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ARTICLE

Study of Lattice Parameter and Nanoparticle Size in Lead Chalcogenides (PbX, X = S, Se & Te)

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Abstract: In the present paper, the structural and electronic properties have been studied with the help of thermodynamic parameter. The lattice parameter and nanoparticle size in lead chalcogenides [(PbX, X = S, Se and Te)] are calculated with the help of fitting parameter under the effect of temperature. The calculated values are in close agreement with the experimental results.

Keywords: Lead chalcogenides, Lattice parameter, Nanoparticle size, Energy band gap.

Introduction

Lead chalcogenides (Pb X, X = S, Se and Te) are narrow band gap (0.2-0.4 eV) semiconductors at lower temperatures. They have unique structural and electronic properties. They have wide technological applications and are used to fabricate various optoelectronic, spintronic and thermo-electronic devices, as well as in nanoscience and nanotechnology [1–9]. Various classes of thermoelectric materials had been developed, such as bismuth telluride for low-temperature applications [10, 11] and germanium telluride for higher-temperature applications [12]. Theoretical and experimental studies have been performed on their structural and electronic properties [13-22]. Those properties have been studied in terms of lattice constant, nanoparticle size and energy band gap under the effect of temperature. Lattice constant and energy band gap are functions of temperature [15-22]. The structural and electronic properties, such as lattice constant (a) and nanoparticle size (R), are calculated. The calculated values are compared with experimental results.

Theoretical Methodology

Lead chalcogenides are narrow band gap semiconductors. Energy band gap and lattice parameter are functions of temperature [24-25]. The crystal structure of lead chalcogenide is of NaCl (B1) type. The coordination number and bond between lead (Pb) and chalcogen {X = S, Se, Te} are 6 and ionic, respectively. The electronic and structural properties were studied in terms of lattice parameter and energy band gap with temperature [23-26]. Various experimental studies have found that lead chalcogenides exhibit strongly anharmonic lattice dynamics [27]. Coulomb interaction and short-range two-body interaction in lead chalcogenides are given by:

$$U_{ij} = \frac{Q_i Q_j}{R_{ij}} + Xe^{\frac{-R_{ij}}{\rho}} - \frac{D_6}{R_{ij}^6} \quad (1)$$

In Eq. 1, the first term describes the long-range Coulomb interaction between two charges. The second term indicates the repulsive potential. The third term represents the dipole-

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dipole interaction Abuckingham potential; where X, ρ and D_6 are fitting parameters. Short-range cation –cation interactions are ignored. Thermodynamic enthalpy in NaCl (B1) structure is given by:

$$H = E + PV. \quad (2)$$

The Gibbs free energy is given by:

$$G = H - TS. \quad (3)$$

According to the classical Heisenberg model, the Hamiltonian is given by:

$$\mathcal{H} = -\frac{1}{2}\sum \vec{S}_i \left(J_1 \sum_j^{nn} \vec{S}_j + J_2 \sum_j^{nnn} \vec{S}_j\right) \quad (4)$$

with normalized spin vectors $\vec{S}_i$ and $\vec{S}_j$ and summation over nearest neighbor and next nearest neighbor.

The energy differences in terms of J_1 and J_2 are given by the following relations:

$$\Delta E_1 = 8J_1$$

$$\Delta E_2 = 6J_1 + 6J_2 .$$

The atomic radius of lead chalcogenide PbX (X=S,Se and Te) is a function of temperature. Then,

$$R(T) = A + BT + CT^2 \quad (5)$$

where A, B and C are the fitting parameters, the values of which are given in Table 1.

The lattice parameter in term of atomic radius is given by the following relation:

$$a(T) = 2\sqrt{2}\,\mathrm{R(T)}.$$

The energy gap is related with temperature and lattice parameter by the following relation:

$$\left[\frac{\partial E_g}{\partial T}\right]_{LATTICE} = \left(\frac{\partial E_g}{\partial a}\right)\left(\frac{\partial a}{\partial T}\right). \quad (6)$$

The forbidden width is a linear function of temperature [28-30]. Then,

$$E_g(T) = E_g(0) + \frac{\partial E_g}{\partial T}\mathrm{T}, \quad (7)$$

$E_g(0)$ being the energy at absolute zero.

