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Investigation of $Mg_xSr_{1-x}O$ Mixed Alloy under High Pressure

Purvee Bhardwaj (Corresponding author)
High pressure Research Lab., Department of Physics, Barkatullah University, Bhopal-462026, India
E-mail: purveebhardwaj@gmail.com

Abstract
The structural and mechanical properties of alkaline earth oxides mixed compound $Mg_xSr_{1-x}O$ ($0 \leq x \geq 1$) have been investigated under high pressure. Phase transition pressures are associated with a sudden collapse in volume. Phase transition pressure and associated volume collapses [$\Delta V (Pt)/V(0)$] calculated from this approach are in good agreement with experiment for the end point members (x=0 and x=1). The results for the mixed crystal counter parts are also in fair agreement with experimental data generated from the application of Vegard's law to data for the end point members.
Keywords: Mixed crystal, Oxide, Volume collapse, Phase transition, High pressure.

1. Introduction

The alkaline earth chalcogenides (AX: A=Be, Mg, Ca, Sr, Ba; X= O, S, Se, Te) form a very important closed shell ionic system. The relative stability of different crystallographic phases and possible high pressure phase transformations among them are interested in alkaline earth oxides XO (X = Mg, Ca, Sr and BaO). Theses oxides have been considered as a typical case for understanding bonding in ionic oxides. Their catalytic properties are important for chemical engineering [1]. This is because of their wide range of applications ranging from catalysis to microelectronics. These oxides are important constituent of earth's lower mantle where pressure reaches up to 140 GPa. The electronic structure of these compounds inside the earth will be considerably changed compared to that at normal pressure. So they are of geophysical interest [2-5]. The alkaline earth chalcogenides are the simplest and ideal ionic solids on which, much experimental and theoretical work have been done in the past. A survey of the literature reveals that, although a large amount of experimental work has been done on the phase transition in alkaline earth chalcogenides [6-9], very scant attention has been paid to their theoretical understanding. These compounds share similar band structures and, in turn have similar physical properties. In order to understand the band structure of these compounds and their rate of change with pressure we examine alkaline earth chalcogenides under pressure from a theoretical point of view. Apart from this, these compounds exhibit interesting phenomena of metallization with the application at further pressure. Metallization is described due to band broadening with increase in pressure and subsequent overlap of filled valence band (p-like valence band of the chalcogen atom) and the conduction band (d-like conduction band of the cation). At normal conditions these compounds crystallize in the NaCl-type (B1) structure (Fm3m) and have both properties of ordinary insulators and properties of semiconductors [6-9].

Among this group of alkaline earth oxides we have selected the simple system of MgO- SrO in the present study. The mixed oxides of Mg and Sr have been investigated by Vegard's law [10]. Present oxides crystallize in NaCl-type structure (B1) at normal conditions with space group *Fm3m* (225). Under pressure, the present oxides suffer a first-order phase transition from the sixfold-coordinated NaCl structure to the eightfold-coordinated CsCl-type structure (B2) with the space group symmetry *Pm3m* (221) [11].

We have applied an extended interaction potential model by including zero point energy effects in TBP for the prediction of phase transition pressures and associated volume collapses in alkaline earth oxide mixed compound $Mg_xSr_{1-x}O$ ($0 \leq x \geq 1$) under high pressure. The zero point energy is the ground state energy of the compound. This term shows a small effect in Gibbs free energy. To make the model realistic this term cannot be ignored completely. The main aim of this work is to provide a model suitable for the study of structural and elastic properties of alkaline earth oxide mixed compound $Sr_xCd_{1-x}O$. 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.

1.1 Potential model and method of calculation

Application of pressure directly results in compression leading to the increased charge transfer (or three body interaction effect [12]) due to the deformation of the overlapping electron shell of the adjacent ions (or non-rigidity of ions) in solids. Also we have considered zero point energy effects, which, is the lowest possible energy that the compound may possess. The energy of the compound is ($\upsilon = (h\upsilon)/\{e^{h\upsilon/kt}-1\}+ (h\upsilon)/2$), here υ, h, t, and k are the frequency, plank constant, temperature and Boltzaman constant of the compound. It is clear from the above expression that even at absolute zero the energy of the compound cannot be zero but at least ($h\upsilon)/2$. 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) [12], 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 temperature T=0K and pressure (P) the Gibbs free energies for rock salt (B1, real) and CsCl (B2, hypothetical) structures are given by:

$$G_{B1}(r) = U_{B1}(r) + PV_{B1}(r) \qquad (1)$$
$$G_{B2}(r') = U_{B2}(r') + PV_{B2}(r') \qquad (2)$$

