

# High Pressure and Temperature Induced Structural, Elastic and Thermodynamical Properties of Samarium Monochalcogenides Alloy of the Type $\text{SmS}_{1-x}\text{Sex}$ [ $x = 0, 0.11, 0.44, 1$ ]

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**Abstract.** The pressure and temperature dependent elastic, mechanical and thermal properties of rock salt to CsCl structures in Samarium monochalcogenides  $\text{SmS}_{1-x}\text{Sex}$  ( $x = 0, 0.11, 0.44, 1$ ) are presented. The enhancement of Young's modulus ( $E$ ) and Bulk modulus ( $BT$ ) with increment in doping is an indicator of brittle nature of  $\text{SmS}_{1-x}\text{Sex}$ . The compressions in volume of  $\text{SmS}_{1-x}\text{Sex}$  ( $x = 0, 0.11, 0.44, 1$ ) is the indicator of mechanical stiffening in lattice at higher pressure and the thermal expansion of  $\text{SmS}_{1-x}\text{Sex}$  at higher temperature shows thermal softening of  $\text{SmS}_{1-x}\text{Sex}$  ( $x = 0, 0.11, 0.44, 1$ ) alloy. From Pugh's and Poisson's ratio we classify  $\text{SmS}_{1-x}\text{Sex}$  ( $x = 0, 0.11, 0.44, 1$ ) as brittle material. The present results are in general in good agreement with experimental data available for the end point members ( $x = 0$  and  $x = 1$ ).

## INTRODUCTION

Rare earth monochalcogenides crystallize in NaCl structure and they show either metallic or semiconducting properties depending on the valence state of the rare earth ions [1]. They are metallic if trivalent and semiconducting if divalent [2]. With the application of pressure, the Sm ions become trivalent with the reduction of radius and change in volume of the crystal. However, there is no change in structure. This isostructural transition is first order transition in SmS while it is continuous in SmSe and SmTe [3].

The high-pressure behavior of the Samarium monochalcogenides  $\text{SmX}$  ( $X = \text{S, Se, Te}$ ) is studied up to 55 GPa using the energy dispersive X ray diffraction technique and synchrotron radiation. SmS shows a phase transition at low pressure (less than 1.8 GPa), retaining the same cubic structure [4]. This phase transition is associated with a considerable volume collapse and a change of color from blue/black to a golden. The above can be attributed to a valence transition of the  $\text{Sm}^{2+}$  ion to  $\text{Sm}^{3+}$  state. A relatively normal compression curve is obtained from this point until 42 GPa, when a previously unobserved phase transition to a CsCl structure starts to occur. This transition, accompanied by a volume collapse of 10% is almost complete at 54 GPa [4]. SmSe undergoes a structural phase transition from the B1 to the B2 phase that starts at 25 GPa and completing at 35 GPa with a volume collapse 6.8%, whereas SmTe undergoes the transition starting at 12.9 GPa and completing at 14 GPa with a volume collapse 6.8% [4]. Earlier, it is reported that this B1 to B2 is followed by electronic transition in the pressure range 1–50 kbar for SmSe and 1–60 kbar for SmTe [5]. A similar transition at 3–9 GPa for SmSe and 6–8 GPa for SmTe is also documented [4].

Although, structure stability and lattice mechanical properties are widely studied in SmX (X = S, Se, Te), less efforts have been made on mixed compounds. A smooth variation of transition pressure and energy gap in SmS<sub>1-x</sub>Se<sub>x</sub> is seen as a function of composition.

## THE METHOD

The SmS<sub>1-x</sub>Se<sub>x</sub> alloy transforms from their initial B1 to B2 structure under pressure. The stability of a particular structure is decided by the minima of Gibbs's free energy,  $G = U + PV - TS$ . The cohesive energy of B1 and B2 phases are:

$$U_{B1} = (-\alpha_M Z e^2 / r) [Z + 2nf(r)] - Cr^{-6} - Dr^{-8} + nb\beta_{ij} \exp[(r_i + r_j - r_{ij}) / \rho] + (n'b/2) [\beta_{ii} \exp((2r_i - kr_{ij}) / \rho) + \beta_{jj} \exp((2r_j - kr_{ij}) / \rho)] + [\{\hbar < \omega^2 >^{1/2} / 2\}] \quad 1$$

$$U_{B2} = (-\alpha'_M Z e^2 / r') [Z + 2mf(r')] - Cr'^{-6} - Dr'^{-8} + mb\beta_{ij} \exp[(r_i + r_j - r'_{ij}) / \rho] + (m'b/2) [\beta_{ii} \exp((2r_i - k'r'_{ii}) / \rho) + \beta_{jj} \exp((2r_j - k'r'_{jj}) / \rho)] + [\{\hbar < \omega^2 >^{1/2} / 2\}] \quad 2$$

