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Structural and thermoelectric properties of $Bi_{0.4}Sb_{1.6}Se_{3x}Te_{3(1-x)}$ quaternary compound

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Abstract. Novel hexagonal rods of $Bi_{0.4}Sb_{1.6}Se_{3x}Te_{3(1-x)}$ ($0.0 \leq x \leq 1.0$) were synthesized successfully through solid-state microwave synthesis. These hexagonal rods were explored using field emission scanning electron microscopy images. The X-ray diffraction results indicate that the powders ($0.0 \leq x \leq 0.8$) can be indexed as the rhombohedral phase, whereas the sample with x=1.0 has an orthorhombic phase structure. The electrical conductivity gradually decreases as Se increased, resulting in an increase in the Seebeck coefficient. Ascribing to the increased Seebeck coefficient for the sample with x=0.8, the maximum power factor is 7.47 mW/mK^2 at 373 K.

Introduction

In recent years, materials with high-performance bulk thermoelectric properties (TE) have been developed with ternary and quaternary chalcogenides containing heavy atoms having isotropic complex structures that are beneficial for the large carrier effective masses and low lattice thermal conductivity associated with such systems [1]. Most compounds are stable in an environment when they can combine with a set of properties that make them appropriate for practical TE applications. Given the versatility in the choice of the suitable electronegativity of the chalcogen elements, obtaining semiconductors with energy gaps useful for TE applications over elevated temperatures is possible. The cornerstone of present-day TE cooling has been the compound, Bi_2Te_3 and its alloys, $Bi_{2-x}Sb_xTe_3$ and $Bi_2Te_{3-x}Se_x$ [2]. Furthermore, a group of chalcogenides, such as $Bi_{2-x}Sb_xTe_{3-y}Se_y$, are among the most studied materials for TE refrigeration and TE power generation use [3, 4]. In the present paper, the first solid-state microwave preparations of ingot $Bi_{0.4}Sb_{1.6}Se_{3x}Te_{3(1-x)}$ ($0.0 \leq x \leq 1.0$) hexagonal rods is presented. These materials were synthesized within as little as 10 minutes of irradiation time. The products were characterized by their structural and electrical properties.

Materials and Methodology

Bi, Sb, Se, and Te powders of high purity (99.999%) were used in the present research to produce six 2 g samples of $Bi_{0.4}Sb_{1.6}Se_{3x}Te_{3(1-x)}$ ($0.0 \leq x \leq 1.0$) ingots using the solid-state microwave synthesis, as reported previously [5]. The samples were irradiated in an 800 W (100% power) MS2147C microwave oven (LG) at 2.45 GHz for 10 min. Bright, whitish-blue plasma was observed emerging from all the ampules from the first minute of microwave exposure. The temperature of the samples was measured using an OS524E infrared thermometer (OMEGA SCOPE) with values ranging from 873-903 K. After microwave irradiation, the reaction ampules were opened, and the products were removed and examined. Selected portions of the ingots were imaged using field emission scanning electron microscopy (FESEM) (Leo-Supra 50VP, Carl Zeiss, Germany). After grinding, the samples were then characterized to determine their crystallization via X-ray diffraction (XRD, PANalytical X'Pert PRO MRD PW3040, Almelo, The Netherlands). Subsequently, $Bi_{0.4}Sb_{1.6}Se_{3x}Te_{3(1-x)}$ ($0.0 \leq x \leq 1.0$) powders were pressed into disk shapes (diameter: 13 mm; thickness: 0.58 mm) via cold pressing at 10 tons. The Seebeck coefficient (S) was determined by the slope of the linear relationship between the thermoelectromotive force and the temperature difference between the two ends of each sample. The electrical conductivity (σ) was measured using the standard four-probe dc method under a vacuum of 10^{-3} mbar within temperatures ranging from room temperature to about 523 K.

Results and discussion

Fig. 1 displays a typical FESEM image of the surface morphology of the ingots $Bi_{0.4}Sb_{1.6}Se_{3x}Te_{3(1-x)}$ ($0.2 \leq x \leq 0.8$) prepared through solid-state microwave synthesis. Hexagonal rods with polished surfaces and different widths and lengths were observed. The diameters of the rods in all samples decreased with increasing Se content (x), which is mainly due to the smaller atomic radius of Se (1.15 Å) compared with that of Te (1.4 Å).

