Theoretical Analysis of High Pressure Phase Transition and Stability of LaTe and SmTe with NaCl-structure

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We have predicted the phase transition pressures and corresponding relative volume change of LaTe and SmTe having NaCl-type structure under high pressure using three body interaction potential (TBIP) approach and found better results with TBIP. In addition, we have checked the conditions for relative stability in terms of modified Born criterion and also found that LaTe and SmTe follow the universal equation of state described by Vinet et al.

1. Introduction

Most Rare Earth (RE) monochalcogenides show NaCl(B_1)$\rightarrow$CsCl(B_2) structural phase transition and attracted the attention of both experimental and theoretical workers. These compounds have attracted attention due to their magnetic and electrical properties [1]. The presence of 4f-electron in these compounds is mainly responsible for these peculiar physical properties. They show metallic nature when the rare earth ion is in trivalent state and semi-conducting when in divalent state. The pressure-volume relationship for divalent rare-earth chalcogenides have been extensively done by high-pressure X-ray diffraction technique [2-4].

Although considered a proper reference material, lanthanum monochalcogenides LaX (X= S, Se, Te) and its high pressure structural properties have been less studied experimentally. Out of these, only LaS show $B_1\rightarrow B_2$ phase transition at around 25GPa in a Silicon oil pressure medium [5]. However, no experimental studies of LaSe and LaTe are known at present. Hence, we refer to the self-consistent Tight Binding Linear Muffin Tin Orbital (TBLMTO) method [6]. Further, Lu et al. [7] reported the local density approximation (LDA) results successfully for electronic structures of LaS and SmS. Theoretical investigation of LaX (X= S, Se, Te) has been done by two-body interaction potential by Varshney et al. [8]. Among divalent rare-earth chalcogenides, SmTe shows $B_1\rightarrow B_2$ phase transition at around 11GPa [4]. The ground state configuration of SmTe is determined from total energy calculation using the self-interaction local-spin-density approximation[4].

Looking at the interesting properties of RETe compounds and the fact that no study has been done using three body interactions, we thought it pertinent to apply three body interaction potential (TBIP) approach. The importance of three body interactions in potential model to improve results has also been emphasized by others like Sims et al. [9]. We have employed our three body interaction potential (TBIP) approach [10-12] to study high pressure behavior. We introduced our three body potential model, which includes the long range Columbic, three body interaction, short range overlap repulsive interaction operative up to second neighbor ions within Hafemeister and Flygare approach [13] incorporated with van der Walls (vdW) attraction due to dipole-dipole and dipole-quadrupole interactions effects [14] and also with zero point energy effects [15,16]. The inclusion of short range (SR), vdW interaction and second neighbor ion (SNI) seems essential as their effects are considerably important as per prediction of the relative stability of crystal structure. The importance of inclusion SR, vdW interaction and SNI has been established in our earlier work [15]. Also we have considered Zero point energy effects, which is the lowest possible energy that the compound may possess and is the ground state energy of the compound. The energy of the compound can be written as $(\varepsilon = (h\upsilon) / \{e^{(h\upsilon)/kt} - 1\} + (h\upsilon)/2)$ where, υ, t, and k are the frequency, temperature and Boltzman constant of the compound, respectively, and h is the Planck constant. It is clear from the above expression that even at absolute zero the energy of the compound

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cannot be zero, but at least 1/2 (*h*υ). This term shows a small effect in Gibbs free energy, but cannot be ignored completely. The Potential model and method of calculation is given in Sec. 2 and result and discussion are given in Sec. 3.

2. Potential model and method of calculations

It is well known that the application of pressure on crystals results in change in its volume that leads to an increased charge transfer (or three-body interaction effects) due to the deformation of the overlapping electron shells of the adjacent ions. The three body interaction arises during lattice vibrations when electron shells of neighboring ions overlap. This overlapping leads to the transfer of charge which interacts with other charges and many body interaction (MBI) takes place, the dominant part of which is the three body interaction [10-12]. This interaction becomes more important due to the decrease in inter ionic spacing of the lattice crystal when pressure gets increased and when anions experience sufficient overlap. Besides, both an enhancement in overlap energy and the transferred charge due to the overlap in electron shells modify the ionic charge, which in its turns modifies the Coulomb energy. The expression for the modified Coulomb energy due to three body interaction (TBI) is

