FINAL TECHNICAL REPORT "FUNDAMENTAL UNDERSTANDING AND THEORECTICAL DESIGN OF NOVEL NANOSTUCTURED SEMICONDUCTOR MATERIALS"

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This research was for the fundamental understanding and theoretical design of novel nanostructured semiconductor materials with a potential impact in the areas of thermoelectrics, solar energy, and the role of impurities and embedded nanoparticles. The most challenging phase of the theoretical research was attacked so as to help understand the underlying fundamental electronic structures, find the key mechanism, and finally suggest design principles for desirable thermoelectric and solar energy materials. This involves developing new insights via theoretical calculations for interfaces, nanostructures, and defect structures including important refinements for electronic structures such as screened exchange (sX)-LDA and model-GW for band gap and band offset problems, optical properties such as dielectric functions and second harmonic susceptibilities, phonon dispersions of guest and host materials including thermal conductivity with the linear response approach, and transport properties including electrical conductivity and Seebeck coefficients using our newly developed transport codes.   Specific materials/properties to be investigated include thermoelectrics (notably PbTe and SnTe as host materials) and transport, optical, and work functions of photovoltaic materials and transparent conducting oxides.

Electronic structure and volume effect on thermoelectric transport in p-type Bi and Sb tellurides

The development of highly efficient thermoelectric (TE) materials is important for refrigeration and energy generation and storage technologies. The efficiency of TE materials is represented by the figure of merit, $ZT = S^2 \sigma T / (\kappa_e + \kappa_L)$, where S is the Seebeck coefficient, σ is the electrical conductivity, and κ_e and κ_L are the electronic and lattice thermal conductivities, respectively. Thus, a higher ZT can be obtained by decreasing the denominator (smaller κ_e and/or κ_L) or by increasing the numerator (larger S and/or σ. Although the thermoelectric materials have been extensively studied for the last decade, there are only a few theoretical simulations of their transport properties.

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Bi$_2$Te$_3$ alloys with peak $ZT \sim 1.0$ are well-known conventional materials for thermoelectric applications near room temperature. In the experiments for Bi$_2$Te$_3$ and Sb$_2$Te$_3$-based alloys, the doping of bismuth and antimony atoms in Sb$_2$Te$_3$ and Bi$_2$Te$_3$, respectively, influences the thermoelectric properties, where it is generally known that the antisite defects are the origin of the current carriers. In addition, recently, the highest ZT value of ~2.4 was reported at 300 K in p-type Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattices. Even though the phonon-blocking/electron-transmitting mechanism in the superlattice was suggested, to our knowledge, the influence of the thickness and volume of each layer for the electronic transport coefficients of S and σ is not well understood. In this work, we first investigate the temperature-dependent behavior of the thermoelectric property in bulk Bi$_2$Te$_3$, (Bi$_{0.5}$Sb$_{0.5}$)$_2$Te$_3$, and Sb$_2$Te$_3$; discuss the role of carrier concentration, band gap, and electronic structure; and compare the results to experiments. Second, we suggest that the dopant size effect by Bi and Sb cation doping can be one of the origins to influence the thermoelectric property, even though both Bi and Sb have the same number of valence electrons, and it is demonstrated that S in Sb$_2$Te$_3$ increases due to the volume expansion associated with the doping of larger Bi atoms.

For the study, we considered the rhombohedral structure for Bi$_2$Te$_3$ and Sb$_2$Te$_3$, and the hexagonal supercell structure for (Bi$_{0.5}$Sb$_{0.5}$)$_2$Te$_3$ where each Bi (Sb) atom has four and two nearest neighbors of Sb (Bi) and Bi (Sb), respectively, in the hexagonal plane. We used experimental lattice constants for Bi$_2$Te$_3$ (a_{BT}=4.386 Å, c_{BT}=30.497 Å) and Sb$_2$Te$_3$ (a_{ST} =4.264 Å, c_{ST}=30.458 Å), and average lattice constants for _Bi0.5Sb0. (Bi$_{0.5}$Sb$_{0.5}$)$_2$Te$_3$. The internal atomic positions in (Bi$_{0.5}$Sb$_{0.5}$)$_2$Te$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ were optimized via force and total-energy minimization. Experimentally, the Sb-doped Bi$_2$Te$_3$ shows p-type character; therefore, we discuss only p-type Bi and Sb tellurides for comparing with experimental results. The electronic structure was calculated using the highly precise all-electron full-potential linearized augmented plane-wave (FLAPW) method in the localdensity approximation (LDA) with spin-orbit coupling (SOC) included by a second variational method. Further, the screened-exchange LDA (sX-LDA) method is used for obtaining correct band gaps at zero temperature. The sXLDA method is known to provide a better description of the excited states and band gaps; in particular, good agreement with the experimental band gap (0.162 eV) was obtained for Bi$_2$Te$_3$ (0.154 eV). To determine the Seebeck coefficient and the electrical conductivity, we employed the distribution function given by Boltzmann's equation in the constant relaxation-time approximation.

Thermoelectric transport properties (Seebeck coefficient, S, and electrical conductivity, σ) of p-type Bi and Sb tellurides are investigated using a first-principles all-electron density-functional approach. We demonstrate that the carrier concentration, band gap, and lattice constants have an important influence on the temperature behavior of S and that the volume expansion by 5.5% in Sb$_2$Te$_3$ results in an increase in S by 33 µV/K at 300 K. We argue that in addition to the electronic structure characteristics, the volume also affects the value of S and hence should be considered as an origin of the experimental observations that S can be enhanced by doping Sb$_2$Te$_3$ with Bi (which has a larger ionic size) in Sb sites or by the deposition of thick Bi$_2$Te$_3$ layers alternating with thinner Sb$_2$Te$_3$ layers in a superlattice, Bi$_2$Te$_3$ / Sb$_2$Te$_3$. We showed that the optimal carrier concentration for the best power factor of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ is approximately 10^{19} cm^{-3}.

