strem Chemicals, 99.9999%, shot) sealed

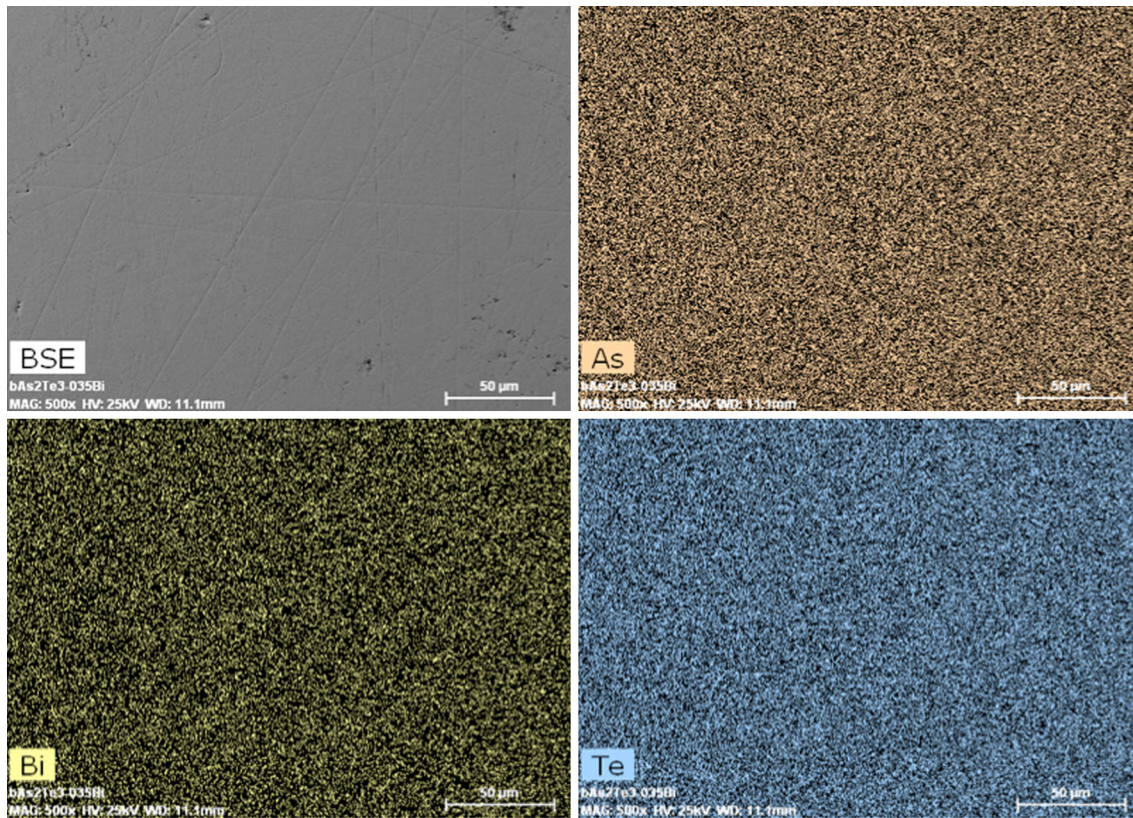


Fig. 2. Scanning electron microscopy (SEM) elemental contrast image of the β -As_{1.965}Bi_{0.035}Te₃ sample in backscattered electron (BSE) mode, together with the corresponding element mapping for As, Bi, and Te. The distribution of the elements is overall homogeneous.

under secondary vacuum in quartz tubes. The tubes were heated slowly up to 923 K at a rate of 10 K min⁻¹, dwelled at this temperature for 2 h, and finally quenched in icy water. The resulting ingots were hand-ground into micron-sized powders and cold-pressed into 10-mm-diameter cylindrical pellets under pressure of 750 MPa. Remarkably, all the obtained ingots showed experimental density higher than 95% of the theoretical value, a situation reminiscent of that observed in (Bi,Sb)₂(Se,Te)₃ compounds.¹ Noteworthy, for this phase, sintering techniques such as hot-pressing or spark plasma sintering could not be used as the temperatures required trigger the phase transition of β - to α -As₂Te₃ that sets in around 423 K.

