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Quantitative analysis on the influence of Nb substitutional doping on electronic and thermal properties of *n*-type $Cu_{0.008}Bi_2Te_{2.7}Se_{0.3}$ alloys

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ABSTRACT

Cation substitutional doping has been shown to be an effective method to modify both the electronic and thermal transport in *p*-type $(Bi,Sb)_2Te_3$-based thermoelectric alloys. However, there are not many studies that have attempted a quantitative analysis on the influence of cation substitution on the electronic and thermal properties of *n*-type $Bi_2(Te,Se)_3$-based alloys. In this work, we report a comprehensive analysis of the influence of substitutional Nb doping on the electrical and thermal conductivity in *n*-type $Cu_{0.008}Bi_2Te_{2.7}Se_{0.3}$ alloys. First, we found that Nb doping increases the carrier concentration of both the electrons and holes, whereas the weighted mobility of the electrons and holes is only slightly modified based on a single parabolic band model. As a result, the bipolar thermal conductivity was increased as the Nb was doped. Next, the contribution of point defect scattering by the Nb substitution on the thermal conductivity of the lattice was quantitatively analyzed using a Debye-Callaway model, and it was concluded that the influence of cation substitutional doping in *n*-type $Bi_2(Te,Se)_3$ is as effective as that in *p*-type $(Bi,Sb)_2Te_3$.

1. Introduction

Due to the problems associated with the use of fossil fuels and nuclear energy, renewable energy generated using thermoelectric or photovoltaic technology has been the focus of recent studies. Among these sources, thermoelectric materials have drawn significant attention over the past several decades owing to their ability to convert a temperature gradient directly into electrical energy and vice versa. Bismuth telluride (Bi_2Te_3) based alloys, developed in the 1950s, are currently the most used bulk thermoelectric alloys used at near room temperature [1,2]. Nevertheless, the widespread application of Bi_2Te_3-based alloys has been constrained because of their low thermoelectric conversion efficiency. The thermoelectric conversion efficiency is evaluated based on the dimensionless thermoelectric figure of merit, which is $zT = S^2 \cdot \sigma \cdot T/\kappa_{tot}$, where S, σ, κ_{tot}, and T denote the Seebeck coefficient, the electrical conductivity, the total thermal conductivity, and the temperature, respectively.

Substitutional or intercalation doping is an effective strategy for increasing the zT value, either by increasing the power factor (which is $S^2 \cdot \sigma$) or by reducing κ_{tot} in many *p*-type $(Bi,Sb)_2Te_3$ alloys [3–11]. However, a quantitative analysis has yet to be conducted with respect to both the electronic and thermal properties together. Moreover, there have been few studies on *n*-type $Bi_2(Te,Se)_3$-based alloys, whose zT should be increased along with the zT of the *p*-type alloys to implement a high module performance. In this work, the influence of substitutional Nb doping on *n*-type $Cu_{0.008}Bi_2Te_{2.7}Se_{0.3}$ was comprehensively examined with respect to the electronic and thermal transport properties using a single parabolic band (SPB) model [12] and the Callaway model [13] as well as previously reported results [14]. Using a single parabolic band model, the band parameters (mainly, the effective mass m^* and deformation potential E_{def}) for the conduction band (CB) and valence band (VB) were fitted to the measured total S and σ (S_{total} and σ_{total}). These parameters enable a careful analysis of the electronic transport properties in view of two carriers, and an estimation of the bipolar thermal conductivity, κ_{bp}. The reduction of the lattice thermal conductivity κ_{latt} was predicted quantitatively from the Debye-Callaway model in order to investigate how effective substitutional Nb doping is in reducing κ_{latt} in *n*-type $Bi_2(Te,Se)_3$ alloys, and the parameters for the fitting were compared with substitutional doping in *p*-type $(Bi,Sb)_2Te_3$ alloys.

2. Experimental

A series of Nb-doped $Cu_{0.008}Bi_{2-x}Nb_xTe_{2.7}Se_{0.3}$ (x = 0, 0.005, 0.01, and 0.02) samples were previously synthesized using a conventional solid-state reaction with a carbon-coated quartz tube for 10 h at 1423 K.