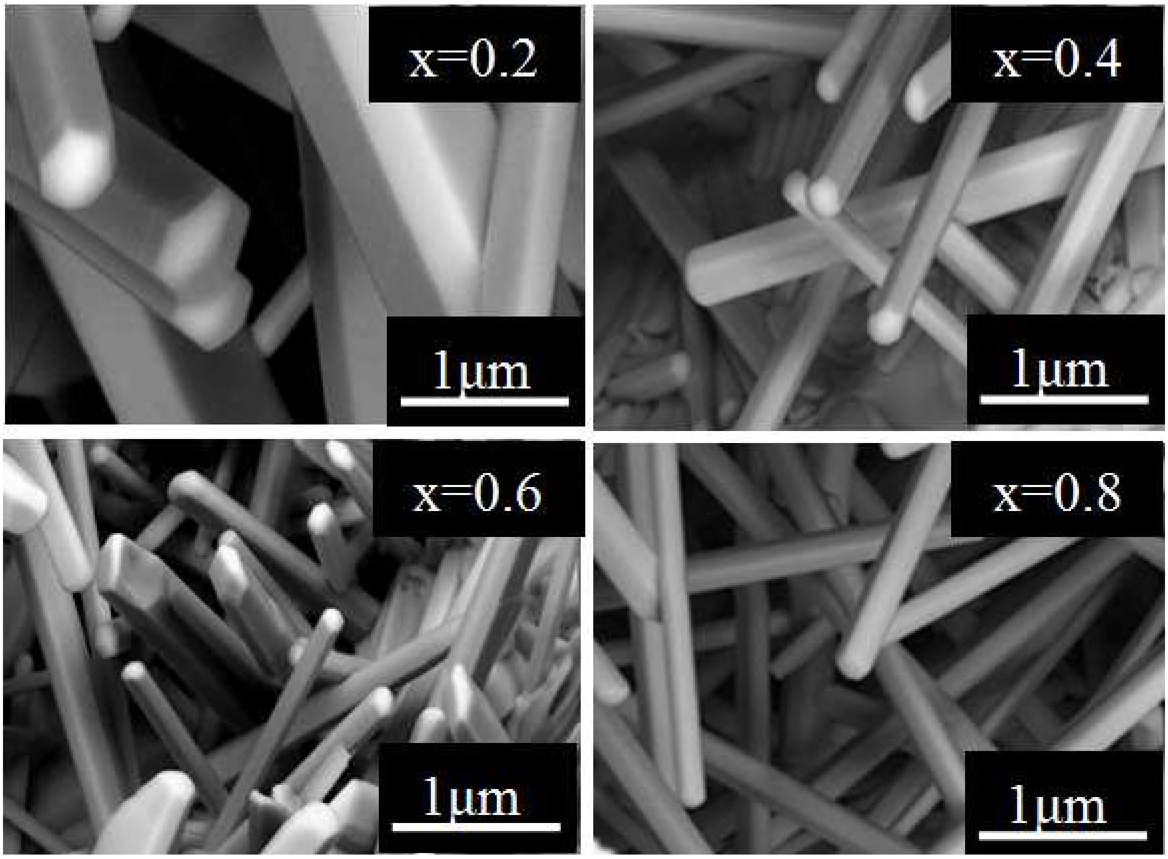

Fig.1 FESEM images of $Bi_{0.4}Sb_{1.6}Se_{3x}Te_{3(1-x)}$ ($0.2 \leq x \leq 0.8$) ingots.

XRD experiments were carried out to determine the structure of the powder samples, and the results are shown in Figs. 2. All the XRD peaks for $Bi_{0.4}Sb_{1.6}Se_{3x}Te_{3(1-x)}$ ($0.0 \leq x \leq 0.8$), which can be indexed as the rhombohedral phase of Bi_2Te_3, Sb_2Te_3, and Bi_2Se_3 (JCPDS 15-0863, 15-0874, and 33-0214, respectively) with a small amount of Sb_2Se_3 phase, appeared as (400), (331), (060), and (412). The diffraction peaks (015) displayed an apparent shift to a higher angle (27.985 to 29.2608°) with increasing Se content. This finding agrees with the FESEM results, which indicates that the nano-rod gradually decreases with Se content and the rhombohedral crystal structure can be represented as a stack of hexagonally arranged atomic layers [5]. In Fig. 2 shows also the XRD pattern of $Bi_{0.4}Sb_{1.6}Se_3$ ($x=1.0$) powder. Most peaks in this pattern can be indexed according to JCPDS 15-0861 for Sb_2Se_3 orthorhombic structure (Pbnm D_{2h}^{16}) with three small peaks of Bi_2Se_3 as (009), (018), and (0012). From this analysis, the solid-state microwave synthesis gives a reasonable indication that Se atoms successfully occupy Te sites in the as-prepared compounds.

