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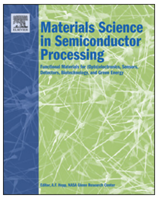

Thermoelectric studies of IV–VI semiconductors for renewable energy resources

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ABSTRACT

In the present study we explore the structural, electronic and thermoelectric properties of IV-VI semiconductors using first principle calculations based on the density functional theory. Generalized gradient approximation (GGA-PBEsol) is used as an exchange-correlation functional for the structural properties of the different crystal phases of these semiconductors. The compounds SnS, SnSe, GeS and GeSe favor orthorhombic structure, lead chalcogenides (PbS, PbSe and PbTe) are stable in the cubic rocksalt structure, while SnS_2 and $SnSe_2$ exist in hexagonal structure. For band structures additional to GGA, modified Becke and Johnson (mBJ) exchange potential is used. These compounds are narrow band gap semiconductors in the energy range 0.2–2.8 eV. These binary IV-VI chalcogenides have direct band gap nature in cubic crystals while indirect in the orthorhombic phases. The post-DFT (BoltzTraP) calculations are performed to estimate Seebeck coefficient, electric and thermal conductivities, power factor and figure of merit of these compounds to check their applicability in thermoelectric devices. Spin orbit coupling effect influences the electronic and thermoelectric properties of these compounds due to the large size of the constituent elements. Further, the total thermal conductivity is computed using ad-hoc calculation with the experimental results. The calculated values of figure of merit for PbS, PbSe, PbTe and SnTe are in the range 0.68–0.77 at room temperature.

1. Introduction

The energy crises make the world eager for energy resources, causing social and economical problems. The globe will become energy desert if new abundant and environmental friendly resources are not identified. One of the solutions to the problem is the recovery of waste heat for useful purposes. Therefore, researchers across the world are searching for efficient thermoelectric materials.

Thermoelectric conversion technology has received increasing attention in the recent years because of the worldwide energy needs and environmental problems. In this regard great progress has been observed in the development of high-performance thermoelectric materials. Thermoelectric generator is a device that converts waste heat into useful energy. Thermoelectric generator is based on Seebeck effect while cooler is based on Peltier effect, containing no moving parts unlike traditional heat engines, refrigerators and air conditioners. These devices could be used reliably for 25–30 years without any repairing operations. Thermoelectric devices have lower efficiency than common used generators but for small applications these devices are very useful for energy harvesting. These devices are useful to harvest waste heat in automobiles, industries and even from human body for wristwatch design by Seiko and Citizen. For high efficiency of thermoelectric devices, recently new approaches are developed in nanowires, thin films and bulk nano-structured materials.

The efficiency of thermoelectric materials is determined by the dimensionless figure of merit ($ZT = S^2\sigma T/\kappa$), which depends on Seebeck coefficient (S), electrical conductivity (σ), thermal conductivity (κ) and absolute temperature. The relationship between thermopower (seebeck coefficient), electrical conductivity and thermal conductivity is quite complex, but it is possible to fluctuate one of the parameters while keeping the others constant with band gap engineering. High ZT means increase in power factor ($S^2\sigma$) and decrease in thermal conductivity without depressing the electric conductivity of a material. An average ZT, in the operating temperature range must be higher than 1 to make a thermoelectric device competitive [1]. There have been persistent efforts to improve ZT values during the past two decade, in (i) superlattices [2], and (ii) bulk materials, [3]. Although high ZT values are reported in superlattice structures, but it has been proven that these materials are difficult to use in large-scale energy-conversion applications because of their limitations of heat transfer and cost. Bulk materials with improved ZT, such as lead

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antimony silver telluride (LAST) and IV-VI monochalcogenide semiconductors are ideal for high-temperature operations [4].

The IV-VI chalcogenides family such as SnSe, SnS, SnTe, PbSe, PbS, PbTe, GeSe, GeS, GeTe, $SnSe_2$, SnS_2 and their alloys are promising materials for thermoelectric generators, optoelectronic devices, temperature sensors, telecommunications, holographic recording systems, memory switching devices, etc. [5–8]. Different physical properties of these semiconductors such as structural, electronic and optical properties are extensively investigated experimentally, however most of the theoretical studies are limited to the understanding of their basic physics and chemistry of the structural phase transitions, electronic band gaps and ferroelectric like behavior at low temperatures [9]. These IV-VI compounds crystallize in different crystal structures. The lead chalcogenides PbS, PbSe, PbTe, GeTe and SnTe adopt the NaCl structure with each atom in an octahedral coordination of six atoms of the other type [10]. The compounds SnS, SnSe, GeS and GeSe have orthorhombic crystal structure with the space group Pnma (#62) [11], except SnSe which occurs in space group Cmcm (#63) [12]. Whereas, $SnSe_2$ and SnS_2 exist in hexagonal crystallographic structure with space group P-3ml (#164) and P3ml (#156) respectively [13,14]. Ettema et al. [10] theoretically reported the structural phase transition of SnS between α (low temperature phase) and β (high temperature phase), having space group Pnma and Cmcm respectively, but α-phase has larger band gap than β. Loa et al. [15] found orthorhombic structural phase transition of SnSe from low pressure phase α (Pnma #62) to high pressure phase (10.5 GPa) β (Cmcm#63) using angle-dispersive synchrotron x-ray powder diffraction method. Below 100 K, the cubic structure of SnTe is changed to rhombohedral structure which is the equilibrium structure of SnTe [14].

