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ELECTRONIC, MECHANICAL AND THERMODYNAMIC PROPERTIES OF 18-VALENCE ELECTRON HALF-HEUSLER ALLOYS LiZnX (X=As,P, and Sb)

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Abstract

Ab-initio calculation has been performed to investigate the electronic, mechanical and thermodynamic properties of half-Heusler alloys LiZnX (X=As,P, and Sb). It is found that these alloys have narrow band gaps making them posses semiconducting properties. Their mechanical properties indicate that they are mechanically stable and all the three alloys are brittle. From their thermodynamic properties, they are found to be stable and posses high Debye temperatures.

Keywords. Half Heusler, Band structure, Density functional theory, Bulk modulus, elastic constant

1. Introduction

Half Heusler alloys have gained huge interest among material scientist and physicist because of the various properties which they exhibit. Such properties include, thermoelectric properties [1], half-metallic properties [2], piezoelectric properties [3], optoelectronic properties [4], etc. Another reason why they have attracted the interest of researchers is because they can be synthesized easily and also can be epitaxially grown on semiconductor [5-6]. Half Heusler alloys are generally known to exist in the form XYZ with the Y being a transition element, Z could be any element in the group 3,4,5 etc while X is taken from group 1, 2 or another transition element. With these possibilities, over a thousand of these half Heusler alloys have been predicted and synthesized [7]. The possibilities of predicting and synthesizing more half Heusler alloys is unlimited hence these compounds could posses unique properties for a particular technological purposes. In this work, we study the electronic, mechanical and thermodynamic properties of a new set of half Heusler alloys. From these properties, we report the true nature of these compounds as to whether they are metals, semiconductors or insulators. We also report the mechanical and thermodynamic stability of the alloys. Our results are compared to available experimental and theoretical results. The rest of the work is organized as follows, Section 2 presents the method used in getting our results, in Section 3, we present the result and discussion and we conclude the work in Section 4.

2. Computational details

Ab-inito calculations as implemented in Quantum Espresso [8] have been performed to compute the structural, electronic, mechanical and thermodynamic properties LiZnX (X=As,P, and Sb). A generalized gradient approximation (GGA) type of exchange-correlation functional based on Perdew, Burke, and Ernzerhof (PBE) is used. The type of pseudopotiential used is the projected augmented wave (PAW). Before the properties were computed, series of optimization were carried out on the kinetic energy cutoff, k-point and the lattice parameter. The values of the optimized kinetic energy cutoff used in this work are 65Ry, 50Ry and 50Ry for LiZnAs, LiZnP and LiZnSb respectively. For the k-points, we used optimized value of 9x9x9, 8x8x8 and 8x8x8 for LiZnAs, LiZnP and LiZnSb respectively. The optimized values of the lattice parameters are presented in Table 1. Having carried out optimization, the various properties were computed. We also used the thermo_pw code [9] to compute the mechanical and thermodynamic properties of the three alloys

3. Results and discussion

3.1 Structural properties

The structural properties of the three Half Heuslers alloys are computed and are presented in Table 1. Since the half Heusler alloys are generally represented as XYZ, they are known to have a space group of F-43m (No. 216). Their structure take the form of a combination of a face centered cubic and a zincblende structure as shown in Fig. 1. The XYZ atoms occupy the

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X(0.00,0.00,0.00), Y(0.25,0.25,0.25), and Z(0.50,0.50,0.50) Wyckoff sites respectively. The optimizes lattice parameters and bulk modulus are obtained by fitting the total energy E as a function of lattice to the Murnaghan equation of state. From Table 1, we compared our results with experimental and theoretical results and they are in good agreement. We observed that the lattice parameters of the three half Heusler alloys increases with increasing atomic mass of P, As and Sb.

Table 1: Computed lattice parameters a, bulk modulus (B), and energy band gap E_g.