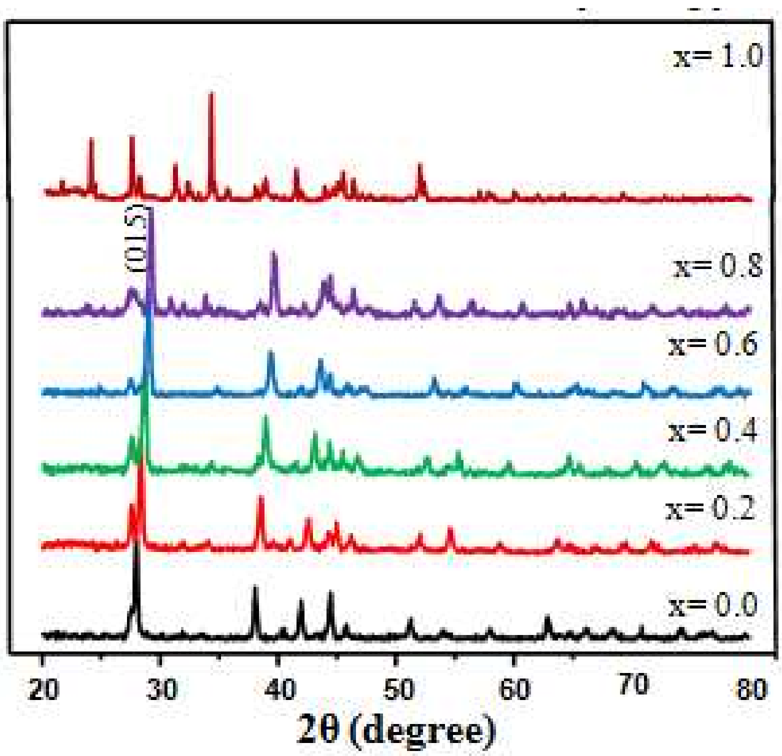

Fig. 2 XRD spectra of (a) (0.0≤x≤0.8) powders, and (b) x=1.0 powder for $Bi_{0.4}Sb_{1.6}Se_{3x}Te_{3(1-x)}$.

Fig. 3 shows the electrical properties (σ, S and power factor $S^2\sigma$) of $Bi_{0.4}Sb_{1.6}Se_{3x}Te_{3(1-x)}$ (0.0≤x≤1.0) as a function of the experimental temperature range (300–523) K. Fig. 3(a) shows that the σ of $Bi_{0.4}Sb_{1.6}Se_{3x}Te_{3(1-x)}$ samples decreased with increasing temperature, implying that the samples all display a degenerate semiconductor character. Two competing factors of carrier concentration and mobility determine σ. Generally, σ decreases considerably from 9.6×10^5 S/m to 4.8×10^5 S/m at 300 K, and from 4.3×10^5 S/m to 1.7×10^5 S/m at 523 K from x=0.0 to x=1.0, respectively. The decrease of σ values is most likely due to the incorporation of Se atoms into the crystal lattice, thus, changing the formation energy of the lattice defects in the $Bi_{0.4}Sb_{1.6}Se_{3x}Te_{3(1-x)}$ mixed crystals [6, 7].

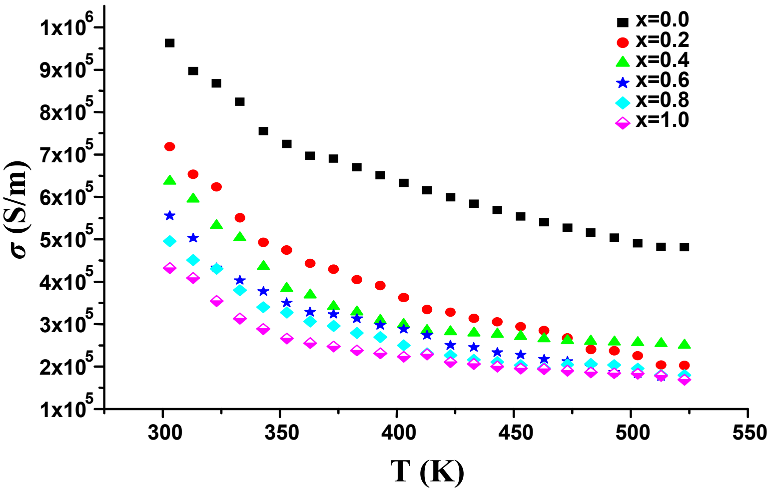

Fig. 3(a): Temperature dependences of σ, $Bi_{0.4}Sb_{1.6}Se_{3x}Te_{3(1-x)}$ (0.0≤x≤1.0).

Fig. 3(b) shows the temperature dependence of the S of the $Bi_{0.4}Sb_{1.6}Se_{3x}Te_{3(1-x)}$ samples. Samples with high Se content exhibited a relatively higher S. The highest value of S obtained is 183 μV/K at 433 K for the sample with x=1.0. For degenerate semiconductors, S can be described using the following equation: $S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3p}\right)^{2/3}$, where k_B is Boltzmann's constant, h is the Plank constant, and m^* is the effective mass. The above relationship shows that S is highly dependent on the carrier concentration and increases with decreasing carrier concentration. Variations in S are understood by assuming that the scattering distance of the charge carrier is independent of energy and degenerate approximations [8].

