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Pressure induced phase transition in $Ba_{1-x}Sr_xTe$ mixed crystal

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We have investigated the phase transition pressures and associated volume collapses in the alkaline earth mixed compound $Ba_{1-x}Sr_xTe$ ($0 \leq x \leq 1$) using a three body potential (TBP) approach and Gibbs free energy. The Gibbs free energy is expressed as a function of charge transfer (or three body interactions) and the pressure. Phase transition pressure and associated volume collapses [$\Delta V (P_t)/V(0)$] 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 Vegards law to data for the end point members.

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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 crystallizing in NaCl-type structure at room conditions except for the MgTe and the Beryllium chalconides.These compounds are technologically important materials having many applications ranging from catalysis to micro electronics. They have also applications in the area of luminescent devices. Among these compounds BaTe and SrTe have been found to under go first order phase transition from the six fold coordinated NaCl-type B1 structure to the eight fold coordinated CsCl-type B2 structure at pressures 6 GPa and 12GPa respectively as it has been shown by high pressure X-ray diffraction experiments. Metallization under sufficiently high pressure is the main phenomenon of interest in these compounds. The common reason for this metallization is the lowering of d-like conduction band relative to p-like valance band, which results in band overlap due to high pressure. An interest in the study of structural and high-pressure behaviour of alkaline earth chalcogenides (AEC) has increased in last two decades [1-12]. These compounds under normal condition crystallize in rock salt structure and show a different phase at high pressure. The new phase often shows different physical and chemical properties. At elevated pressures the AEC compounds undergo pressure induced structural phase transition from six fold coordinated NaCl to more closed eight fold coordinated CsCl structure. Metallization under sufficiently high pressure is the main phenomenon of interest in these compounds. The common reason for this metallisation is the lowering of d-like conduction band relative to p-like valance band, which results in band overlap due to high pressure. The band gap between p-like valance and d-like conduction band states in AEC compounds range from 2.5 to 6.0ev. In the past H.G. Zimmer and Thomas et. al. [13] had studied the structural phase transition in BaTe and SrTe. Later B. S. Rao [14] investigated the structural phase transition using an interionic potential approach. In recent years the structural phase transition due to high pressure in BaTe and SrTe is investigated by A. Chakrabarti [2], U.K. Sakalle [15]. R. Khenata [16], and M. Dadsetani [17]. They studied B1 (NaCl) to B2 (CsCl) phase transition phenomena in these compounds. In the recent past, many efforts were made to interpret the experimental results by using a variety of theoretical models. Most of these approaches target to predict the metallization phenomena through band overlap by using different methods of band structure calculations, such as linear muffin-tin orbitals (LMTO) and tight binding approximation [12]. Most of the studies emphasized that overlap of bands at high pressure causes metallization in the AEC compounds. However, some of these theories fail to predict the transition pressure and volumes cohesive properties even with a reasonable order of magnitude [12]. Also the high-pressure structural behavior, interionic forces and several other static and dynamical properties cannot be predicted through band structure approaches.

Phase transition phenomena and structure stability in BaTe and SrTe have been studied by many physicists [1, 2, 14, 15]. How ever such studies for their mixed counter parts are lacking. This obvious from the fact that BaTe and SrTe transforms from B1 (NaCl) to B2 (CsCl) phase at 6Gpa and 12Gpa. So the difference in phase transition pressure in end point members is high (i.e.). From X-ray structure analysis it has been observed that the mixed ionic crystals are formed by the mixture of pure components and are truly crystalline and their lattice constants change linearly with concentration from one pure member to another[18,19]. So experimental data for mixed compounds can be generated by applying Vegards law to experimental values available for end point members [20, 21]. As we have already studied mixed system of $Ba_{1-x}Sr_xTe$ successfully using three-body potential approach and minimization technique, same approach has been applied in the present work.

Motivated from the above mentioned success of the TBP model in III-V and II-VI compound semiconductor, we thought it pertinent to apply it for the prediction of phase transition pressures and associated volume collapses in AEC mixed compound $Ba_{1-x}Sr_xTe$ ($0 \leq x \leq 1$). For this purpose, we have used the first and second neighbour distances. The results, obtained by us have shown a reasonably good agreement with experimental data generated by applying Vegards law to experimental values available for end point members (BaTe and SrTe). In addition to the prediction of phase transitions and relative stability of crystal structures of mixed systems, the present work includes the study of pressure derivatives of second order elastic constants (C_{11}, C_{12}, C_{44}), their combinations $S = (C_{11}-C_{12})/2$ and bulk modulus $k = (C_{11}+2C_{12})/3$. The essentials of the theoretical formalism and the computational method are present in section 2.The computed results are reported and discussed in section 3.

