Structural Phase Stability of SrO and CaO at high Pressure and high Temperature

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Abstract- **To study the phase transition, elastic properties of SrO and CaO at very high pressure and high temperatures a realistic interaction potential model with polarization (RIPPM) is developed by including temperature effects. The present model includes long-range Coulombic, three-body interaction forces, short-range overlap repulsive forces operative up to next nearest neighbor ions and electronic polarizability effects. We have investigated phase transition pressures, volume collapses, elastic behavior at different pressures as well as elevated temperatures and found results well suited with available experimental data.**

Keywords – Phase transition, elastic properties, electronic polarizability and volume collapses.

I. INTRODUCTION

The group of divalent metal oxides (DMOs) has paid the attention of researchers both theoretically and experimentally as they provide a link between largely covalent semiconductors and highly ionic halides [1]. These DMOs are generally crystallized in rock-salt structure at room temperature and transforms to CsCl structure. DMOs are also important geophysically because inside the earth their electronic structure is considerably varies under normal pressure. SrO has presented much interest because of its applications in various technologies ranging from catalysis to microelectronics and also used in refractory system [2]. CaO is considered as prototype oxide and play an important role in the modern spintronics [3].

Many theoretical studies have been carried out to study the static structural properties of SrO and CaO. Aguado et al. [4] predicted the B_1-B_2 transition at 31.8 GPa and 63 GPa using ab initio molecular dynamic method in case of SrO and CaO. Bhardwaj et al. [5] has shown the three-body interaction potential (TBIP) model approach successfully explains the comparable results of the lattice static and dynamical properties of the divalent metal oxides. A theoretical study of the phase transition and high-pressure behavior of CaO and SrO using density functional theory (DFT) was carried out by Ghebouli et al. [3].

For high pressure studies of DMOs, several phenomenological, semi empirical and microscopic models [6, 7] was used. These models are mostly based on two-body forces and are not adequate to explain the breakdown of the Cauchy violation relation $C_{12}\neq C_{14}$, which is quite important for the alkaline earth and the transition metal oxides [8]. For the study of these DMOs, the TBI are mostly considered due to the smallness of the nearest neighbor separations because solid compresses at high pressure which was investigated by Singh [8]. The importance of three body interactions in potential model to improve results has also been emphasized by other's works [9-12]. It had been found that TBI potential is comparatively better than the two body potential for the prediction of phase transition pressures and relative volume collapses. Allan et al. [13] performed the calculations at 300K of divalent metal oxides using two-body potentials and a simple shell model. Sunm et al. [14] obtained the static and thermal equation of state (EOS) and intrinsic anharmonicity in EOS from the static and ab initio molecular dynamics simulations.

The theoretical analysis of pressure-induced phase transition of EuS and EuSe including the role of temperature have been studied by Gour et al. [11] using a realistic interaction potential model (RIPM). Recently,

Bhardwaj et al. [15] have computed an investigation of SrS under high pressure including the role of temperature with RIPM. We had studied [16] theoretically the phase transition of rare-earth antimonides with $TBIPE_p$ model which had been carried by assuming the equilibrium at 0K instead of room temperature. As less work is reported on high-pressure phase transition at high temperature in SrO and CaO and there is no study available using realistic model for the same so we developed a realistic interaction potential model with polarization (RIPPM) including temperature to study the phase transition and elastic properties of SrO and CaO at high pressures and elevated temperatures.

II. Proposed Algorithm

Under high pressure, there is change in volume of the crystal, which leads to an increased charge transfer (TBI) [8] due to deformation of the overlapping electron shells of the adjacent ions. This interaction becomes more important to consider due to the decrease in inter-ionic spacing of the lattice crystal ions experience sufficient overlap on increasing pressure. The enhancement in overlap energy causes the modification in the ionic charge as charge is transferred due to the overlap in electron shells, which in turn modifies the Coulomb energy by a factor $\left[1+\left(\frac{2n}{z}\right) f(r)\right]$, where n is the number of electrons in outermost shell, z is ionic charge of the compound and $f(r)$ is the TBI parameter which depends on the nearest neighbor distance (r) [8] as

$$f(r) = f_0 e^{-r/\rho} \tag{1}$$

Where f_0 is a constant and ρ is the range parameter.