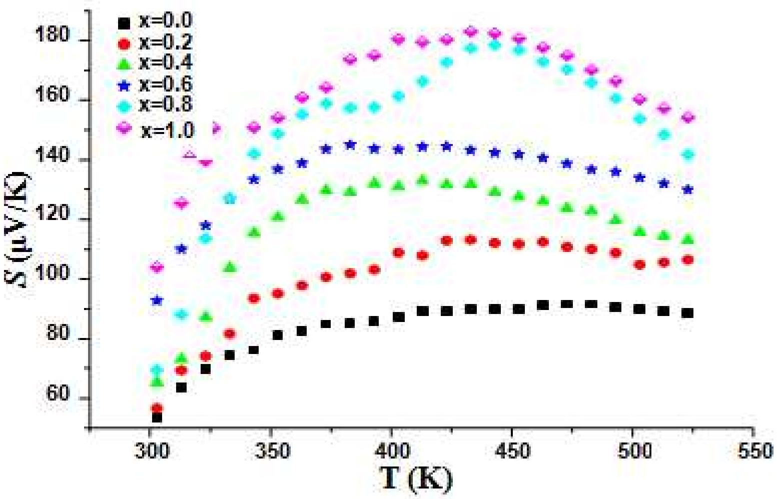

Fig. 3(b): Temperature dependences of S, $Bi_{0.4}Sb_{1.6}Se_{3x}Te_{3(1-x)}$ ($0.0 \leq x \leq 1.0$).

Power factor ($S^2\sigma$) was calculated from the measured S and σ, as shown in Fig. 3(c). $S^2\sigma$ of $Bi_{0.4}Sb_{1.6}Se_{3x}Te_{3(1-x)}$ increased with an increase in Se content. $S^2\sigma$ reached a maximum of 7.47mW/mK^2 when the content of Se reached 0.8 at 373 K, which is larger than that reported by Cui et al. and Kim et al. [7, 9].

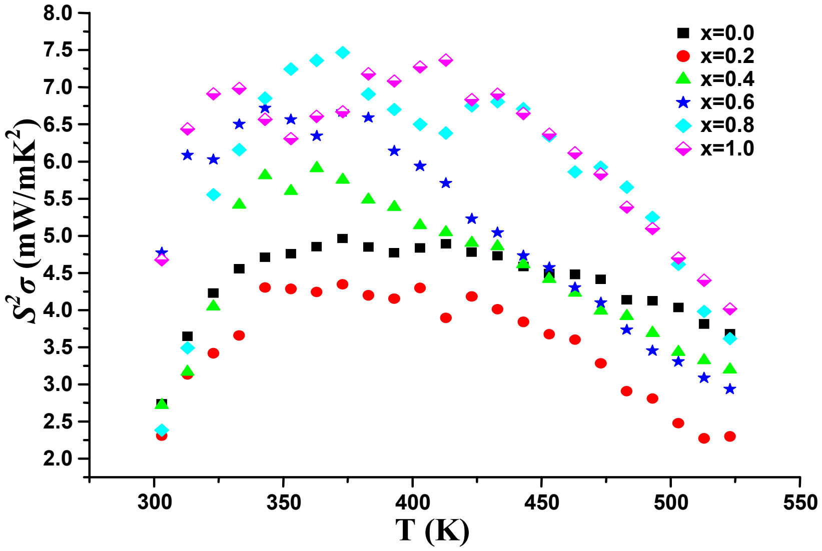

Fig. 3(c): Temperature dependences of $S^2\sigma$, $Bi_{0.4}Sb_{1.6}Se_{3x}Te_{3(1-x)}$ ($0.0 \leq x \leq 1.0$).

Summary

Hexagonal rods of $Bi_{0.4}Sb_{1.6}Se_{3x}Te_{3(1-x)}$ ($0.0 \leq x \leq 1.0$) ingots were prepared via solid-state microwave synthesis. The alloying of Se in $Bi_{0.4}Sb_{1.6}Te_3$ changed the crystal structure from rhombohedral ($0.0 \leq x \leq 0.8$) to orthorhombic ($x=1.0$). The substitution of Se with Te atoms effectively increased the Seebeck coefficient. The maximal power factor measured in the present work was 7.47 mW/mK^2 at 373 K for the x=0.8 sample. A moderate Seebeck coefficient of about 159 μV/K indicates the potential to improve the TE properties of this material through Se substitution optimization. The single crystal hexagonal rods are spontaneously grown as aggregates on the nanoscale. In future, these rods can be carefully captured out of the ingot, and fabrication of metal contacts via electron beam lithography can be utilized to produce thermoelectric power devices.

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