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:

$$U_{B_1}(r) = \frac{-\alpha_m z^2 e^2}{r} - \frac{(12\alpha_m z e^2 f(r))}{r} - [\frac{C}{r^6} + \frac{D}{r^8}]$$
$$+ 6b\beta_{ij} \exp[(r_i + r_j - r)/\rho] + 6b\beta_{ii} \exp[(2r_i - 1.414r)/\rho] \qquad (3)$$
$$+ 6b\beta_{jj} \exp[(2r_j - 1.414r)/\rho] + (0.5)h\langle \omega^2 \rangle^{1/2}{}_{B_1}$$

$$U_{B2}(r') = \frac{-\alpha'_m z^2 e^2}{r'} - \frac{(16\alpha'_m z e^2 f(r'))}{r'} - [\frac{C'}{r'^6} + \frac{D'}{r'^8}]$$
$$+ 8b\beta_{ij} \exp[(r_i + r_j - r')/\rho] + 3b\beta_{ii} \exp[(2r_i - 1.154r')/\rho] \qquad (4)$$
$$+ 3b\beta_{jj} \exp[(2r_j - 1.154r')/\rho] + (0.5)h\langle \omega^2 \rangle^{1/2}{}_{B_2}$$

With α_m and α'_m as the Madelung constants for NaCl and CsCl structure respectively. C(C') and D(D') are the overall Vander Waal coefficients of B1 (B2) phases, β_{ij} (i,j=1,2) are the Pauling coefficients. Ze 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 $\langle \omega^2 \rangle^{1/2}$ as the mean square frequency related to the Debye temperature (θ_D) as

$$\langle \omega^2 \rangle^{1/2} = k\theta_D/h \qquad (5)$$

Here, θ_D can be expressed as [13,14]

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

With B_T and μ as the Bulk modulus and reduced mass of the compounds.

These lattice energies consists of long range Coulomb energy (first term), three body interactions corresponding to the nearest neighbour separation r (r') (second term), vdW (van der Waal) 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 indicates zero point energy effect term.

The mixed crystals, according to the virtual crystal approximation (VCA) [10], 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 $Mg_xSr_{1-x}O$ alloy have shown that they vary linearly with the composition (x), and hence they follow Vegard's law:

$$a(A_x B_{1-x} C) = (1-x) a(AC) + xa(BC) \qquad (6)$$

The values of these model parameters are the same for end point members. 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 instructive to point that the mixed crystals, according to the virtual crystal approximation, are regarded as an array of average ions whose masses, force constants and effective charges are considered to scale linearly with concentration. It is convenient to find the three parameters for both binary compounds. Furthermore, we assume that these parameters vary linearly with x and hence follow Vegard's law:

$$b(A_x B_{1-x} C) = (1-x) b(AC) + xb(BC) \qquad (7)$$
$$\rho(A_x B_{1-x} C) = (1-x) \rho(AC) + x\rho(BC) \qquad (8)$$
$$f(r)(A_x B_{1-x} C) = (1-x) f(r)(AC) + xf(r)(BC) \qquad (9)$$

1.1.1 Results and Discussion

The Gibbs free energies in eq. (1) and (2) contain three model parameters [b, ρ, $f(r)$]. The values of these model parameters have been computed using the following equilibrium conditions.

$$\left[\frac{dU}{dr}\right]_{r=r_0} = 0 \qquad (10)$$

and the bulk modulus

$$B = \frac{1}{9kr_0}\left[\frac{d^2U}{dr^2}\right]_{r=r_0} \qquad (11)$$

Where k is the crystal structure dependent constant and r_0 is the lattice constant and U is the lattice energy. The input parameters have been given in Table-1. After using the input parameters and these equilibrium conditions the model parameters have been calculated. These three model parameters have also been given in Table-1 at different concentrations. These model parameters have been plotted with concentration in Fig 1. Taking the value of model parameters we have used minimization technique for calculating the phase transition pressure and volume collapse of the present oxides. At the phase transition pressures, the crystals undergo structural phase transition associated with a sudden change in volume. The discontinuity in volume at the transition pressure shows the first order phase transition.

The computed values of phase transition pressures and volume collapses have been given in Table-2. These values have been compared with available experimental [3] and theoretical results [9] for end point members. The variations of phase transition pressure with concentration (x) have been plotted in Fig. 2. The variations of volume collapse with concentration (x) have been plotted in Fig. 3. The values for different concentrations (x) have been compared with pseudo-theoretical (interpolated from the theoretical values of the two end crystals) calculations.

