Structural elastic and thermal properties of $\text{Sr}_x\text{Cd}_{1-x}\text{O}$ mixed compounds – a theoretical approach

PURVEE BHARDWAJ*

High pressure Research Lab., Department of Physics, Barkatullah University, Bhopal-462026, India

In the present paper, the structural and mechanical properties of alkaline earth oxides mixed compound $\text{Sr}_x\text{Cd}_{1-x}\text{O}$ ($0 \leq x \leq 1$) under high pressure have been reported. An extended interaction potential (EIP) model, including the zero point vibrational energy effect, has been developed for this study. Phase transition pressures are associated with a sudden collapse in volume. Phase transition pressure and associated volume collapses $[\Delta V(\text{Pt})/V(0)]$ calculated from this approach are in good agreement with the experimental values for the parent compounds ($x = 0$ and $x = 1$). The results for the mixed crystal counterparts are also in fair agreement with experimental data generated from the application of Vegard's law to the data for the parent compounds.

Keywords: *oxide; alloy; volume collapse; phase transition; high pressure*

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1. Introduction

The pressure induced phase transformation is a vital subject in precise computational studies [1–6]. In recent time, the transition-metal monoxide CdO has been predicted to undergo a high pressure phase transformation from NaCl-type (B1) to CsCl-type (B2) structure at 89 GPa pressure [7]. First-principles calculations of the crystal structures, and the computation of phase transition and elastic properties of cadmium oxide (CdO) have been carried out with the plane-wave pseudo-potential density functional theory method by Peng et al. [8]. The experimental research on the compressibility and phase transition of CdO up to 176 GPa at room temperature, using high-resolution angular-dispersive X-ray diffraction from synchrotron source combined with the diamond anvil cell technique, has been carried out by Liu et al. [9]. The first-principles calculations of the elastic and thermodynamic properties for CdO in both the B1 (rocksalt) and B2 (cesium chloride) phases have been performed within the framework of density functional theory, using the pseu-

dopotential plane-wave method by Li et al. [10]. Schleife et al. [11] studied the phase transition pressure of CdO from NaCl (B1) to CsCl (B2) at 85 GPa using total energy calculations in the framework of density functional theory. CdO is one of the most extensively studied semiconductor materials. It is widely used in the production of solar cells, light-emitting diodes and liquid crystal displays, etc. [12, 13]. Hence, to study this semiconductor, it is essential to attain the high pressure structural, mechanical and thermo dynamical properties of CdO.

In the family of alkaline earth oxides, strontium oxide is one of the most important compounds for high pressure study. The present oxide crystallizes in rock salt NaCl-type (B1) structure at normal conditions and transforms into caesium chloride CsCl-type (B2) structure at high pressure. The predicted value of transition pressure for SrO is nearly 100 GPa, which is higher than its observed value 36 GPa [14]. The lattice parameters and the crystal structure of SrO (NaCl-type structure) have been investigated to 34 GPa at 23 ± 3 °C by means of X-ray diffraction employing a diamond anvil press. Static-compression experiments to 59 GPa, employing X-ray diffraction through a diamond cell,

*E-mail: purveebhardwaj@gmail.com

demonstrate that strontium oxide (SrO) transforms from its initial B1 (NaCl-type) to B2 (CsCl-type) structure at 36 ± 4 GPa on the ruby fluorescence scale with 13 % volume collapse at the transition pressure [15]. The high-pressure structural, elastic and thermophysical properties of SrO have been investigated using the three-body potential modified by incorporating the covalency effects [16].

The structural electronic and optical properties of $\text{Cd}_{1-x}\text{Sr}_x\text{O}$ have been calculated using density functional theory by Khan et al. [17]. They concluded that $\text{Cd}_{0.50}\text{Sr}_{0.50}\text{O}$ is an anisotropic material. The study of mixed alloy of SrO and CdO has not been performed experimentally. We have applied an extended interaction potential model by including zero point vibrational energy effects in TBP (Three Body Potential) for the prediction of phase transition pressures and associated volume collapses in alkaline earth oxide mixed compound $\text{Sr}_x\text{Cd}_{1-x}\text{O}$ ($0 \leq x \leq 1$) under high pressure. This zero point vibrational energy term shows an insignificant effect on Gibbs free energy but to make the model realistic it cannot be ignored completely. The main aim of this work is to provide a model suitable for the study of structural, elastic and thermophysical properties of alkaline earth oxide mixed compound $\text{Sr}_x\text{Cd}_{1-x}\text{O}$. The remaining part of this paper is organized as follows: the method of calculation is given in section 2; the results and conclusion are presented and discussed in section 3.

