

High Pressure Induced Structural Phase Transition and Elastic Properties of Some Alkaline Earth Mono Selenides

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Abstract – The structural and elastic properties of some alkaline earth mono-selenides (AESe : AE = Ca, Sr, Ba) under pressure have been investigated using a two body inter ionic potential approach with modified ionic charge ($Z_m e$). This method has been found quite satisfactory in case of the rare earth compounds. The equation of state curve, structural phase transition pressure from NaCl (B1) to CsCl (B2) phase and associated volume collapse at transition pressure of alkaline earth selenides (AESe) obtained from this approach, so have been compared with experimentally measured data reveal good agreement. We have also investigated bulk modulus, second (C_{11} , C_{12} & C_{44}) and third order (C_{111} , C_{112} , C_{123} etc.) elastic constants and pressure derivatives of second order elastic constants at ambient pressure which shows predominantly ionic nature of these compounds. First time, we have calculated the Poisson ratio, Young and Shear modulus of these compounds.

Keywords: High pressure behavior, Equation of state, structural phase transition, second order elastic constants, third order elastic constants.

I. Introduction

High pressure research on structural phase transformations of alkaline earth chalcogenides (AEC) has been approaching a stage of systematic study and understanding of a series of material with analogous physical and chemical properties. At high pressure, most of these compounds first undergo a structural phase transition from NaCl (B1) phase to CsCl (B2) structural phase [1-2]. A phenomenon of interest in these compounds is metallization, which occurs after first order phase transition by increasing pressure further. Most of the theoretical approaches predict that the metallization phenomenon through band overlap by using different methods of *ab initio* calculations. The elastic properties define the properties of material which play an important role in providing valuable information about the binding characteristic between adjacent atomic planes, anisotropic character of binding and structural stability of these compounds. These AEC (AEC: AE = Be, Mg, Ca, Sr, Ba; C = O, S, Se, Te), compounds form a closed-shell ionic system crystallized in the NaCl-type (B1) structure at ambient conditions except for BeO and MgTe (crystallize in the wurtzite structure) and beryllium chalcogenides (crystallize in the zinc-blende structure)

[3,4]. An interesting feature in the electronic band structure of the AEC is that there are no d electrons in the valence band. The band gaps in the AEC compounds range from about 2.5 to 6.0 eV. Experimentally, the high pressure structural phase transformation and equation of states of alkaline earth selenides (AESe; AE= Ca, Sr, Ba) compounds have been measured by means of energy-dispersive x-ray diffraction techniques [3, 5, 6]. It was found that they transform from NaCl (B1) phase to the CsCl (B2) structure at 38GPa, 14 GPa and 6 GPa respectively for CaSe, SrSe and BaSe. Several theoretical studies have been carried out to observe structural and elastic properties of these compounds. Jha et al [7] have investigated structural phase transformation and equation of states of CaSe using three body interaction (TBI) potential. Also, different methods of band structure calculation such as linear muffin tin orbital [LMTO] [8], tight binding approximation [9], full potential linearized augmented plane wave (FP-LAPW) method [4] were performed to calculate structural, cohesive, metallization and elastic properties of calcium chalcogenides. The structural, electronic and elastic properties of SrX (X: S, Se, Te) compounds have been calculated from first principle by Khenata et al [10].

Also, theoretical studies such as linearized augmented plane wave (LAPW) method by Weir and Krakauer for BaSe and BaTe [11], augmented-spherical wave method within local density approximation (LDA-ASW) by Carlsson and Wilkins [12] for BaS, BaSe and BaTe, tight binding linear muffin orbital (TB-LMTO) by Kalpana *et al* [13], linear muffin tin orbital (LMTO) by Syassen *et al* [14]. Recently, Bouhemadou *et al* [15] have used the full potential augmented plane plus local orbitals method (FP-APW+lo) and reported the structural, electronic, elastic and high pressure properties in these compounds.

These *ab initio* calculations have shown that overlap of bands at high pressure causes metallization in the AEC compounds. However, some of these theories failed to predict phase transition pressure, volume and cohesive properties even with a reasonable order of magnitude [9].

In the present study, we have investigated structural and elastic properties of some alkaline earth selenides using two body interionic potential with modified ionic charge ($Z_m e$) described in next section.