Herein, first two terms are energies including long-range Coulomb and charge transfer effect. Third and fourth terms are van-der Waals attraction energies. Fifth and Sixth terms are short-range repulsive energy due to overlap repulsion between ions. Last term is the lowest possible energy of the system and is due to the zero point energy. The charge transfer force parameter and the force parameter arises due to covalent nature i.e.  $f(r) = f_{cti} + f_{cov}$ . The charge transfer between ions of S and Sm atoms is denoted in terms of a force parameter  $f_{cti}$  and covalency  $f_{cov}$  [30 - 32].

Alloy, according to the virtual crystal approximation (VCA) are regarded as any array of average ions whose masses, force constants and effective charges are considered to scale linearly with concentration (x). The measured data on lattice constants in SmS<sub>1-x</sub>Se<sub>x</sub> have shown that they vary linearly with the composition (x), and hence they follow Vegard's law [6]:

$$a(ABxCl_{1-x}) = (1-x)a(AB) + xa(AC) \quad 3$$

With these understanding of interatomic potential in SmS<sub>1-x</sub>Se<sub>x</sub>, we have four material parameters, namely, modified ionic charge; hardness, range, force parameter [ $Zm, b, \rho, f(r)$ ]. Values of them can be deduced from equilibrium conditions [15 – 29]

## RESULTS AND DISCUSSION

We use experimental data on lattice constant ( $a$ ) [4] the bulk modulus ( $B_T$ ), [4], ionic ( $Ze$ ), effective charge ( $e_s^*$ ) and the second order aggregate elastic constant  $C_{12}$  ( $C_{44}$ ) in [7] for end members of SmS<sub>1-x</sub>Se<sub>x</sub> ( $x = 0, 0.11, 0.44, 1$ ) for determining the material parameters. The computed material parameter of hardness ( $b$ ), range ( $\rho$ ), and non-central forces arose due to charge transfer ( $f_{cti}$ ) and covalency ( $f_{cov}$ ) for SmS<sub>1-x</sub>Se<sub>x</sub> and is illustrated in Table

As a next step, we have estimated the transition pressure  $P_T$  for SmS<sub>1-x</sub>Se<sub>x</sub>. The Variation of Gibb's free energy for B1 and B2 phases with pressure is illustrated in Figure 1(a-d). The calculated values of transition pressure  $P_T$  are 40.4 (SmS), 36.3 (SmS<sub>0.89</sub>Se<sub>0.11</sub>), 32.5 (SmS<sub>0.56</sub>Se<sub>0.44</sub>) and 24.2 (SmSe) GPa compared with available experimental data [4]. Compressions in SmS<sub>1-x</sub>Se<sub>x</sub> at higher pressure indicate the mechanical stiffening of lattice.

Figure 2 (b) discerns the variation of  $V_T/V_0$  as functions of temperature in B1 phase. Here,  $V_T$  symbolizes the