The computed values of bulk modulus have been given in Table-3 at different concentrations (x). The variation of bulk modulus with concentrations (x) has been plotted in Fig. 5. The variation of lattice constants with concentrations (x) has been plotted in Fig. 6. The values of lattice constants (a) have also been listed in Table-3 at different concentrations (x). The values of bulk modulus and lattice constants have been compared with available experimental [1] and theoretical results [7] for end point members. The values for different concentrations (x) have been compared with pseudo-experimental values (interpolated from the experimental values of the two end crystals) and pseudo-theoretical (interpolated from the theoretical values of the two end crystals) calculations.

The present extended interaction potential (EIP) model have been applied to study the structural properties of alkaline earth oxides mixed compound $Mg_xSr_{1-x}O$ ($0 \leq x \geq 1$) under high pressure. Phase transition pressure and associated volume collapses calculated from this approach are in good agreement with experiment for the end point members (x=0 and x=1). The results for the mixed crystal are also in good agreement with pseudo-experimental values and pseudo-theoretical calculations generated from the application of Vegard's.

Finally, it may be concluded that in general, our values are near to available experimental and theoretical data for the end point members and pseudo-experimental and pseudo-theoretical data for mixed concentration. The successful predictions achieved from the present model is that it has considered overlap repulsion effective up to second neighbour ions and including the zero point energy effect.

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Table-1 Generated model parameters of $Mg_xSr_{1-x}O$ alloy at different concentration

Alloy/ Concentration	Input parameters		Model parameters		
	r_0 (Å)	B (GPa)	b(10^{-12} ergs)	ρ(Å)	f(r)
$Mg_xSr_{1-x}O$ 0	2.580[a]	160[a]	1.423	0.214	0.1273
0.25	-	-	1.329	0.2002	0.1457
0.5	-	-	1.235	0.1865	0.1642
0.75	-	-	1.141	0.1727	0.1826
1	2.107[a]	90.6[b]	1.047	0.159	0.2011

a-ref [8], b-ref [5].

Table-2 Phase transition pressure (GPa) and volume collapse of $Mg_xSrd_{1-x}O$ alloy at different concentrations

Alloy/ Concentration	Phase Transition Pressure (GPa)			Volume Collapse (%)		
	Present	Expt.	Others	Present	Expt.	Others
$Mg_xSr_{1-x}O$ 0	80	36±4[a]	88[b]	6.23	13.0[a]	4.5[b]
0.25	110.5	-	116.5	6.12	-	4.62
0.5	141	-	145	5.90	-	4.75
0.75	171.5	-	173.5	5.67	-	4.83
1	202	>120[a]	202[b]	5.45	-	5.0[b]

a-ref [3], b-ref [9].

Table-3 Lattice constants and bulk modulus of $Sr_xCd_{1-x}O$ alloy at different concentrations.

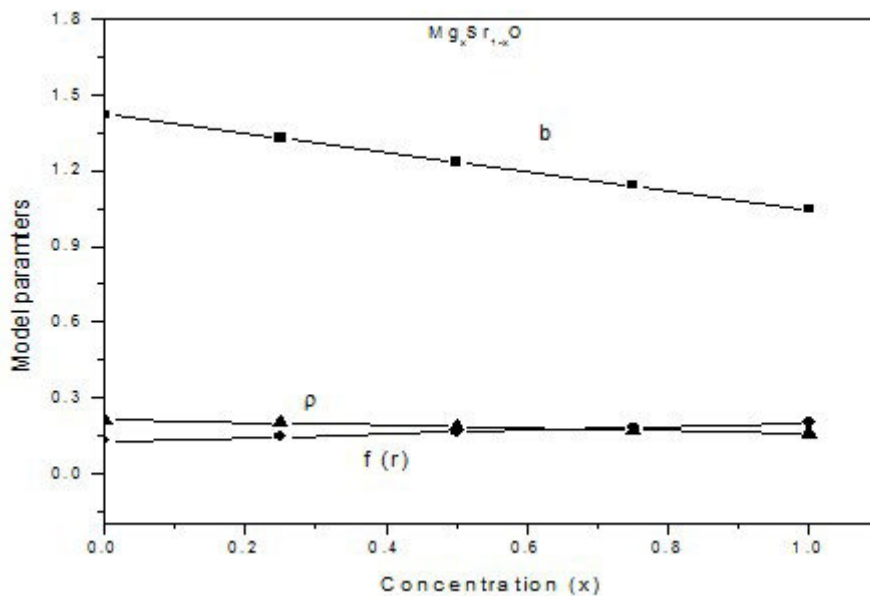| Alloy/ Concentration	Lattice constants (Å)			Bulk modulus (GPa)		
	Present	Expt.	Others	Present	Expt.	Others
$Mg_xSr_{1-x}O$ 0	4.197	4.213[a]	4.192[b]	157	160[a]	198.722[b]
0.25	4.416	4.449	4.450	139.37	142.65	177.48
0.5	4.636	4.686	4.709	121.75	125.3	156.25
0.75	4.855	4.923	4.967	104.125	109.95	135.01
1	5.075	5.160[a]	5.226[b]	86.5	90.6	113.781[b]

a-ref [1], b-ref [7].