$$\Phi_m(r_0) = \Phi^c + \Phi^T \tag{1}$$

$$\Phi_m(r_0) = [-\alpha_M Z^2 e^2 / r]\,[1+(2n/Z)\, f(r_0)] \tag{2}$$

Here α_M is the Madelung constant (1.7476 for NaCl and 1.7629 for CsCl structure solids), r_0 is the equilibrium nearest neighbor (nn) ion separation, n is the number of nearest neighbor (nn), and f(r) is the TBI parameter which is dependent on the nearest neighbor distance (r) as [12]

$$f(r) = f_0 \exp(-r/\rho) \tag{3}$$

These effects have been incorporated in the Gibbs free energy (G=U+PV-TS) as a function of pressure (P). Here, U is the internal energy, which at T= 0 K is equivalent to the lattice energy and S is the vibrational entropy at absolute temperature T. Since theoretical calculations are done at T= 0 K, the Gibbs's free energy is equivalent to enthalpy. At T= 0 K and pressure P, the Gibbs free energies for rock salt (B_1, real) and CsCl (B_2, hypothetical) structures are given by

$$G_{B_1}(r) = U_{B_1}(r) + PV_{B_1} \tag{4}$$

$$G_{B2}(r') = U_{B2}(r') + PV_{B2} \tag{5}$$

with V_{B_1} (=2.00 r^3) and V_{B2} (=1.54 r^3) as the unit cell volumes for B_1 and B2 phases, respectively. The first terms in the energies (4) and (5) are lattice energies for B_1 and B_2 structures and they are expressed as:

$$U_{B_1}(r) = [-(\alpha_m z^2 e^2)/r] - [(12\alpha_m z\, e^2\, f(r))/r] + 6b\,\beta_{ij} \exp[(r_i + r_j - r)/\rho] + 6b\,\beta_{ii} \exp[(2r_i - 1.41r)/\rho] + 6b\,\beta_{jj} \exp[2r_j - 1.41r)/\rho] - \{(C_{ij}r^{-6} + D_{ij}r^{-8})\} + (0.5)\, h\, \langle\omega^2\rangle^{1/2}{}_{B1} \tag{6}$$

$$U_{B2}(r') = [-(\alpha'_m z^2\, e^2/r')] - [(16\alpha'_m z e^2\, f(r'))/r'] + 8b\,\beta_{ij} \exp[(ri + r_j - r')/\rho] + 3b\beta_{ii} \exp[(2r_i - 1.154r')/\rho] + 3b\,\beta_{jj} \exp[2r_j - 1.154\, r')/\rho] - \{(C'_{ij}r'^{-6} + D'_{ij}r'^{-8})\} + (0.5)\, h\, \langle\omega^2\rangle^{1/2}{}_{B2} \tag{7}$$

Here, ze is the ionic charge, r_i (r_j) is the ionic radii of i(j) ions, ρ is the range parameter, b is the hardness parameter, C_{ij} and D_{ij} are the van der Walls coefficients from dipole-dipole and dipole-quadrupole interactions, r(r') is the inter ionic separation for B_1 (B_2) phases and β_{ij} is the Pauling coefficients defined as

$$\beta_{ij} = 1 + \frac{z_i}{n_i} + \frac{z_j}{n_j} \tag{8}$$

where, $z_i\,(z_j)$ and $n_i\,(n_j)$ denote the valence and number of electrons in the outermost orbit of cations (anions).

These lattice energies consist of long-range Coulomb energy (first term), three body interactions corresponding to the nearest neighbor separation r (r') for B_1(B2) phases (second term), energy due to the overlap repulsion represented by Hafemeister and Flygare (HF) type potential (i, j) ions (third term) and extended up to the second neighbor ions (fourth and fifth terms), vdW interaction (sixth term), and the last term indicates the zero point effect term in eqns.(6) and (7).