The enthalpy of lead chalcogenide crystal is defined as:

$$H \approx H_{ELEC} + H_{VIB}^0 + H_{VIB}(T) + H_{ROT}(T) + H_{TRANS}(T) + RT \quad (8)$$

where, H_{ELEC} is the electronic component of enthalpy, H_{VIB}^0 is the vibrational component of enthalpy (main State), $H_{VIB}(T)$ is the vibrational component of enthalpy, $H_{ROT}(T)$ is the rotational component of enthalpy, $H_{TRANS}(T)$ is the trans. component of enthalpy, R is the universal gas constant and T is the temperature.

The entropy of the crystal is the sum of following components:

$$\Delta S = S_{TRANS} + S_{VIB} + S_{ELECT} - nR[\ln(nN_0) - 1] \quad (9)$$

where, N_0 is the Avogadro constant and N is the number of moles in the molecules.

The Gibbs free energy of the crystal is determined in term of the entropy of individual members of molecules of reagent Pb and X = (S, Se and Te). Then,

$$\Delta G = H_{Pb} - H_X + \frac{1}{2}\sum_{i\varepsilon Pb} h\nu_i - \frac{1}{2}\sum_{j\varepsilon X} h\nu_j - T\,(S_{VIB}^{Pb} - S_{VIB}^{X} + S_{ROT}^{Pb} - S_{ROT}^{X} + S_{TRANS}^{Pb} - S_{TRANS}^{X}) \quad (10)$$

where, H_{Pb} is the enthalpy of lead, H_X is the enthalpy of chalcogen [X = S, Se and Te], S_{VIB}^{Pb} is the entropy of lead due to vib. component, S_{VIB}^{X} is the entropy of chalcogen due to vib. component, S_{ROT}^{Pb} is the entropy of lead due to rot. component, S_{ROT}^{X} is the entropy of chalcogen due to rot. component, S_{TRANS}^{Pb} is the entropy of lead due to trans. component and S_{TRANS}^{X} is the entropy of chalcogen due to trans. component.

The particle size of PbX (X = S, Se and Te) has been calculated by effective mass of holes and electrons. Now, the carrier effective mass of a hole is given by:

$$m_h^* = 1.44\, m_e^* \quad (11)$$

where m_e^* be the carrier effective mass of an electron.

Generally, electrons and holes are in the conduction band and valence band, respectively. Both achieved the lowest energy for an optical transition from valence band to conduction band. Then, the expression for the radius of nanoparticle is given by:

$$R^{,2} = \frac{h^2}{8(\Delta E_{gT} - \Delta E_g)}\left[\frac{1}{m_e^*} + \frac{1}{m_h^*}\right] \quad (12)$$

where, ΔE_{gT} is the energy gap at 4.2K and 300K, respectively and ΔE_g is the energy gap at 0K.

The structural properties have been predicted by lattice parameter and are shown in Figs. 1, 2 and 3. In Figs. 1, 2 and 3, the lattice parameter is the linear function of temperature. The values of

lattice parameter and nanoparticle size are calculated. The calculated values of lattice parameter and nanoparticle size are shown in Tables 1 and 2, respectively. Finally, our calculated values are in close agreement with the experimental results.

TABLE 1. Variation of atomic radius and lattice parameter with temperature for lead chalcogenides (PbX, X=S, Se and Te).