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The ingots were pulverized using a high-energy ball mill for 5 min, and sieved powders (size < 45 μm) were sintered through a spark plasma sintering technique at 723 K and 30 MPa for 2 min [14]. The density of the samples ranged from 7.51 to 7.55 gcm^{-3}, which is higher than 96% of the theoretical density [14]. The lattice parameters a and c of the samples were measured between 4.34 and 4.36 Å and 30.16–30.47 Å, respectively, showing no distinct tendency. Then, the temperature-dependent thermoelectric transport properties were evaluated in the direction perpendicular to the pressing direction. The carrier concentrations were determined using a Hall measurement in a van der Pauw configuration. Details on the sample preparation and measurement of the thermoelectric properties are described in detail in the previous report [14].

3. Results and discussion

The σ values at room temperature slightly decrease from 862 Scm^{-1} for undoped $Bi_2Te_{2.7}Se_{0.3}$ to 797 Scm^{-1} for 0.02 Nb doping as the Nb doping increases, whereas the magnitude of S at room temperature increases from −178 to −192 μVK^{-1}. As a result, the power factor ($S^2\cdot\sigma$) increases slightly from 2.73 to 2.97 mWm^{-1}K^{-2} through Nb doping (see Fig. 1 in ref.14).

To understand the variation in the observed electronic transport behavior in Nb-doped samples, we first analyzed the effects of Nb doping in $Cu_{0.008}Bi_2Te_{2.7}Se_{0.3}$ on the electronic transport properties by applying a two-band model based on a single parabolic band model (SPB) [12]. With this model, CB and VB can be estimated from Eqs. (1)–(3) [11]:

$$\sigma_{tot} = \sigma_p + \sigma_n, \tag{1}$$

$$S_{tot} = \frac{\sigma_p S_p - \sigma_n |S_n|}{\sigma_p + \sigma_n}, \tag{2}$$

$$R_H = \frac{R_H \sigma_p + R_H \sigma_p}{(\sigma_p + \sigma_n)^2}. \tag{3}$$

Here, σ_p, σ_n S_p, S_n, R_{Hp}, and R_{Hn} are the electrical conductivities for VB (p) and CB (n), Seebeck coefficients for VB and CB, and Hall coefficients for VB and CB, respectively. The σ_{tot} and S_{tot} values are derived from the total contributions of VB and CB (bipolar conduction). The calculated σ_{tot} and S_{tot} values of the samples were fitted to the measured σ and S [14] by fitting the effective mass m^* and deformation potentials E_{def} of VB and CB, the main fitted parameters of which are shown in Table 1. Details of the fitting process and the material parameters are described elsewhere [15]. Herein, we used a band gap E_g value of 0.2 eV for the n-type $Bi_2(Te,Se)_3$ alloys [16]. In addition, the weighted mobility U, which is a product of the non-degenerate mobility (μ_o, as in Eq. (4)) and $(m^*)^{3/2}$ ($U = \mu_0\cdot(m^*)^{3/2}$), is calculated for the electrons and holes (U_{CB} and U_{VB}), as shown in Table 1. The value of U provides information on how the changes in m^* and E_{def} together influence the charge transport.

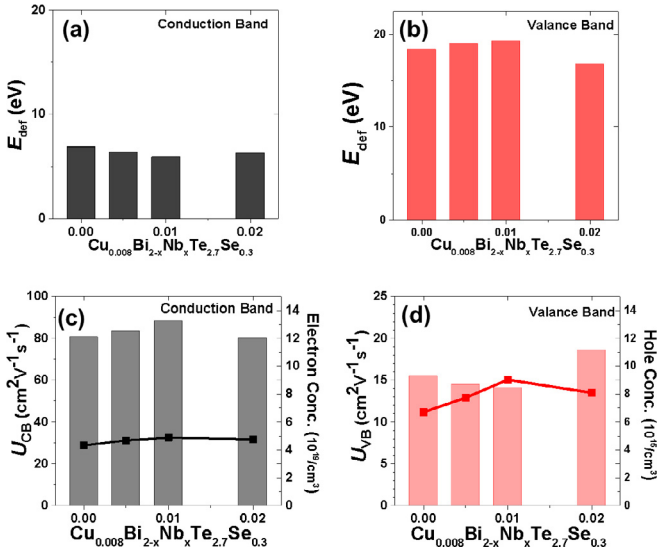

Fig. 1. Deformation potential, weighted mobility of valance band (VB) and conduction band (CB) as a function of x in $Cu_{0.008}Bi_{2-x}Nb_xTe_{2.7}Se_{0.3}$ at 300 K.

