

Theoretical investigations of structural and thermal properties of PbS and PbSe

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Abstract

First-principles calculations are performed to investigate the structural, elastic and thermal properties of PbS and PbSe in rocksalt structure using the full-potential linearized augmented plane wave method. In this approach, the generalized gradient approximation (GGA) of Perdew et al. was used for exchange correlation potentials. Results are given for lattice constant, bulk modulus and elastic constants are in agreement with experimental and theoretical data. The quasi-harmonic Debye model, using a set of total energy versus volume calculations obtained with the FP-LAPW method which is applied to study the thermal . Temperature effects on the structural parameters, thermal expansions, heat capacities and Debye temperatures are determined from the non-equilibrium Gibbs functions.

1. Introduction

The lead salts semiconductors PbS, PbSe and PbTe have been subject of many experimental and theoretical works. They have been largely used in infrared detectors, as infrared lasers in fiber optics, as thermoelectric materials, in solar energy panels, and in window coatings [1,2]. One of their interesting properties is their narrow fundamental energy band gap [3,4]; that is why, these IV–VI semiconductors are useful in optoelectronic devices such as lasers and detectors [5–7]. They are used in medical diagnostic and atmospheric pollution control [8]. The small energy gap of lead chalcogenides semiconductors is one of the most important properties leading to the experimental interest in these materials. Experimental researches have been performed on their structural and band properties [9,10], electronic structure [11,12], and optical properties [13,14]. Many theoretical studies of electronic structures of these semiconductors are carried out using different methods of calculations. We can cite: the FP-LMTO method [15], FP-LAPW method [16–18], pseudopotential method [19,20] and orthogonalized-plane-wave method [21]. All of the theoretical calculations founded a direct band gap at the L point of the Brillouin zone for all three compounds. These materials crystallize in the rocksalt structure at ambient temperature and pressure.

This article gives a systematic theoretical analysis of the structural, elastic and thermodynamic properties of PbS and PbSe compounds by using the full-potential-linearized-augmented plane wave (FP-LAPW) method in the framework of density functional theory (DFT), with the generalized gradient approximation (GGA).

The rest of the paper has been divided in three parts. In Section 2, we briefly describe the computational techniques used in this study. The most relevant results obtained for the structural, elastic and thermodynamic properties of PbS and PbSe compounds are presented and discussed in Section 3. Finally, in Section 4 we summarize the main conclusions of our work.

2. Computational method

The calculations were performed using the full potential linear augmented plane wave (FP-LAPW) method [22] within the framework of the density functional theory (DFT) [23, 24] as implemented in the Wien2k code [25]. For the exchange-correlation potentials, we have used the generalized gradient approximation [26] (GGA).

The self-consistent calculations are considered to be converged only when the calculated total energy of the crystal converged to less than 1 mRyd. In the FP-LAPW method, the wave function and potential are expanded in spherical harmonic functions inside non-overlapping spheres surrounding the atomic sites (muffin-tin spheres) and a plane wave basis set in the remaining space of the unit cell (interstitial region) is used. The muffin-tin radius R_{MT} were assumed to be 2.5, 2.1 and 2.3 a.u. for Pb, S and Se, respectively. The maximum l value for the wave functions expansion inside spheres was confined to $l_{max} = 10$. The plane wave cut off of $K_{max} = 8.0/R_{MT}$ (R_{MT} is the smallest muffin-tin radius) is chosen for the expansion of the wave functions in the interstitial region while the charge density was Fourier expanded up to $G_{MAX} = 14$. The k integration Meshes of 45 special k -points were chosen in the irreducible wedge of the Brillouin zone for the compound. All these values have been chosen in a way to ensure the convergence of the results.

3. Results and discussion

3.1. Structural properties

In order to calculate the ground state properties of PbS and PbSe, the total energies are calculated in rocksalt structure. The calculated total energies are fitted to the Murnaghan's equation of state [27] to determine the ground state properties such as the equilibrium lattice constant a and the bulk modulus B . The calculated equilibrium parameters (a and B) in NaCl structure are given in Table 1 which also contains results of the previous first principle calculations as well as the experimental data. Our calculated lattice constants and (bulks) are slightly larger (less) than the experimental works. This is essentially due to the GGA. These results are also in good agreement with previous first-principles calculations [29].

We also calculate the elastic constants (C_{11} , C_{12} and C_{44}) for the three compounds using the numerical first-principles method. Results of elastic constants are presented in Table 1. The traditional mechanical stability conditions on the elastic constants in cubic crystals are known to be $C_{11} - C_{12} > 0$, $C_{11} + 2C_{12} > 0$, $C_{11} > 0$ and $C_{44} > 0$. Our results for elastic constants in Table 1 obey these stability conditions. Our values are relatively closed to those of Ref. [32].

Table 1. Structural and elastic parameters of PbS and PbSe. The calculated results GGA are compared with the experimental data. The bulk modulus B and elastic constant Cij are in the unit of GPa. Note that the DFT results correspond to T = 0 K.