2. Model and computational method

Application of pressure directly results in compression, leading to the increased charge transfer (or three body interaction effect [18]) due to the deformation of the overlapping electron shells of the adjacent ions (or non-rigidity of ions) in solids. We have also considered the effects of zero point energy, which is the lowest possible energy that the compound may possess. The energy of the compound is $(\epsilon = (h\nu)/[e^{h\nu/kT} - 1] + (h\nu)/2)$, where ν , h , T , and k are the frequency, Planck constant, temperature and Boltzmann constant of the com-

pound, respectively. It is clear from the above expression that even at absolute zero the energy of the compound cannot be zero but at least $h\nu/2$. Hence, there arises a need to include the zero point energy term in TBP approach for better agreement with experimental approaches.

These effects have been incorporated in the Gibbs free energy ($G = U + PV - TS$) as a function of pressure and three body interactions (TBI) [18], which are the most dominant among the many body interactions. Here, U is the internal energy of the system equivalent to the lattice energy at temperature near zero and S is the entropy. At the temperature $T = 0$ K and pressure (P), the Gibbs free energies for rock salt (B1, real) and CsCl (B2, hypothetical) structures are given by:

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

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

with $V_{B1} (=2.00r^3)$ and $V_{B2} (=1.54r'^3)$ as unit cell volumes for B_1 and B_2 phases, respectively. The first terms in 1 and 2 are lattice energies for B_1 and B_2 structures and they are expressed as [18]:

$$\begin{aligned} U_{B1}(r) = & \frac{-\alpha_m z^2 e^2}{r} - \frac{(12\alpha_m z e^2 f(r))}{r} - \left[\frac{C}{r^6} + \frac{D}{r^8} \right] \\ & + 6b\beta_{ij} \exp[(r_i + r_j - r)/\rho] \\ & + 6b\beta_{ii} \exp[(2r_i - 1.414r)/\rho] \\ & + 6b\beta_{jj} \exp[(2r_j - 1.414r)/\rho] \\ & + (0.5)h\langle\omega^2\rangle_{B1}^{\frac{1}{2}} \end{aligned} \quad (3)$$

$$\begin{aligned} U_{B2}(r') = & \frac{-\alpha'_m z^2 e^2}{r'} - \frac{(16\alpha'_m z e^2 f(r'))}{r'} - \left[\frac{C'}{r'^6} + \frac{D'}{r'^8} \right] \\ & + 8b\beta_{ij} \exp[(r_i + r_j - r')/\rho] \\ & + 3b\beta_{ii} \exp[(2r_i - 1.154r')/\rho] \\ & + 3b\beta_{jj} \exp[(2r_j - 1.154r')/\rho] \\ & + (0.5)h\langle\omega^2\rangle_{B2}^{\frac{1}{2}} \end{aligned} \quad (4)$$

with α_m and α'_m as the Madelung constants for NaCl and CsCl structure respectively. $C(C')$ and $D(D')$ are the overall van der Waals coefficients of

B1 (B2) phases, β_{ij} ($i, j = 1, 2$) are the Pauling coefficients; e is the ionic charge and b (ρ) are the hardness (range) parameters, $r(r')$ are the nearest neighbour separations for NaCl (CsCl) structure, $f(r)$ is the three body force parameter.

The term $\langle \omega^2 \rangle^{\frac{1}{2}}$ is the mean square frequency related to the Debye temperature (θ_D) as:

$$\langle \omega^2 \rangle^{\frac{1}{2}} = k\theta_D/h$$

Here, θ_D can be expressed as [19, 20]:

$$\theta_D = (h/k)[(5rB)/\mu]^{\frac{1}{2}}$$

with B and μ as the bulk modulus and reduced mass of the compounds.

These lattice energies consist of long range Coulomb energy (first term), three body interactions corresponding to the nearest neighbour separation $r(r')$ (second term), vdW (van der Waals) interaction (third term), energy due to the overlap repulsion represented by Hafemeister and Flygare (HF) type potential and extended up to the second neighbour ions (fourth, fifth and sixth terms), and last term which indicates zero point energy effect.

