High Pressure Phase Transition and Allied Behavior of Samarium Compounds

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A theoretical study of the phase transition of samarium monochalcogenides using three-body interaction potential model is carried out at high pressure. The three-body interaction potential includes long range Coulombic, three-body interaction forces and short range overlap repulsive forces operative up to next nearest neighbor ions. We have investigated phase transition pressures, volume collapses, elastic behavior, stability criteria and various thermo physical properties at various high pressure. The results found are well suited with available experimental data. In this paper third order elastic constants are also reported for the first time which helps in understanding the nature of interionic forces in ionic solids which paved the experimentalist to work in specific direction.

1. Introduction

The samarium monochalcogenides (SmX; X = S, Se, Te) crystallize in NaCl structure and are semiconducting with unusual gap structure (except SmO) [1, 2]. Valence instabilities are observed in SmS, SmSe, and SmTe [2–6]. The theoretical description of Sm and Eu compounds is a challenge due to the $4f$-electrons. The electronic structures of SmX [X = N, P, As, Sb, Bi, O, S, Se, Te, Po] compounds were calculated using the self--interaction corrected local-spin density approximation (LSDA) [7]. Recently, the electronic structure and optical spectra of SmS, SmSe, SmTe were calculated with the LSDA+U approach [8]. The transition from semiconductor to metal under pressure was studied by X-ray scattering [9]. High pressure resistivity studies on Sm chalcogenides reveal that SmTe, SmSe undergo a continuous pressure induced semiconductor to metal transition while for SmS this transition is discontinuous. Sm chalcogenides in their high pressure phase are metallic conductors [10]. Rooyman [11] reported a discontinuous isostructural transition near 40 kbar with 15% volume decrease due to valence transition of Sm divalent to the trivalent state. Compressibility of monochalcogenides of Sm was investigated on nearly 30 GPa using high pressure X-ray diffraction technique [12].

SmTe exhibits phase transition from NaCl type to CsCl type at pressure of about 11 ± 1 GPa [13]. Among the other samarium monochalcogenides SmS is one of the most studied systems. Using X-ray diffraction technique and synchrotron radiation Le Bihan et al. [2] studied monochalcogenides of Sm up to a pressure of 55 GPa.

SmS and SmSe exhibit a phase transition from NaCl to CsCl type structure at 42 and 25 GPa [2]. At pressure less than 1.8 GPa SmS shows considerable volume collapse and change of colour but retains the same cubic structure [14]. Earlier, we had studied the high pressure phase transition phenomenon, elastic and various thermo-physical properties of SmTe and EuO successfully [15]. For SmS, at zero pressure, the Sm ions are in a divalent insulating state, the so-called black phase [16]. SmS has been a typical system showing valence instability and undergoes a pressure-induced first-order phase transition [17] and at a very high pressure the Sm will be in a trivalent metallic state and between the two limits the valence of Sm is intermediate [18]. This transition occurs discontinuously from divalent to an intermediate valence at the well known black-to-gold phase transition [14].

2. Potential model and method of calculation

During lattice vibration, ions suffer an appreciable overlap and their electron shells get deformed and charge gets transferred between overlapping ions, these transferred charges interact and give rise to long range many body interactions [19] in which the main contribution is due to three body interactions (TBI). In ionic crystal the existence of three body interactions and its influence on lattice mechanical properties of ionic solids is well established and explained through quantum as well as classical mechanical theories by Singh and coworkers [19]. It is well known fact that the application of pressure on crystals results in reduction in its volume which leads to an increased charge transfer which is three body interaction effects [20–22] due to the deformation of overlapping electron shells of the adjacent ions. These effects have been incorporated in the Gibbs free energy ($G = U + PV - TS$)

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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 in the vibrational entropy. The Gibbs free energies for rock salt ($B1$ real) and CsCl ($B2$; hypothetical) structures at $T = 0$ K and at ambient pressure are given by

$$G_{B1}(r) = U_{B1}(r) + PV_{B1}, \tag{1}$$

$$G_{B2}(r') = U_{B2}(r') + PV_{B2}, \tag{2}$$

with V_{B1} $(= 2.00r^3)$ and V_{B2} $(= 1.54r^3)$ as the unit cell volumes for B_1 and B_2 phases, respectively. The first terms in Eqs. (1) and (2) represents lattice energies for $B1$ and $B2$ structures and they are expressed as