In RIPPM model, the effect of TBI is incorporated to obtain the stability condition for a crystal structure in the expression of Gibbs free energy, (G=U+PV-TS). Here U is the internal energy; S is the vibrational entropy at room temperature. Since at absolute zero, the Gibbs free energy is equivalent to enthalpy (H) when calculated theoretically. In RIPPM approach, we have taken account of the room temperature T=300 K in the pressure induced theoretical calculations as well as electronic polarizability for achieving better results which are comparable with the experimental data. The Gibbs free energies for rock salt (B_1) and CsCl (B_2) structure at room temperature can be stated by:

$$G_{B_1}(r) = U_{B_1}(r) + PV_{B_1} - TS_1 \tag{2}$$

$$G_{B_2}(r') = U_{B_2}(r') + PV_{B_2} - TS_2 \tag{3}$$

With (=2.00r^3) and (=1.54r'^{3}) as the unit cell volumes, and are the entropies for and phases, respectively.

$$\Delta G = \Delta H - T\Delta S \tag{4}$$

The terms and are the lattice energies for and structures and they are expressed as

$$U_{B_1} = \left[\frac{-(\alpha_m e^2 z^2)}{r}\right] - \left[\frac{(12\,\alpha_m e^2 z f(r))}{r}\right] + \frac{\alpha_e e^2}{r^4} + 6\beta_{ij}\exp\left(\frac{r_i + r_j - r}{\rho}\right) + 6\beta_{ii}\exp\left(\frac{2r_i - 1.414\,r}{\rho}\right) + 6\beta_{jj}\exp\left(\frac{2r_j - 1.414\,r}{\rho}\right) \tag{5}$$

$$U_{B_2} = \left[\frac{-(\alpha'_m e^2 z^2)}{r'}\right] - \left[\frac{(16\,\alpha'_m e^2 z f(r'))}{r'}\right] + \frac{\alpha_e e^2}{r'^4} + 8\beta_{ij}\exp\left(\frac{r_i + r_j - r'}{\rho}\right) + 3\beta_{ii}\exp\left(\frac{2r_i - 1.154\,r'}{\rho}\right) + 3\beta_{jj}\exp\left(\frac{2r_j - 1.154\,r'}{\rho}\right) \tag{6}$$

Here, $r_i(r_j)$ is the ionic radii of i(j) ions, ρ (b) are the range (hardness) parameters and α_e is the electronic polarizability.The first term in equations (5) and (6) are long-range Coulomb energy, second terms are three body interaction forces for and phases, third term is electronic polarizability [16] and remaining terms are overlap repulsive term extended up to next nearest neighbor ions within Hafemeister and Flygare approach [17]. Now the entropy differences in the last terms of equations (2) and (3) can be calculated from the relation used by Shanker et al. [18, 19].

$$S_1 - S_2 = \int_1^2 \left[\frac{(C_1 - C_2)}{T}\right] dT \tag{7}$$

Here 1 and 2 stand for and phases, and are the specific heats of two phases at constant pressure. Their values can be calculated by the relation

$$C_i = \frac{\beta V_i B_T}{\gamma_i} \tag{8}$$

Where, γ and β are the Gruneisen parameter and linear isothermal temperature coefficient respectively. We can calculate the Gruneisen parameter (γ) by well known formula [10] as

$$\gamma = -\frac{r_0}{6}\left[\frac{U'''(r_0)}{U''(r_0)}\right] = \frac{-r_0}{6\rho} \tag{9}$$

Here, U'''(r) and U''(r) are the third and second derivatives of lattice energy.

To interpret the elastic behavior of SrO and CaO, we have calculated the second order elastic constants (SOECs) at room temperature and at higher temperatures. The inclusion of temperature effects for obtaining elastic constants in the present study provides better comparability with experimental work [1]. Earlier work by Jog et al. [7] was based on the estimation of the SOEC at absolute zero.The expressions of SOECs are as follows:

$$C_{11} = \frac{e^2}{4r_0^4}\left[-5.112\ z\{z+12\ f(r)\} + A_1 + \left(\frac{A_2+B_2}{2}\right) + 9.3204\ r_0 f'(r)\right]$$

$$C_{12} = \frac{e^2}{4r_0^4}\left[0.226\ z\{z+12\ f(r)\} - B_1 + \left(\frac{A_2-5B_2}{2}\right) + 9.3204\ r_0 f'(r)\right] \tag{10}$$

(11)