The crystal structure was determined by powder x-ray diffraction (PXRD) at 300 K with a Bruker D8 Advance instrument using monochromated Cu K _{α} 1 radiation. The chemical homogeneity of the samples was checked by scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDXS) using a Quanta FEG (FEI).

The thermoelectric properties were measured simultaneously between 5 K and 300 K on parallelepiped-shaped samples cut with a diamond wire-saw (typical dimensions 2 mm \times 3 mm \times 7 mm) using the thermal transport option (TTO) of a physical property measurement system (PPMS, Quantum Design). Fine Cu wires were brazed to

the samples to ensure good electrical and thermal contacts, in a four collinear contacts setup. Owing to the anisotropic crystal structure of the studied compounds, the transport properties were measured on samples cut both parallel and perpendicular to the pressing direction. The Hall coefficient R_H was measured at 300 K on the perpendicular-cut samples (same as used for the TTO) with the AC transport option of the PPMS. The magnetic field was swept between -0.5 T and $+0.5$ T. The hole concentration p and Hall mobility μ_H were estimated from $p = 1/eR_H$ and $\mu_H = R_H/\rho$.

RESULTS AND DISCUSSION

Figure 1 presents the PXRD patterns (Fig. 1a) obtained for the illustrative $x = 0.025$ sample (all diffraction patterns being very similar) together with the evolution of the lattice parameter with x (Fig. 1b) and a sketch of the crystal structure of this compound (Fig. 1c). All reflections could be indexed to the $R\bar{3}m$ space group with an additional peak ascribed to nonquantifiable AsTe impurities ($Fm\bar{3}m$, $a = 5.778$ Å) present for all compositions. Due to the anisotropy of the crystal structure, all samples showed preferred orientation, resulting in slight renormalization of the relative intensities of the Bragg peaks. Rietveld refinements against the PXRD patterns led to good fits, allowing precise

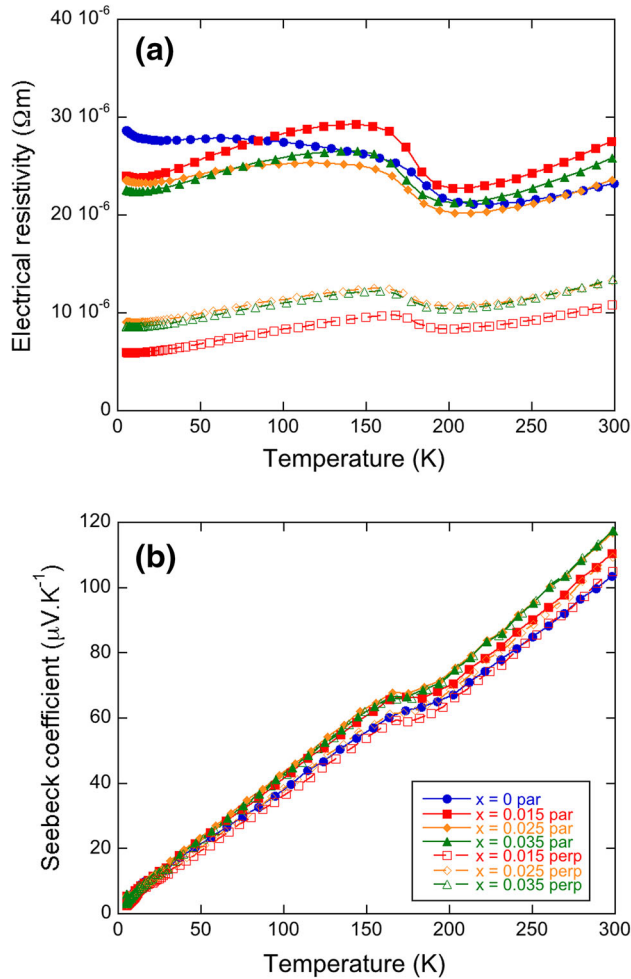


Fig. 3. Temperature dependence of electrical resistivity ρ (a) and thermopower α (b) of polycrystalline β -As_{2-x}Bi_xTe₃ samples. Measurements performed parallel and perpendicular to the pressing direction are represented by filled and open symbols, respectively. The composition color code is identical in both panels.

determination of the hexagonal lattice parameters of β -As_{2-x}Bi_xTe₃ (Fig. 1b). The values inferred for the binary compound are in agreement with literature data ($a = 4.0473$ Å, $c = 29.5018$ Å). The unit cell volume expanded monotonically with increasing Bi content up to $x = 0.035$ as a result of a simultaneous increase along the a and c axes. However, the expansion was not linear, hinting at a saturation threshold at higher x . These data are consistent with effective insertion of Bi into the crystal structure of β -As₂Te₃.