$$\begin{aligned}
U_{B1}(r) = & \left[-(\alpha_m z^2 e^2)/r\right] - \left[(12\alpha_m z e^2 f(r))/r\right] \\
& + 6b \exp\left((r_i + r_j - r)/\rho\right) \\
& + 6b \exp\left((2r_i - 1.41r)/\rho\right) \\
& + 6b \exp\left((2r_j - 1.41r)/\rho\right),
\end{aligned} \tag{3}$$

$$\begin{aligned}
U_{B2}(r) = & \left[-(\alpha'_m z^2 e^2)/r'\right] - \left[(16\alpha'_m z e^2 f(r'))/r'\right] \\
& + 8b \exp\left((r_i + r_j - r)/\rho\right) \\
& + 3b \exp\left((2r_i - 1.154r')/\rho\right) \\
& + 3b \exp\left((2r_j - 1.154r')/\rho\right).
\end{aligned} \tag{4}$$

These lattice energies consist of long-range Coulomb energy [first terms in Eq. (3) and Eq. (4)], three-body interactions corresponding to the nearest neighbor separation r (r') [second terms in Eqs. (3) and (4)] and energy due to the overlap repulsion represented by Hafemeister and Flygare (HF) type potential [21, 22] and extended up to the second neighbour ions (rest of the terms). In Eqs. (3) and (4) three-body potential parameter depends on inter ionic separation and expressed as $f(r) = f_0 e^{-r/\rho}$ with f_0 being a constant. Three model parameters are used in Eqs. (3) and (4), viz. $[\rho, b, f(r)]$ the value of which have been determined from the knowledge of the cohesive energy $U(r)$ and its first order derivative following the equilibrium condition given below

$$\left[\frac{dU}{dr}\right]_{r=r_0} = 0$$

$$\text{and} \quad B_1 + B_2 = -1.165z(z + 12f(r)). \tag{5}$$

To understand the elastic and anharmonic properties of the proposed compounds we have calculated the second order elastic constants (SOEC's), their pressure derivatives and third order elastic constants (TOEC's). Their calculation will provide knowledge of interionic forces in the crystal. These (SOEC's) are functions of the first and second-order derivatives of the short range potentials, their calculation will provide a check on the accuracy of short range forces in these materials [21, 22]. The basic theory for deducing the expressions of the second, third and higher order elastic constants is described somewhere else [23]. We have obtained SOEC's, their pressure derivatives and third order elastic constants with the help of relations given in [24].

TOEC's furnish accurate information about the repulsive interactions as their contributions are dominant in the higher derivatives of the potential energy. Also they

provide information regarding the thermal expansion and the temperature and pressure dependence of the second order elastic constants. The expressions for TOEC's for NaCl phase are taken from Shanker et al. [23].

Exploiting the TBIP model we have calculated various thermo physical properties of SmS and SmSe. We have calculated the compressibility (β), molecular force constant (f), infrared absorption frequency (ν_0), the Debye temperature (Θ_D), the Grüneisen parameter (γ) and anharmonicity (A) of these compounds. These thermo physical properties provide us the interesting information about substances, viz. the Debye temperatuture (Θ_D) shows the structural stability, defect availability and the strength of bonds between the elements. The expressions of these thermo physical properties are taken from [24].

In the same sequence compressibility (β) is given by well known relation

$$\beta = \frac{3Kr_0}{f}, \tag{6}$$

where molecular force constant (f) is

$$f = \frac{1}{2}\left[\Phi_{kk'}^{SR}(r) + \frac{2}{r}\Phi_{kk'}^{SR}(r')\right]. \tag{7}$$

Here, $\Phi_{kk'}^{SR}(r)$ are the short range nearest neighbor part which is given by the last three terms in Eqs. (3) and (4). This force f leads to the infrared absorption frequency which is deduced by the knowledge of the reduced mass (μ):

$$\nu_0 = \frac{1}{2\pi}\left(\frac{f}{\mu}\right)^{1/2}. \tag{8}$$

This frequency is utilized to calculate the Debye temperature as follows:

$$\Theta_D = \frac{h\nu_0}{k},$$

where h and k are the Planck and Boltzmann constants, respectively.