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

(12)

III. Experiment and Result

The present RIPPM contains three model parameters $[\rho, b, f(r)]$ namely range, hardness and three-body force parameter. Their values have been determined from the knowledge of lattice parameter and by solving the equilibrium conditions as defined in our work [11]

$$\left[\frac{dU}{dr}\right]_{r=r_0} = 0 \text{ and } \left[\frac{dU}{dr}\right]_{r=r_0} = 9kr_0B_T$$

The difference in Gibb's free energy $\Delta G = (G_{B_2}(r') \sim G_{B_1}(r))$ approaches zero at phase transition pressure (P_t). At P_t these oxides undergo a sudden collapse ($B_1 \rightarrow B_2$) in volume showing first-order phase transition. We have calculated P_t at different high temperatures with the knowledge of isothermal expansion coefficients (β) and using the Eqn.4 at different high temperatures. The relative stability of the two phases was obtained by minimizing the lattice energies in both real and hypothetical phases at different pressures corresponding to equilibrium inter-ionic separation r (r') using the model parameters for both compounds are listed in table 1.

Table 1 Input parameters and model parameters.

Compounds	Input parameters			Model parameters		
	r_o (Å)	B_T (GPa)	α_e (Å^3)	b (10^{-12}erg)	ρ(Å)	f(r)
SrO	2.580[a]	91	2.9[b]	0.6513	0.4705	-0.0128
CaO	2.405[a]	110	2.2[b]	0.8419	0.4702	-0.0125

a. Ref. [21], b ref. [22]

The phase transition pressures and volume collapses of both compounds are listed in table 2. The calculated value of phase transition pressure of SrO and CaO are 36.7 GPa and 75 GPa are in reasonable agreement with experimental value (P_t= 36±4 GPa and 70±10 GPa). The variation of ΔG with pressure for SrO and CaO are shown in fig. 1 and fig. 2. It is clear from the table 2, fig.1and fig. 2 that phase transition pressure P_t at high temperature decreases with the increase of temperatures because the Gibbs free energy difference decreases with the rise of temperature while the volume difference increases due to the increase of inter ionic separations *r* at high temperatures. The trends shown by present work in case of SrO and CaO resembles with the B_1-B_2 phase transition of MgO [1]. The values of relative volume change (Vp/Vo) associated with various compressions have been

obtained and plotted against the corresponding phase transition pressures in fig. 3 and 4 for SrO and CaO . The calculated value of volume collapses are in good agreement with other theoretical values. It is also clear from the Table 2 that the volume collapses decrease slightly with the increase of temperature because due to the minimization of the lattice energies at different pressures and due to the inclusion of TΔS in the equation (5) and (6), the minimized energy variess for their respective phases i.e. the interionic separation (r) varies which causes change of volume collapses.

Compounds	Temperature (K)	Transition Pressure (GPa)	Volume collapse (%)
SrO	0	36.7 (present)	10.9 (present)
		36±4 (exp)[a]	13 (exp)[a]
		88 (other)[c]	4.5 (other)[c]
	300	33	11.2
	600	30	11.5
	900	27	11.8
	1200	24	12.1
CaO	0	75 (Present)	10.3 (Present)
		70 ±4 (exp)[a]	11(exp)[a]
		106 (other)[c]	5.5 (other)[c]
	300	71	10.6
	600	67	10.8
	900	64	11
	1200	50	11.3

[a]Ref. [23], [b]Ref. [6], [c]Ref. [24]

In order to check the mechanical stability and the inter-atomic behavior of our model, we have computed the elastic constants of present compounds at various pressures at elevated temperatures. Constant C_{11} relates the compression stress and strain along the x, y and z axes. The constant C_{12} relates the compression stress in one direction to the strain in another direction. The constant C_{44} relates the shear stress and strain in the same direction [25]. The elastic constants C_{12} and C_{44} are less affected by pressure as they related to the volume change due to transverse strain. We have plotted the variation of elastic constants with different temperature (0K, 300K, 600K, 900K, 1200K) at different pressure of SrO and CaO in fig.5-10. The calculated values of, $C_{11,}$ C_{12} and C_{44} are in good agreement with other theoretical values.

