



First principles study of thermoelectric properties of Li-based half-Heusler alloys



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ABSTRACT

Thermoelectric materials with good figures of merit are being sought for perpetually. In this paper, thermoelectric properties of LiYZ ($Y = \text{Be, Mg, Zn, Cd}$ and $Z = \text{N, P, As, Sb, Bi}$) have been studied employing first principles density functional theory based calculations followed by the solutions of Boltzmann transport equations under relaxation time approximation. Calculated Seebeck coefficients are quite large and are comparable to that of PbTe , a well known thermoelectric material. Doping dependence of the transport coefficients are calculated under rigid band approximation. Except LiZnSb , all the compounds have larger values of power factors for p-type doping than those for n-type doping. The optimal p- and n-type doping levels corresponding to the maximum thermoelectric power factors of these compounds have been calculated, which are important parameters for guiding experimental works.

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1. Introduction

The world at present is facing two major problems relating to energy. One is the energy crisis and another is its environmental impact arising from conventional ways of utilizing energy resources. The first problem is driving research for alternative energy resources and the second problem concerns better ways of utilizing the energy resources. Thermoelectricity is considered to be one of the potential ways towards addressing both these problems [1–3]. However, the efficiency of a thermoelectric device is too low to compete with the conventional ways of producing electricity [4,5]. The thermoelectric performance of a thermoelectric material is determined by its figure of merit, ZT given by $ZT = S^2 \sigma T/k$, where T is the absolute temperature, S is Seebeck coefficient (also known as thermopower), σ is electrical conductivity and k is the thermal conductivity which is the sum of electronic and lattice contributions to thermal conductivity. With the renewed interest in thermoelectricity, mainly from 1990, the figure of merit has reached above 1 from about 0.5 in 1950 [6]. In order to have larger figure of merit, we need to have a large value for $S^2 \sigma$ (also known as power factor) and a small value for thermal conductivity. Though there is no theoretical upper limit for the figure of merit, it is challenging to achieve higher values because of the conflicts between the three transport properties S , σ , k . Thus, a compromise has to be reached among these conflicting parameters to enhance the figure of merit.

Half-Heusler materials are considered to be potential thermoelectric materials [7–9] because of their large temperature stability. Furthermore, they offer the possibility of alloying, which can reduce thermal conductivity due to mass fluctuation [2]. Recently Carrete et al. [10] studied thermal conductivity of a large number of half-Heusler alloys (HHs) from the view point of their thermoelectric prospects. Many HHs have been studied over the years with the main focus on MnNiSn ($M = \text{Ti, Zr, Hf}$) [7,9,11]. These HHs have total valence electron count (VEC) equal to 18 in their primitive unit cell. Yang et al. carried out first principles based electronic structure calculations for a large number of HHs having VEC 18 [12]. They further studied thermoelectric properties by calculating thermoelectric transport properties employing Boltzmann transport equations, and found reasonable agreement with experimental results for Seebeck coefficients and the corresponding optimal doping levels. In this paper, we follow a similar approach to investigate the thermoelectric properties of Li-based Nowotny–Juza phase ($X^I Y^{II} Z^V$) [13] HHs having VEC = 8 in their primitive cell. There exists reports for the synthesis of some of Li-based $X^I Y^{II} Z^V$ HHs [14–16]. There are *ab initio* studies as well with view point of their optoelectronic [18] and piezoelectric [19] prospects, however the study for their thermoelectric properties is lacking.

2. Computational approach

Our calculations involve three main steps: (i) optimization of lattice parameter for each systems, (ii) calculation of band structure, followed by (iii) solution of Boltzmann Transport Equations for calculating thermoelectric properties. The first two sets of cal-

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calculations were carried out using the full-potential linearized augmented plane wave (LAPW) method [20] as implemented in the WIEN2k code [21]. The value of $R_{MT}K_{max} = 9$ was chosen for all the calculations, where R_{MT} corresponds to the minimum of the muffin tin radii of the atoms in the unit cell and K_{max} corresponds to the cut-off for the interstitial plane wave part of the basis. The muffin tin radii for Li, Be, N were set to 2.2 a.u. and for Mg, P, Zn, As, Cd, Sb, Bi they were set to 2.5 au. The choice of these radii ensured no charge leakage out of the muffin tins. The lattice parameters were optimized using Perdew–Burke–Ernzerhof (PBE) generalized gradient functional [22] for the approximation of the exchange correlation functional along with $18 \times 18 \times 18$ k -mesh. The band structures were calculated using modified Becke–Johnson (mBJ) potential [23] implemented within WIEN2k along with a finer $34 \times 34 \times 34$ k -mesh. The choice of using mBJ potential was for obtaining correct semiconducting electronic structures. For example, LiCdN and LiCdAs were found to be metallic within PBE approach where as within mBJ approach they are found to be semiconducting.

