Novel natural super-lattice materials with low thermal conductivity for thermoelectric applications: A first principles study

P.C. Sreeparvathy, V. Kanchana [*]

Department of Physics, Indian Institute of Technology Hyderabad, Kandi, 502 285, Sangareddy, Telangana, India

A B S T R A C T

A systematic study which reveals the low thermal conductivity and high thermopower on a series of natural superlattice structures in the form BaXFCh (X: Cu, Ag, Ch: S, Se, Te), LaXSO (X: Cu, Ag) and SrCuTeF are presented. Low thermal conductivity is predicted by combining elastic constants and few well established models. The electronic properties reveal the highly two dimensional nature of band structure in the valence band, and this is confirmed through effective mass calculations. The huge difference in effective mass along different crystallographic directions in valence band introduces anisotropy in the transport properties for hole doping, and 'a' axis is found to be more favourable. In addition to these, the parameter A ($S^2\sigma/\tau T/\kappa_e/\tau$), which can decouple the relaxation time is also calculated, and it reveals the possibility of good thermoelectric properties in these compounds. Our results are comparable with prototype thermoelectric materials, and show better values than traditional TE materials.

1. Introduction

Thermoelectric materials have drawn attention as alternative energy source decades ago, and the wide range of applications and its unique properties made them attractive till today [1]. For commercial applications, the efficiency of the TE materials has to improve, but the conflicting requirements limits the efficiency. The performance of a TE material is defined by the dimensionless figure of merit, zT, given by $zT = \frac{S^2\sigma T}{\kappa}$, where S, σ, κ and T are the thermopower, the electrical conductivity, the thermal conductivity, and the absolute temperature, respectively. κ includes both the electronic κ_e, and the lattice contributions κ_l, i.e, $\kappa = \kappa_e + \kappa_l$. Seebeck coefficient, electrical conductivity and thermal conductivity are the conflicting parameters. Several methods have been adapted to improve the efficiency of a thermoelectric material, and these methods mainly focus on enhancing the power-factor or to suppress the lattice thermal conductivity. Supperlattice is one of the emerging technique which can elevate the efficiency of TE properties by these two methods. The impact of two dimensional quantum well structures on thermoelectric properties have attracted long back itself [2], as there would be more number of controlling parameters to tune the value of zT (figure of merit) compared to normal bulk structures, which means that the thickness also plays a role in these structures. Since the charge carriers in the 2D quantum well structure are confined in a plane

(which will be within the plane of layer), the scattering effect along the perpendicular direction will be very less, and that leads to a constant mobility in the plane, whereas the phonons are not confined in any plane, so the interface scattering will be playing a significant role, leading to reduction of lattice thermal conductivity [2]. In addition to this, the thermopower value is also found to be higher in the quasi two dimensional structures. The origin of the large Seebeck coefficient is discussed in the previous study by Kuroki, and they explained that the peculiar band model referred as "pudding-mold" which contain the combination of highly flat and dispersed band [3], could be the reason for high Seebeck coefficient. As we mentioned, superlattice structure can enhance the TE efficiency, but the practical difficulties like lattice mismatch and reproducibility will constrain the production. On this basis, the search for natural superlattice materials which have inherent 2D electronic structure properties are highly demanding. Recent study on Na_xCoO_2 revealed the potential TE property [4], which mainly emerged due to two dimensional electronic structure [5]. Electron doped $FeAs_2$ revealed large Seebeck coefficient due to quasi one dimensional band structure [6]. Layered crystal structures are always interesting to analyse, and the distinct properties of these materials are decided by the bonding within the layers and the bonding between two layers, specifically the weak bonding nature between two layers of the system introduce dimensional reduction. The high temperature superconductivity in La based layered

---

* Corresponding author.
   E-mail address: kanchana@iith.ac.in (V. Kanchana).

material is an example [7]. Later on, this approach is generalized as new chemistry for zintl-phase compounds, which involves construction of crystal structures out of charge compensating layers, specifically a stable cationic layer, e.g. SrF or LaO, and an anionic functional layer, e.g. FeAs, to make compounds like LaFeAsO [7] or SrFeAsF [8]. The interaction between these two charged layers is Coulombic. The competing charge flow between these two layers makes this zintl-type of compounds more significant for the present research world. The layered crystal structures makes the compounds two-dimensional with quasi-flat electronic structure leading to less dispersive bands at the band edges, resulting in high thermopower in these type of zintl compounds enabling them as good thermoelectric candidates. The hetrolayered '1111' type compounds have attracted because of several properties, like ionic conductivity, moderate temperature super conductivity and many more [7,9]. The compounds like BiCuSeO [10], SrAgSF [11] have drawn attention to thermoelectricity also. We present further investigation on these series to explore the potential compounds for thermoelectric applications. An ideal thermoelectric material for device application should have, high mechanical strength, high melting point, high Seebeck coefficient, high electrical conductivity and low thermal conductivity. From this point of view we have done an extensive study on this present compounds, which reveals their mechanical, electronic and transport properties. We have chosen zintl-type compounds in the form of BaCuChF (Ch = S, Se, Te), BaAgFCh (Ch = S, Se, Te), SrCuTeF, LaCuSO, LaAgSO for this purpose.