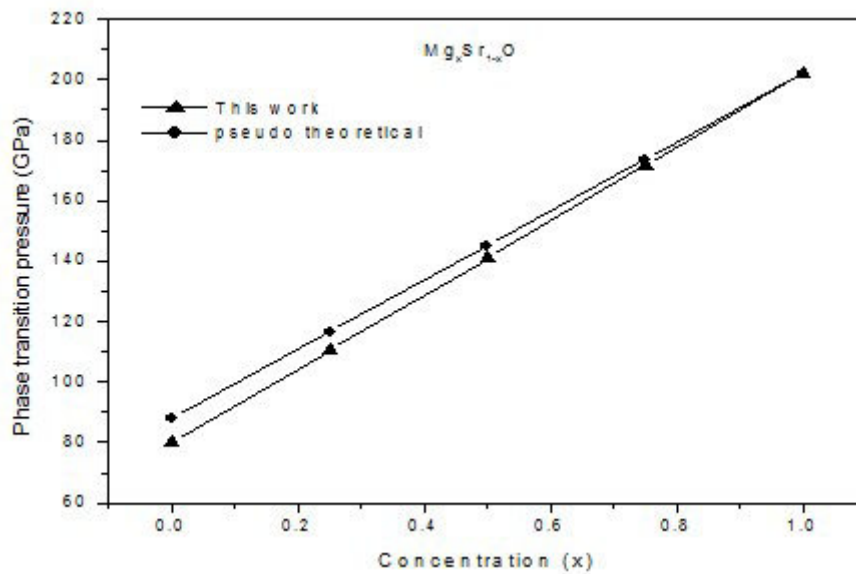Figure 1. Variation of model parameters with concentrations (x)

Figure 2. Variation of phase transition pressure with concentration (x). Solid triangles represent present work and solid circles represent pseudo-theoretical work
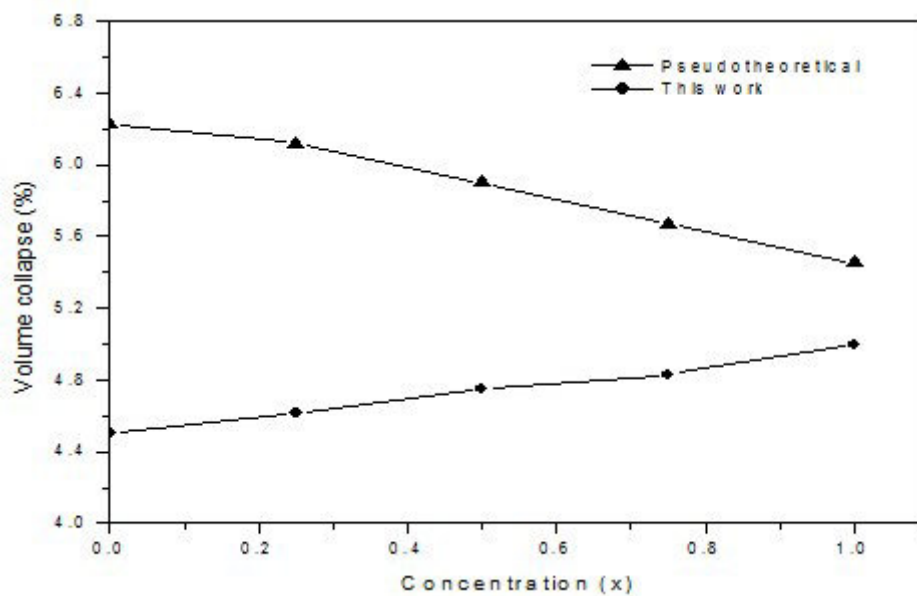

