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Enhanced Seebeck coefficient by energy filtering in Bi-Sb-Te based composites with dispersed Y_2O_3 nanoparticles

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A B S T R A C T

The incorporation of ceramic nanoparticles in the bulk thermoelectric matrix is one of the new strategies to boost the Seebeck coefficient. In this research, different weight percentages of Y_2O_3 (2, 4, and 6) nanoparticles (NPs) were incorporated into the pre-alloyed BiSbTe powder for making nanocomposites (NCs) by mechanical milling. The resultant NCs powders were subsequently consolidation by spark plasma sintering (SPS) at 450 °C. The existence of Y_2O_3 nano-inclusions was confirmed by x-ray diffraction and TEM-SAED analysis. The hardness of the nanocomposites was significantly improved (>49%) compared to that of pure BiSbTe, and this was attributed to grain-boundary hardening and to a dispersion strengthening mechanism. The electrical conductivity decreased while the Seebeck coefficient significantly improved (45%) at room temperature for the NCs to which 2 wt% Y_2O_3 was added. This was due to the scattering of carriers through the energy filtering effect. The electronic component of the thermal conductivity greatly contributed to the reduction of total thermal conductivity (22%) in BiSbTe NCs to which 6 wt% Y_2O_3 was added. A peak ZT of 1.24 was achieved for BiSbTe/(2 wt%) Y_2O_3 NCs due to reduction in their thermal conductivity and improved Seebeck coefficient values.

1. Introduction

Due to serious concerns regarding the exhaustion of natural sources (e.g., fossil fuels), there has been renewed interest in the development of alternative renewable energy sources. Among the various alternative energy sources, thermoelectric (TE) power generation is one of the best, due to its unique benefits, which include no moving parts, high reliability, operation over a wide range of temperatures, and environmental compatibility. The energy conversion efficiency of a thermoelectric device is strongly dependent on its thermoelectric figure of merit, ZT ($ZT = (\alpha^2\sigma/\kappa)T$, where α is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity). There are two ways to improve the figure of merit of the constituent materials. The selected TE material can be made to exhibit a high power factor ($\alpha^2\sigma$), or can be made to exhibit low thermal conductivity (κ). However, achieving a perfect combination of these is difficult because the parameters are interdependent [1–3].

The use of Bi-Sb-Te alloy for energy conversion at room temperature is of great interest due to their special features. To increase the performance of TE devices for use in a wide variety of practical applications, many researchers have focused research on improving the figure of merit of BiSbTe-based materials. The figure of merit of these materials is about 1.0, using various traditional approaches [4,5]. In addition to the figure of merit, mechanical properties should also improve for practical applications. Recently, the use of thermoelectric nanocomposites has been put forward as a promising way to enhance TE efficiency as well as mechanical properties. The TE efficiency is achieved by significantly reducing thermal conductivity by a massive scattering mechanism (both phonons and charge carriers scattering), and by greatly improving the power factor via an energy filtering approach. Also, the mechanical properties are considerably increased due to formation of fine and complex grains structures in the matrix. Recently, Jung et al. reported that the mechanical properties such as hardness is gradually increased after addition of B_4C nanoparticles in $Bi_{0.4}Sb_{1.6}Te_3$. This is attributed to the effective blocking of cracks by nanoparticles in matrix [6]. Y. C. Dou et al. showed that the Seebeck coefficient is dramatically increased (>20%) after dispersion of SiO_2

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nanoparticles in BiSbTe. This is attributed to enhanced carrier scattering caused by an energy filtering effect (EFE) on interface potentials [7]. Although electrical conductivity decreases due to carrier scattering at interfaces, it is partially compensated by an increase in Seebeck coefficient due to the increased EFE caused by the scattering of carriers at interface potentials [8].

According to the Mott relation, the Seebeck coefficient: α of a degenerate semiconductor, is given by Ref. [9,10],

$$\alpha = \frac{\pi k_B^2 T}{3q}\left[\frac{d\,ln(\,\sigma(E))}{dE}\right] \text{ at } E = E_f$$
$$= \frac{\pi k_B^2 T}{3q}\left[\frac{1}{p}\frac{dp(E)}{dE} + \frac{1}{\mu}\frac{d\mu(E)}{dE}\right] \text{ at } E = E_f \quad (1)$$

where q is the carrier charge, E is the energy, $\mu(E)$ is the carrier mobility ($\mu = q\tau/m^*$), $p(E)$ and $\mu(E)$ are the energy dependent carrier density and mobility, k_b is the Boltzmann constant, m^* is the effective mass, and E_f is the Fermi energy. According to the free electron gas model, Eq. (1) can be expressed in terms of a scattering parameter, λ (with relaxation time, $\tau = \tau_0 E^{\lambda-1/2}$) as

$$\alpha \approx \frac{\pi k_B^2 T}{3q}\left[\frac{N(E)}{p} + \frac{\lambda - \frac{1}{2}}{E}\right] \text{ at } E = E_f \quad (2)$$

where N(E) is the electronic density of states (DOS). Eq. (2) states that the Seebeck coefficient can be enhanced by increasing the scattering parameter, λ which corresponds to the EFE [10]. In the present work, yttria (Y_2O_3) has been chosen to be incorporated into the BiSbTe matrix, because it is a good oxygen scavenger that promotes high inclusion stability when dispersed in the host matrix [11,12]. In this research, p-type BiSbTe + x wt% Y_2O_3, (x = 0, 2, 4, and 6) nanocomposite powders were fabricated via high-energy ball milling, and subsequently consolidated by spark plasma sintering. The effect of Y_2O_3 dispersion on microstructure, mechanical properties and thermoelectric properties are systematically studied. In addition, the possibility of energy filtering effects to enhance the Seebeck coefficient and simultaneously decrease in thermal conductivity of the NCs was elucidated.