2. Computational details

The electronic band structures were calculated by means of full-potential linear augmented plane wave (FP-LAPW) method based on first-principles density functional theory as implemented in the WIEN2k code [12]. The structural optimisation is carried out to compute the ground state properties within the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) potential [13], using the experimental parameters with an energy convergence criterion of 10^{-6} Ry per formula unit. The traditional exchange-correlation potential of Local-Density Approximation (LDA) or Generalized Gradient Approximation (GGA) schemes for the exchange-correlation underestimate the band gaps of semiconductors, and we have used the modified GGA known as the Tran-Blaha modified Becke-Johnson [14] potential (TB-mBJ) [15]. For k-space integrations a $12 \times 12 \times 5$ k-mesh was used. The self-consistent calculations included spin-orbit coupling. The carrier concentration (p for holes and n for electrons) and temperature (*T*) dependent thermoelectric properties like thermopower (*S*), electrical conductivity scaled by relaxation time (σ/τ) were calculated using the BOLTZTRAP [16] code, within the Rigid Band Approximation (RBA) [17,18] and the constant scattering time (τ) approximation (CSTA). In the RBA the band structure is assumed unaffected by doping, which only leads to a shift of the chemical potential. For semiconductors it is a good approximation for calculation of the transport properties, when the doping level is not too high [18–23]. In CSTA, the scattering time of electrons is assumed to be independent of the electron energy, while it may depend on carrier concentration and temperature. A detailed discussion of the CSTA is given in Refs. [24–26], and references therein. The only situation where the CSTA can fail is when bipolar conduction is significant, which happens in narrow-gap materials. The phonon dispersion of investigated compounds is calculated using pseudo potential method implemented in Quantum espresso program. Electron localization function (ELF) is calculated using VASP [27].

3. Results and discussions

3.1. Structural properties

The speciality of the investigated compounds originate from the crystal structure itself, where all the compounds crystallize in tetragonal structure with alternative layers of conducting X_2Ch_2 (X: Cu Ag, Ch: S, Se,

Te) and insulating Ba_2F_2 segments, see Fig. 1. The structural parameters are optimized using experimental values, and the obtained lattice parameters agree with the experimental values as seen in Table 1. To comment more on structural properties, we have calculated the bond lengths of all the investigated compounds, and are represented in Table 2. It is observed that in BaCuSF, Cu—S bond has more ionic character compared to Ba—F bond, where Cu—S bond length is more close to the sum of the radius of cation and anion, and the same trend is followed for BaCuSeF and BaCuTeF. Among these three compounds, Cu—Te bond in BaCuTeF is found to be more ionic. In the case of BaFAgS, Ag—S bond is found to be more ionic compared to Ba—F bond, and same trend is followed down the column in periodic table. While comparing BaCuSF and BaAgSF, it is observed that all bond length are higher for BaFAgS, and same trend is observed for Se and Te based compounds. In addition to this, Ba—Cu distances in BaCuChF compounds are lesser than Ba—Ag distances in BaAgFS compounds, which might be due to the weak bonding nature of Ag in these compounds, and this is further discussed in the upcoming section. Estimation of bond angle will help to understand the bond distortions, and are represented in Table 2. It is found that in BaCuSF, the bond angle of Ba—F bond is more tetragonally distorted compared to Cu—S bond, where ideal tetragonal bond is 109.5°, and Cu—S bond angle has almost same angle as tetragonal. Bond angles for Ba—F, and X-Ch are found to increase from S to Te, and compared to Cu compounds Ag based compounds have higher bond angle for all the bonds as seen in Table 2. The more distorted bonds may lead to soft lattice and introduce more anharmonicity in lattice thermal conductivity [28]. Now let us analyse the nature of charge density in investigated compounds, and for this we have represented the charge density of [100] plane of BaFAgS (See Fig. 2). From the figure it is evident that along 'xy' plane there is a charge flow, but there is no charge flow along 'z' direction, and this may lead to a huge anisotropy along 'z' direction in the system. For further analysis we have calculated the electron localization function (ELF) for the investigated compounds and in Fig. 3 we have shown the ELF for BaFAgS. ELF can help to identify the chemistry of bonds, and a value close to unity indicate the more covalent character. In Fig. 3 we can see the Ba, S, and F atoms shows this (see the red color), but around Ag atom we found very less ELF value, which indicate the weak Ag bonds in this series. Our results are in line with the previous results for prototype compounds [28].

Moving to electronic structure, we have calculated the band structure using TB-mBJ functional to predict proper band gap of investigated compounds. In Table 1, we have given the band gap using both PBE and TB-mBJ functionals, and from this it is quite clear that the PBE functional underestimate the band gap, and further calculations were performed using TB-mBJ functional only. Fig. 4 represents the band structure of one of the investigated compound, since all the compounds have very similar band structure. The earlier study on these compounds revealed the role of spin-orbit coupling [29], and our calculations also included spin orbit coupling. As we discussed earlier, the investigated compounds crystallize
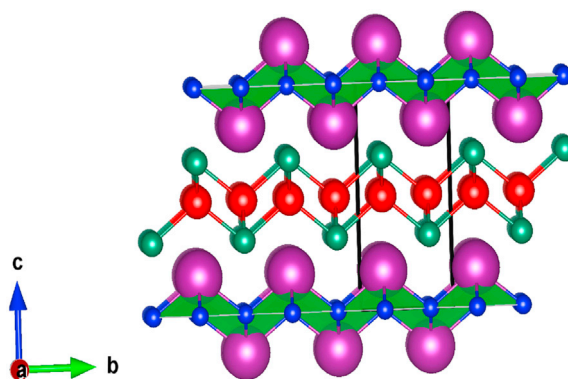

Fig. 1. Crystal structure of investigated compounds.