The mixed crystals, according to the virtual crystal approximation (VCA) [21], 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 alkaline earth oxide mixed $\text{Sr}_x\text{Cd}_{1-x}\text{O}$ alloy have shown that they vary linearly with the composition (x), and hence, they follow Vegard's law:

$$a(A_xB_{1-x}C) = (1-x)a(AC) + xa(BC) \quad (5)$$

The values of these model parameters are the same for the parent compounds. The values of these parameters for their mixed crystal components have been determined from the application of Vegard's law to the corresponding measured data for AC and BC. It is convenient to find the three parameters (masses, force constants, and effective charges) for both binary compounds. Furthermore, we assume that these parameters vary linearly with x and hence, they follow Vegard's law:

$$b(A_xB_{1-x}C) = (1-x)b(AC) + xb(BC) \quad (6)$$

$$\rho(A_xB_{1-x}C) = (1-x)\rho(AC) + x\rho(BC) \quad (7)$$

$$f(r)(A_xB_{1-x}C) = (1-x)f(r)(AC) + xf(r)(BC) \quad (8)$$

3. Results and discussion

The Gibbs free energies contain three model parameters [b , ρ , $f(r)$]. The values of these model parameters have been computed using the following equilibrium conditions:

$$\left[\frac{dU}{dr} \right]_{r=r_0} = 0 \quad (9)$$

$$B_1 + B_2 = -1.165Z_m^2 \quad (10)$$

where $Z_m^2 = Z(Z + 12f(r))$.

Using these model parameters and the minimization technique, phase transition pressures of alkaline earth oxide mixed $\text{Sr}_x\text{Cd}_{1-x}\text{O}$ alloy have been computed for the parent compounds. The lattice constants and bulk modulus have been taken as input parameters of the parent compounds. These input parameters and calculated output parameters are listed in Table 1. The output model parameters have been given at different concentration (x).

3.1. Structural properties

The change in minimized Gibbs free energy of both the phases has been plotted versus pressure in Fig. 1. The plot represents the changes in the Gibbs free energy at different concentrations (x). The phase transition occurs when the change in Gibbs free energy ΔG approaches zero ($\Delta G \rightarrow 0$). At phase transition pressure (P_t) these compounds undergo a (B1 – B2) transition associated with a sudden collapse in volume showing a first order phase transition. The calculated values of phase transition pressures have been listed in Table 2 at different concentrations (x). The variation of phase transition pressure with concentration has been plotted in Fig. 2.

At elevated pressures, the crystals undergo structural phase transition associated with a sudden change in the arrangement of the atoms. The

Table 1. Generated model parameters of $\text{Sr}_x\text{Cd}_{1-x}\text{O}$ alloy at different concentrations.

$\text{Sr}_x\text{Cd}_{1-x}\text{O}$ alloy concentration (x)	Input parameters			Model parameters		
	r_0 (Å)	B (GPa)	$b(10^{-12}$ ergs)	ρ (Å)	f(r)	
0	2.385 ^a	150 ^a	3.16	0.168	0.11302	
0.25	–	–	5.2075	0.17925	0.123132	
0.5	–	–	7.255	0.1905	0.133575	
0.75	–	–	9.3025	0.20175	0.143825	
1	2.581 ^b	91 ^b	11.35	0.213	0.15413	

a – ref. [9], *b* – ref. [14]

Table 2. Phase transition pressure (GPa) and volume collapse of $\text{Sr}_x\text{Cd}_{1-x}\text{O}$ alloy at different concentrations.

$\text{Sr}_x\text{Cd}_{1-x}\text{O}$ alloy concentration (x)	Phase Transition Pressure (GPa)			Volume Collapse (%)		
	Present	Exp.	Others	Present	Exp.	Others
0	90	90.6 ^a	85 ^c	5.8	–	6.5 ^e
0.25	86	77.95	85.75	5.425	–	6.0
0.5	82	65.30	86.50	5.05	–	5.5
0.75	78	52.65	87.25	4.675	–	5.0
1	74	36 ± 4 ^b	88 ^d	4.3	13.0 ^b	4.5 ^c

a – ref. [8], *b* – ref. [15], *c* – ref. [11], *d* – ref. [14], *e* – ref. [10].