The effective inter-ionic potential described for NaCl [B_1] and CsCl [B2] structures contain three model parameters [ρ, b, f(r)]: range, hardness and the three body interaction. To calculate these parameters, we have employed the following equilibrium conditions.

$$[d(U)/dr]_{r=r_0} = 0 \quad \text{and} \quad [d^2U/dr^2] = 9k\, r_0\, B_T \tag{9}$$

Now, in the last term $\langle\omega^2\rangle^{1/2}$, the mean-square frequency relates to the Debye temperature (Θ_D) as

$$\langle\omega^2\rangle^{1/2} = k\,\Theta_D/h \qquad (10)$$

Here, Θ_D can be expressed by well known Blackman's formula described in [16]:

$$\Theta_D = (h/k)\,\sqrt{[(5r_0B_t)/\mu\ ]} \qquad (11)$$

where, B_t and μ are the bulk modulus and reduced mass of the compounds.

To understand elastic properties of these monotellurides, we have calculated second order elastic constants (SOEC), (C_{11} C_{12} and C_{44}) and their pressure derivatives at 0 K, since these elastic constants are functions of first and second order derivatives of short range potential, so their calculation will provide knowledge about the effect of short range forces on these materials following Jain et al. [17]. The expression for SOE constants is given as:

$$C_{11} = e^2/4r_0^4\ [-\ 5.112z\ \{z+12f(r)\} + A_1 + (A_2 + B_2)/\ 2] + 9.30z\ (rdf/dr)] \qquad (12)$$

$$C_{12} = e^2/4r_0^4\ [1.391z\ \{z + 12f(r)\} + (A_2 - B_2)/4 + 9.30z\ (rdf/dr)] \qquad (13)$$

$$C_{44} = e^2/4r_0^4\ [2.556z\ \{z+12f(r)\} + B_1 + (A_2 + 3B_2)/\ 4)\ ] \qquad (14)$$

In equations (12) to (14), the first term represents the long-range Coulomb interaction, the second term represents the contribution due to TBIP and the remaining ones contribute overlap repulsion expressed in terms of the short range parameters (A_1, B_1) and (A_2, B2) for the nearest neighbor (nn) and next nearest neighbor (nnn) ions. These expressions are given in our earlier paper [12] .

3. Result and discussion

Using the measured values of the equilibrium lattice constant (r_0) and isothermal bulk modulus (B_T) with K=2 for B_1 phase, the model parameters thus calculated are given in Table 1 and are used to compute the results presented and discussed below. For simplicity, we have taken account of only a single set [ρ , b, f(r)] in B_1–phase and the same set is used in B_2 phase. The reason for this is that during the phase transition from $B_1 \rightarrow B_2$ the atomic distribution takes a different arrangement and they get arranged in CsCl structure after phase transition. Inter-ionic separation changes are calculated by the minimizing technique. The parameter f(r) is inter-ionic separation (r) dependent and it is therefore changed accordingly.

Table 1: Ionic radii r_i, r_j , inter ionic separation r_0 and range ρ are given in (A^o).

Compounds	Input parameters				Model parameters		
	r_i	r_j	r_0	B_T (GPa)	b(10^{-19}J)	ρ	f(r)
LaTe	1.04[c]	2.21[c]	3.215[a]	52.8[a]	58.21	0.38	0.091
SmTe	1.19[c]	2.21[c]	3.295[b]	37.6[b]	4.85	0.44	-0.008

[a] reference(8) [b] reference(4) [c] reference(23)

We have followed the technique of minimization of $U_{B_1}(r)$ and $U_{B_2}(r')$ at different pressures in order to obtain their inter ionic separations r and r' corresponding to B_1 and B_2 phases. First, we have evaluated the corresponding Gibbs free energies $G_{B_1}(r)$ and $G_{B_2}(r')$ and their respective differences $\Delta G = (G_{B_2}(r) - G_{B_1}(r'))$. Then, we have plotted ΔG against pressure (P), as shown in Fig. 1, for LaTe and SmTe. The phase transition pressure (P_t) is the pressure at which ΔG approaches zero.

We have also computed the relative volume changes V(P)/V(0) and plotted them against the pressure as depicted in Fig. 2 for LaTe and SmTe. It is clear from Fig. 2 that phase transition $B_1 \rightarrow B_2$ occur at about 18 GPa and 12 GPa for LaTe and SmTe, respectively, and the calculated volume collapses using TBIP model are 8.6% for LaTe and 9% for SmTe, respectively. These are close to experimental values and also given in other works. The phase transition pressures and relative volume change for SmTe are calculated by two-body approach as given by Varshney et al. [8] for LaTe and shown in Table 2.