2. Essentials of theory and computational method

The application of pressure on the crystals causes the decrease in their volume, which in turn leads to an increased charge transfer (or three-body interaction effects) due to the existence of the deformed (or exchange) charge between the overlapping electron shells of the adjacent ions. This overlapping leads to the transfer of charges which when interacts with an other distant charges rise to many body interactions (MBI). The dominant part of MBI is three body interactions (TBI) [22]. To understand this mechanism, let us designate A, B and C ions with positions (lk), (l'k') and (l"k") in an ionic crystal having an ionic charge ±Ze with l and k as the cell and basis indices as shown in Fig 1. Also, C is the nearest neighbour (nn) of ion A and separated by a distance $r = |r(lk,l'k')$ and B is any distance $|r(lk,l''k'')|$ ion a distance Apart from A.

$$dq_k = \pm zef_k r(lk,l''k'') = \pm Zef_k f(r)$$

The occurrence of the above transferred charge leads to a modified charge of A (or C) as

$$z_m e = z_k e + nef_k r(lk,l''k'') \cong z_k e[1+(2n/z) f_k r(lk,l''k'')]^{1/2}$$

Here, n is the number of the nearest neighbour (nn) ions, e is the electronic charge, f_k (r) is the intrinsic potential force and [1+(2n/z)f(r)]. The expression for the modified columbic energy due to the three body potential (TBI) is

$$\phi_m(r) = \phi^c + \phi^T$$

$$\phi_m(r) = [-\alpha_M z^2 e^2 / r][1+(2n/z) f(r)]$$

Where, α_M is the Madelung constant , which is 1.7476(1.7629) for NaCl (CsCl) structure, r is the equilibrium nn ion separation and n is the number of nn ions, f(r) is the TBI parameter and is independent on the nearest neighbour ion distance as

$$f(r) = f_0 \exp(-r/\rho)$$

These effects have been incorporated in the Gibbs free energy (G =U+PV-TS) as a function of pressure (P) and three-body interaction (TBI). Here U is the internal energy. The Gibbs free energies for rock salt (B_1, real) and CsCl (B_2, hypothetical) structures are given by

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

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

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 the energies (3) and (4) are lattice energies for B_1 and B_2 structures and they are expressed as:

$$U_{B_1}(r) = \frac{-\alpha_m z^2 e^2}{r} - \frac{(12\alpha_m z e^2 f_m(r))}{r} - [\frac{C}{r^6} + \frac{D}{r^8}] + 6b\beta_{ij} exp[(r_i + r_j - r)/\rho] + 6b\beta_{ii} exp[(2r_i - 1.414r)/\rho] + 6b\beta_{jj} exp[(2r_j - 1.414r)/\rho] \tag{3}$$

$$U_{B2}(r') = \frac{-\alpha'_m z^2 e^2}{r'} - \frac{(16\alpha'_m z e^2 f_m(r'))}{r'} - [\frac{C'}{r'^6} + \frac{D'}{r'^8}] + 8b\beta_{ij} exp[(r_i + r_j - r')/\rho] + 3b\beta_{ii} exp[(2r_i - 1.154r')/\rho] + 3b\beta_{jj} exp[(2r_j - 1.154r')/\rho] \tag{4}$$

Here, the first term in the above eqs. (5) and (6) is the long range Coulomb energy modified with three body interactions $r(r')$,$\alpha_m(\alpha'_m)$ are the Medlung constants for B1-B2 phases. The remaining terms correspond to the overlap repulsion represented by Hafemister and Flygare (HF) type potential [23]. The lattice energies given by eqs. (5) and (6) contain only three model parameters (b,ρ,f(r)), whose values have been determined from the knowledge of the cohesive energy U(r) at $r=r_0$ and its first and second order space derivatives depicting the equilibrium condition

$$[dU(r)/dr]_{r=r0} = 0$$

And $$[d^2U/dr^2] = 9kr_0B_T$$

Here, B_T is isothermal bulk modules and k=2 for B1 phase.

