Enhancement Thermoelectric Properties of Cu\textsubscript{x}-doped Nanostructure Bi-Sb-Te Thermoelectric Materials by Spark Plasma Sintering

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Abstract. Nanostructure Cu\textsubscript{x}-doped Bi\textsubscript{0.5}Sb\textsubscript{1.5-x}Te\textsubscript{3} thermoelectric materials was successfully prepared by Mechanical alloys and spark plasma sintering. In the research, the crystallinity, particle size, and chemical composition were characterized by XRD, EDS, respectively. Thermoelectric properties with a maximum ZT value up to 1.17 has been obtained at 407 K in prepared Cu\textsubscript{0.04}-doped Bi\textsubscript{0.5}Sb\textsubscript{1.46}Te\textsubscript{3} sample. The achieved higher ZT value is attributed that Cu as doping at the Sb sites introduced additional holes to enhance carrier mobility and Cu dopants interrupted the periodicity of lattice vibration to decrease lattice thermal conductivity. It is suggested that the as-prepared nanostructure Cu\textsubscript{x}-doped Bi\textsubscript{0.5}Sb\textsubscript{1.5-x}Te\textsubscript{3} thermoelectric materials has high potential for thermoelectric energy conversion application.

1. Introduction

Recently, energy demand has a huge increase all over the world. Thermoelectric materials (TE) play a very key role in new energy fields due to their ability to convert heat directly into electricity [1]. Because of their high reliability and environmentally friendliness, thermoelectric materials are applied widely in some hi-tech fields such as space power generation, industry facility and a variety of cooling applications.

Bismuth telluride-based alloys are a kind of very extensively used commercial thermoelectric materials for ambient temperature application. At present, a common manufacture method to fabricate thermoelectric materials is to employ the means of electrodeposition[2], solvothermal method [3], hot extrusion [4], thin films [5], etc. Nevertheless, these means have some disadvantageous that is either intricate manufacture process or high cost. Nowadays, spark plasma sintering (SPS) technique is an attractive approach to fabricate novel materials [6]. The dominating characteristic of spark plasma sintering is the pressed reaction mass are effectively heated by the spark plasma. Thus, the reacting matter are sintered uniformly and rapidly, and dense samples with subtle crystal particle can be obtained in a very short holding time.

Moreover, current available thermoelectric devices have low efficiency in comparison with heat engine[7]. Nowadays nano-structure thermoelectric materials have already attracted many attention owing to the improvement in performance of thermoelectric devices through establishing nanostructure novelty material which have already been fabricated by advanced methods and techniques for instance nanocomposites[8], quantum dots[9], and superlattices [10].
In this content, the nano-structure Cu\textsubscript{x}-doped Bi\textsubscript{0.5}Sb\textsubscript{1.5-x}Te\textsubscript{3} (x mol.%, x = 0, 0.004, 0.008, 0.012) thermoelectric alloys are successfully synthesised by high-energy ball milling and SPS and its thermoelectric performances are also elaborated subsequently.

2. Experimental
The starting raw materials are high-purity Sb(99.999%), Cu(99.999%), Bi (99.999%) and Te (99.999%) powders which were loaded to a zirconium-coated steel jar with zirconium balls to carry out high-energy ball milling at 450 rpm with a ball-to-powder weight ratio of 20:1 for 20h in argon atmosphere. The as-prepared precursor materials were then sintered using spark plasma sintering approach under axial compressive stress of 50 MPa in vacuum at 693 K for 8 minutes to fabricate Bi-Sb-Te alloys with diameter of 15 mm and thicknesses of 2 mm.

The synthesized Cu\textsubscript{x}-doped nanostructure Bi\textsubscript{0.5}Sb\textsubscript{1.5-x}Te\textsubscript{3} alloys were characterized through X-ray powder diffraction using a X’Pert PRO X-ray diffractometer. The sintered Bi-Sb-Te alloys were cut into rectangular bar specimens of 10 mm×2 mm ×2 mm in size with a diamond saw, then were polished with SiC emery paper. The bars were polished to carry out σ, k, and S measurements. The Seebeck coefficient and the electrical resistivity were measured simultaneously adopting ULVAC ZEM-2. The total thermal conductivity were determined through the density (ρ), specific heat capacity (C\textsubscript{p}), and thermal diffusivity (D) values. The density (ρ) was calculated by the Archimedes method. The laser flash technique through TC-7000H system (ULVAC-RIKO) was adopt to measure the thermal diffusivity.