II. Method of calculation

The interionic potential for the alkaline earth selenides (AESe: AE= Ca, Sr, Ba) in the framework of the rigid ion model is expressed as [16].

$$U(r) = \sum_{ij} Z_m^2 e^2 / r_{ij} + \sum_{ij} b \beta_{ij} \exp[(r_i + r_j - r_{ij}) / \rho_{ij}] + \sum_{ij} C_{ij} r_{ij}^{-6} + \sum_{ij} D_{ij} r_{ij}^{-8} \quad (1)$$

which includes long-range Coulomb (first term), Hafemeister and Flygare form of short-range repulsive (second term) and van der Waals multipole interactions (third and fourth terms). $Z_m e$ is the modified ionic charge due to Coulomb screening effect. r_{ij} is the nearest neighbor separation. $r_i(r_j)$ are the ionic radii of ions $i(j)$. The range and hardness parameters ρ and b in the short-range part of the crystal energy are determined from the knowledge of lattice parameters, bulk modulus and the equilibrium condition

$$\left. \frac{dU(r)}{dr} \right|_{r=r_0} = 0 \quad (2)$$

where r_0 is the equilibrium interionic separation. The input data and model parameters for AESe compounds are presented in Table 1. Thermodynamically a phase transition is said to occur when changes in the structural details of the phase are caused by a variation of the free energy. The AESe compounds transform from their initial NaCl(B1) to CsCl(B2) structure under pressure. The stability of a particular structure is decided by the minima of the Gibbs free energy, given by

$$G = U + PV - TS \quad (3)$$

where U is the internal energy (eq. (1)), which at 0 K corresponds to cohesive energy, S the vibrational entropy at absolute temperature T , pressure P , volume V .

The Gibbs free energies $G_{B1}(r) = U_{B1}(r) + 2P r^3$ for NaCl (B1) and $G_{B2}(r) = U_{B2}(r) + (8/3)(3)^{1/2} P r^3$ for CsCl (B2) phases become equal at the phase transition pressure P_t at temperature 0K. Such a theoretical approach has been found to predict most of the crystal

properties of rare-earth chalcogenides [16] and transition metal mono-nitrides compounds [17, 18] satisfactorily. In the present paper, we have also calculated the second order elastic constants (SOEC) from the following expressions, derived from the interionic potential (eq. 1) [16]

$$C_{11} = \alpha[-5.112Z_m^2 + A_1 + 1/2(A_2 + B_2)] \quad (4)$$

$$C_{12} = \alpha[0.226Z_m^2 - B_1 + 1/4(A_2 - 5B_2)] \quad (5)$$

$$C_{44} = \alpha[2.556Z_m^2 + B_1 + 1/4(A_2 + 3B_2)] \quad (6)$$

Here, $\alpha = e^2/4r_0^4$, $A_1 = A_{12}$, $B_1 = B_{12}$, $A_2 = (A_{11} + A_{22})$ and $B_2 = (B_{11} + B_{22})$, and are expressed as: $A_{ij} = 2V/e^2 (d^2\Phi_{ij}(r) / dr^2)$ and $B_{ij} = 2V/e^2 (1/r_{ij} (d\Phi_{ij}(r) / dr))$ where $\Phi_{ij}(r)$ is the short-range potential in eq. (1) and V is the unit cell volume. The expressions for the third order elastic constants (TOEC) can be derived as follows

$$C_{111} = \alpha[37.556Z_m^2 + C_{1-3}A_1 + 1/4(C_2 - 3A_2 - 9B_2)] \quad (7)$$

$$C_{112} = C_{166} = \alpha[-4.786Z_m^2 + 1/8(C_2 - 3A_2 - 3B_2)] \quad (8)$$

$$C_{123} = C_{144} = C_{456} = \alpha(2.717Z_m^2) \quad (9)$$

with $C_{1(2)} = A_{1(2)}^2 / B_{1(2)}$. The expressions for the pressure derivatives of second order elastic constants (dB/dP , dC_{44}/dP , dS/dP) can be derived from the combination of SOEC and TOEC constants for NaCl structure using their standard relations [16]. The expression for the shear modulus S' can be written as

$$S' = (C_{11} - C_{12}) / 2 \quad (10)$$

and E is the Young modulus calculated using the formula

$$E = (C_{11} - C_{12})(C_{11} + 2C_{12}) / (C_{11} + C_{12}) \quad (11)$$

We use these two relations to calculate the Poisson ratio as

$$\sigma = C_{12} / (C_{11} + C_{12}) \quad (12)$$

III. Results and discussion

The input data and model parameters for AESe compounds are given in the Table 1, where r_0 , B_0 and b & ρ represent equilibrium interatomic separation, bulk modulus and short range parameters, respectively. It is observed that the calculated values of model parameters follow a systematic trend of variation in AESe compounds. The equation of state (P - V curve) along with the variation of Gibbs energy $\Delta G (= G_{B1} - G_{B2})$ with pressure for the CaSe, SrSe and BaSe have been presented in Figures 1-3(a, b).