	Lattice constant a (Å)	Bulk modulus B(GPa)	Elastic constant parameters		
			C ₁₁	C ₁₂	C ₄₄
PbS					
This work	6.011	51.9	111.81	22.21	20.60
Experiment	5.940 ^a	52.9 ^a	124.0 ^d	33.0 ^d	23.0 ^d
Other	6.012 ^b	52.1 ^b	135.1 ^e	16.9 ^e	20.4 ^e
calculations					
PbSe					
This work	6.224	47.8	122.16	10.31	17.91
Experiment	6.130 ^c	54.1 ^c	123.7 ^d	19.3 ^d	15.9 ^d
Other	6.222 ^b	47.5 ^b	123.6 ^e	12.2 ^e	17.6 ^e
calculations					

3.2. Thermal effects: quasi-harmonic Debye model

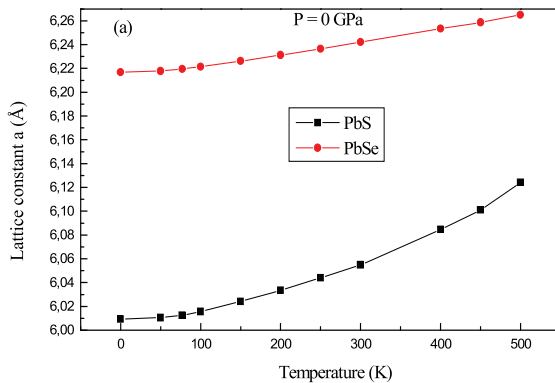
To investigate the thermodynamic properties of PbS and PbSe compounds under high temperature, we apply the quasi-harmonic Debye model [33], in which the non-equilibrium Gibbs function $G^*(V; P, T)$ can be written in the form of:

$$G^*(V; P, T) = E(V) + PV + A_{vib}[\theta(V); T] \quad (6)$$

where $E(V)$ is the total energy per unit cell, PV corresponds to the constant hydrostatic pressure condition, $\theta(V)$ is the Debye temperature, and A_{vib} is the vibrational term, which can be written using the Debye model of the phonon density of states as [34, 35]:

$$A_{vib}(\theta, T) = nkT \left[\frac{9\theta}{8T} + 3 \ln \left(1 - e^{-\theta/T} \right) - D\left(\frac{\theta}{T}\right) \right] \quad (7)$$

where n is the number of atoms per formula unit, $D(\theta/T)$ represents the Debye integral, and for an isotropic solid, θ is expressed as [24]:



$$\theta_D = \frac{\hbar}{k} \left[6\pi^2 V^{1/2} n \right]^{1/3} f \left(\sigma \sqrt{\frac{B_S}{M}} \right) \quad (8)$$

M being the molecular mass per unit cell and B_S the adiabatic bulk modulus, approximated by the static compressibility [23]:

$$B_S \cong B(V) = V \frac{d^2 E(V)}{dV^2} \quad (9)$$

$f(\sigma)$ is given by Refs [23, 27]; the Poisson σ is taken as 0.25 [43].

Therefore, the non-equilibrium Gibbs function $G^*(V; P, T)$ as a function of $(V; P, T)$ can be minimized with respect to volume V .

$$\left[\frac{\partial G^*(V, P, T)}{\partial V} \right]_{P, T} = 0 \quad (10)$$

By solving Eq.(10), one can obtain the thermal equation of state (EOS) $V(P, T)$. The heat capacity C_V and the thermal expansion coefficient α are given by [36].

$$C_V = 3nk \left[4D\left(\frac{\theta}{T}\right) - \frac{3\theta/T}{e^{\theta/T} - 1} \right] \quad (11)$$

$$S = nk \left[4D\left(\frac{\theta}{T}\right) - 3 \ln \left(1 - e^{-\theta/T} \right) \right] \quad (12)$$

$$\alpha = \frac{\gamma C_V}{B_T V} \quad (13)$$

Where γ is the Grüneisen parameter, which is defined as:

$$\gamma = - \frac{d \ln \theta(V)}{d \ln V} \quad (14)$$

Through the quasi-harmonic Debye model, one could calculate the thermodynamic quantities of any temperatures and pressures of compounds from the calculated $E-V$ data at $T = 0$ and $P = 0$.

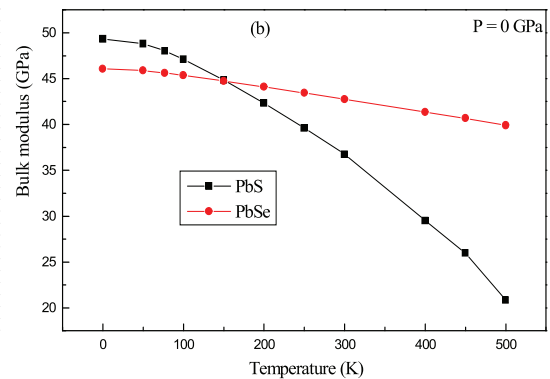


Fig. 1. Variation of (a) lattice constant a (Å) and (b) bulk modulus B (GPa) with temperature for PbS and PbSe at pressure 0 GPa.