Table 3. Elastic constant C11, C12 and C44of compound SrO

Compound	Elastic constants	Temperature (K)	Pressure (GPa)				
			0	10	20	30	40
SrO	C_{11}	0	138	142	146	152	161
		300	135	139	143	149	158
		600	132	135	140	146	155
		900	129	132	137	143	152
		1200	126	129	134	140	149
	C_{12}	0	72	74.1	76.4	78.6	40.7
		300	71.7	77.4	75	77.4	79.5
		600	70.5	72.5	74.7	76.7	78.6
		900	69.6	71.4	77.7	75.2	77
		1200	68.6	70.6	72	74.4	76
	C_{44}	0	94.2	96.7	98.4	100.7	102
		300	97.4	94.5	96.6	98.7	100.7
		600	92.2	97.6	95.4	97.5	98.5
		900	91.1	92.7	94.5	96	96.9
		1200	90	90.9	97	94.6	95.7

Table 4 Elastic constant $C_{11,}$ C_{12} and $C_{44}$of compound CaO

Compound	Elastic constants	Temperature (K)	Pressure (GPa)					
			0	15	30	45	60	75
CaO	C_{11}	0	151	170	187	192	205	215
		300	147	164	178	186	199	206
		600	176	158	171	178	191	199
		900	127	150	167	170	182	191
		1200	118	147	156	161	172	187
	C_{12}	0	71.5	74.6	77.4	79.7	81.4	87.5
		300	70.6	77.4	76.7	78.7	80.5	82.6
		600	79.4	72.5	75.5	77.4	89.5	81.6
		900	78.6	71.6	74.6	76.5	78.6	80.8
		1200	77.7	70.8	77.5	75.4	77.7	79.9
	C_{44}	0	98.11	104.2	109.5	114	117.8	122
		300	91.1	102	107.8	112	116	120.2
		600	99.9	100.1	106	110.4	114.9	118
		900	94	98	104.7	108	112.2	116.9
		1200	92	95.11	102	105.9	110.11	114