Compounds		a(Å)	B(GPa)	E_g (eV)
LiZnAs	This work	5.94	54.79	0.38
	experiment	[a]5.93		
	others	[b]5.76	[b]67	
LiZnP	This work	5.73	52.90	1.22
	experiment	[c]5.76		
	others	[b]5.58	[b]76	
LiZnSb	This work	6.33	40.38	0.43
	others	[d]6.32	[d]44.4	[e]0.54

[a][10], [b][11], [c][12], [d][13] and [e][14]

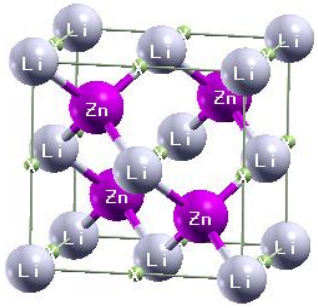

Figure 1: Crystal structure of LiZnX (X=As, P and Sb) HH alloys

3.2 Electronic properties

The electronic properties of LiZnX (X=As, P, and Sb) have been computed and are presented in Figs 2, 3, and 4 in the form of band structures and partial density of states (PDOS). From our results, it is observed that they all have narrow band gaps indicating that they have semiconducting properties. The three alloys are observed to be a direct band gap semiconductors. The band gap values are presented in Table 1. The band gap of LiZnP is the highest of the three followed by LiZnSb. The PDOS of LiZnAs is dominated by the As-1s, Zn-2p and Li-2s orbital around the 1-3eV. It is observed that there is hybridization of these three orbitals. In the negative region of the energy, the hybridization is between the As-2p and Zn-2p orbitals. Around the fermi energy, the gap splitting is between the As-1s and As-2p orbitals. For LiZnP and LiZnSb, the orbitals that undergo hybridization are clearly shown in Figs 3 and 4 respectively. The band gap splitting is among P-2p and P-1s orbital for LiZnP while for LiZnSb, the band gap splitting is among Sb-2p and Sb-1s orbitals.

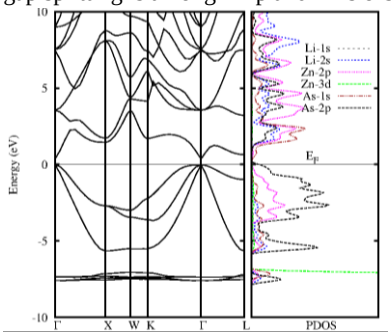

Figure 2: Band structure and PDOS of LiZnAs.

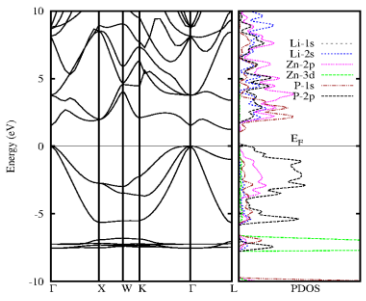

Figure 3: Band structure and PDOS of LiZnP.

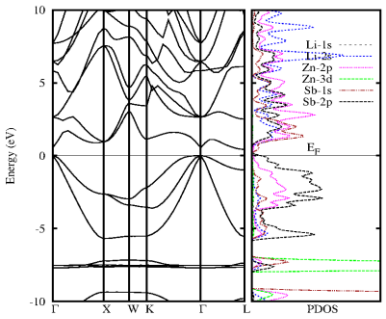

Figure 4: Band structure and PDOS of LiZnSb.

3.3 Mechanical and Thermodynamic Properties

The mechanical properties of LiZnX (X=As, P and Sb) have been computed and are presented in Table 2. From the mechanical stability criteria presented in eq. 1, it is observed that the three alloys satisfy the stability criteria hence they are mechanically stable.