$$\mu_0 = \frac{e\pi\hbar^4 v_l^2 d}{\sqrt{2}E_{def}^2 m^*(kT)^{3/2}} \tag{4}$$

Fig. 1 shows E_{def}, U, and the calculated carrier concentrations for CB and VB, which represent the transport characteristics of the electrons and holes. In Fig. 1(a) and (b), E_{def} for CB decreases (whereas E_{def} for VB increases) as the Nb doping increases except at x = 0.02, at which a sudden drop in the carrier concentration occurs for some unknown reason. The value of U_{CB} for CB increases, whereas U_{VB} for VB decreases, as the Nb doping increases except at x = 0.02. Therefore, it can be concluded that the electrons become more mobile, whereas the holes become less mobile, as the Nb doping increases, which implies that σ increases if the carrier concentrations remain the same. However, the observed reductions of σ in the Nb-doped samples [14] result from a large increase (~29%) in the hole concentration (minority carrier) from 6.96 × 10^{15} to 9.03 × 10^{15} cm^{-3} for x = 0.01, as compared to the slight increase in the observed electron concentrations (~13%) (Table 1). Nevertheless, the reduction of σ is compensated with an increase in S, and in turn the power factor is slightly increased [14].

The bipolar conduction of electrons and holes, as analyzed above, also affect κ_{tot}. From the fitted parameters of VB and CB in Table 1, κ_{bp} was estimated from the individual σ_p, σ_n, S_p, and S_n values along with the total σ_{tot} and S_{tot} values, as described in Eq. (4) [11]:

$$\kappa_{bp} = (S_p{}^2\sigma_p + S_n{}^2\sigma_n - S_{total}^2\sigma_{total})\,T. \tag{4}$$

The calculated κ_{bp} is shown in Fig. 2. The value of κ_{bp} was increased ~45%, from 0.22 Wm^{-1}K^{-1} of the un-doped sample to 0.32 Wm^{-1}K^{-1} of x = 0.02 at 440 K. This increase in κ_{bp} is mainly due to the increase in the hole concentration with Nb doping, as analyzed above using a two-band model. The Nb substitutional doping for the Bi site induces holes, which are minority carriers, and thus it enhances the bipolar conduction, which is considered to be detrimental to the thermal conductivity, particularly at a high temperature.

The experimental κ_{latt} was then predicted by subtracting the electronic thermal conductivity κ_{elec} and κ_{bp} from the measured κ_{tot}, as shown in Fig. 3(a), whereas κ_{elec} was estimated using the simple Lorenz number L equation (a function of the total S) [17], as indicated in Eq. (5):

$$L = 1.5 + \exp(-\frac{|S|}{116}). \tag{5}$$

Eq. (5) can simply describe the Lorenz number L with the experimental S based on the two-band model [17]. In addition, the sum of κ_{bp} and κ_{latt} (which is equivalent to κ_{tot} - κ_{elec}) is also shown in Fig. 3(b).

The experimental κ_{latt} (symbols in Fig. 3(a)) was fitted based on a calculation of the theoretical κ_{latt}, which can be predicted using the Callaway equation below:

$$\kappa_{latt} = \frac{k_B}{2\pi^2 v}(\frac{k_B T}{\hbar})^3 \int_0^{\Theta_D/T} \tau_{tot}(z)\frac{z^4 e^z}{(e^z-1)^2}dz, \tag{6}$$

where k_B, v, T, $\hbar$, Θ_D, τ_{total}, and z are the Boltzmann constant, phonon group velocity, temperature, Planck constant divided by 2π, Debye temperature, total phonon relaxation time, and $\hbar\omega/kT$ (ω = the phonon frequency), respectively. Therefore, the determination of τ_{tot} describes the theoretical κ_{latt}.

The τ_{tot} value of the undoped and Nb-doped $Cu_{0.008}Bi_2Te_{2.7}Se_3$ samples can be described using the individual phonon relaxation times