The important Grüneisen parameter (γ) [24] is given by

$$\gamma = -\frac{r_0}{6}\left[\frac{\Phi_{kk'}'''(r)}{\Phi_{kk'}''(r)}\right]. \tag{9}$$

Here, $\Phi_{kk'}'''(r)$ and $\Phi_{kk'}''(r)$ are the third and second derivatives of cohesive energy. The elastic anisotropic parameter of a cubic crystal is defined in [24, 25] as

$$A = \frac{2C_{44} + C_{12}}{C_{11}} - 1. \tag{10}$$

3. Result and discussion

We have followed the technique of minimization of $U_{B1}(r)$ and $U_{B2}(r')$ at different pressures in order to obtain the interionic separations r and r' corresponding to $B1$ and $B2$ phases. Input and model parameters are tabulated in Table I and Table II respectively. Now $\Delta G = (G_{B2}(r') - G_{B1}(r))$ are plotted against pressure (P) as shown in Fig. 1 for SmS and SmSe. The phase transition pressure (P_t) is the pressure at which ΔG approaches zero. It is clear from Fig. 2 that phase transition

$B1 \to B2$ occurs at about 41.9 GPa and 24.9 GPa for SmS and SmSe respectively, which are close to the experimental phase transition pressure 42 GPa and 25 GPa [2]. Concisely we point that from TBIP approach the estimated value of P_t is in good agreement with experimental values which are listed in Table III and furthermore we have estimated relative volume change with pressure for SmS and SmSe which are shown in Fig. 2, the magnitude of relative volume changes at the transition pressure for SmS and SmSe are 6.5% and 8.7%, respectively. We have also calculated the bulk modulus and listed in Table IV for SmS the calculated value suited with the experimental value [26]. The pressure variation have been shown in Fig. 4. The cohesive energies for both the phases viz. $B1$ and $B2$ are listed in Table IV.
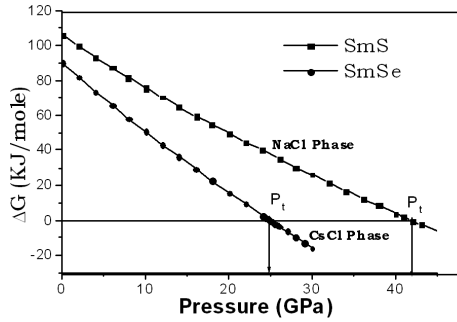

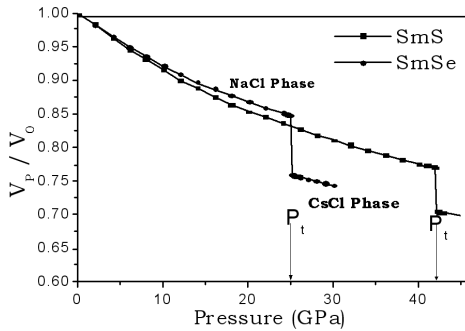Fig. 1. Variation of Gibbs free energy with pressure.

Fig. 2. Variation of relative volume change with pressure.

TABLE I

Input data.

Comp.	r_i [Å]	r_j [Å]	r_0 [Å]
SmS	1.19^a	1.84^b	2.98^b
SmSe	1.19^a	1.91^b	3.11^b

^{a} Ref. [2], ^{b} Ref. [32]

The SOEC's of SmS are well suited with experimental work [27], while the SOEC's of SmSe are not available up to present study. The variation of these SOEC's with pressure are well shown in Fig. 3a for SmS and
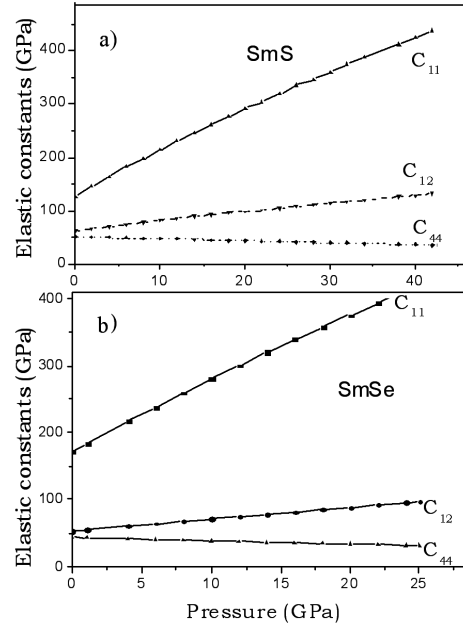

Fig. 3. (a) Variation of C_{11}, C_{12} and C_{44} with pressure P (GPa) for SmS. (b) Variation of C_{11}, C_{12}, and C_{44} with pressure P (GPa) for SmSe.
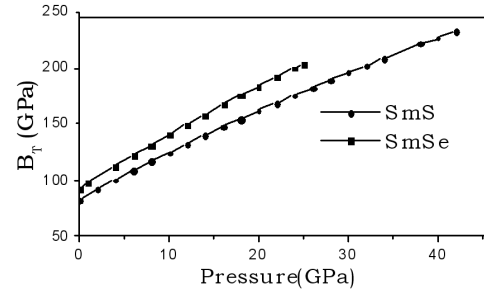

Fig. 4. Variation of B_T with pressure P (GPa).