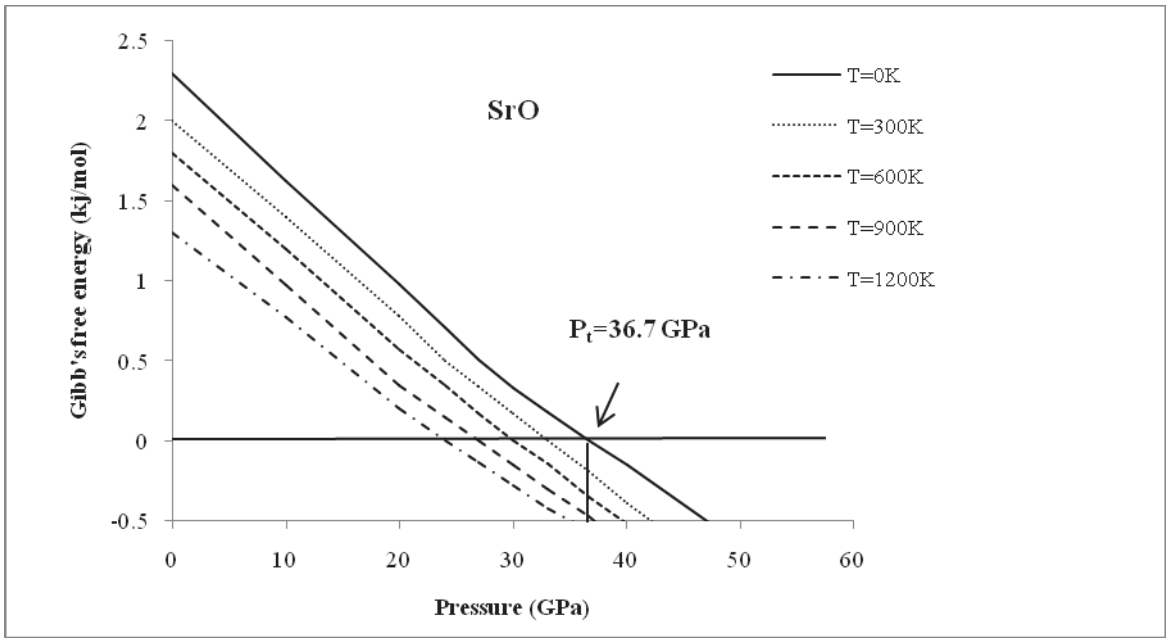

Fig 1. Variation of Gibbs free energy with pressure of SrO

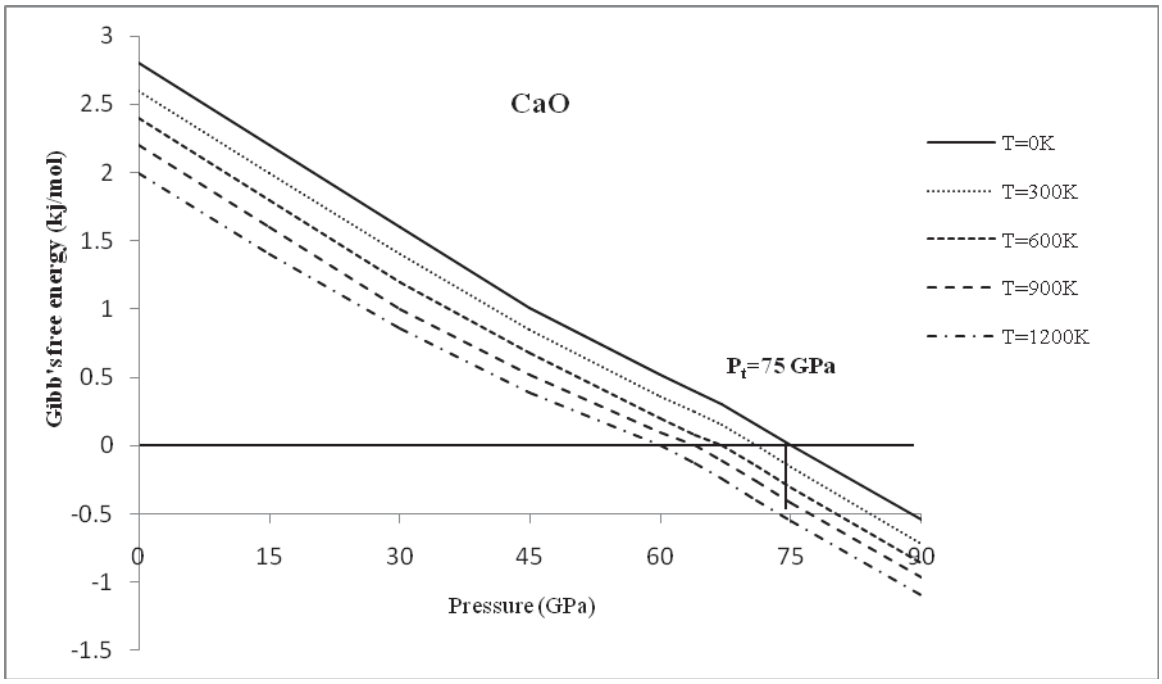

Fig 2. Variation of Gibbs free energy with pressure of CaO

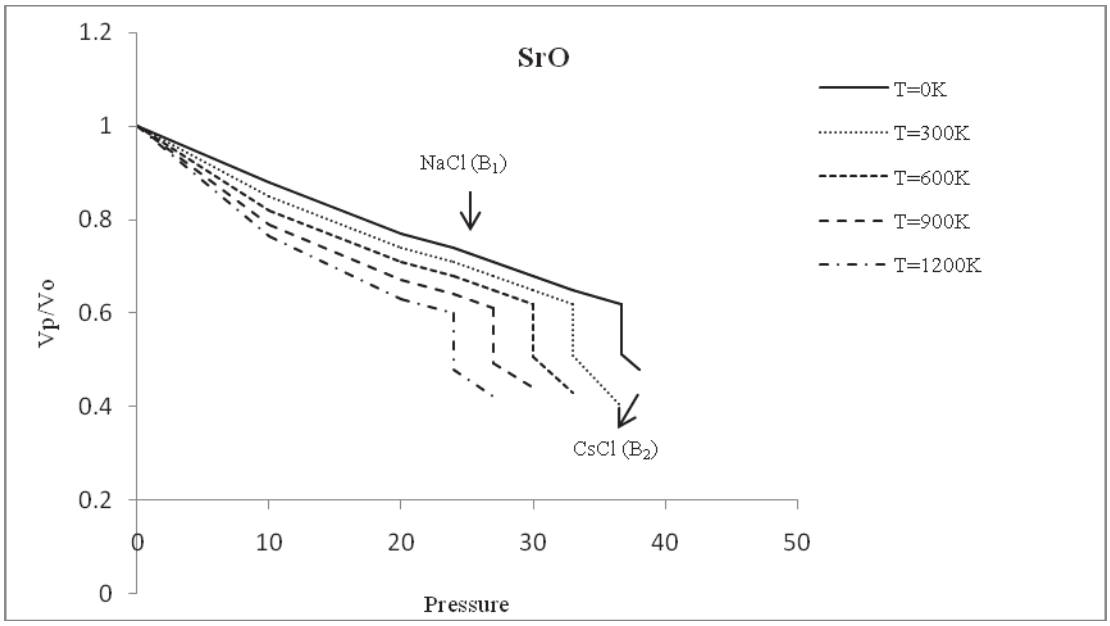

Fig 3. Variation of Vp/Vo with pressure of SrO

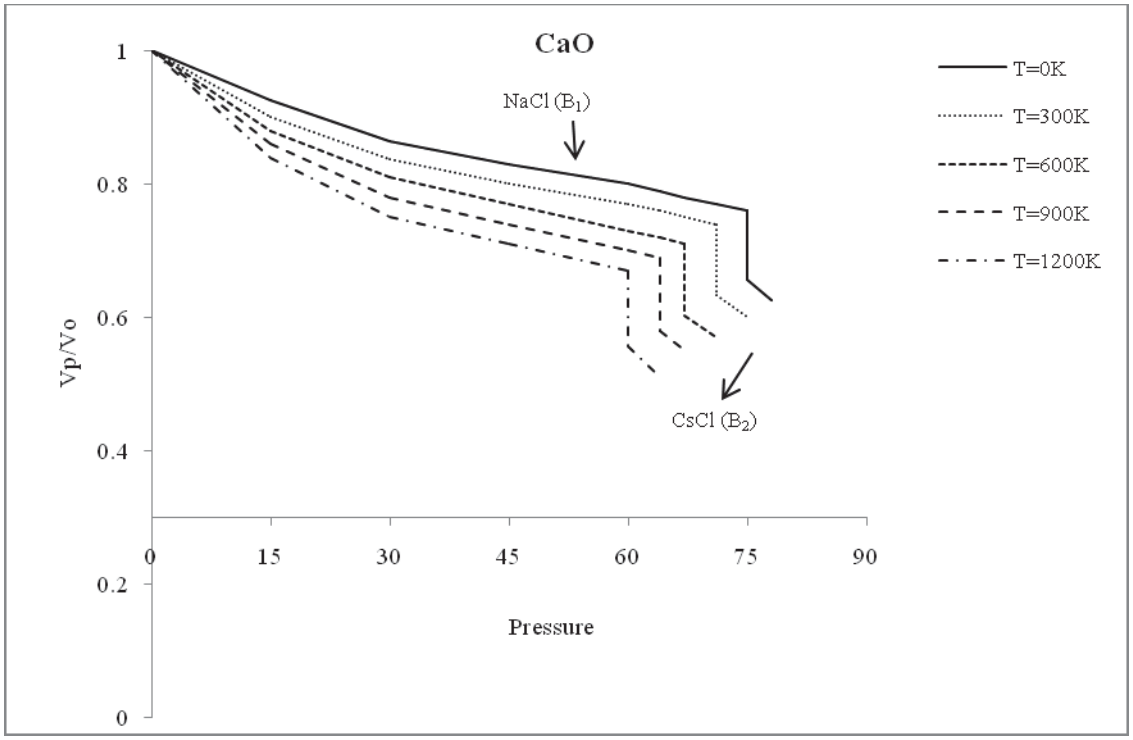

Fig 4. Variation of Vp/Vo with pressure of CaO

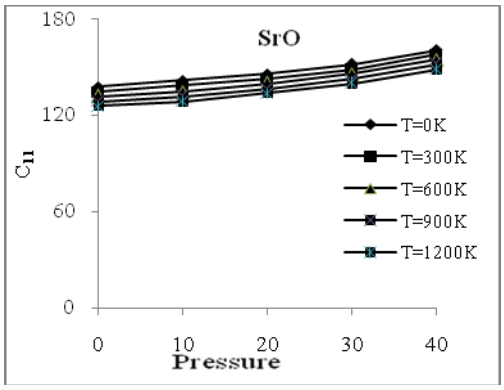

Fig 5. Variation of C11 with pressure for SrO

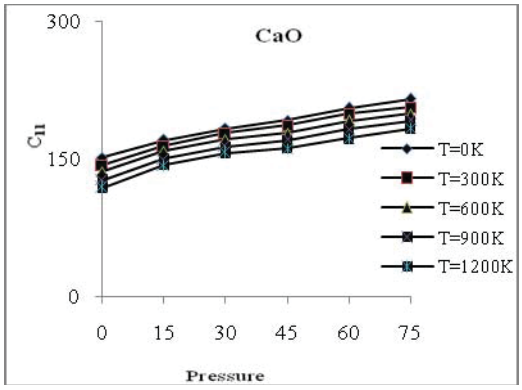

Fig 8. Variation of C11 with pressure for CaO

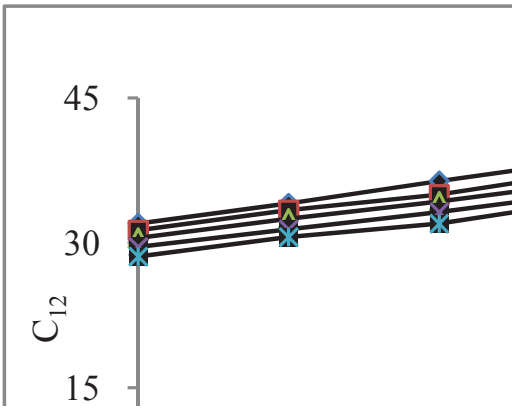

Fig 6. Variation of C12 with pressure for SrO

Fig 9. Variation of C12 with pressure for CaO