Scanning electron microscopy (SEM) and x-ray mapping further revealed an overall homogeneous distribution of the different elements in the samples regardless of the composition, as displayed for the $x = 0.035$ specimen in Fig. 2.

The temperature dependences of ρ and α measured parallel and perpendicular to the pressing direction are displayed in Fig. 3a and b, respectively. The values of ρ exhibit noticeable anisotropy with a

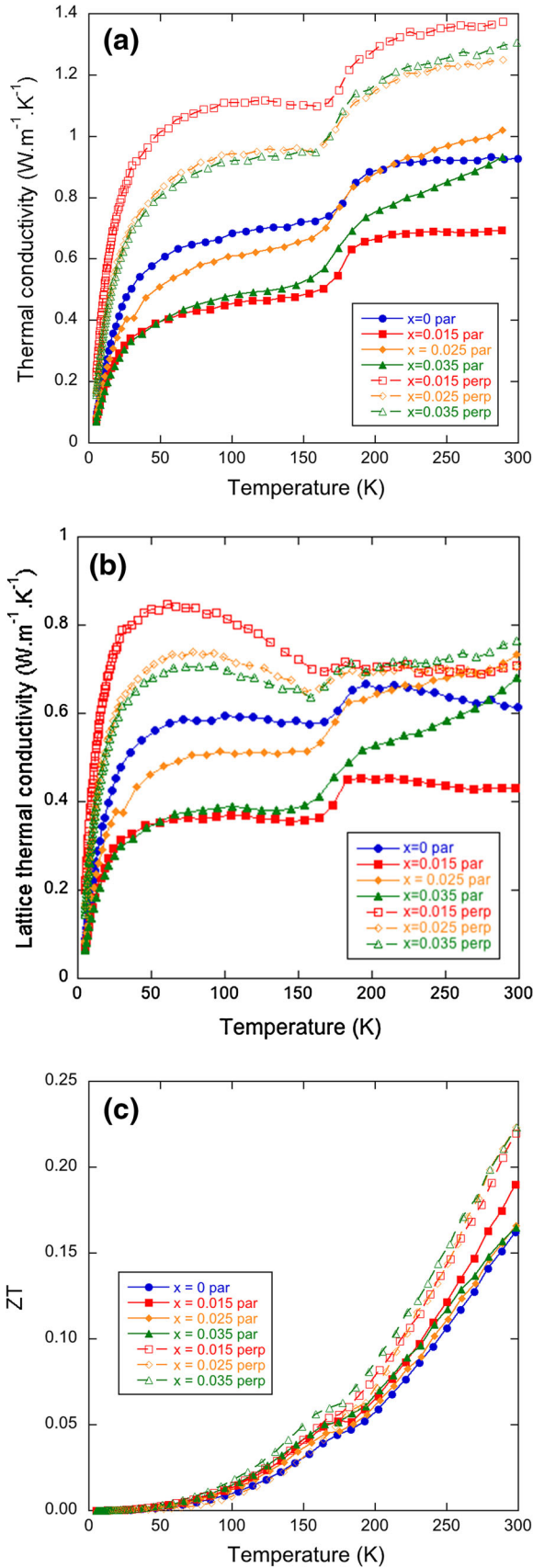
Table I. Hall carrier concentration (p) and mobility (μ_H) in the β -As_{2-x}Bi_xTe₃ system at 300 K, deduced from samples measured perpendicular to the pressing direction

x	0	0.015	0.025	0.035
p (10^{19} cm ⁻³)	8.4	7.1	6.8	8.0
μ_H (cm ² V ⁻¹ s ⁻¹)	48.6	81.2	69.5	57.8