Fig. 3b for SmSe. The combination of these SOEC's, $C_L = (C_{11} + C_{12} + 2C_{44})/2$ and $C_S = (C_{11} - C_{12})/2$ are calculated from Shanker et al. [23] and listed in Table IV. The results we obtained are well suited with the first order character of the transition for these compounds and are similar to the earlier reported pressure dependence of elastic stiffness PbTe and SnTe having the NaCl structure with B_1 to B_2 structural phase transition [28]. According to the Vukcevich [29] the stable phase of a crystal is one in which the shear elastic constant C_{44} is non-zero (for

TABLE II

Model parameters for samarium monochalcogenides.

Comp.	b [10^{-19} J]	ρ [Å]	$f(r)$
SmS	0.38	0.35	-0.0095724
SmSe	0.36	0.28	-0.0076146

TABLE III

Phase transition pressure and relative volume collapse.

Comp.	Phase transition pressure [GPa]		Volume collapse [%]
	Present	Exp.	Present
SmS	41.9	42[a]	6.5
SmSe	24.9	25[a]	8.7

[a] Ref. [2]

TABLE IV

Calculated bulk modulus and cohesive energy.

Comp.	B_T [GPa]		μ [10^{-24} g]	Cohesive energy	
	Present	Exp./others		U_1 (B_1) [kJ/mol]	U_2 (B_2) [kJ/mol]
SmS	83	89[a]/53.4[b]	43.86	−2923.56	−2817.37
SmSe	92.2	40 + 5[c]/43.9[b]	85.94	−2874.87	−2784.36

[a] Ref. [2], [b] Ref. [7], [c] Ref. [29]

mechanical stability) and which has the lowest potential energy among the mechanically stable lattices. The value of C_{44} for SmS and SmSe are positive and satisfy the above stability condition. We have later on followed the Born criterion for a lattice to be mechanically stable which states that the elastic energy density must be a positive definite function of strain. This requires that the principal minors (the eigenvalues) of the elastic constant matrix should all be positive. Thus using the above stability criterion for NaCl structure in terms of the elastic constants as followed by Singh et al. [20, 21] are

$$B_T = \frac{1}{3}(C_{11} + C_{12}) \succ 0, \quad C_S = \frac{1}{2}(C_{11} - C_{12}),$$

$$C_{44} \succ 0. \tag{11}$$

The C_{44} and C_S are the tetragonal and shear modulus of a cubic crystal. Also, the estimated tetragonal moduli of these compounds are $C_{44} = 0.523 \times 10^{12}$ dyn/cm² and $C_{44} = 0.44 \times 10^{12}$ dyn/cm², respectively, and shear moduli are $C_S = 0.320 \times 10^{12}$ dyn/cm² and $C_S = 0.452 \times 10^{12}$ dyn/cm² for SmS and SmTe, respectively, which are well suited with the above elastic stability criterion. Demarest et al. [30] proposed a slight modification of the Born stability criterion that a phase transition take place when the ratio $\frac{C_{44}}{B_T}$ reaches a critical value in the neighborhood of 0.14 and 0.2. From Table IV it is inferred that we have obtained the same trends from TBIP and hence also well satisfied the above stability criterion. We have also shown the trends of $\frac{C_{44}}{B_T}$ with pressure and shown in Fig. 5. The values of $\frac{C_{44}}{B_T}$ for these monochalcogenides decrease with pressure but could not reach zero up to phase transition pressure as defined above. This shows that our calculated elastic constants with this TBIP are well suited with the stability criterion.