Temperature K	PbS $R(t)=\frac{a}{2\sqrt{2}}$ A = 2.082 (Å) B = $0.367\times10^{-4}(\text{Å}\,K^{-1})$ C = $2.938\times10^{-8}(\text{Å}\,K^{-2})$ Calc.	PbS Exp.[28-30]	PbSe $R(t)=\frac{a}{2\sqrt{2}}$ A = 2.157 (Å) B = $3.136\times10^{-5}(\text{Å}\,K^{-1})$ C = $0.417\times10^{-7}(\text{Å}\,K^{-2})$ Calc.	PbSe Exp.[28-30]	PbTe $R(t)=\frac{a}{2\sqrt{2}}$ A=2.277(Å) B = $0.371\times10^{-4}(\text{Å}\,K^{-1})$ C = $2.867\times10^{-8}(\text{Å}\,K^{-2})$ Calc.	PbTe Exp.[28-30]
0	2.082		2.157		2.277	
4	2.082		2.158		2.278	
75	2.085		2.159		2.280	
150	2.088		2.165		2.283	
225	2.091		2.166		2.286	
300	2.095		2.170		2.290	
375	2.100		2.175		2.295	
400	2.101		2.176		2.296	
525	2.109		2.184		2.304	
600	2.114		2.190		2.309	

TABLE 2. Nanoparticle size of lead chalcogenides at different temperatures and band gaps.

Compound	Energy gap $(\Delta E_g)\ at\ 0K$ eV Exp. [16]	Energy gap $(\Delta E_g)\ at\ 4K$ eV	Particle size (R') nm	Energy gap $(\Delta E_g) at$ 300K eV	Particle size (R') nm
PbS	0.290	0.20	5.42	0.26	9.39
PbSe	0.170	0.18	16.27	0.23	6.64
PbTe	0.190	0.65	2.4	0.69	2.03

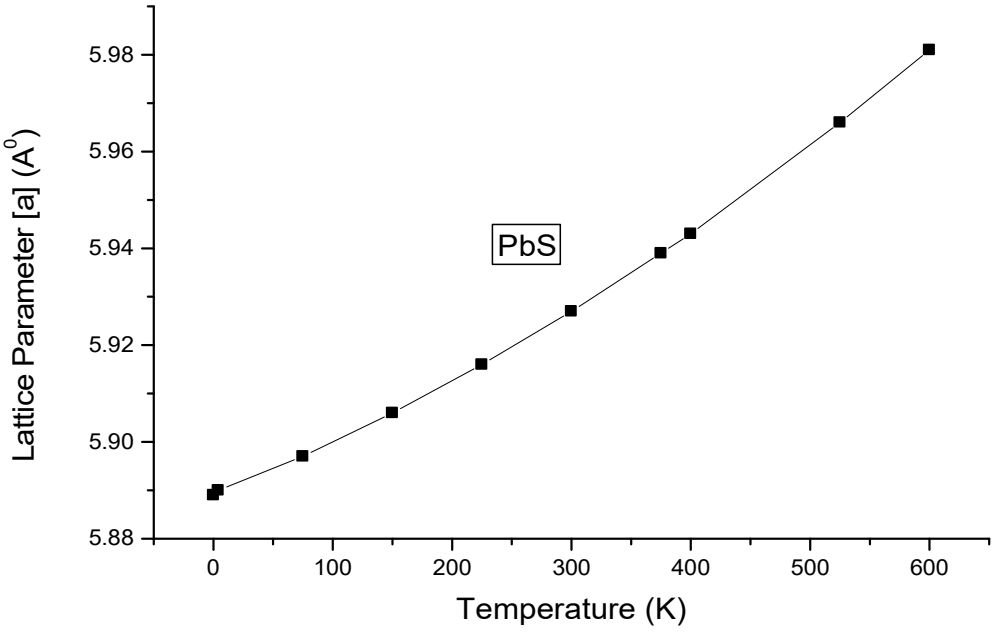

FIG. 1. Lattice parameter with temperature for PbS.

