



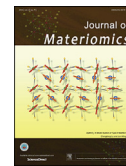
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J Materiomics 2 (2016) 273–279



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Synergistic effects of Lanthanum substitution on enhancing the thermoelectric properties of β -Zn₄Sb₃

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Received 22 March 2016; revised 28 May 2016; accepted 2 June 2016

Available online 21 June 2016

Abstract

A core challenge of thermoelectric research is decoupling the otherwise inversely interdependent properties electrical conductivity, thermopower, and lattice thermal conductivity offering synergistic effects. Herein, we present a systematic study in which we have substituted Lanthanum into the Zn-site in β -Zn₄Sb₃ compound. We observed that La-substitution not only simultaneously enhances electrical conductivity and thermopower over a wide temperature range but also substantially reduces the lattice thermal conductivity. These synergistic effects of La-substitution are discussed in terms of the substitution-induced variation in carrier concentration and effective mass as well as stronger phonon scattering by point defects. As a result, a ~30% increase of the power factor and a ~23% reduction in the lattice thermal conductivity led to a state-of-the-art $ZT \sim 1.3$ at 648 K for the bulk sample of β -La_{0.01}Zn_{3.99}Sb₃.

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Keywords: Thermoelectric; Band engineering; Rare earth; Phonon scattering

1. Introduction

In the wake of increasing energy demand and the environmental detriments of using fossil fuels, the requirement for alternative energy technologies has stimulated research of energy-related materials including thermoelectrics, the simplest technology for heat-to-electricity conversion. The conversion efficiency of a thermoelectric (TE) material is gauged by its dimensionless figure of merit, $ZT = (\sigma S^2/\kappa)T$, where σ , S , κ are the electrical conductivity, thermopower, and total thermal conductivity, respectively. κ can be expressed as the sum of the carrier thermal conductivity κ_e and the lattice

thermal conductivity κ_L . A high ZT value requires a low κ_L and a high power factor $PF = \sigma S^2$. In recent decades, most advances in enhancing ZT values were made by reducing κ_L via nanostructuring [1,2], “phonon liquid” [3,4], all-scale hierarchical microstructures [5,6], anharmonicity [7], phonon localization due to random stacking [8], complex crystal structures [9], phase diagram approach [10] and alloying [11]. As κ_L of start-of-the-art TE materials approaches the “amorphous limit” [12,13], the room for further reduction of κ_L declines.

Now is the time to shift the focus of TE research to enhancing the PF . PF is a function of σ and S , both of which depend on the electron band structure and the scattering mechanisms. Attention should especially concentrate on S , because PF increases with the square of S but only proportional to σ . According to the Mott relation, S for a degenerate semiconductor can be expressed as:

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Peer review under responsibility of The Chinese Ceramic Society.

$$S = \frac{\pi^2 k_B^2 T}{3q} \left[\frac{\partial \ln(\sigma(E))}{\partial E} \right]_{E=E_F}$$

$$= \frac{\pi^2 k_B^2 T}{3q} \left[\frac{1}{p} \frac{\partial p(E)}{\partial E} + \frac{1}{\mu} \frac{\partial \mu(E)}{\partial E} \right]_{E=E_F} \quad (1)$$

with the carrier mobility $\mu(E) = q\tau/m^*$ in the Drude model, where q is the carrier charge, E the energy, $p(E)$ and $\mu(E)$ the energy dependent carrier concentration and mobility, k_B the Boltzmann constant, m^* the effective mass, and E_F the Fermi energy, respectively. In most cases where non-resonant scattering dominates, the relaxation time τ follows a power law behavior $\tau = \tau_0 E^{\lambda-1/2}$, where λ is the scattering parameter and τ_0 a constant. Eq. (1) indicates that S increases with increasing electron density of states (eDOS) near E_F [14]. However, due to the inverse inter-dependence of σ and S , improving S often impairs σ . Consequently, the simultaneous increase of σ and the S must result in synergistic effects. In this work, we show this by taking the example of La-substituted β -Zn₄Sb₃.

β -Zn₄Sb₃ is a promising class of novel TE materials featuring a glasslike low κ_L and a relatively high PF in the temperature range of common applications [15]. Calculations predict that substitution with f -elements such as rare earth elements may introduce additional density of states near the Fermi level, thus, enhancing the thermopower. Indeed, substituting β -Zn₄Sb₃ with Sm (6s²4f⁶), Pr (6s²4f³) and Gd (6s²4f⁶5d¹) enhances the power factor [16–18]. This begs the question of the effect of substituting β -Zn₄Sb₃ with La (6s²5d¹), the only rare earth element without f -electrons. To date, studies on the effect of La-substitution on the TE properties of β -Zn₄Sb₃ are scarce. The prime motivation of this work is, therefore, to reveal the role of f -electrons in rare earth element substituted β -Zn₄Sb₃.