3. Results and Discussion
Figure 1 shows the XRD patterns of the Cu\textsubscript{x}-doped Bi\textsubscript{0.5}Sb\textsubscript{1.5-x}Te\textsubscript{3} (x mol.%, x = 0, 0.004, 0.008, 0.012) thermoelectric materials alloys . It is clearly indicated that in Fig. 1, XRD pattern of the synthesized alloys can be indexed to the pattern of rhombohedral Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} with the space group R-3m (JCPDS No. 00-049-1713). All the diffraction lines are assigned well to Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} crystalline phase; therefore the result indicates the Cu-doped Bi-Sb-Te sample is monophasic which were prepared by spark plasma sintering method. Moreover, without supernumerary peaks being found in the XRD patterns show the Cu element was successfully doped into the lattice of Bi-Sb-Te alloys. It indicates that the Cu doped method does not change the structure of the matrix nor does it create the second phase. The atomic radius of Cu (135 pm) is approximate to that of Sb atoms (145 pm), therefore, substitution of the Bi site by some Cu atoms is feasible.

![Figure 1. XRD patterns for as-synthesized Cu\textsubscript{x}-doped Bi\textsubscript{0.5}Sb\textsubscript{1.5-x}Te\textsubscript{3} samples](image-url)
Also, it can be seen from the XRD patterns that the diffraction peaks are broadened, which shows the fine character of the samples. The average crystallite size can be calculated from the full width at half maximum (FWHM) of the diffraction peaks using Scherrer’s equation \( D = \frac{k \lambda}{\beta \cos \theta} \). The average crystallite sizes of the particles synthesized are about 85 nm through calculation from the Scherrer’s formula.

Figure 2 indicates a lattice-resolved high-resolution TEM (HRTEM) image of the as-prepared sample, which shows the prepared alloy is well-crystallized and without any displaces. Meanwhile, the lattice spacing of 0.23nm is clear and distinct in the HRTEM image, corresponding to the (015) plane of the space group R-3m \( \text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3 \), which indicated the prepared Cu-doped \( \text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3 \ ( x = 0.008) \) sample has similar crystal structure as \( \text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3 \).

![Figure 2. High-resolution TEM image of the as-prepared Cu-doped Bi0.5Sb1.5xTe3 (x = 0.008) sample](image)

Figure 3 show the EDS spectrum of as-prepared Cu-doped \( \text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3 \ ( x = 0.008) \) sample. Semiquantitative EDS results give the normalized chemical composition of the as-prepared sample. The chemical composition of \( \text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3 \ ( x = 0.008) \) sample is Bi, Sb, and Te, while the quantities of Cu are too scarce to be detected. The EDS measurement is also helpful to get a quantitative estimate of the chemical element ratio. Table 1 indicated the chemical composition of the as-prepared alloy.

**Table 1.** Composition of obtained \( \text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3 \ ( x = 0.008) \) alloy detected by EDS

| Element | Bi    | Sb    | Te    |
|---------|-------|-------|-------|
| Wt%     | 16.59 | 26.85 | 56.56 |
| At%     | 10.68 | 29.67 | 59.65 |

![Figure 3. The EDS spectrum of as-prepared Bi0.5Sb1.5xTe3 (x = 0.008) sample](image)
Figure 4 indicated the thermal conductivity values of as-prepared Cu$_x$-doped Bi$_{0.5}$Sb$_{1.5}$,Te$_3$ alloys detected at different temperature from 298k to 523k. The thermal conductivity monotonically decrease with temperature rising for all the Cu$_x$Bi$_{0.5}$Sb$_{1.5}$,Te$_3$($x = 0.004$–$0.012$) samples below 450K, thereafter gets gradually steady values with temperature elevated. The lattice thermal conductivity of materials makes a great contribution to the total thermal conductivity K. In the Cu$_x$-doped Bi$_{0.5}$Sb$_{1.5}$,Te$_3$ samples, the decreasing contribution of lattice thermal conductivity after Cu-doping was caused through the variation in scattering of phonons. This scattering of phonons can be triggered owing to the defects generated by filling of Sb cation vacancies by Cu atoms.