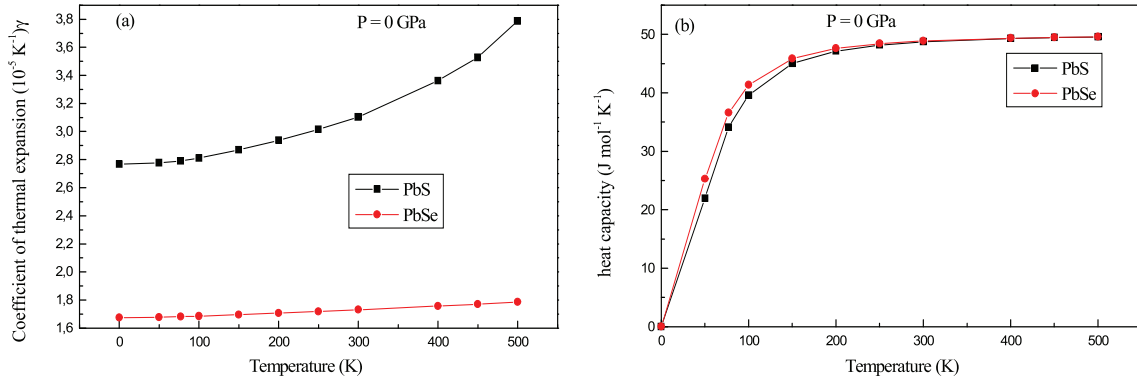


Fig. 2. Variation of (a) Coefficient of thermal expansion (10^{-5} K^{-1}) and (b) heat capacity ($\text{J mol}^{-1} \text{ K}^{-1}$) with temperature for PbS and PbSe at pressure 0 GPa.

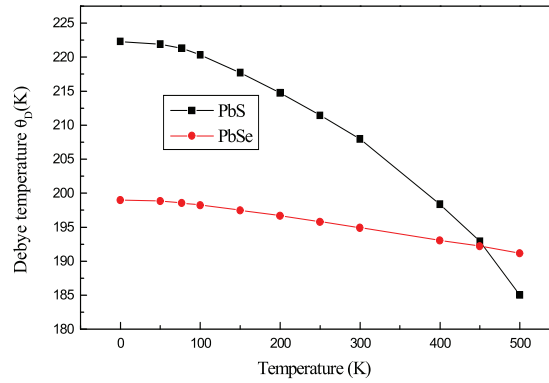


Fig. 3. Variation of Debye temperature (K) with temperature for PbS and PbSe at pressure 0 GPa.

The temperature effects on the lattice constant and bulk modulus are illustrated in Fig. 1(a) and (b), respectively. The lattice constant for the two compounds rises with increasing temperature but the rate of increase is very reduced for PbSe. The bulk modulus of both compounds decreases with temperature. One can notice that from 150 K the bulk modulus for PbSe becomes higher than for PbS. This explains why PbSe is a hard material at high temperature when compared to PbS.

The variations of the thermal expansion coefficient $\alpha(T)$ as a function of the temperature are plotted in Fig. 2(a). However, at low temperatures the thermal expansion coefficient increases for the two materials but for the high temperature shows a parabolic behavior for PbS and gradually tends to a linear increase at higher temperatures for PbSe. Fig. 8(b) illustrates the heat capacity $C_V(T)$ as a function of temperatures. It is found that when $T > 300$ K, the heat capacity $C_V(T)$ is dependent on the temperature T . This is due to the approximations of the Debye model used here. However, the anharmonic effect on heat capacity $C_V(T)$ is suppressed at high temperatures, and $C_V(T)$ is close to the Dulong–Petit limit. The specific heat capacity at high temperature of the two materials does not depend much on temperature and tends to approach $50 \text{ J mol}^{-1} \text{ K}^{-1}$. At $T = 0$ K. The heat capacity $C_V(T)$ are in agreement with the theoretical values [32], see Table 4.

Fig. 3 displays the dependence of the Debye temperature θ_D on temperature. It can be seen that θ_D is nearly constant from 0 to 100 K and decreases linearly with increasing temperature

from $T > 100$ K for PbSe. Our calculated θ_D at zero pressure and zero temperature is equal to 222.29 K, 199.10 K for PbS and PbSe, respectively.

4. Conclusion

In this study, we have presented a complete theoretical analysis of the structural and thermal properties of PbS and PbSe compounds by using the FP–LAPW method. The use of the GGA for the exchange–correlation potential permitted us to obtain good structural parameters.

The thermal properties of PbS are different from PbSe. The dependency of the lattice constant, bulk modulus, thermal expansion, heat capacities and Debye temperatures on temperature is predicted. We conclude that the heat capacity for the two materials at high temperature is given by the law of Dulong and Petit.

5. References

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