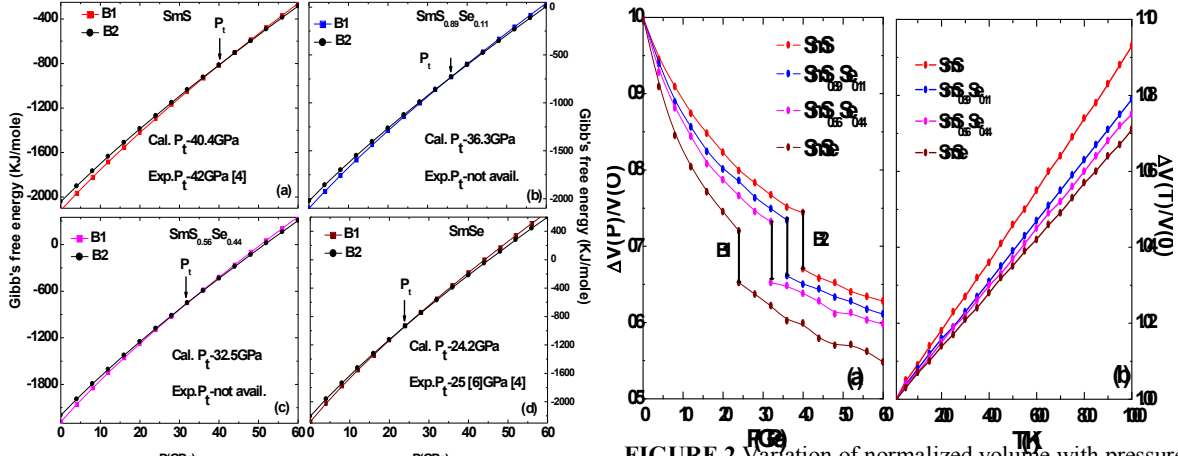


FIGURE 1. Variation of Gibb's free energy for B1 and B2 phases with pressure.

FIGURE 2. Variation of normalized volume with pressure and temperature.

volume at various temperatures and  $V_0$  at zero temperature and zero pressure volumes, respectively. A step increase in the ratio  $V_T/V_0$  with increasing temperature infers expansion of  $\text{SmS}_{1-x}\text{Se}_x$  lattice and is susceptible to temperature.

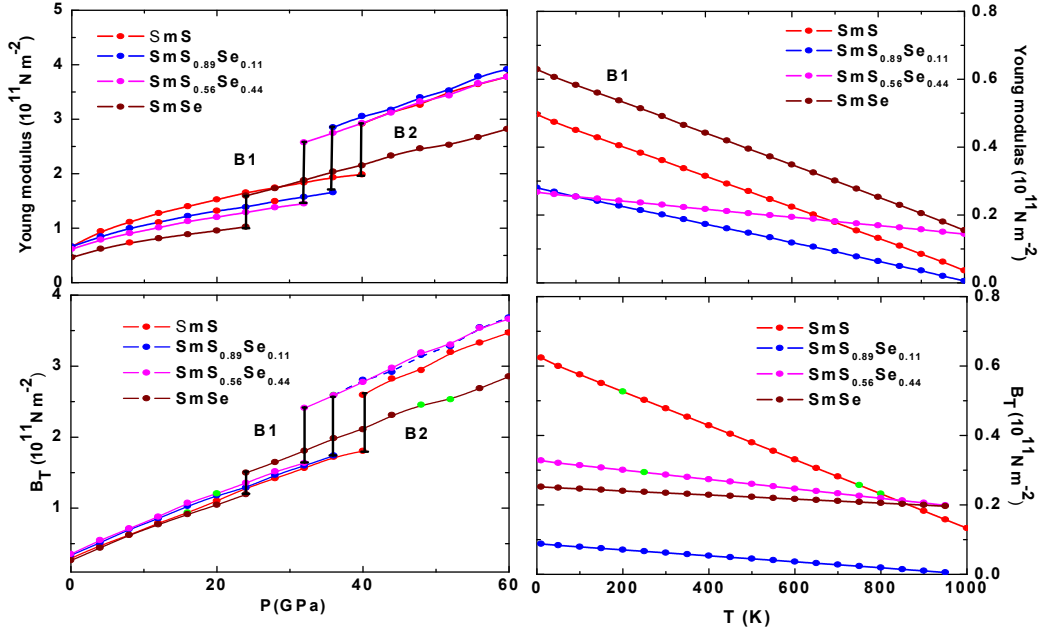


FIGURE 3. Variation of Young's modulus ( $E$ ) and Bulk modulus ( $B_T$ ) with pressure and temperature.

On the other hand,  $\text{SmS}_{1-x}\text{Se}_x$  is compressed at higher pressures as shown in Figure 2 (a). Henceforth,  $\text{SmS}_{1-x}\text{Se}_x$  lattice is thermally softened and mechanical stiffened. The normalized volume  $V_T/V_0$  dependences on temperature is not known for  $\text{SmS}_{1-x}\text{Se}_x$  but the calculated values of volumes collapse are 7.4 ( $\text{SmS}$ ), 7.3 ( $\text{SmS}_{0.89}\text{Se}_{0.11}$ ), 8.0 ( $\text{SmS}_{0.56}\text{Se}_{0.44}$ ) and 6.8 ( $\text{SmSe}$ ) % consistent with available experimental data [4].