Fig. 1. Variation of ΔG (KJ/mole) with pressure for $\text{Sr}_x\text{Cd}_{1-x}\text{O}$ at different concentrations (x).

Fig. 2. Variation of phase transition pressure with concentration (x). Solid circles represent pseudo-experimental, solid squares represent pseudo-theoretical and solid triangles represent present results.

atoms are rearranged into new positions leading to a new structure. The discontinuity in volume at the transition pressure is obtained from the phase diagram. The relative volume changes $V(P)/V(0)$ corresponding to the values of r and r' at different concentrations (x) are plotted versus pressure

in Fig. 3. The values of relative volume changes $V(P)/V(0)$ have been plotted versus different concentrations (x) in Fig. 4. The values of phase transition pressures and volume collapses have been

compared with available experimental [8, 15] and theoretical results [10, 11, 14] for the parent compounds. The values for different concentrations (x) have been compared with pseudo-experimental values (interpolated from the experimental values of the two parent crystals) and pseudo-theoretical (interpolated from the theoretical values of the two parent crystals) calculations.

Fig. 3. Variation of relative volume change V/V_0 with pressure at different concentrations (x).

Fig. 4. Variation of relative volume change V/V_0 with concentration (x). Solid squares represent pseudo-theoretical and solid triangles represent present work results.

3.2. Elastic properties

The theoretical study of second order elastic constants of cubic crystals has been carried out

by the method of homogeneous finite deformation. The mechanical elastic constants depend on the configuration of a crystal. Elastic properties are important for the solid crystals because they are related to equations of state (EOS), phonon spectra, specific heat, thermal expansion, Debye temperature etc. The values of elastic constant give valuable information about the structure stability and the bonding characteristics between atoms.

The information of second order elastic constants (SOECs) and their pressure derivatives are significant for the understanding interatomic forces in solids. The expressions of second order elastic constants [22–24] are as follows:

$$C_{11} = (e^2/4a^4)[-5.112Z(Z + 12f(r)) + A_1 + (A_2 + B_2)/2 + 9.3204za f'(r)] \quad (11)$$

$$C_{12} = (e^2/4a^4)[0.226Z(Z + 12f(r)) - B_1 + (A_2 - 5B_2)/4 + 9.3204za f'(r)] \quad (12)$$

$$C_{44} = (e^2/4a^4)[2.556Z(Z + 12f(r)) - B_1 + (A_2 + 3B_2)/4] \quad (13)$$

Using model parameters (b , ρ , $f(r)$), pressure derivatives of bulk modulus have been computed, whose expressions are as follows:

$$\frac{dB}{dp} = -(3\Omega)^{-1} \times \left[13.980Z(Z + 12f(r)) + C_1 - 3A_1 + C_2 - 3A_2 - 167.7648za f'(r) + 41.9420za^2 f''(r) \right] \quad (14)$$

with

$$B = \frac{1}{3}(C_{11} + 2C_{12}), \quad S = \frac{1}{2}(C_{11} - C_{12})$$

and

$$\Omega = -2.330Z(Z + 12f(r)) + A_1 + A_2 + 21.9612za f'(r)$$

The values of A_i , B_i , and C_i ($i = 1, 2$) have been evaluated from the knowledge of b , ρ and vdW coefficients.

Calculations of the bulk elastic properties play a vital role in the physics of solid state. The bulk elastic properties of a material determine how much it will compress under a given amount of external pressure. To test the mechanical stability of our model, we have computed the elastic properties of proposed materials. The computed values of bulk modulus have been given in Table 3 at different concentrations (x). The variation of bulk modulus versus concentrations (x) has been plotted in Fig. 5. The variation of lattice constants versus concentrations (x) has been plotted in Fig. 6. The values of lattice constants (a) have also been listed in Table 3 for different concentrations (x). The values of bulk modulus and lattice constants have been compared with available experimental [9, 14] and theoretical results [3, 4, 8] for the parent compounds. The values for different concentrations (x) have been compared with pseudo-experimental values (interpolated from the experimental values of the two parent crystals) and pseudo-theoretical (interpolated from the theoretical values of the two parent crystals) calculations.

Fig. 5. Variation of bulk modulus (GPa) with concentration (x). Solid circles represent pseudo-experimental, solid squares represent pseudo-theoretical and solid triangles represent present results.