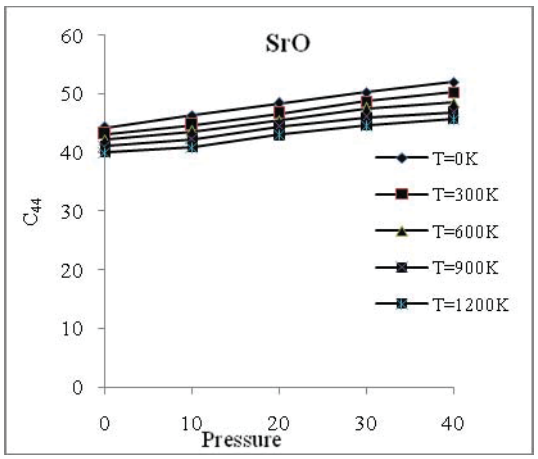

Fig 7 Variation of C44 with pressure for SrO

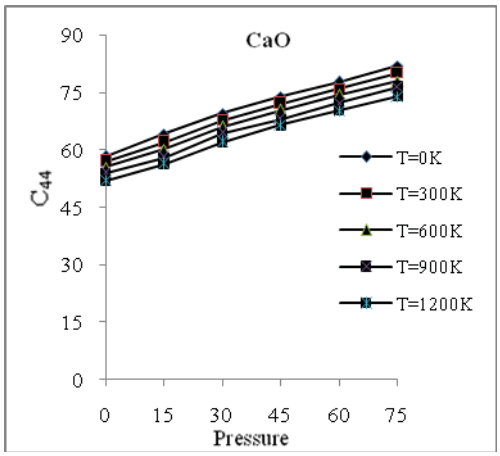

Fig 10 Variation of C44 with pressure for CaO

IV.CONCLUSION

It may be concluded from our investigation that

1. The pressure-induced phase transition from B_1 to B_2 structure analysis should be done at elevated temperature (T=300K, 600K, 900K and 1200K) rather than at $T = 0$K.
2. Calculated phase transition pressures and volume collapses are in general in reasonable agreement with the available experimental [22] and theoretical data [23].
3. The present realistic interaction potential model with polarization (RIPPM) is appropriately suitable for describing phase transition phenomenon and elastic properties of SrO and CaO.
4. The calculation for second order elastic constants have been performed at various pressure and elevated temperature which have not been performed experimentally yet.
5. The inclusion of TBI with temperature and electronic polarizabilty has improved the prediction of phase transition pressures over those obtained from the two body potential and TBI without temperature effect.

The success achieved in the present work can be ascribed to the realistic approach of our model.

ACKNOWLEDGEMENT

The authors are thankful to UGC, New Delhi, India and MP Council of Science and Technology (MPCST) Bhopal, India for financial assistances.

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