The pressure dependence of the Young's modulus ( $E$ ) and Bulk modulus ( $B_T$ ) of  $\text{SmS}_{1-x}\text{Se}_x$  is sketched in Figure 3 (a-d). It is inferred that Young's modulus ( $E$ ) and Bulk modulus ( $B_T$ ) enhances in both phases with the

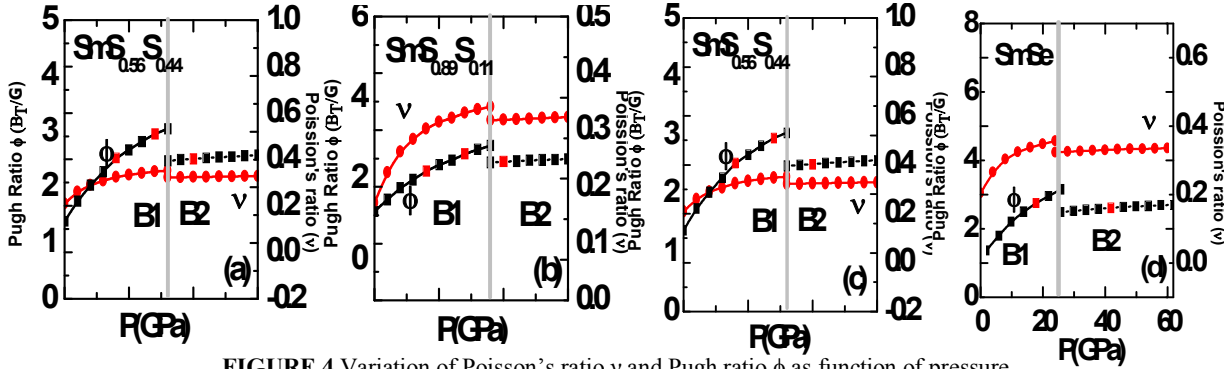


FIGURE 4. Variation of Poisson's ratio  $\nu$  and Pugh ratio  $\phi$  as function of pressure.

enhancement of pressure. We also note that as the doping concentration of Se increases discontinuity gap at transition pressure decreases from SmS to SmSe. This concluded higher level of doping concentration decreases stiffness of material. The calculated value of Bulk modulus ( $B_T$ ) 29.2 (SmS), 33.7 ( $\text{SmS}_{0.89}\text{Se}_{0.11}$ ), 35.4 ( $\text{SmS}_{0.56}\text{Se}_{0.44}$ ) and 26.1 (SmSe) GPa is in good agreement with available data [7].

TABLE I. Estimated and input crystal data: lattice constant ( $a_0$ ), bulk modulus ( $B_T$ ), second order elastic constant  $C_{12}$  ( $C_{44}$ ), hardness (b), range ( $\rho$ ), charge transfer parameter  $f(r)$  for  $\text{SmS}_{1-x}\text{Se}_x$  ( $x = 0, 0.11, 0.44, 1$ ) in B1 phase at zero pressure.

Solids	Input Parameters				Model Parameters		
	$a_0$ (Å)	$B_T$ (GPa)	$C_{12}$ (GPa)	$C_{44}$ (GPa)	$b(10^{-12}$ erg)	$\rho$ ( $10^9$ cm)	$f(r)$ ( $10^{-3}$ )
SmS	5.970[4]	89.8[4]	12[7]	26[7]	1.05	3.09	1.226
$\text{SmS}_{0.89}\text{Se}_{0.11}$	6.127 [6]	89.8 [4]	11.9 [6]	25.8 [6]	1.455	3.187	1.308
$\text{SmS}_{0.56}\text{Se}_{0.44}$	6.599[6]	89.8 [4]	11.6[6]	25.1[6]	2.671	3.477	1.569
SmSe	6.220 [4]	40 [4]	10.8 [6]	21.4 [7]	4.735	3.97	2.067

The temperature dependence of the tensile strength as Young's modulus ( $E$ ) and Bulk modulus ( $B_T$ ) of  $\text{SmS}_{1-x}\text{Se}_x$  ( $x = 0, 0.11, 0.44, 1$ ) is illustrated in Figure 3 (a-d). A decreasing trend is inferred with increase in temperature.

From Figure 4 (a-d), the ratio  $\phi$  ( $= B_T/GH$ ) shows that (a) at zero pressures,  $\text{SmS}_{1-x}\text{Se}_x$  ( $x = 0, 0.11, 0.44, 1$ ) are ductile in NaCl phase, and (b) with increased pressure brittle nature  $\phi$  ( $= B_T/GH$ )  $> 1.75$  is documented in CsCl phase. Hence,  $\text{SmS}_{1-x}\text{Se}_x$  ( $x = 0, 0.11, 0.44, 1$ ) is ductile only at zero pressure and become brittle after structural phase transformations.

