Computational Materials Science 83 (2014) 496–503

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Structural and optoelectronic properties of PbS_xSe_{1-x}, PbS_xTe_{1-x} and $PbSe_xTe_{1-x}$ via first-principles calculations

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ARTICLE INFO

Article history:
Received 5 October 2013
Accepted 22 October 2013
Available online 15 November 2013

Keywords:
DFT
Lead chalcogenides
Covalent bonding
Band gap
Optical properties

ABSTRACT

Using first-principle technique of full-potential linearized augmented plane-wave method, we have studied the structural, electronic and optical properties of PbS_xSe_{1-x}, PbS_xTe_{1-x} and $PbSe_xTe_{1-x}$ ternary alloys. For exchange–correlation potential the generalized gradient approximation (GGA) has been used. Lattice constants, bulk moduli, charge densities, density of states and band structures of parent binary compounds and their ternary alloys in the rocksalt structure are presented. The results reveal that the incorporation of 'S' and 'Se' atoms in PbSe, and PbTe reduces the band gaps. The bonding nature is studied via electron charge density plots. Absorption coefficient, optical conductivity and reflectivity are also discussed to exploit the interaction of these materials to photons in varied frequencies.

1. Introduction

Lead chalcogenide semiconductors have been used largely as thermoelectric materials, infrared detectors, inside fiber optics as infrared lasers, in window coating and in panels which are used for solar energy utilization [1,2]. These materials have small fundamental energy bandgap [3,4]. Due to this property these materials are very useful in opto-electronic equipments importantly includes the lasers and detectors [5–7]. These materials are also used in the control of atmospheric pollution and especially in medical diagnostics [8]. Experimental works have been done on the structural [9,10], electronic [11,12], and optical [13,14] properties of these materials.

These materials exist in rock salt structure. Many theoretical techniques have been used to investigate the electronic structure of the herein studied compounds [15–22]. Theoretically the fundamental bandgap in these compounds is found at L-symmetry point in Brillouin zone. The ferroelectricity in these materials [23] is reported by Lebedev and Sluchinskaya and investigated the quaternary solid solution sample of $PbS_xSe_yTe_{1-x-y}$ at low temperature with the electrical and X-ray method [24]. Zogg et al. [25] have studied the photovoltaic infrared sensor array in monolithic lead chalcogenide in silicon. The examination of the vacuum evaporated $PbS_{1-x}Se_x$ thin films were done by Kumar et al. [26]. Schoolar et al. realized the multi-spectral photovoltaic infrared detectors of PbS_xSe_{1-x} [27].

In this work the electronic, structural and optical properties of PbS_xSe_{1-x}, PbS_xTe_{1-x}, and $PbSe_xTe_{1-x}$ alloys are calculated to predict their applications on the basis of band structure and optical spectra. The determination of these properties is done by using FP-LAPW as implemented in "WIEN2K" [28].

2. Method of calculations

In the present density functional calculations, FP-LAPW method with Wu–Cohen generalized gradient approximation (GGA) [29] is used to solve Kohn–Sham equation [30]. In the full potential scheme the wave function, potential and charge density are expanded into two different basis. The wave function is expanded in spherical harmonics in the atomic spheres while outside the spheres (interstitial regions) it is expanded in plane wave basis. The potential is also expanded in the same manner:

$$V(r) = \begin{cases} \sum_{lm} V_{lm}(r) Y_{lm}(r) & (a) \\ \sum_{k} V_K e^{ikr} & (b) \end{cases} \quad (1)$$

where Eq. (1a) is for inside and Eq. (1b) is for outside of the atomic sphere. Inside the sphere the maximal value of l for the wave function is expanded to $l_{max} = 10$ and is spherically symmetric while outside the sphere it is constant. The muffin-tin radii (R_{MT}) are chosen in such a way that there is no charge leakage from the core and to achieve better energy eigenvalues convergence. The R_{MT}

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http://dx.doi.org/10.1016/j.commatsci.2013.10.033

were taken to be 2.5 a.u. for Pb, S, Se, and Te. The wave functions in the interstitial region were expanded in plane waves with a cut-off $R_{MT}K_{max} = 7$, where R_{MT} denotes the smallest muffin-tin radius and K_{max} gives the magnitude of the largest K vector in the plane wave expansion. For the structural properties the integrals over the Brillouin zone are performed up to 35 k-points in the irreducible Brillouin zone.

3. Results and discussions

3.1. Structural properties

The structural properties of the alloys PbS_xSe_{1-x}, PbS_xTe_{1-x} and $PbSe_xTe_{1-x}$ ($x = 0$, 0.25, 0.5, 0.75, and 1) are calculated by energy minimization process. The equilibrium structure parameters, such as; lattice constant, bulk modulus and its pressure derivative are evaluated by fitting unit cell energy versus unit cell volume using Birch–Murnaghan equation of state [31].