Lead chalcogenides have been extensively studied theoretically and experimentally due to their potential applications in thermoelectric energy converters and electronic devices. The experiments as well as first principle calculations confirm direct band gap nature of these materials [9,16]. PbX (X=Se, S, Te) crystallize in NaCl-type structure at lower pressure, where adopt orthorhombic structure in the pressure range 2.5–6 GPa, however on further increase in pressure (13–25 GPa) they transform to CsCl-type structure, metallic and superconductors [16]. Wiedemeier et al. [17] investigated the structure of GeS and GeSe by using X-ray diffraction technique. They predict that GeSe transfers from orthorhombic to cubic phase with increasing temperature while GeS (space group Pnma, #62) melts before transformation to other structure, but Durandurdu [18] theoretically predicts NaCl type structure as high pressure phase of GeS (space group Cmcm, No. 63). Edwards et al. [19] studied the electronic structure of GeTe both for low temperature rhombohedral phase and high temperature cubic phase by using SEQQUEST and ABINIT plane-wave pseudo-potentials method in DFT.

Thermoelectric properties of pure and doped IV-VI semiconductors are extensively studied experimentally and there are also available some theoretical results on these compounds in different crystal structures. Tan et al. [20] investigated the thermoelectric properties of SnS both in pure and doped form. Cheng et al. [21] investigated thermoelectric properties of SnSe doped with Ag and measured ZT=0.6. The thermoelectric power factor of SnS, SnSe, GeS, and GeSe are theoretically calculated as 21.25, 20.07, 30.25 and 35.03 $\mu W\,cm^{-1}\,K^{-2}$ for n-type concentration and 14.70, 23.48, 15.03 and 15.02 $\mu W\,cm^{-1}\,K^{-2}$ respectively for p-type concentration at 300 K [22]. Seebeck coefficient, electric and thermal property of lead chalcogenides are calculated both in pure and doped form [23–27].

The above extensive literature confirms the versatility of these compounds in different device applications. In the present theoretical studies structural, electronic and thermoelectric properties of IV-VI binary compounds in different crystal structures are investigated.

2. Method of calculations

We make use of the density functional calculations in the frame work of full potential linearized augmented plane-wave (FPLAPW) method as implemented in the Wien2k package [28]. For the calculation of structural and electronic properties exchange and correlation interactions are described using the generalized gradient approximation (GGA-PBEsol) [29] and modified Becke-Johnson (mBJ) exchange potential [30]. Both local density approximation (LDA) and generalized gradient approximation (GGA) are somewhat successful in calculating the structural properties but fails to reproduce experimental band gaps of semiconductors and insulators. Recently Tran and Blaha develop modified Becke and Johnson (mBJ) approximation for the exchange potential for the calculation of the band structures, whereas the correlation potential comes from the original LDA or GGA [30]. The mBJ exchange potential is an empirical relation of the form:

$$v_{x,\sigma}^{mBJ}(r) = c v_{x,\sigma}^{BR}(r) + (3c-2)\frac{1}{\pi}\sqrt{\frac{5}{12}}\sqrt{\frac{2t_\sigma(r)}{\rho_\sigma(r)}} \tag{1}$$

where $\rho_\sigma(r)$ is the spin dependent density of states, $t_\sigma(r)$ is the kinetic energy density and $V_{x,\sigma}^{BR}$ (r) is the Becke-Roussel potential, and c is density dependent parameter given by:

$$c = \alpha + \beta\left(\frac{1}{V_{cell}}\int_{cell}\frac{|\nabla\rho(r')|}{\rho(r')}d^3r'\right)^{\frac{1}{2}} \tag{2}$$

In this equation, $\alpha = -0.012$ and $\beta = 1.023$ bohr1/2 are two free parameters. The values of these parameters are generally fixed by experiments for compounds. The mBJ calculations are computationally as cheaper as ordinary LDA or GGA calculations. As a general result, this potential causes a rigid displacement of the conduction bands toward higher energies with respect to the top of the valence band, with small differences in the dispersion at some regions of the Brillouin zone but reproducing, in general, the characteristic behavior of the bands for each semiconductor according to experiment [31]. mBJ offer high-precision and accurate calculations of electronic band structures which is required to quantify accurately thermoelectric coefficients. Spin-orbit coupling (SOC) is a relativistic effect and is an interaction of particles that depends on the values and mutual orientations of the particles, orbital and spin angular momenta and that leads to the fine-structure splitting of the system's energy levels. We include the spin-orbit coupling in our calculations by using the second variational method [32] programmed in the WIEN2K code. The second variational method, which makes use of the scalar-relativistic basis, is based on the reduction of the original basis. In the first step of this approach, the scalar-relativistic part of the Hamiltonian is diagonalized in the scalar-relativistic basis. In the second step, the full Hamiltonian matrix including SOC is constructed using the eigen functions of the first step Hamiltonian [33].

In full potential scheme, the wave functions inside the non-overlapping spheres are expanded as spherical harmonics up to angular momentum $l=10$. Plane wave expansion is used in the remaining space of the unit cell (interstitial region) fixing the parameter $R_{MT}/K_{\max}=7$. The atomic spheres are used in such a way that no charge leakage occurred. The Brillouin zone integration is performed with a 200 k-point for the self-consistency cycle which is taken to be converged when the forces on the atoms fell below 1.0 mRy/a.u. Whereas to calculate the thermoelectric parameters a dense k mesh of 50,000 k points is used in this work as the