Table 2: Calculated transition pressures and volume collapses.

Comp.	Transition	Transition Pressure(GPa)			Volume Collapes		
		Present TBIP	Exp. and other	Two-body	Present	Exp. and other	Two-body
LaTe	$B_1 \rightarrow B_2$	18	16.5[a]	(16.8)[b]	8.6%	(8.2%)[a]	(7.2%)[b]
SmTe	$B_1 \rightarrow B_2$	12	(11)[c]	13.5	9%	(9.1%)[c]	8.7%

[a] reference(8) [b] reference(9) [c] reference(4)

Furthermore, to test our TBIP model we have used the Vinet universal equation of state (EOS) for these compounds on the guidelines of Recio et al. [18]. The P-V data can be expressed by the equation.

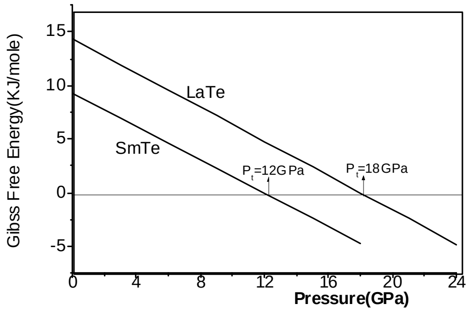

Fig-1

Variation of Gibbs free energy differences ΔG(KJ/mol) against pressure (GPa) for LaTe and SmTe.

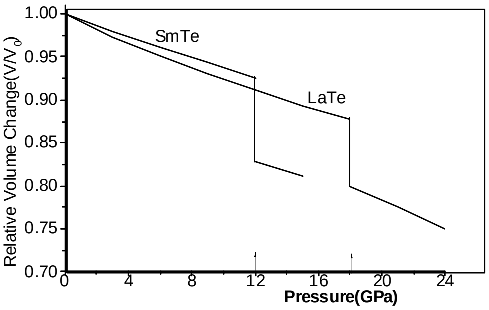

Fig-2

Variation of relative volume with pressure for LaTe, and SmTe.

$$\ln H = \ln B_0 + (3/2)(B_0' - 1)(1 - x) \qquad (15)$$

Here H and x are defined as

$$H = Px^2/(3(1 - x) \quad \text{and} \quad x = V/V_0 \qquad (16)$$

The curve representing B_1 (B_2) phases computed from above equation (14) are shown in thick (thin) lines in Fig. 4. We have fitted the VEOS to our TBIP P-V data. In this way, we carried out a comparison not with the experiments, but simply created a sort of consistency of the empirical behavior in many real solids.

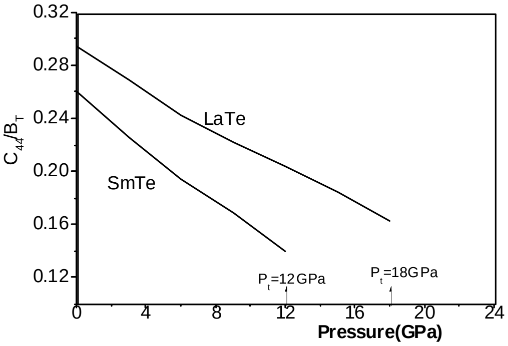

Fig-3

Variation of C_{44}/B_T with pressure for LaTe, and SmTe.

Since the study of elastic constant and their combinations is important to understand the elastic properties and their inter-atomic behavior, we have computed the second-order elastic constants (SOEC) and their combinations, which are shown in Table-III. The quantities C_{44} and C_S are the shear and tetragonal moduli of a Cubic crystal. It is necessary for lattice to satisfy the Born criterion for mechanically stable state. For this purpose, the elastic energy density must be a positive definite quadratic function of the strain. In order to fulfill the above criterion, the principal minor (eigen values) of the elastic constant matrix should all be positive.