The calculated values of the equilibrium lattice constant (a), bulk modulus (B), pressure derivatives of the bulk modulus B' and the minimum energy for binary compounds and their ternary alloys are summarized in Tables 1–3 along with available experimental and theoretical data. Our computed values of lattice parameters are in excellent agreement with the experimental data. The variations of the calculated lattice constant (a) and bulk modulus (B) versus concentration (x) for PbS_xSe_{1-x}, PbS_xTe_{1-x} and $PbSe_xTe_{1-x}$ are displayed in Figs. 1 and 2. In view of Fig. 1, it is clearly seen that the calculated lattice parameters at different compositions for PbS_xSe_{1-x} and $PbSe_xTe_{1-x}$ alloys exhibit tendency to Vegard's law [32] with a marginal upward bowing parameters equal to −0.032 and −0.079 Å, respectively. In the case of PbS_xTe_{1-x} alloy, a large deviation from Vegard's law with upward bowing parameter equals to −0.2125 Å is observed. The physical origin of this significant deviation could be mainly due to the large mismatch of the lattice constants of the parent binary compounds of this alloy. We can also remark that the lattice constant value decreases with the increase of concentration. The reason for the decrease in lattice constant is due to the decrease in the atomic radii of the anion with increase in concentration 'S' atom in PbSe, PbTe and of 'Se' atom in PbTe compound. The squeezing effect is due to the difference in atomic radii of chalcogens (S < Se < Te). It is observed from Fig. 2 that the variation of the bulk modulus versus composition shows a significant deviation from the linear concentration dependence (LCD) with downward bowings equal to 6.673 and 4.08 GPa for PbS_xTe_{1-x} and $PbSe_xTe_{1-x}$, respectively. A small deviation from Vegard's law is found for PbS_xSe_{1-x} alloy with a downward bowing parameter equal to 0.983 GPa. It is obvious from Fig. 2 that the incorporation of selenide and sulfide in PbTe and sulfide in PbSe increases the bulk modulus values and consequently improves their hardness.

Table 1
Calculated lattice parameter a (Å), bulk modulus B (GPa), pressure derivatives of the bulk modulus B' and total ground state unit cell energy E_0 (Ry.) for PbS_xSe_{1-x} compared to the experimental and theoretical works.

	Present (GGA)	Experimental	Others
PbSe			
a (Å)	6.095	6.117[a], 6.124[c,d], 6.130[f]	6.196[b], 6.098[e], 6.215[k], 6.222[j]
B (GPa)	55.7	54.1[a]	49.1[b], 48.8[k], 47.5[j]
B'	5.00		
E	−46714.19		
$PbS_{0.25}Se_{0.75}$			
a(Å)	6.05		6.174[l], 6.071[m], 6.073[n]
B (GPa)	56.60		48.2[l], 49.8[m], 49.211[n]
B'	5.000		
E	−182795.32		
$PbS_{0.5}Se_{0.5}$			
a (Å)	6.00		6.122[l], 6.125, 6.128[n]
B (GPa)	57.80		49.7[l], 48.4[m], 47.462[n]
B'	5.00		
E	−89366.86		
$PbS_{0.75}Se_{0.25}$			
a (Å)	5.958		6.069[l], 6.174[m], 6.179[n]
B (GPa)	59.74		50.8[l], 47.5[m], 46.783[n]
B'	5.00		
E	−174672.15		
PbS			
a (Å)	5.895	5.929[a], 5.939[c,d], 5.940[f]	6.012[b], 5.906[e], 6.012[j]
B (GPa)	60.7	52.9[a]	53.3[b], 53.2[j]
B'	5.00		
E	−42652.61		

[a] Ref. [33].
[b] Ref. [16].
[c] Ref. [3].
[d] Ref. [11].
[e] Ref. [34].
[f] Ref. [15].
[g] Ref. [35].
[h] Ref. [36].
[i] Ref. [37].
[j] Ref. [38].
[k] Ref. [17].
[l] Ref. [39].
[m] Ref. [2].
[n] Ref. [1].

Table 2
Calculated lattice parameter a (Å), bulk modulus B (GPa), pressure derivatives of bulk modulus B' and total ground state unit cell energy E_0 (Ry.) for PbS_xTe_{1-x} compared to the experimental and theoretical works.

	Present (GGA)	Experimental	Others
PbTe			
a (Å)	6.42	6.462[a], 6.462[c,d], 6.460[f]	6.565[b], 6.440[e], 6.572[k], 6.570[j]
B (GPa)	44.44	39.8[a]	41.4[b], 40.3[k], 38.7[j]
B'	5.00		
E	−55446.977320		
$PbS_{0.25}Te_{0.75}$			
a (Å)	6.333		6.45[j], 6.450[l]
B (GPa)	47.51		40.8[j], 39.462[l]
B'	5.000		
E	−208993.672446		
$PbS_{0.5}Te_{0.5}$			
a (Å)	6.208		6.31[j], 6.325[l]
B (GPa)	50.879		45.12[j], 44.368[l]
B'	5.0000		
E	−98099.637063		
$PbS_{0.75}Te_{0.25}$			
a (Å)	6.067		6.18[j], 6.188[l]
B (GPa)	55.233		49.2[j], 45.744[l]
B'	5.0000		
E	−183404.901999		
PbS			
a (Å)	5.895	5.929[a], 5.939[c,d], 5.940[f]	6.012[b], 5.906[e], 6.012[j]
B (GPa)	60.73	52.9[a]	53.3[b], 53.2[j]
B'	5.00		
E	−42652.6084		

[a] Ref. [33].
[b] Ref. [16].
[c] Ref. [3].
[d] Ref. [11].
[e] Ref. [34].
[f] Ref. [15].
[g] Ref. [35].
[h] Ref. [36].
[i] Ref. [37].
[j] Ref. [38].
[k] Ref. [17].
[l] Ref. [1].