Figure 4. Temperature dependence of thermal conductivity for as-prepared Cu$_x$-doped Bi$_{0.5}$Sb$_{1.5}$,Te$_3$ samples

Figure 5 indicated the temperature dependence of electrical conductivity for all Cu$_x$-doped Bi$_{0.5}$Sb$_{1.5}$,Te$_3$ samples . As Cu content was increased , the electrical conductivity $\sigma$ values were improved as well. At 300 K temperature, the electrical conductivity $\sigma$ for different Cu content sample is about $13.92 \times 10^4$ S/m, $15.98 \times 10^4$ S/m, $18.57 \times 10^4$ S/m, respectively ,which is almost 3-4 times larger than that in the none Cu-doped sample. With the Sb atoms were substituted by Cu atoms, the hole concentration of the as-prepared samples were increased owing to Cu atoms having fewer electrons in the outermost orbital than Sb atoms. Moreover, the electrical conductivity of the as-prepared samples decreases when the temperature was elevated because the lattice vibration increases with a incremental temperature, therefore, the scattering effect from lattice vibration is heightened, thus the carrier mobility can be suppressed [11].

Figure 5. Temperature dependence of electrical conductivity for Cu$_x$-doped Bi$_{0.5}$Sb$_{1.5}$,Te$_3$ samples
The Seebeck coefficients (S) of the as-synthesised Cu\textsubscript{x}-doped Bi\textsubscript{0.5}Sb\textsubscript{1.5-x}Te\textsubscript{3} samples at 298K-523 K are indicated in Figure 6. The Seebeck coefficient (S) indicated a positive value which declared p-type conduction (hole conduction). The Seebeck coefficient (S) at about 300K temperature decreases with increasing Cu content, from 219 μVK\textsuperscript{-1} to 112 μVK\textsuperscript{-1}, which is consistent with the incremental hole concentration. With the increase of Cu content (x from 0.004 to 0.012), the Seebeck coefficient gradually decreases, meantime the peak shifts to the elevated temperature was observed also.

Figure 6. Temperature dependence of Seebeck coefficients for as-prepared Cu\textsubscript{x}-doped Bi\textsubscript{0.5}Sb\textsubscript{1.5-x}Te\textsubscript{3} samples

Figure 7 indicates the temperature dependence of ZT of the as-synthesised samples, which ZT is equal to \( s^2 \sigma TK^{-1} \), calculated from the measured \( \sigma \), K and S values[12]. It can be seen from the Figure 7 that all samples with Cu-doped samples show outstanding ZT values at a relatively high temperature. The peak value of ZT appears at elevated temperature of 370-440 K which were compared with other values ranging from room temperature to 360 K. A maximum ZT value of 1.17 was attained for Cu\textsubscript{0.004}Bi\textsubscript{0.5}Sb\textsubscript{1.496}Te\textsubscript{3} at 407 K owing to chiefly benefits from the significant increase in electrical conductivity.

Figure 7. Temperature dependence of ZT for as-prepared Cu\textsubscript{x}-doped Bi\textsubscript{0.5}Sb\textsubscript{1.5-x}Te\textsubscript{3} samples
4. Conclusions
Nanostructure Cu$_x$-doped Bi$_{0.5}$Sb$_{1.5-x}$Te$_3$ thermoelectric materials was effectively synthesised by an spark plasma sintering method in a short time due to the spark plasma effect between the reactant particles. XRD indicated a rhombohedral structure with the space group R-3m pure samples. A maximum ZT value up to 1.17 was got at 407 K in the as-synthesised Cu$_{0.04}$-doped Bi$_{0.5}$Sb$_{1.496}$Te$_3$ sample. The swinging ZT improvement was derived from distinct increase in electrical conductivity and decline in thermal conductance. Therefore, the spark plasma sintering is a versatile method to prepare Cu$_x$-doped Bi$_{0.5}$Sb$_{1.5-x}$Te$_3$ thermoelectric materials for potential application of thermoelectric energy conversion.

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6. References
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