TABLE 1
 INPUT DATA AND MODEL PARAMETERS

^aRef.[3], ^bRef. [5], ^cRef.[6], ^dRef.[2].

Solid	Input data			Model parameters	
	r_0 (Å)	B_t (GPa)	Z_m^2	$b(10^{-19}J)$	$\rho(\text{Å})$
CaSe	2.958 ^a	51 ^a	2.586	4.694	0.340
SrSe	3.117 ^b	45 ^b	2.4647	3.902	0.317
BaSe	3.296 ^c	43.4 ^d	2.146	3.606	0.304

It is seen from the Figures 1 -3(a, b), we have predicted structural phase transition from B1 to B2 structure at 38.5, 14.8 and 6.1 GPa with relative volume change 5%, 8% and 11.20% for the CaSe, SrSe and BaSe, respectively.

TABLE 2
 PHASE TRANSITION AND COHESIVE PROPERTIES
 OF AESe (AE = Ca, Sr, Ba) COMPOUNDS. ^aRef.[3], ^bRef. [5],
^cRef.[6]

Solids	B_0 (GPa)	$\left(\frac{dB_0}{dP}\right)$	$\left(\frac{dS'}{dP}\right)$	$\left(\frac{dC_{44}}{dP}\right)$	S' (GPa)	E (GPa)	σ
CaSe							
Pres.	50.76	4.60	4.36	-0.0708	32.51	80.63	0.239
Expt.	51 ^a	4.2 ^a	-	-	-	-	-
SrSe							
Pres.	47	4.98	5.14	-0.3012	38.13	120.04	0.182
Expt.	45 ^b	4.50 ^b	-	-	-	-	-
BaSe							
Pres.	38.15	5.34	5.83	-0.455	35.41	81.10	0.145
Expt.	-	-	-	-	-	-	2
LDA	43.4±24	4.42 ^c	-	-0.69 ^c	-	-	-
	5.95 ^c	-	-	-	-	-	-

In the Table 2, we have presented the calculated values of phase transition pressures, percentage of volume collapses, equilibrium interionic separations and cohesive energies of these compounds and these results are compared with available experimental [3, 5, 6] and show an excellent agreement. Since, we have calculated difference in cohesive energies ΔG from B1 to B2 phases at zero pressure and 0K temperature, are positive quantities which indicate that NaCl structure is more stable than CsCl structure in these compounds.

TABLE 3
 SECOND AND THIRD ORDER ELASTIC CONSTANTS
 OF AESe (AR = Ca, Sr, Ba) COMPOUNDS IN GPa.
^cRef.[4], ^fRef. [19], ^gRef.[20], ^hRef.[21], ⁱRef.[15]

Solids	Equilibrium interionic separation in Å		Cohesive energy in KJ/mole		Change in cohesive energy in KJ/mol.	Phase transition pressure in GPa	Relative vol. change in %
	$R_1(B1)$	$R_2(B2)$	$U_1(B1)$	$U_2(B2)$			
					U_2-U_1	P_t	$\Delta V/V_0$
CaSe	2.960	3.140	-	-	72.60	38.5	5.0
Pret.	2.958 ^a	-	1900.4	1827.	-	38 ^a	7.7 ^a
Exp.	-	-	0	80	-	-	-
SrSe	3.120	3.270	-	-	50.81	14.8	8
Pret.	3.117 ^b	-	1744.3	1693.	-	14 ^b	107 ^b
Exp.	-	-	3	52	-	-	-
BaSe	3.300	3.430	-	-	31.48	6.1	11.20
Pret.	3.2965 ^c	-	1455.6	1424.	-	6 ^c	13.9 ^c
Exp.	-	-	4	2	-	-	-

In the Table 3, we have presented the calculated values of second order (SOEC) and third order (TOEC) elastic constants of AESe compounds for B1 phase and compared SOEC (C_{11} , C_{12} and C_{44}) with available theoretical data [4, 15, 19, 20, 21]. It can be noted from

the Table 3, the calculated values of C_{11} are little lower and C_{12} little higher than the corresponding theoretical one. This is not a serious limitation of the present theoretical model. It can be seen from the table that $C_{11} - C_{12} > 0$, $C_{11} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$. This condition obeys criteria of mechanical stability in these compounds [22, 23]. To the best of our knowledge, there is no experimental data of SOEC available for comparing our results.