The mixed crystals, according to the virtual crystal approximation (VCA) (Elliot and Leath, 1976), 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 $Ba_{1-x}Sr_xTe$ have shown that they vary linearly with the composition (x), and hence they follow Vegards law:

$$a(A_{1-x}B_xC) = (1-x)\,a(AC) + x\,a(BC) \quad (7)$$

The values of these model parameters are the same for end point members (AC- SrTe) and (BC- BaTe). The values of these parameters for their mixed crystal components have been determined from the application of Vegards 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 Vegards law:

$$b(Ba_{1-x}Sr_xTe) = (1-x)\,b(BaTe) + x\,b(SrTe) \quad (8)$$

$$\rho(Ba_{1-x}Sr_xTe) = (1-x)\,\rho(BaTe) + x\rho(SrTe) \quad (9)$$

$$f(r)(Ba_{1-x}Sr_xTe) = (1-x)\,f(r)(BaTe) + x\,f(r)(SrTe) \quad (10)$$

3. Discussion and conclusion

The Three Body potential described in the preceding section for NaCl (B_1) CsCl (B_2) structures contain three model parameters [b ρ, f(r)], namely range, hardness and three body interaction parameter. To calculate these parameters we employed the first and second order space derivatives of lattice energy and equilibrium condition. We have followed the technique of minimization of U_{B1} (r) and U_{B2} (r') at different pressures in order to obtain inter ionic separation r and r, for B_1 and B_2 phases respectively. We have evaluated the corresponding $G_{B1}(r)$ and $G_{B2}(r')$ and their respective differences $\Delta G = (G_{B1}(r) - G_{B2}(r'))$. The pressure at which ΔG approaches zero is the phase transition pressure (P_t).

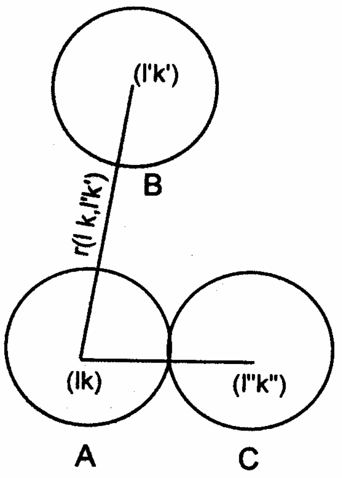

Fig. 1. Schematic representation of three body interactions model showing the three ions A, B and C with positions (lk,l'k',l"k").

The three model parameters [b ρ, f(r)] are listed in Table 1.A look at the Table 2 exhibits dk/dp, ds/dp and dc_{44}/dp calculated from TBPM are in good agreement with experimental results [1, 13] than reported by others. In Fig: 2 the Gibbs free energy difference $\Delta G = (G_{B1}(r) - G_{B2}(r'))$ have been plotted against the pressure (P). It is seen from Fig: 2 that the present TBP model correctly predicts the relative stability for both the competitive phases as the volume of ΔG at P=0 are positive, for all the concentrations, which is the required criterion [24]. This prediction from TBP model has the same success as has been found in cases of perfect crystals i.e. BaTe, SrTe. In Fig: 2 the pressure variations of ΔG have been depicted for $Ba_{1-x}Sr_xTe$ at different concentrations to obtain the phase transition pressure (P_t).

Table 1. Model parameters for $Ba_{1-x}Sr_xTe$ ($0 \le x \le 1$).

Crystal	b	ρ	f(x)
BaTe	3.4998	0.2320	0.7587
$Ba_{75}Sr_{25}Te$	2.9915	0.2352	0.0734
$Ba_{50}Sr_{50}Te$	2.4833	0.2385	.07101
$Ba_{25}Sr_{75}Te$	1.9750	0.24170	.06862
SrTe	1.6448	0.2450	.06615

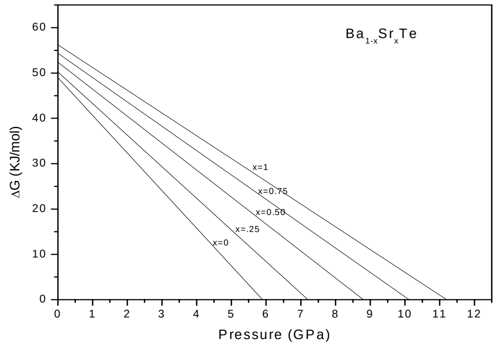

Fig. 2. The Gibbs free energy difference $\Delta G = (G_{B1}(r) - G_{B2}(r'))$ have been plotted against the pressure (P).