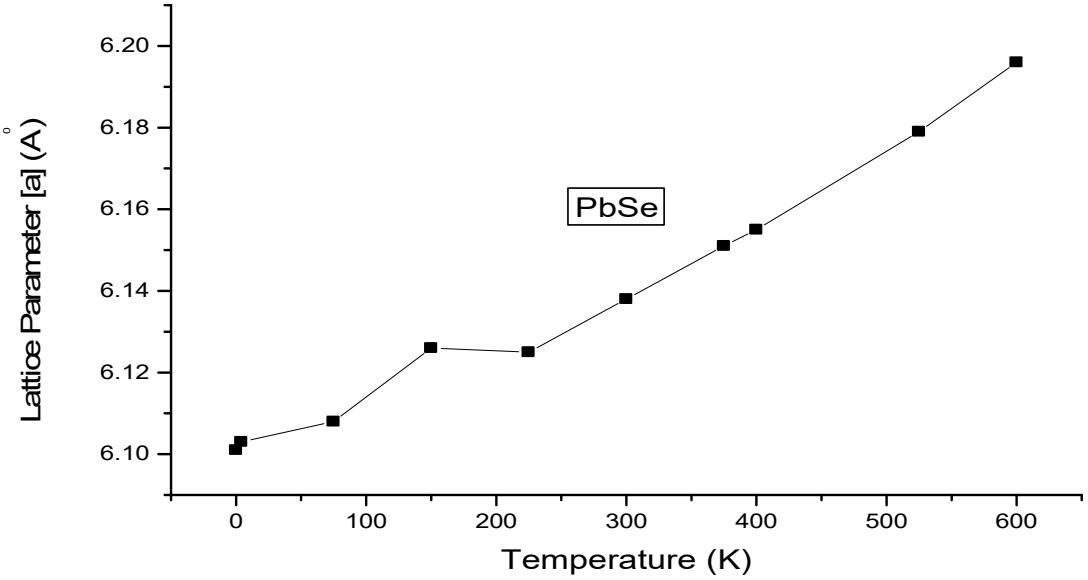

FIG. 2. Lattice parameter with temperature for PbSe.

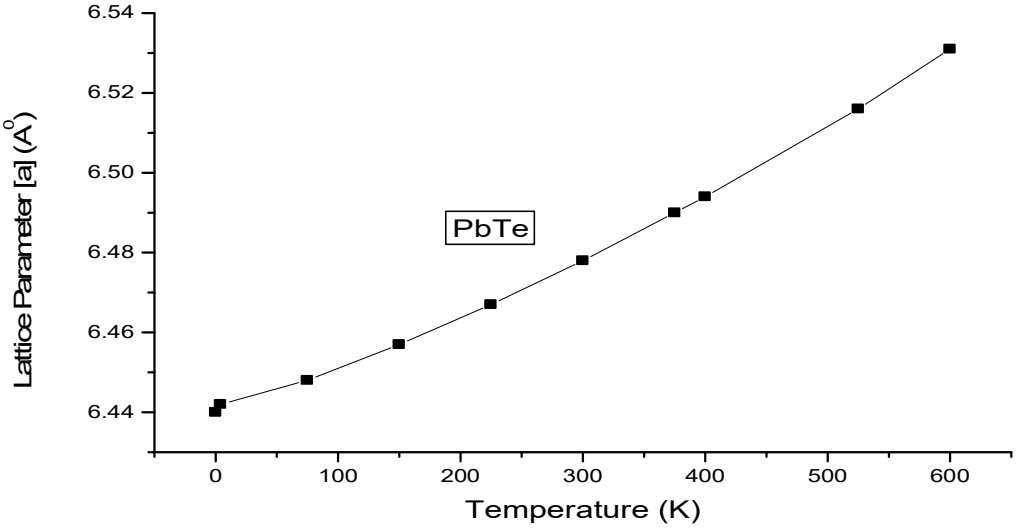

FIG. 3. Lattice parameter with temperature for PbTe.

Results and Discussion

In this method, the lattice parameter and nanoparticle size in lead chalcogenides [(PbX, X = S, Se and Te)] have been studied under the effect of temperature. We have studied the structural and electronic properties and calculated the lattice parameter and nanoparticle size of given compounds at different temperatures. The values of lattice parameter and nanoparticle size in various temperatures are shown in Tables 1 and 2, respectively. The variations of lattice parameter with temperature are predicted in Fig. 1, Fig. 2 and Fig. 3 for PbS, PbSe and PbTe, respectively. The values of lattice parameter are a linear function of temperature. The fitting parameters have been taken different for different compounds. During the electronic transition, the values of nanoparticle size have been calculated and are shown in Table 2. Our calculated values of Tables 1 and 2 are in close agreement with experimental results.

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