In summary, using a first-principles density-functional approach, we have calculated the transport coefficients for pure and mixed Bi and Sb tellurides. We showed that the carrier concentration, electronic structure, and volume have an important influence on the temperature

dependent S, such as the peak location and the slope. We found that the optimal carrier concentration for the best power factor of Bi_2Te_3 and Sb_2Te_3 is approximately 10^{19} cm^{-3}. This may give a good insight to fabricate more efficient thermoelectric materials and devices.

"Electronic structure and volume effect on thermoelectric transport in p-type Bi and Sb tellurides", (M. S. Park, J. H. Song, J. E. Medvedeva, M. Y. Kim, I. G. Kim, A. J. Freeman), Physical Review B, **81**, 155211 (2010)

Electronic structure and transport properties of doped PbSe

PbTe-based materials, including nanostructures, alloys, and also the 2% Tl-doped bulk materials, have shown good properties in thermoelectric applications. Compared with PbTe, another lead chalcogenide, PbSe has several advantages with respect to thermoelectric application. First of all, selenium is much more abundant than tellurium, which can reduce the cost of related devices. Second, bulk PbSe has a smaller lattice thermal conductivity than PbTe, which is beneficial for a larger figure of merit. Third, bulk PbSe has a higher melting temperature than PbTe (1082°C versus 924°C), which means a possibly better thermal stability. In this study, we investigate the electronic structures and transport properties of PbSe doped with a serial of impurities including cation-site substitutional impurities (Na, K, Rb; Mg, Ca, Sr; Cu, Ag, Au; Zn, Cd, Hg; Ga, In, Tl; Ge, Sn; As, Sb, Bi) and anion-site substitutional impurities (P, As, Sb; O, S, Te), using first-principles band structure calculations. We calculate the difference between the DOS of the doped samples and the pure host sample to find a local increase near the Fermi level. The chemical trends and the nature of impurity states are well described using the linear combination of atomic orbitals (LCAO) picture. Within the framework of Boltzmann theory, using the constant relaxation time approximation and rigid band model, the transport properties and the power factor for the semiconducting doped samples are calculated. We find that (1) changes in the DOS of PbSe due to different impurities are very similar with those that happen to PbTe; (2) there is a significant enhancement of the power factor in cation-site Au- and As-doped PbSe; (3) with the impurity concentration in this work (3.125%), Tl doping does not improve the thermoelectric properties of PbSe; (4) the HMA method is not applicable for PbSe, so it is not universal.

Understanding the electronic structure and transport properties of doped PbSe for its thermoelectric applications is an urgent need. Using a first-principles approach, we first explored the band structures of PbSe doped with a series of impurities, including cation-site substitutional impurities (Na, K, Rb; Mg, Ca, Sr; Cu, Ag, Au; Zn, Cd, Hg; Ga, In, Tl; Ge, Sn; As, Sb, Bi) and anion-site substitutional impurities (P, As, Sb; O, S, Te). Then we calculated the density of states (DOS) difference between the doped samples and pure host sample, which is a useful quantity to recognize the possibility of improving transport properties. The exhibited chemical trends and the nature of the impurity states are well explained with a simplified linear combination of atomic orbitals (LCAO) picture. Finally, we calculated the transport properties of these doped systems within the framework of Boltzmann theory and constant relaxation time approximation. Typical competing behavior between the electrical conductivity and Seebeck coefficient is exhibited, and a significant enhancement of thermoelectric power factor is found in the cation-site Au-doped p-type samples, and cation-site As-doped n-type samples.

In summary, we calculated the band structures, density of states (DOS), change in DOS, Seebeck coefficients, electrical conductivities, and power factors of PbSe doped with various impurities. From our results and previous investigations, we conclude the following:

(i) The effects of the same impurity in PbSe and PbTe are very similar.

(ii) Impurity-p or -d orbitals are much more efficient than impurity-s orbitals to resonate with or to perturb the host bands. They are also more efficient to produce a local increase of the DOS. The former impurities include As, Sb, and Bi doped on the cation site, P, As, and Sb doped on the anion site, and Cu, Ag, and Au doped on the cation site. The latter impurities include Zn, Cd, and Hg doped on the cation site.

(iii) The impurity states near E_F in PbSe doped with Ga, In, and Tl are host states perturbed by the deep impurity-s states. We did not find an enhancement of the power factor in PbSe:Tl.

(iv) We did not find an enhancement of the power factor in PbSe:O. The highly mismatched isoelectronic doping method is not a good method to enhance the power factor of PbSe. PbSe is a kind of "$5e$" compound because Pb and Se have an average of five valence electrons, whereas ZnSe is a kind of "$4e$" compound. We believe that the highly mismatched isoelectronic doping method may be good for the $4e$ compounds but not for the $5e$ compounds.

(v) PbSe:Au is a good candidate for p-type thermoelectric materials because of resonance states and a local increase of the DOS, compared with PbSe:Na.

(vi) PbSe:As$_c$ is very likely to be a good candidate for n-type thermoelectric materials because of resonance states and a local increase of the DOS, compared with PbSe:I; further, PbSe:Zn and PbSe:Cd may be good candidates for n-type thermoelectric materials because of an additional energy pocket. But for all the n-type samples, more delicate investigations are needed because of the neglect of spin-orbit coupling in this study.

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