In Table 4, we have presented the calculated values of pressure derivatives (dB_0/dP , dS'/dP , dC_{44}/dP) of second order elastic constants for B1 phase and compared with available data [12, 13,]. We have reported Bulk modulus (B_0), Shear modulus (S'), Young modulus (E) and Poisson's ratio (σ) for AESe compounds. The calculated values of bulk modulus are shown good agreement with experimental and theoretical data. To the best of our knowledge no experimental and theoretical results of TOEC available. These calculated values are only our predictions. The theoretical calculated Poisson's ratio (σ) of CaSe, SrSe and BaSe are 0.239, 0.182 and 0.1452, respectively. As we know that for a perfectly incompressible material the Poisson's ratio would be exactly 0.5. This allows drawing the conclusion that our compounds are not much compressible. We have presented the variation of the second order elastic constants C_{11} and C_{44} with pressure in the Figs. 4-6. We observed that C_{11} increases linearly with increase pressure but C_{44} decreases linearly, showing the reduction in resistance to shear as the phase transition is approached. The variations of second order elastic constants (C_{11} , C_{44}) with respect to pressure can reveal many important features of the short range forces at high pressure.

TABLE 4
 BULK MODULUS (B_0), PRESSURE DERIVATIVES OF SECOND
 ELASTIC CONSTANTS, SHEAR MODULUS (S'), YOUNG
 MODULUS (E) AND POISSON'S RATIO (σ) AESe
^aRef. [3], ^bRef. [5], ^cRef. [6], ^eRef.[15],

Solids	Theory	C_{11}	$C_{12} = C_{44}$	C_{111}	$C_{112} = C_{166}$	$C_{123} = C_{144} = C_{456}$
CaSe	Present	94.98	29.96	-	-	52.92
e	GGA	95.17 ^e	25.56 ^e	414	94.	-
	LDA	106.76 ^e	23.12 ^e	.86	19	-
	Pseudo	115 ^f	18 ^f	-	-	-
	potenti	155.25 ^g	55.75 ^g	-	-	-
	al	-	-	-	-	-
	Tight	-	-	-	-	-
	bindin	-	-	-	-	-
	g	-	-	-	-	-
SrSe	Pres.	98.1	21.89	-	-	72.73
e	FP_LA	5	13.4 ^h	673	72.	-
	PW	120 ^h	-	.05	73	-
	-	-	-	-	-	-
BaSe	Present	64.04	11.19	-	-	21.6
e	FP-	87 ⁱ	12 ⁱ	563	38.	-
	APW+	-	-	.7	4	-
	lo	-	-	-	-	-

IV. CONCLUSION

We have presented structural and elastic properties of alkaline earth selenides, namely CaSe, SrSe and BaSe using a two body interionic potential approach with modified ionic charge. These compounds show structural phase transformation from NaCl type to CsCl type structure at 38.5, 14.8 and 6.1 GPa under high pressure with relative volume change 5%, 8% and 11.20% for the CaSe, SrSe and BaSe, respectively. The phase transition pressure decreases with increasing the size of alkaline earth ion. The calculated values of second and third order elastic constants and second order pressure derivatives predict partially ionic nature of these compounds.

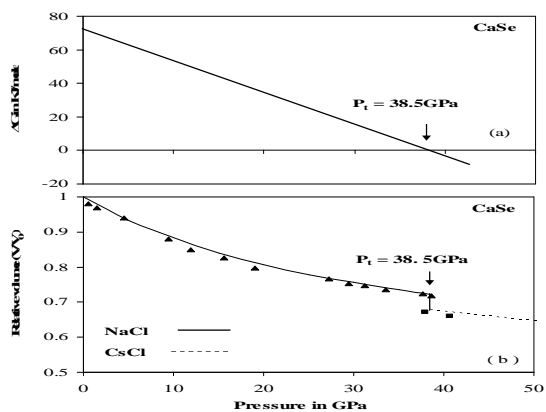


Fig. 1 (a) Variation of ΔG with pressure for CaSe. (b) Equation of state for CaSe. Symbols (▲, ■) represent experimental points taken from Ref. [3] corresponding to B1 and B2 phases, respectively.

