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Investigation of $GaBi_{1-x}Sb_x$ based highly mismatched alloys: Potential thermoelectric materials for renewable energy devices and applications

S. AlFaify [a, **, 1], Bakhtiar Ul Haq [a, *, 1], R. Ahmed [b, c, ***], Faheem K. Butt [d, e], M.M. Alsardia [f]

[a] Advanced Functional Materials & Optoelectronics Laboratory (AFMOL), Department of Physics, Faculty of Science, King Khalid University, P.O. Box 9004, Abha, Saudi Arabia
[b] Department of Physics, Faculty of Science, Universiti Teknologi Malaysia, UTM, Skudai, 81310, Johor, Malaysia
[c] Centre for High Energy Physics, University of the Punjab, Quid-e-Azam Campus, Lahore, Pakistan
[d] Physik-Department ECS, Technische Universität München, Garching, Germany
[e] Department of Physics, Division of Science and Technology, University of Education, College Road, Township, Lahore, Pakistan
[f] Department of Physics, Sungkyunkwan University, Suwon, 440-746, Republic of Korea

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ABSTRACT

The high-performance thermoelectric materials are considered a potential resource for clean and sustainable energy. Highly mismatched alloys (HMAs), that are admired for the dramatic modifications in their electronic band structures can essentially play important role in developing high-performance thermoelectric materials. Here, we explore the potential of $GaBi_{1-x}Sb_x$ based HMAs for their thermoelectric applications via density functional theory coupled with the Boltzmann transport theory. To perform a comprehensive analysis, four different Sb alloying compositions such as GaBi, $GaBi_{0.875}Sb_{0.125}$, $GaBi_{0.75}Sb_{0.25}$, and $GaBi_{0.625}Sb_{0.375}$, are considered. It is found that the Sb replacement over Bi in $GaBi_{1-x}Sb_x$ has stimulated two major modifications in the electronic band structure: the band-gap enhancement, and contraction in the curvature of conduction band minimum. These features have remarkably evolved the thermoelectric properties of $GaBi_{1-x}Sb_x$ as a function of Sb contents. The significant increase in Seebeck coefficient and decrease in the electrical conductivity of $GaBi_{1-x}Sb_x$ alloy as a function of Sb content have resulted in large values of thermoelectric power factor as well as the figure of merit (ZT). Considerable improvement in the ZT values as a function of Sb has been recorded that approaches to ~1.0 for $GaBi_{0.625}Sb_{0.375}$ at room temperature. The occurrence of optimal thermoelectric coefficient values, at attainable doping levels below the Fermi level reveals the predominantly p-type nature of the $GaBi_{1-x}Sb_x$. Hence, $GaBi_{1-x}Sb_x$ ($GaBi_{0.625}Sb_{0.375}$ in particular) exhibits interesting thermoelectric properties at room temperature, and is therefore believed to be good candidate material for room temperature based thermoelectric devices and applications.

1. Introduction

The escalating increase in the environmental pollution due to the globalization, the industrial revolution and increased population demands for the alternative and renewable sources. Therefore researchers have shown a remarkable interest in the quest for finding new and improved methods and resources to bring clean, abundant and renewable sources of energy to the society in harmony with nature. This worldwide demand can be accomplished for example, by new and highly efficient energy generating devices based on materials that are earth-abundant and non-toxic. Such motives have made thermoelectrics one of the fascinating topics in the field of sustainable energy utilization [1,2]. The feature of direct inter-conversion between heat energy and electrical energy for

* Corresponding author.
** Corresponding author.
*** Corresponding author. Department of Physics, Faculty of Science, Universiti Teknologi Malaysia, UTM, Skudai, 81310, Johor, Malaysia.
E-mail addresses: saalfaify@kku.edu.sa (S. AlFaify), bakhtiar@kku.edu.sa (B. Ul Haq), rashidahmed@utm.my (R. Ahmed).
[1] These authors contributed equally.

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power generation or refrigeration reveals the significant potential of thermoelectric materials in solving the energy crises that likely can make essential contributions to reducing the carbon-based fuels and cutting energy waste [3]. The efficiency of these materials in terms of converting heat into electrical energy is characterized by the dimensionless figure of merit. The figure of merit, $ZT = S^2\sigma T/\kappa$ is determined by Seebeck coefficient (S), absolute temperature (T), electrical conductivity (σ), and thermal conductivity. To attain a high value of ZT, a large value of the Seebeck coefficient, high electrical conductivity, and low thermal conductivity are needed simultaneously. However, the conflicting correlation between these parameters is the major complexity in achieving the maximum ZT value. Maximizing the ZT value is, therefore, demanding for optimized values of a number of parameters such as carrier concentration, effective masses of charge carriers, and the electronic/lattice thermal conductivity that have been the subject of significant ongoing research in recent years.