twofold increase in ρ in the parallel with respect to the perpendicular direction. Except for the binary compound, which displays a slightly lower electrical resistivity than the other compounds, no clear trend with the Bi content can be observed. This conclusion also holds true for the anisotropy, which hardly evolves with increasing x . However, a clear change in the temperature dependence behavior can be observed around 175 K for each sample. This change reflects a structural transformation of β -As₂Te₃ into an analogous monoclinic structure β' -As₂Te₃.⁹ The values of α are positive, indicating transport dominated by holes, with an almost linear increase for each sample along the whole temperature range. At 300 K, substitution of Bi for As leads to a slight increase in α from 103 μ V K⁻¹ for $x = 0.0$ to 117 μ V K⁻¹ for $x = 0.025$ and 0.035. The change in the slope observed at 175 K is consistent with that observed in the ρ data and is thus ascribed to the $\beta \rightarrow \beta'$ structural transition. Anisotropy is observed between the two measuring directions, fading out for $x = 0.035$. Compared with the effects of As/Sn substitution, where a strong increase in both the electrical resistivity and thermopower was observed up to Sn content of 0.035, these two properties hardly evolve upon isoelectronic substitution of Bi for As at 300 K.

Table I presents the Hall carrier concentration (p) and Hall mobility (μ_H) measured at 300 K for $x = 0, 0.015, 0.025,$ and 0.035 . Only a very subtle evolution can be observed between the three Bi-substituted samples, while the value of p for the nonsubstituted compound lies at slightly higher values, below 10^{20} cm⁻³. Mobility values at 300 K firstly increase from the initial value of 49 cm² V⁻¹ s⁻¹ for the binary compound to the very high value of ~ 81 cm² V⁻¹ s⁻¹ for $x = 0.015$. For higher x , the electronic mobility constantly decreases down to 58 cm² V⁻¹ s⁻¹ for $x = 0.035$.

Figure 4a shows the temperature dependence of the total thermal conductivity λ . The anisotropic behavior is similar to that displayed by the electrical resistivity data, albeit opposite, with thermal conductivity in the parallel direction considerably lower than in the perpendicular direction. Compared with the As_{2-x}Sn_xTe₃ compounds, the decrease in the λ values due to Bi substitution is less marked. Given the monotonic increase in the electrical resistivity upon Sn substitution,⁸ in contrast to the moderate evolution observed here, the



◀Fig. 4. Temperature dependence of total thermal conductivity λ (a), lattice thermal conductivity (b), and dimensionless figure of merit ZT (c) of polycrystalline β - $\text{As}_{2-x}\text{Bi}_x\text{Te}_3$ samples. Measurements performed parallel and perpendicular to the pressing direction are represented by filled and open symbols, respectively. The composition color code is identical in both panels. It is likely that the thermal conductivity above 200 K is overestimated due to radiation issues, hence leading to a slight underestimation of ZT .

electronic contribution to λ is considerably lower in the former with respect to the latter, resulting in a stronger decrease in λ on substituting Sn for As. The values range between $0.7 \text{ W m}^{-1} \text{ K}^{-1}$ and $1 \text{ W m}^{-1} \text{ K}^{-1}$ in the parallel direction, while the values for the Sn-substituted compounds decreased to around $0.5 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K.⁸ Figure 4b shows the lattice thermal conductivity as a function of temperature, calculated by subtracting the electronic contribution λ_e as estimated using the Wiedemann–Franz law ($\lambda_e = T \cdot L / \rho$, where $L = 2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ is the Lorenz number). The observed lattice thermal conductivities range from 0.8 W/(m K) to slightly above 0.4 W/(m K) at 300 K, bearing in mind that due to the experimental setup, room-temperature thermal conductivity is always slightly overestimated (due to difficulties in estimating radiation losses in a direct measurement).

A remarkable feature rarely observed in the Bi_2Te_3 family of compounds is the absence of a dielectric peak at low temperatures, mimicking the temperature dependence of a glass.¹⁰ However, in contrast to other materials such as tetrahedrites,¹¹ these samples do not display all the features required to conduct thermally “as a glass.” The $\beta \rightarrow \beta'$ structural transition upon cooling is also evidenced in the thermal conductivity curves by a sudden decrease near 175 K owing to enhanced disorder in the β' compared with the β structure.