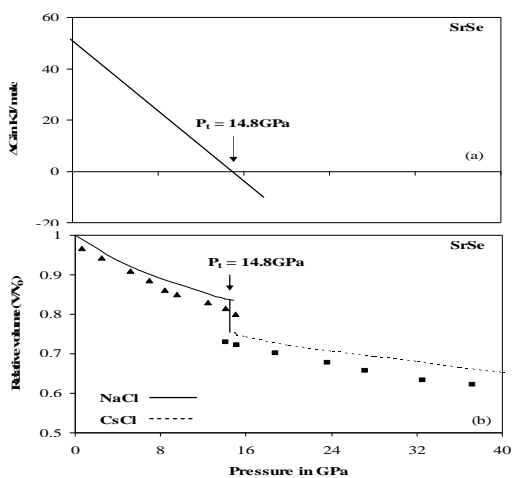


Fig. 2 (a) Variation of ΔG with pressure for SrSe. (b) Equation of states for SrSe. Symbols (▲, ■) represent the experimental data points taken from Ref. [5] corresponding to B1 and B2 phases, respectively.

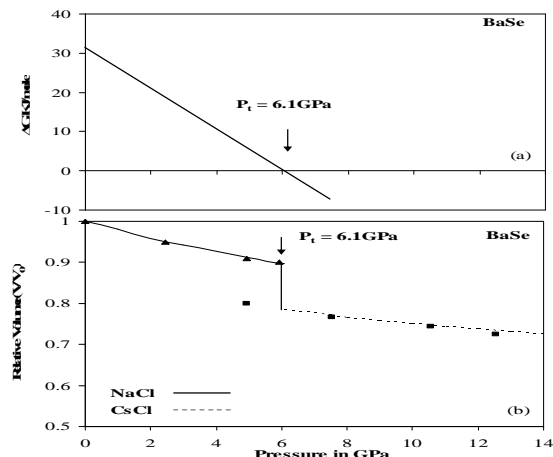


Fig. 3 (a) Variation of ΔG with pressure for BaSe. (b) Equation of states for BaSe. Symbols (▲, ■) represent the experimental data points taken from Ref. [6] corresponding to B1 and B2 phases, respectively.

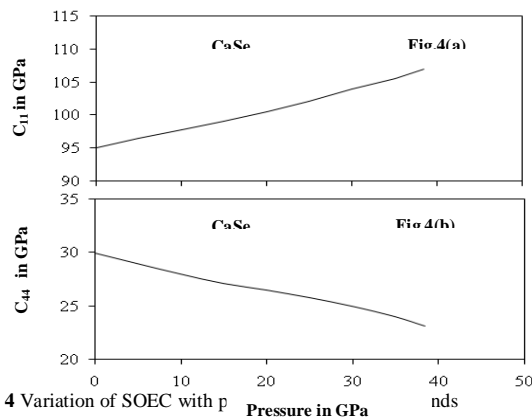


Fig. 4 Variation of SOEC with p Pressure in GPa nds
 (a) C_{11} , (b) C_{44}

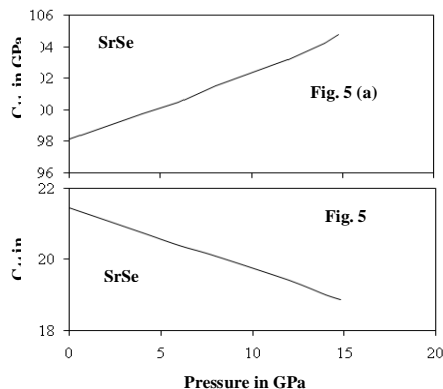


Fig. 5 Variation of SOEC with pressure for SrSe compounds
 (a) C_{11} , (b) C_{44}

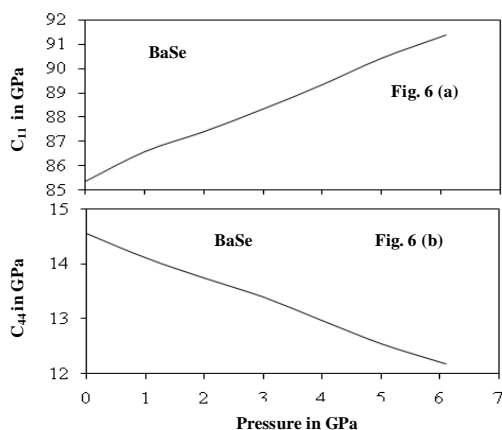


Fig. 6 Variation of SOEC with pressure for BaSe compounds

(a) C_{11} , (b) C_{44}

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