We will demonstrate that La-substitution of β -Zn₄Sb₃ has synergistic effects by simultaneously reducing the electrical resistivity due to a higher carrier concentration, enhancing the thermopower due to an enhanced effective mass, and reducing the lattice thermal conductivity due to point defect scattering of heat-carrying phonons. As a result, the ZT of β -La_{0.01}Zn_{3.99}Sb₃ reaches values of up to 1.3 at 648 K.

2. Experimental procedure

2.1. Sample preparation

Polycrystalline β -(Zn_{1-x}La_x)₄Sb₃ ($x = 0, 0.005, 0.0075, 0.01, \text{ and } 0.0125$) samples were synthesized by melting high-purity elemental Zn (99.9999%, powder), Sb (99.999%, powder) and La (99.999%, powder) according to the nominal composition. An excess of Zn of about 1% was added to compensate for the Zn loss during synthesis. The evacuated and sealed quartz glass tubes with the starting materials were heated at 1023 K for 12 h and then quenched in cold water. The as grown β -(Zn_{1-x}La_x)₄Sb₃ ($x = 0, 0.005, 0.0075, 0.01, \text{ and } 0.0125$) ingot was hand-ground into a fine powder and hot pressed at a pressure of 600 MPa in vacuum at 650 K for 1 h to get disc-shaped samples for TE property characterization.

2.2. Sample characterization

Sample phases were checked by X-ray powder diffraction on a Philips-X PERT PRO[®] diffractometer using Cu-K α radiation. Electrical resistivity ρ ($= 1/\sigma$) and thermopower S were measured on a ZEM-3 (ULVAC-RIKO[®]) in Helium atmosphere in the range of 300 K–650 K. Hall coefficients R_H were measured on a physical property measurement system (PPMS, Quantum Design[®]) at room temperature. The hole concentration p was estimated using the relationship $p = 1/eR_H$, where e is the elementary charge. The Hall mobility μ was calculated using the relationship $\mu = \sigma R_H = R_H/\rho$. The thermal diffusivity α was measured with a NETZSCH LFA-457[®] apparatus in the range of 300 K–650 K in an argon atmosphere using cylinder disks (2–3 mm in thickness) coated with graphite. The total thermal conductivity κ was calculated according to $\kappa = DC_p\alpha$, where C_p is the isobaric specific thermal capacity measured on a differential scanning calorimeter (DSC, Perkin-Elmer[®]) in argon atmosphere and D the density measured by the Archimedes method.

3. Results and discussion

3.1. Phase characterization

XRD patterns of the β -(Zn_{1-x}La_x)₄Sb₃ ($x = 0, 0.0005, 0.0075, 0.01, \text{ and } 0.0125$) samples are shown in Fig. 1(a). All reflections can be indexed to β -Zn₄Sb₃ (JCPDS #89-1969; space group $R\bar{3}c$) and no secondary phase is detected. Upon La substitution, the refinement lattice constant a obviously increases (Fig. 1(b)) accompanied by an increase of the FWHM as demonstrated for the reflection at $2\theta \approx 25.3^\circ$ (Table 1). Both observations are consistent with a substitution of Zn²⁺ with La³⁺. The host lattice increase originates from the larger ionic radius of La (ionic radius La³⁺: ~1.06 Å vs. ionic radius Zn²⁺: ~0.74 Å).

3.2. Thermoelectric properties

Fig. 2(a) shows the temperature dependence of the electrical conductivity ($\sigma = 1/\rho$) of all β -(Zn_{1-x}La_x)₄Sb₃ samples. All samples follow a similar pattern exhibiting a shallow minimum near 500 K, which is ascribed to the onset of the bipolar effect [15,19]. Importantly, σ increases with increasing La-substitution, which can be attributed to an increased carrier concentration (Table 1).

The temperature dependence of the thermopower S of β -(Zn_{1-x}La_x)₄Sb₃ is displayed in Fig. 2(b). As with σ , all samples exhibit the same temperature dependence. S is positive in the whole temperature range indicating a p -type conduction effected by means of holes. Magnitude and temperature dependence of S are typical of degenerate semiconductors. In general, S increases linearly with increasing temperature in the range of 300 K–500 K before reaching a plateau between 500 K and 550 K indicating the onset of the bipolar effect.

We have made two interesting observations: (i) trivalent La (3+) substituting divalent Zn (2+) increased the carrier (hole)

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