Using the results from band structure calculations, the transport calculations were performed employing the BoltzTraP [24] code. For the calculation of thermoelectric power factor ($S^2\sigma$), the values for Seebeck coefficient and electrical conductivity are required. The electrical conductivity and the Seebeck coefficient tensors as a function of temperature and the chemical potential can be written as

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

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

where Ω is the volume of the unit cell, f_o is the Fermi-Dirac distribution function and e is the electronic charge. The kernel of the Eqs. (1) and (2) is the energy projected transport distribution tensor $\sigma_{\alpha\beta}(\varepsilon)$, which contains the system dependent information, and can be expressed as

$$\sigma_{\alpha\beta}(\varepsilon) = \frac{e^2}{N} \sum_{i\mathbf{k}} \tau_{i,\mathbf{k}} v_{\alpha}(i, \mathbf{k}) v_{\beta}(i, \mathbf{k}) \frac{\delta(\varepsilon - \varepsilon_{i,\mathbf{k}})}{d\varepsilon}, \quad (3)$$

where N is the number of k -points, i is the band index, \mathbf{k} is the wave vector and $v_{\alpha}(i, \mathbf{k})$ is the group velocity, which can be obtained from the band structure calculations as

$$v_{\alpha}(i, \mathbf{k}) = \frac{1}{\hbar} \frac{\partial \varepsilon_{i,\mathbf{k}}}{\partial k_{\alpha}}, \quad (4)$$

where \hbar is the reduced Planck constant.

The wave vector dependent relaxation time appearing in the expression for transport distribution tensor (Eq. (3)) is difficult to be determined from first principles calculations and hence Eq. (3) is solved under constant relaxation time approximation (RTA) [25]. The RTA is based on the assumption that the relaxation time does not vary strongly with energy on the scale of $k_B T$, where k_B is the Boltzmann constant. In fact the calculation of transport coefficients involves the derivative of Fermi function whose magnitude varies significantly within a small energy window about $10k_B T$ (0.26 eV for $T = 300$ K) near the chemical potential, and τ is assumed to remain nearly constant within this small energy range. Thus, it turns out to be a reasonably good approximation and has been able to successfully describe the transport coefficients of many materials [24,26–28]. Within RTA, the Seebeck coefficient can be calculated without any adjustable parameter. However, the electrical conductivity has to be calculated with respect to the relaxation time and hence instead of calculating the absolute power factor $S^2\sigma$, we calculate the power factor with respect to relaxation time ($S^2\sigma/\tau$). This is a reasonable approach for studying

qualitative trend of thermoelectric properties of a particular class of materials.

3. Result and discussions

A typical crystal structure of a Nowotny–Juza phase half-Heusler compound with common formula XYZ is shown in Fig. 1. The crystal structure corresponds to MgAgAs type structure with space group $F\bar{4}3m$ (space gr. no. 216). The structure can be assumed to be derived from the combination of a rock-salt type (NaCl) structure with a zinc-blende type structure. The most electropositive element X (Li in our case) and the element with intermediate electronegativity Y (Be, Mg, Zn, Cd) build the rock-salt type structure. The zinc-blende type structure is built from the most electronegative element Z (N, P, As, Sb, Bi) and the element with the intermediate electronegativity Y. Thus, the Wyckoff positions for X, Y and Z are $4b(0.5, 0.5, 0.5)$, $4a(0, 0, 0)$ and $4c(0.25, 0.25, 0.25)$ respectively. Thomas [29] has carried out extensive *ab initio* studies for the crystal structures of various types of HHs and has found the aforementioned structure to be the most favorable for the Nowotny–Juza phase (I–II–V) HHs.

Now we present and analyze the results of electronic structure calculations and then we will discuss the transport properties relating thermoelectric performance. The calculated lattice parameters obtained using PBE-GGA functional and band gaps using TB-mBJ potential along with the corresponding available experimental values are listed in Table 1. As can be seen in Table 1, the optimized lattice parameters agree very well with the available experimental lattice parameters for LiMgZ [30,32], LiZnZ [33–35] and LiCdZ [14] except for the case of LiCdAs where our calculated value is about 2% larger than the experimental value [36]. Unlike general underestimation of band gaps due to the well known limitation of ground state density functional theory using local or semilocal approximations, our calculated band gaps under TB-mBJ approach are closer to the available experimental values. In fact we find some overestimated values in the cases of LiMgN, LiZnP, LiZnAs and highly overestimated band gap for LiCdP. However, our calculated lattice parameters (including the case of LiCdAs) as well as band gaps agree very well with previous calculations [18]. Except LiZnBi and LiCdBi, all the alloys show insulating behavior within TB-mBJ approach. LiZnBi and LiCdBi show metallic behaviour, which could not be further confirmed as there is no any literature report for these two alloys. Since metallic systems are not good for thermoelectric prospects mainly because they cannot maintain thermal gradient, we exclude these two compounds from study of thermoelectric properties. The band gaps of other remaining alloys range from as low as 0.21 eV (for LiCdN) to relatively high value of 4.23 eV (for LiBeN).

Fig. 2 shows the plot for density of states (DOS) for some selected HHs. The dominant states at valence band maxima (VBM) of these HHs come from atoms at Z positions, and the analysis of orbital projected DOS (not shown in Fig. 2 for the sake of clarity) reveals that these are p-states of Z. The dominant states at conduction band minima (CBM) are the strongly s–p hybridized states coming from s orbital of Y and p orbital of Z along with a small contribution from Li-s states. Similar composition of DOS at band edges is found for all the remaining HHs. If we analyze the variation of band gap (see Table 1), we find with few exceptions the variation of band gaps follow two kinds of general trends: (i) with XY fixed the band gap decreases with increasing atomic number of Z and (ii) with XZ fixed the band gap decreases with increasing atomic number of Y. In either case there is increase in average atomic number, $\langle Z \rangle$ in XYZ, and hence the band gap decreases linearly with the increasing average atomic number, $\langle Z \rangle = 1/N \sum_i^N Z_i$, where N is the number of atoms in the unit cell.

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