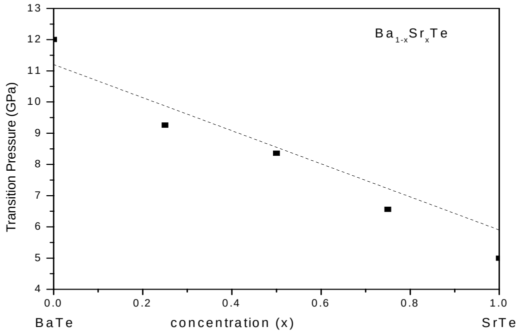

Fig. 3. The variation of transition pressures with composition (x).

We have plotted the variation of transition pressures with composition (x) in Fig. 3 and compared with their experimental and psuedoexperimental values (interpolated from the experimental values of the two end crystals). It is obvious from Figs. 2 and 3 that composition dependence of the transition pressure obtained presently are in closer agreement with their experimental values. The values of P_t at different compositions have been obtained from the linear interpolation between the transition pressures of the two end crystals. Relative volumes $\Delta V_{(P)}/V_{(0)}$ for different concentrations have been plotted against pressure for $Ba_{1-x}Sr_xTe$ in Fig. 4. The values of volume collapses -$\Delta V_{(Pt)}/V_{(0)}$ obtained from Fig. 4 are plotted in Fig. 5 with the variation of concentration (x) and they are compared with experimental results are closer to experimental values than reported by others.

Table 2. Pressure derivatives of BaTe and SrTe.

Pressure derivatives		BaTe	SrTe
dk/dp	(present) (exp.)	6.0821 7^a	5.8783 5^b
ds/dp	(present) (exp.)	6.9583 -	6.1553 -
dc_{44}/dp	(present) (exp.)	-0.7432 -	-0.3562 -

a-ref [13], b-ref [1]

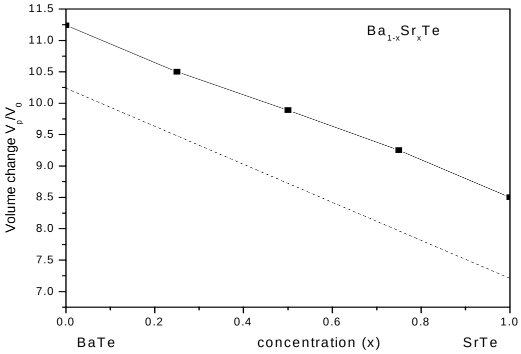

Fig. 4. Relative volumes $\Delta V_{(P)}/V_{(0)}$ for different concentrations have been plotted against pressure.

An overall assessment shows that in general, our values are near to experimental data and they are better matching than other theoretical data. The success achieved in the present investigation can be ascribed to the inclusion of the charge transfer (or three body) they seems to be of great importance at high pressure when the inter-ionic potential reduces considerably and the coordination number increases.

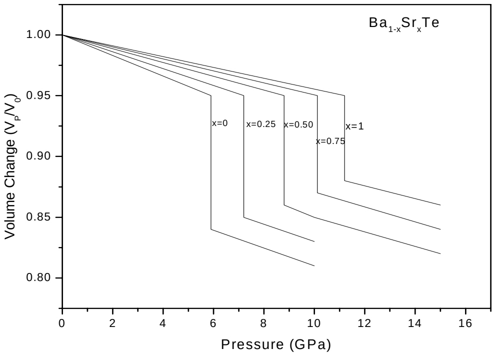

Fig. 5. The values of volume collapses - $\Delta V_{(Pt)}/V_{(0)}$ obtained from fig: 3 are plotted in Fig. 4 with the variation of concentration (x).

The pressure derivatives of second order elastic constants presented in Table 2 show that these values obtained from the TBP model are in better agreement with their available experimental data and others.. It is clear that during the phase transition from NaCl to CsCl, the volume discontinuity in pressure volume phase diagram identifies the same trend as the experimental approach. On the basis of above it may be concluded that the present three body potential model is adequately suitable for describing the phase transition phenomena and elastic properties of the mixed crystal $Ba_{1-x}Sr_xTe$.

Finally, it may be concluded that $Ba_{1-x}Sr_xTe$ transforms from NaCl to CsCl phase. The TBP model has been found to explain the phase transitions, relative stability and pressure derivatives of mixed $Ba_{1-x}Sr_xTe$ crystal with success.

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