The anharmonic properties of proposed compounds are obtained by computing the pressure derivative of the bulk moduli $\frac{dB_T}{dP}$, shear-moduli $\frac{dS}{dP}$ and the tetragonal moduli $\frac{dC_{44}}{dP}$ at zero pressure and third order elastic constants (TOEC's). We have therefore, deducted these pressure derivative and TOEC which are listed in Table VI and
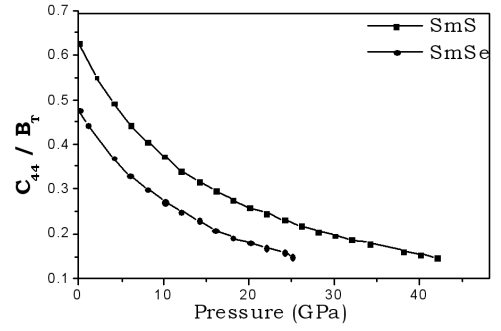
Fig. 5. Variation of C_{44}/B_T with pressure P (GPa).

The calculated values of elastic constants SOEC's (10^{12} dyn/cm²).

TABLE V

Comp.	C_{11}		C_{12}		C_{44}		C_{44}/B_T
	Present	theor. /exp.	Present	theor. /exp.	Present	theor. /exp.	Present
SmS	1.26	1.2[a]	0.61	0.11[a]	0.52	0.25[a]	0.16
SmSe	1.22	–	0.32	–	0.44	–	0.15

[a] Ref. [26]

Table VII, respectively. It is true that the comparison of the experimental and theoretical results is not possible but we have compared these values with those of the other monochalcogenides and our values are better with their values.

In continuation the TOEC's at zero pressure are given in Table VII for SmS and SmSe which show that the C_{111}, C_{112}, C_{166} are negative while that of C_{123}, C_{144}, C_{456} are positive. The present studies on TOEC's reveal that their behavior is just opposite to the behavior of SOEC. It is also evident from the experimental values of TOEC's for alkali halide viz. NaCl, KCl, etc. that the Cauchy discrepancies among the TOEC's are not very large and are of about the same order as those among the SOEC, viz. ($C_{11} - C_{12}$). This result, according to our present TBIP shows better resemblance which is most inspiring. However the experimental studies on the TOEC's of the system of solids under consideration are relatively difficult and only measurements available up to present date are the pressure derivatives of the SOEC.

Apart from elastic constants, we have investigated various important physical properties like the Debye temperature (Θ_D) and Grüneisen parameter (γ) and are well tabulated in Table VIII. These thermo-physical properties provide us the interesting information about these Sm compounds. The Debye temperature is important property as it relates to many physical properties viz.

TABLE VI

Variation of second order elastic constants with pressure and combination of SOEC's.

Comp.	$\frac{dB_T}{dP}$	$\frac{dS}{dP}$	$\frac{dC_{44}}{dP}$	$C_S = (C_{11} -C_{12})/2$	$C_L = (C_{11}+ C_{12} + 2C_{44})/2$
SmS	4.994	3.289	0.234	0.320	1.46
SmSe	5.713	4.740	0.037	0.459	1.56

Calculated TOEC's.

TABLE VII

Comp.	C_{111}	C_{112}	C_{123}	C_{144}	C_{166}	C_{456}
SmS	-21.43	-2.99	0.96	0.78	-2.27	0.75
SmSe	-32.23	-2.78	0.82	0.67	-2.06	0.65

Calculated thermophysical properties.

TABLE VIII

Comp.	f [10^4 dyn/cm]	v_0 [10^4 dyn/cm]	Θ_D [K]	γ	α_V/C_V [10^3 J]	A
SmS	6.69	6.22	297.33 [178^a]	1.52	7.91	1.27
SmSe	7.89	4.82	230.52	1.89	8.11	0.38

^{a} Ref. [28]

the specific heat and melting temperature. Moreover, the Debye temperature (Θ_D) reflects its structural stability, the strength of bonds between its constituents, structure defects availability, and its density. At low temperature the vibration excitations arise only from acoustic vibrations. Hence at low temperature the value of Θ_D calculated from elastic constants is the same as that determined from specific heat measurements [27]. Our values for the Debye temperature are calculated from well known Blackman formula and their values for SmS and SmSe are 297.33 K and 230.52 K, respectively. Direct evidence of experimental values for the Debye temperature of solids under study is not known yet but our results are closed to same class of compound viz. LaS and LaSe [31].

Also, our values of Grüneisen parameter (γ) seem to be more realistic as they are close in magnitude to the measured values of alkali halides and other monochalcogenides having NaCl type structure [21]. It is arguable that the deduced values of γ are consistent with the Raman scattering measurements and the values calculated from the knowledge of phonon frequencies (long--wavelength phonons) as a function of crystal volume.

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