From Figure 4 (a-d) the Poisson's ratio  $\nu$  shows that (a) at zero pressure  $\text{SmS}_{1-x}\text{Se}_x$  are brittle in nature, (b) in the NaCl phase,  $\text{SmS}_{1-x}\text{Se}_x$  shows the brittle nature with increasing pressure, (c) at zero pressure, the value of  $\nu$  is about

0.121, 0.172, 0.209 and 0.205 for  $\text{SmS}_{1-x}\text{Se}_x$  close to the brittle limit of 0.33 and (d) at high pressures i.e., in CsCl

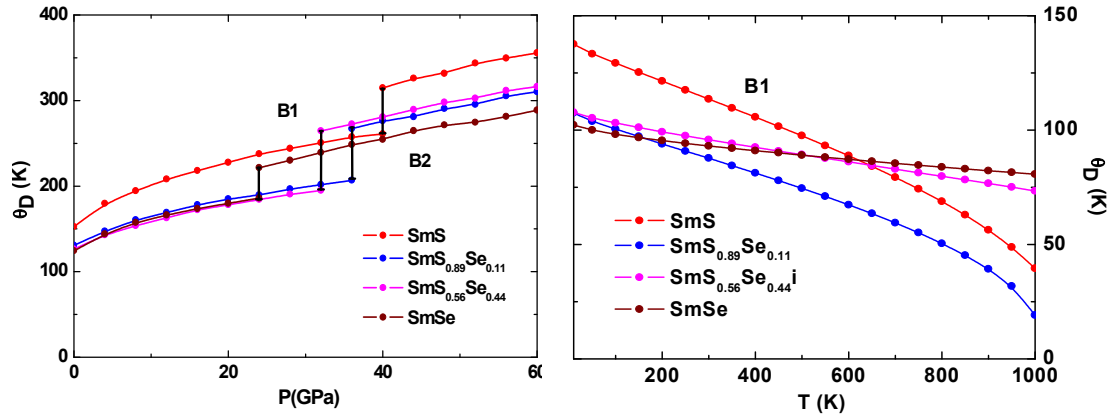


FIGURE 5. Variation of Debye Temperature ( $\theta_D$ ) as a function of pressure and temperature.

phase again it documents the brittle nature ( $\nu < 0.33$ ). Thus, Frantsevich rule confirms the brittle nature of  $\text{SmS}_{1-x}\text{Se}_x$ .

We further compute Debye temperature ( $\theta_D$ ) to shed further light on mechanical stiffened and thermal softened characteristics of  $\text{SmS}_{1-x}\text{Se}_x$ . The Debye temperature as functions of pressure is plotted in Figure 5 (a). At zero pressure,  $\theta_D$  is about 152.6 (SmS), 130.7 ( $\text{SmS}_{0.89}\text{Se}_{0.11}$ ), 126.1 ( $\text{SmS}_{0.56}\text{Se}_{0.44}$ ) and 124.2 (SmSe). It is noticed that with enhanced pressure,  $\theta_D$  increases in B1 phase for  $\text{SmS}_{1-x}\text{Se}_x$ . The gap at transition pressure in Debye temperature decreases as doping concentration increases except  $\text{SmS}_{0.56}\text{Se}_{0.44}$ . On the other hand,  $\theta_D$  also showed an increase in B2 phase. Enhanced  $\theta_D$  in B1 phase at higher pressure indicates the mechanical stiffening of lattice.

Figure 5 (b) displays the variation of the Debye temperature as functions of temperature at zero pressure. It is worth commenting from high pressure and high temperature Debye temperature behavior that a) the pressure dependent Debye temperature infers the mechanical stiffened bulk modulus due to Sm-Sm, S-S, Se-Se and Sm-S bond compression and bond strengthening due to lattice vibration and b) the thermal softening of bulk modulus results from bond expansion and bond weakening due to thermal stress in  $\text{SmS}_{1-x}\text{Se}_x$  in rock salt structure.

## CONCLUSION

We have focused on the high temperature and pressure dependent structural, elastic, and thermodynamical studies in rock salt and cesium chloride structure of  $\text{SmS}_{1-x}\text{Se}_x$  ( $x = 0, 0.11, 0.44, 1$ ). From the knowledge of Gibbs's free energies in rock salt and cesium chloride structure, we determine the pressure induced first order structural phase transition and volume collapse. Compressions at higher pressure indicate the mechanical stiffening of lattice. The phase transition pressure and volume collapse are consistent with earlier observations.

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