Figure 3. Variation of volume change with concentrations (x). Solid triangles represent present work and solid circles represent pseudo-theoretical work.
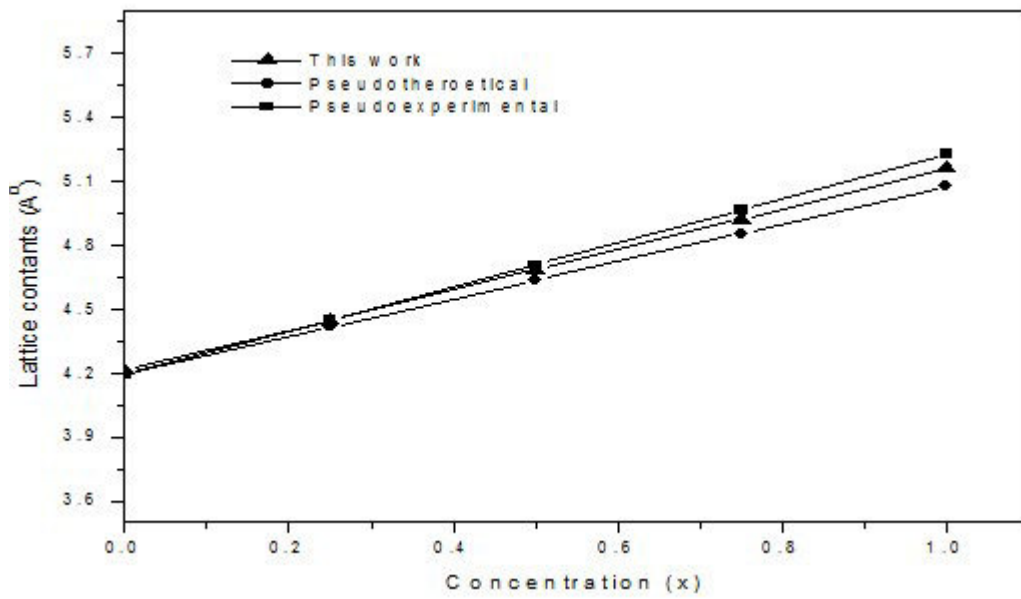
Figure 4. Variation of lattice constants a (Å) with concentration (x). Solid circles represent pseudo-theoretical, solid squares represent pseudo-experimental and solid triangles represent present work.
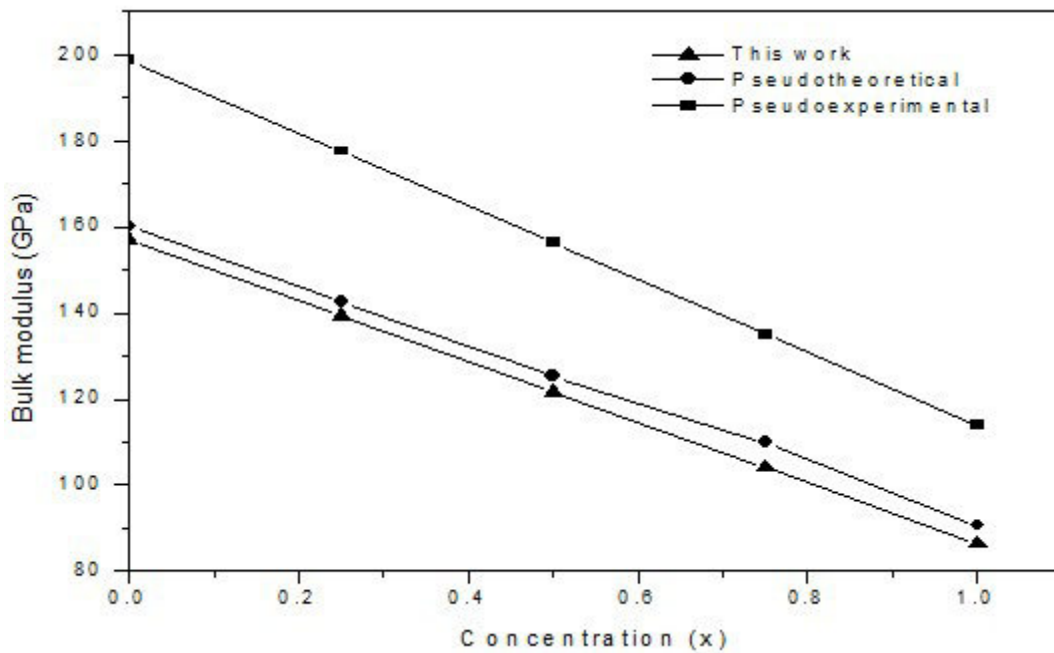

Figure 5. Variation of bulk modulus (GPa) with concentration (x). Solid circles represent pseudo-theoretical, solid squares represent pseudo-experimental and solid triangles represent present

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