2. Experimental procedure

A stoichiometric amount of Bi, Sb, and Te high-purity granules were weighed to synthesize the p-type Bi_2Te_3 + 75% Sb_2Te_3 (hereafter referred to as BiSbTe) alloy powder by a rapid solidification process (RSP) [13]. In order to prepare the p-type BiSbTe/Y_2O_3 nanocomposite powders, different weight percentages (2, 4, and 6) of Y_2O_3 nanoparticles (size of 30–70 nm) were dispersed into the RSP powder via a high-energy ball milling process. The milled nanocomposite powders are shown in Fig. S1 (See supplementary information). The few of nanocomposite powders are agglomerated with each other due to cold welding that takes place during the ball milling [14]. Subsequently, the nanocomposite powders were consolidated by spark plasma sintering (SPS) at 400 °C. Zirconia (ZrO_2) balls and jars were used in the present experiment as the milling media.

The microstructural analysis of nanocomposite powder and bulk samples was done using field emission scanning electron microscopy (SEM- MIRA LMH II (TESKAN), Czech Republic). Electron diffraction and high-resolution transmission electron microscopy (HRTEM) was performed on a JEOL 2010 microscope operated at 200 kV. The phase structure of prepared samples was analyzed using X-ray diffraction (XRD, MiniFlex-600, Rigaku, Japan) with monochromatic Cu-Kα radiation (0.1541 nm) at angles of 10–70°. The relative density of the nanocomposite bulks was measured using the Archimedes method. The Vickers hardness of the NC samples was measured 15 times by a micro Vickers hardness tester at different locations, and averaged to provide the final value. The carrier concentration and hall mobility were calculated using the high temperature hall measurement system (ECOPIA, HMS3500, HT55T5). The temperature dependence of thermoelectric properties such as the Seebeck coefficient and electrical conductivity, were measured over the temperature range of 300–500 K using a thermoelectric power (TEP-1000, Seepel, Inc. co) measuring system. Thermal diffusivity (D) was measured by the laser flash method (LFA 457 system, Netzsch Instruments, Inc.). Specific heat (Cp) was measured by Perkin elmer DSC-8000. The thermal conductivity ($\kappa = DC_p d$) was calculated from the heat capacity (C_p), the density (d), and the thermal diffusivity (D). The thermoelectric figure of merit (ZT) was calculated from the Seebeck coefficient, electrical conductivity, and thermal conductivity.

3. Results and discussion

Fig. 1 shows the XRD patterns of the p-type BiSbTe + x wt% Y_2O_3, (x = 0, 2, 4, and 6) nanocomposite (a) powders and their (b) bulk

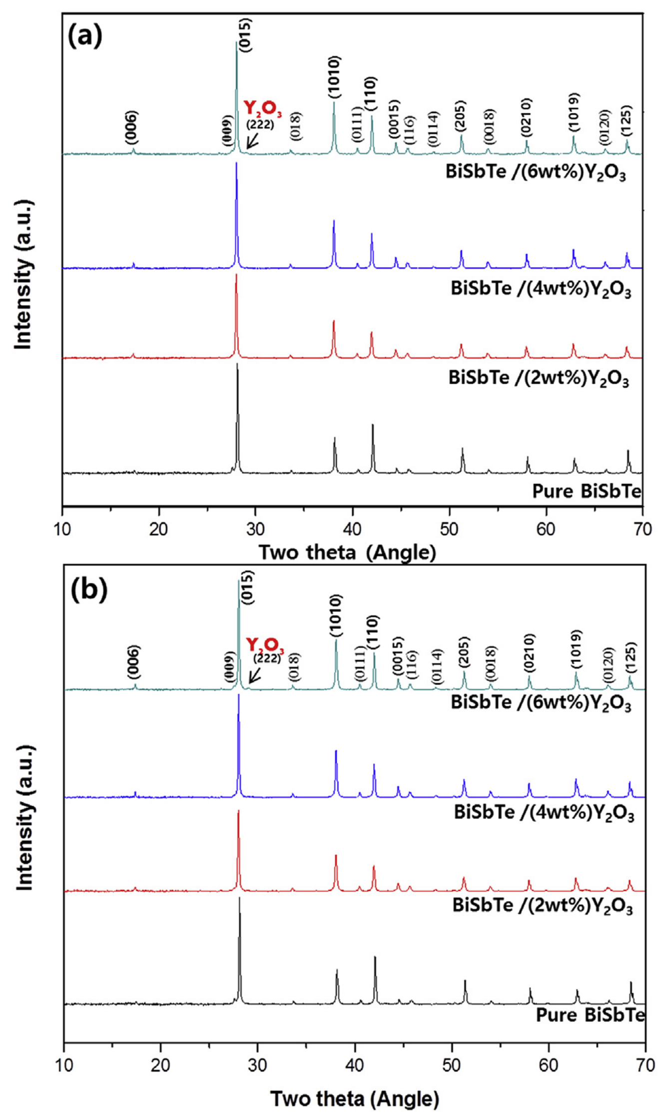

Fig. 1. XRD pattern of BiSbTe/(x-wt%)Y_2O_3 (x = 0, 2, 4 and 6 wt%) nanocomposite (a) powders and (b) SPS-ed bulk samples.