Literature shows that relatively high ZT values materials, ranging from 0.6 to 1.1 (at 773–823 K), have been reproduced by employing different approaches such as doping [3,4], microstructure modulation [5,6] and band structure engineering via alloying [7,8]. Alloying of materials (semiconductors in particular) is a pronounced approach offering numerous opportunities for tailoring new dimensions into their physical properties for any desired applications [9–14]. Literature also illustrates that alloying has often been practiced among iso-electronic semiconductors holding relatively well-matching properties for achieving the characteristics as demanded for electronic and optoelectronic applications [10–17]. Such conventional alloys are typically represented by the relation $A_{(1-x)}B_{(x)}C$, where A and B represents the cations usually belongs to group-II or III elements and the anions C is taken from the corresponding VI or V. However, with swift advances in the fabrication and characterization techniques, a new trend of alloying has been established, where the alloying constituents are chosen to be highly mismatched in terms of their physical properties, and this novel class of materials is therefore named as a highly mismatched alloys (HMAs) [16,18–23]. They are now described by the relation $XY_{(1-x)}Z_{(x)}$, with X being the cation from II or III and, Y and Z are the corresponding anions. In contrast to conventional alloys, the host anions are replaced by elements that exhibit enhanced physical properties in HMAs. The capability of HMAs to bring in dramatic evolution in the physical properties, particularly the electronic band gap on account of minor compositional change has triggered the high interest of the scientific community. It is therefore believed that the capability of dramatic modifications in the electronic band structure of HMAs can possibly provide sufficient room for the enhanced thermoelectric performance.

Although many HMAs have been explored for the applications in electronics, optoelectronics, a deep understanding of their thermoelectric coefficients is scarce so far [14,24,25], that demands further investigations in order to develop a useful guide for enhancing their thermoelectric properties. In this paper, we attempted the designing of highly mismatched alloys (HMAs) based on $GaBi_{1-x}Sb_x$ with tunable band gap/band structure and subsequent modulation in thermoelectric properties. The aim of the present study is to examine the potential of the $GaBi_{1-x}Sb_x$ for thermoelectric applications in the framework of density functional theory in conjunction with the Boltzmann transport theory. To explore the dependence of thermoelectric properties $GaBi_{1-x}Sb_x$ on the alloying concentration and temperature, we looked into different compositions of these HMAs such as GaBi, $GaBi_{0.875}Sb_{0.125}$, $GaBi_{0.75}Sb_{0.25}$, and $GaBi_{0.625}Sb_{0.375}$, at 300 K, 600 K, and 900 K to this end.

1.1. Research methodology

In the present DFT based electronic structures study, the calculations are done by the full potential linearized-augmented-plus-local-orbital (FP-L(APW+lo)) method. The basis set used is therefore realized by dividing the unit cell into two regions namely: the interstitial region and the non-overlapping spheres centered on the atoms. In the interstitial region, the wave functions are represented by the plane wave basis set, where inside the spherical region, are augmented by the atomic-like wave function. The wave functions inside the spherical region (muffin-tin spheres) have been expanded up to $l_{max} = 10$, where for the convergence of eigenvalues in the interstitial region, energy cutoff $K_{max} = 8.0/R_{MT}$ (Ryd) $^{1/2}$ was taken into account. The electronic-structure related calculations are performed by the modified Becke-Johnson (mBJ) exchange potential [26–28] including the spin-orbit coupling (SOC) through the second variational procedure [29,30]. Different compositions of $GaBi_{1-x}Sb_x$ are realized by constructing so-called supercells with 16 atoms/cell. To achieve the ground state, geometry optimization was performed by relaxing the ionic positions and cell size. The R_{MT} values were chosen for Ga, Bi and Sb as 2.08 a.u, 2.30 a.u, and 2.30 a.u respectively. The Fourier-expanded charge density was truncated at $G_{max} = 16$ au^{-1}. The Brillion Zone (BZ) integration has been done using Monkhorst–Pack special k-points approach [31]. For good convergence of energy, the integrals over the special BZ are performed up to 256 ($8 \times 8 \times 8$) k-points. The total energy was found to be converged to 10^{-5}Ryd/unit cell in our present self-consistent computations for well-defined results. Calculations based on the mentioned computational details were executed by WIEN2k code [32].

The results of the electronic structure calculations have been used for the calculations of thermoelectric properties within a semiclassical Boltzmann theory under a constant scattering time approximation as implemented in the BoltzTraP code [33]. A brief summary of the adopted method for the calculations of electrical conductivity, Seebeck coefficient, power factor (PF), and ZT value has been given in the following, whereas a detailed explanation of the Boltzmann transport theory can be found elsewhere [34,35]. The mentioned thermoelectric coefficients have been determined as a function of chemical potential (μ) and temperature using the following equations.

$$\sigma_{\alpha\beta}(T,\mu) = \frac{1}{\Omega}\int \Sigma_{\alpha\beta}(\varepsilon)\left[-\frac{\partial f_0(T,\varepsilon,\mu)}{\partial\varepsilon}\right]d\varepsilon, \tag{1}$$

$$S_{\alpha\beta}(T,\mu) = \frac{1}{eT\Omega\sigma_{\alpha\beta}(T,\mu)}\int (\varepsilon-\mu)\Sigma_{\alpha\beta}(\varepsilon)\left[-\frac{\partial f_0(T,\varepsilon,\mu)}{\partial\varepsilon}\right]d\varepsilon, \tag{2}$$

where α and β are Cartesian indices of the tensor quantities. Symbols e, Ω and f_o represent the electronic charge, volume of the unit cell and the Fermi–Dirac distribution function of the carriers respectively.

The energy projected transport distribution function represented by $\Sigma_{\alpha\beta}$ is central term in equations (1) and (2) and can be defined as

$$\Sigma_{\alpha\beta}(\varepsilon) = \frac{e^2}{N}\sum_{i,k}\tau v_\alpha(i,k)v_\beta(i,k)\delta(\varepsilon-\varepsilon_{i,k}), \tag{3}$$

where $v_\alpha(i,k) = \frac{1}{\hbar}\frac{\partial\varepsilon_{i,k}}{\partial k_\alpha}$ represents the group velocity, and i, k, N, and τ mentioned in Eq. (3) are used for the band index, wave vector, the total number of k-points used for the BZ sampling and relaxation