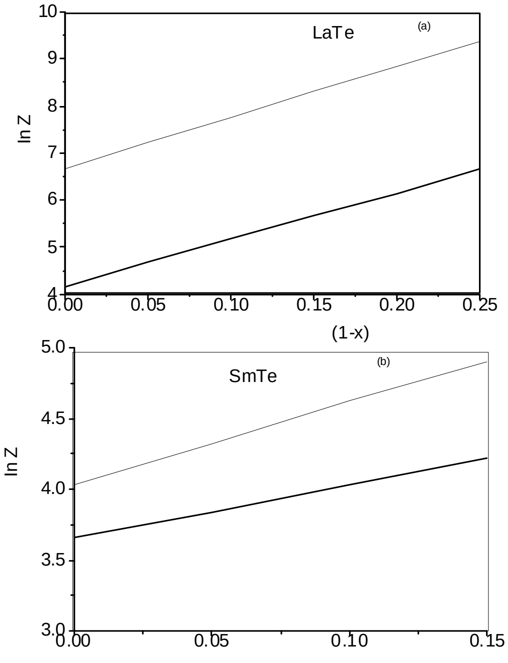

Fig-4

Thick and thin solid curves represent Vinet equation of state (VEOS) (a) for LaTe (b) for SmTe.

Since the tetragonal modulus $C_S = (C_{11} - C_{12})/2$ for PbTe and SnTe increases linearly with pressure, the pressure-induced change in C_{44} decreases slightly for PbTe and SnTe. Also, the pressure dependence of the corresponding stiffness $1/3\ (C_{11} + C_{12} + 2C_{44})$ is linear for PbTe and SnTe. Hence TBIP confirmed that the features of LaTe and SmTe show the same trends as reported for pressure dependence elastic stiffness for PbTe and SnTe possessing the NaCl structure [19]. Vukcevich [20] also stated the high pressure stability criterion for ionic crystal, the stable phase of a crystal is one in which the shear elastic constant C_{44} is non-zero (for mechanical stability) and which has the lowest potential energy among the mechanically stable lattices. Thus the stability of NaCl-type structure in terms of elastic constants should satisfy the following conditions

$$B_T = 1/3\ (C_{11} + 2C_{12}) > 0, \quad C_{44} > 0 \quad \text{and}$$

$$C_S = (C_{11} - C_{12})/2 > 0 \tag{17}$$

The estimated shear moduli are C_{44}=16.2 GPa and C_{44}= 9.8 GPa and tetragonal moduli are C_S = 55.5 and C_S =39.9GPa for LaTe and SmTe, which are well suited for the above elastic stability criterion for RETe compounds. From Table 3, our estimated C_{44} for LaTe and SmTe are positive and hence the above stability criterion is satisfied for ionic crystal. Musgrave and Pople [21] pointed out that if either C_{44} or $C_S = (C_{11} - C_{12})/2$ goes to zero as the pressure is increased, then the structure becomes unstable and the crystal transforms by a spontaneous shear. Also, in the case of B1-structure, C_{44} decreases up to P_t but the phase transition to the B_2 – structure takes place before the C_{44} reaches zero. Demarest et al. [22] proposed a slight modification of the Born stability criterion that a phase transition takes place when the ratio C_{44} / B_T reaches a critical value in the neighborhood of 0.14 and 0.2. Along the same guide lines, we have obtained exactly the same trends from TBIP that are tabulated in Table 3 and shown in Fig. 3. The deviation from Cauchy relations between second order elastic constants as well as the third order elastic constants can be more significantly expressed in terms of TBIP approach.

Table 3: Calculated elastic constants and their combinations (GPa).

Comp.	C_{11}	C_{12}	C_{44}	C_{44}/B_T	$C_S = ½(C_{11} - C_{12})$	$C_L = ½\ (C_{11}+C_{12} + 2C_{44})$
LaTe	135	24	16.2	0.294	55.5	95.7
SmTe	92.4	12.4	9.8	0.14	39.9	57.6

Finally, we have noticed that during the crystallographic transition from NaCl to CsCl, the volume discontinuity in pressure-volume phase diagram identifies the same trends as the experimental data and these results are well fitted with Vinet (EOS). In order to judge the stability of these compounds, we have computed elastic constants and plotted C_{44}/B_T with different pressures and hence the trends shown from TBIP are consistent with the requisites of first-order phase transition. On the basis of above work, it is concluded that the TBIP approach is adequately suitable for the prediction of $B_1 \rightarrow B_2$ phase transition pressures and associated volume collapses in RETe compounds.

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