$C_{11} > 0$, $C_{44} > 0$, $C_{11} > C_{12}$ and $C_{11}+2C_{12} > 0$, $C_{11}-C_{12} > 0$ (1)

where C_{11}, C_{12} and C_{44} are the elastic constant usually associated with cubic materials. From Table 2, it is observed that the Young modulus of LiZnP is highest when compared to LiZnAs and LiZnSb indicating that it is the most resistive to volume deformation. The shear modulus of the three alloys are very close and this parameter indicate the resistive nature to shear efomation. The B/G ratio of the three compounds are below the critical value of 1.75 indicating that they are all brittle in natue. The Poisson's ratio for many metals and alloys ranges from 0.25 to 0.35 and from our results, the three alloys do not fall in this range which agrees with the result of the B/G ratio that they are brittle. The thermodynamic properties are presented in Table 3 and the specific heat capacities at constant volume, entropies, internal energies and free energies are presented in Fig. 5. From Table 3 it is observed that the Debye temperature of LiZnP is the highest among the three alloys indicating that it attains highest temperature where further increase in temperature will not affect the specific heat capacity. LiZnSb posseses the highest specific heat capacity indicating that more heat is needed to raise its temperature by one degree. The average sound velocity of LiZnP is the highest when compared to the othe two alloys. The zero point energy is the internal energy of a material at zero temperature, and from the results, LiZnP has the highest. From Fig. 5(a), it is observed that at lower temperatures the T^3 law is satisfied while at higher temperatures the Dulong-Petit limit is attained for the three alloys. The results for the three alloys in entropies, internal energies and free energies as shown in Fig.5 (b), (c) and (d) respectively, are close.

Table 2: The calculated elastic constants C_{11}, C_{12} and C_{44}, Young modulus E, shear modulus G, anisotropy A, B/G ratio and the Poisson's ratio v of LiZnX (X=As, P and Sb).

Compound		LiZnAs	LiZnP	LiZnSb
C_{11} *(GPa)*	*This work*	79.20	77.84	68.98
	Others	[a]123	[a]145	
C_{12} *(GPa)*	*This work*	42.58	40.43	26.09
	Others	[a]40	[a]41	
C_{44} *(GPa)*	*This work*	49.78	59.71	44.67
	Others	[a]65	[a]75	
E(GPa)	*This work*	83.01	90.78	78.26
	Others	[a]104	[a]127	
G(GPa)	*This work*	33.35	31.81	33.27
	Others			
A	*This work*	2.72	3.19	2.08
B/G	Others	[a]1.64	[a]1.41	1.21
v	*This work*	0.2447	0.2085	0.1760
	Others	[a]0.2445	[a]0.2193	-

[a][11]

Table 3: The calculated specific heat capacity C_v(J/Kmol) at 300K, Debye temperature θ_D(K), zero point energy E_o(kJ/Nmol), and the average sound velocity V_{av}(m/s) for the three compounds.

Compounds	C_v	θ_D	E_o	V_{av}
LiZnAs	70.6	339.9	9.37	2905
LiZnP	68.4	409.9	11.51	3447
LiZnSb	71.4	299.8	8.42	2786

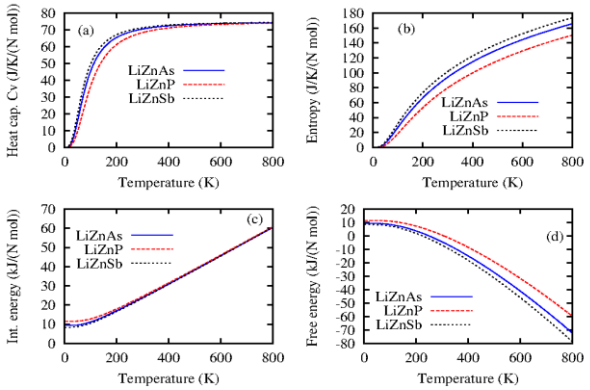

Figure 5: Thermodynamic properties of LiZnX (X=As, P and Sb) with (a) indicating the specific heat capacity, (b) the entropy, (c) internal energy and (d) the Gibb's free energy

4. Conclusion

The electronic properties of LiZnX (X=As, P and Sb) alloys from ab initio calculation show that the three half Heusler alloys have narrow band gaps showing that they are in a class of semiconductor. Mechanically the three alloys are stable and brittle since their B/G are lesser than the critical value of 1.75. They have also been found to be thermodynamically stable.

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