3.3. Thermophysical properties

Thermophysical properties are very important for solid state materials. These properties are used

Fig. 6. Variation of lattice constants a (Å) with concentration (x). Solid circles represent pseudo-experimental, solid squares represent pseudo-theoretical and solid triangles represent preset work.

to study various structural and non structural behaviour of materials at temperature and pressure change. To study the thermophysical properties, the values of the Debye temperature, molecular force constant and Restsrahlen frequency have been computed for the present compounds. In Debye theory the Debye temperature (θ_D) is the temperature of a crystal's highest normal mode of vibration.

The Debye temperature (θ_D) is given by the expression [25]:

$$\theta_D = \frac{h\nu}{k_B} \quad (15)$$

where h is the Planck constant and k_B is the Boltzmann constant:

$$\nu_0 = \frac{1}{2\pi} \left(\frac{f}{\mu} \right)^{\frac{1}{2}} \quad (16)$$

where μ is the reduced mass, ν_0 is the Restsrahlen frequency, as defined in our earlier paper [11, 12], and f is the molecular force constant given by:

$$f = \frac{1}{3} \left[U_{kk'}^{SR}(r) + \frac{2}{r} U_{kk'}^{SR}(r) \right]_{r=r_0} \quad (17)$$

with $U_{kk'}^{SR}(r)$ as the short range nearest neighbour ($k \neq k'$) part of $U(r)$ is given by the last three terms in equations 3 and 4.

Table 3. Lattice constants and bulk modulus of $\text{Sr}_x\text{Cd}_{1-x}\text{O}$ alloy at different concentrations.

$\text{Sr}_x\text{Cd}_{1-x}\text{O}$ alloy concentration (x)	Lattice constants (Å)			Bulk modulus (GPa)		
	Present	Exp.	Others	Present	Exp.	Others
0	4.8032	4.77 ^a	4.6531 ^c	156	150 ^a	163 ^d
0.25	4.9059	4.8675	4.74407	140.50	135.25	147.44
0.5	5.0087	4.965	4.83505	125.00	120.50	131.885
0.75	5.1115	5.0625	4.92602	109.50	105.75	116.327
1	5.2143	5.16 ^b	5.017 ^c	94	91 ^b	100.77 ^e

a – ref. [9], *b* – ref. [14], *c* – ref. [8], *d* – ref. [3], *e* – ref. [4].

Table 4. Thermo-physical properties of $\text{Sr}_x\text{Cd}_{1-x}\text{O}$ alloy at different concentrations.

$\text{Sr}_x\text{Cd}_{1-x}\text{O}$ alloy concentration (x)	f (10^4dyn/cm)	ν_0 (10^{12} Hz)	θ_D (K)	γ
0	1.24	4.8706	347.58	1.39
0.25	1.395	5.9826	410.27	1.45
0.5	1.550	5.6109	472.97	1.51
0.75	1.705	5.9810	535.66	1.57
1	1.86	6.3512	598.36	1.64

The values of the Grüneisen parameter (γ), have been calculated from the relation:

$$\gamma = -\frac{r_0}{6} \left[\frac{\phi'''(r)}{\phi''(r)} \right]_{r=r_0} \quad (18)$$

The computed values of thermophysical properties molecular force constant (f), Reststrahlen frequency (ν_0), Debye temperature (θ_D) and Grüneisen parameter (γ) have been given in Table 4. These thermo physical properties have been listed at different concentrations (x) for $\text{Sr}_x\text{Cd}_{1-x}\text{O}$ alloy.

4. Conclusions

In conclusion, extended interaction potential EIP model has been applied to investigate the structural, mechanical and thermophysical properties of alkaline earth oxides mixed compound $\text{Sr}_x\text{Cd}_{1-x}\text{O}$ ($0 \leq x \leq 1$) under high pressure. Phase transition pressure and associated volume collapses calculated from this approach are in good agreement with the experimental values for the parent compounds ($x = 0$ and $x = 1$). The results for the mixed crystal counterparts are also in fair agreement with

pseudo-experimental values and pseudo-theoretical calculations generated from the application of Vegard's law to the data for the parent compounds.

An overall assessment shows that in general our values are close to the available experimental and theoretical data for the parent compounds and pseudo-experimental and pseudo-theoretical data for mixed concentration. The successful predictions achieved from the present model can be considered as remarkable in view of the fact that it has considered overlap repulsion effective up to second neighbour ions including the zero point vibrational energy effect.

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