Figure 4c depicts the temperature dependence of ZT in this series of compounds. The $\beta \rightarrow \beta'$ structural transition is perceivable around 175 K for all compositions. Owing to compensation effects between the electrical and thermal transport properties, the ZT values appear to vary negligibly with x within experimental uncertainty. A peak ZT value of 0.22 at 300 K is obtained concomitantly for $x = 0.015, 0.025,$ and 0.035 . However, the anisotropy of the transport properties is not compensated in ZT , giving rise to values higher by 25% in the perpendicular direction with respect to the parallel direction. Interestingly, all the Bi-substituted compounds showed ZT values very similar to those obtained in the Sn-doped compounds,⁸ suggesting that similar thermoelectric performance (i.e., $ZT > 0.6$) may emerge at higher temperatures.

CONCLUSIONS

We report the low-temperature thermoelectric properties of polycrystalline samples of β - $\text{As}_{2-x}\text{Bi}_x\text{Te}_3$ for

$x = 0.0, 0.015, 0.025,$ and 0.035 . Similar ZT values of 0.22 were obtained at 300 K for all the Bi-substituted samples. Remarkably, these values are similar to those revealed by Sn-doped compounds, suggesting that high ZT values could be achieved above 400 K. Concomitantly, As substitution in the Bi₂Te₃ system remains scarcely studied to date and should be evaluated in relation to the present results on Bi-substituted β -As₂Te₃ phases. As for the Bi₂Te₃ system, the influence of several substitutions and the thermoelectric performance of other solid solutions based on β -As₂Te₃ remain to be investigated for full assessment of its potential as a thermoelectric material for use in room- or mid-range temperature applications.

REFERENCES

1. D.M. Rowe, *Thermoelectrics Handbook: Macro to Nano* (Boca Raton: CRC Press, 2006).
2. H.J. Goldsmid, *Thermoelectric Refrigeration* (New York: Plenum, 1964).
3. J. Snyder and E. Toberer, *Nat. Mater.* **7**, 105 (2008).
4. V.G. Yakushev and V.A. Kirinsky, in *Doklady Akad. Nauk SSSR* (1969), pp. 882.
5. H.W. Shu, S. Jaulmes, and J. Flahaut, *Mater. Res. Bull.* **21**, 1509 (1986).
6. H.W. Shu, S. Jaulmes, and J. Flahaut, *J. Solid State Chem.* **74**, 277 (1988).
7. J.-B. Vaney, G. Delaizir, E. Alleno, O. Rouleau, A. Piarristeguy, J. Monnier, C. Godart, M. Ribes, R. Escalier, A. Pradel, A. Goncalves, E. Lopes, G.J. Cuello, P. Ziolkowski, E. Mueller, C. Candolfi, A. Dauscher, and B. Lenoir, *J. Mater. Chem. A* **1**, 8190 (2013).
8. J.B. Vaney, J. Carreaud, G. Delaizir, A. Pradel, A. Piarristeguy, C. Morin, E. Alleno, J. Monnier, A.P. Goncalves, C. Candolfi, A. Dauscher, and B. Lenoir, *Adv. Electron. Mater.* **1**, 1400008 (2015).
9. C. Morin, S. Corallini, J. Carreaud, J.B. Vaney, G. Delaizir, J.C. Crivello, E.B. Lopes, A. Piarristeguy, J. Monnier, C. Candolfi, V. Nassif, G.J. Cuello, A. Pradel, A.P. Goncalves, B. Lenoir, and E. Alleno, *Inorg. Chem.* **54**, 9936 (2015).
10. A.J. Minnich, *Nat. Nanotechnol.* **8**, 392 (2013).
11. Y. Bouyrie, C. Candolfi, S. Pailhes, M.M. Koza, B. Malaman, A. Dauscher, J. Tobola, O. Boisron, L. Saviot, and B. Lenoir, *PCCP* **17**, 19751 (2015).