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Qualitative Study of Stuructural Phase Transition of Mixed Heavy Metal Halide $Ag_xrb_{1-X}i$ under High Pressure

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ABSTRACT: In our current work the theoretical studies of application of high pressure on the phase transition of mixed crystal halides $Ag_xRb_{1-x}I$ have been made for the different values of x. The current work involves the technique of two body potential model involving the long range Coulomb's electrostatic forces, van der Waal's forces and short range repulsive forces. This model has been used to determine the phase transition pressure, volume collapses and Gibb's free energy in terms of pressure for Zinc-Blende and tetragonal structure. The conclusion of the current investigating work tries to emphasize on the stability of complex crystal structures and its enhanced applicability.

KEY WORDS: Gibb's eneergy, Zinc-Blende structure, vander Waal's force, Coulomb's force, volume collapse.

I. INTRODUCTION

The first and foremost detailed theoretical investigations of tetragonal/NaCl(B1) – Zinc blende(B3) transformation were done by Jacobs[1-5]. He employed a crude semi-empirical Born-Mayer[2] potential energy with nearest neighbour interaction. His calculation of phase transition pressure did not agree with the existing experimental results available then in the scientific literature.

Experimentally several investigators [6-15] observed that both AgI and CuI undergo a first order transition from tetragonal to Rocksalt structure on addition of pressure.

Very few theoretical attempts have been made to explain the structural properties of an intermediate phase transition of the compounds in a systematic manner. Hence there is a need to investigate the effect of high pressure on the structural stability of silver and copper iodide using a suitable interionic interaction energy model.

Several workers[16-25] also confirmed that the heavy metal halides and other compounds also undergo structural phase transition under pressure. Under high pressure these materials finally transform to a more dense six-fold coordinated Rocksalt structures. They behave as photographic materials and ionic conductors. At higher temperature these compounds act as superionic conductors[6]. Their elastic, anharmonic, vibrational, dielectric and phase transition transformations have been studied by several experimental and theoretical workers. Strikingly, such studies for their mixed crystal counterparts are lacking till to date. counterparts are lacking till to date. Investigation of phase transformation and volume collapse has not yet been carried out of $Ag_xRb_{1-x}I$, $Cu_xRb_{1-x}Br$, etc mixed crystals. Here the range of concentration x varies from 0, 0.2, 0.4, 0.6, 0.8 to1.0 for each mixed crystal. These values of thermodynamic properties, anharmonic properties and associated volume collapses of each mixed crystal are of high academic interest at present. They completely lie within Phillipse criteria[7].

The phase transition pressure(Pt) is computed by minimizing the Gibb's free energy at different pressures[8]. Then equilibrium lattice interionic separation of Zinc blende and Rocksalt structures of heavy metal halides and their composites are obtained. This is a new approach to achieve phase transition pressure and associated volume collapses.

II. METHOD &CALCULATION

The interionic interaction potential energy in the framework of two-body interaction potential for the ZnS and NaCl structures is given as

$$U(r) = -\sum_{ij} \frac{\alpha_M z^2 e^2}{r_{ij}} - \frac{C}{r^6} - \frac{D}{r^8} + b\sum_{ij} \beta_{ij} \exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right) \quad (1)$$

The above expression written in more explicit form for ZnS and tetragonal structures is written as

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$$U_{B3}(r) = -\frac{\alpha_M z^2 e^2}{r_{ij}} - \frac{C}{r^6} - \frac{D}{r^8} + nb\beta_{ij}\exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right) + n_i b\beta_{ii}\exp\left[\frac{2r_i - Kr_{ij}}{\rho}\right] + n_i b\beta_{jj}\exp\left[\frac{2r_j - Kr_{ij}}{\rho}\right] \quad (2)$$

$$U_{BT}(r) = -\frac{\alpha_M' z^2 e^2}{r'} - \frac{C}{r^6} - \frac{D}{r^8} + n'b\beta_{ij}\exp\left(\frac{r_i + r_j - r_{ij}'}{\rho}\right) + n_1' b\beta_{ii}\exp\left[\frac{2r_i - Kr_{ij}'}{\rho}\right] + n_1' b\beta_{jj}\exp\left[\frac{2r_j - Kr_{ij}'}{\rho}\right] - \frac{C'}{r'^6} - \frac{D'}{r'^8} \quad (3)$$

Where $\alpha_M(\alpha_M')$ are the Madelung constants for ZnS and tetragonal structure. (n, n') and (n_I n_I') are the nearest and the next-nearest neighbours for ZnS and tetragonal structures C(C') and D(D') are overall van der Waal's coefficients due to dipole-dipole(d-d) and diploe-quadruploe(d-q) interaction constants to be estimated by Slater-Kirkwood variational(SKV) approach.[11-13].According to the virtual crystal approximation the mixed crystals are regarded as a regular arrangement of average ions whose masses, force constant and effective charges are considered to scale linearly with concentration x. The measured values vary linearly with concentration x according to Vegard's law.

β_{ij} are Pauling coefficients defined as

$$\beta_{ij} = 1 + \frac{Z_i}{n_i} + \frac{Z_j}{n_j} \quad (4)$$

Where $Z_i(Z_j)$ and $n_i(n_j)$ are the valencies and the number of electrons in the outermost orbit of cations(anions) respectively. b and ρ are the hardness and range potential model parameters which are obtained from the crystal equilibrium conditions

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

$$\left|\frac{d^2U(r)}{dr^2}\right|_{r=r_0} = 9Kr_0B_0 \quad (5)$$

Here K = crystal constant. B_0 is the bulk modulus and r_0 is the equilibrium ionic radius

Phase Stability : An isolated phase of a systemis stable when the values of Gibb's Free energy G is minimum. The expression for G is given as

$$G = U + PV - TS \quad (6)$$

as a function of pressure(P) and volume(V). Here U is the internal energy which is equivalent to lattice/cohesive energy at 0K. S is the vibrational entropy at absolute temperature T.

At 0K and pressure P, The Gibb's free energy for Zns and tetragonal structure(B_T) is given by

$$G_{B3} = U_{B3}(r) + PV_{B3}(r) \quad (7)$$

$$G_{BT} = U_{BT}(r) + PV_{BT}(r) \quad (8)$$

Where U_{B3} and U_{BT} are the lattice energy for Zns and tetragonal structures.

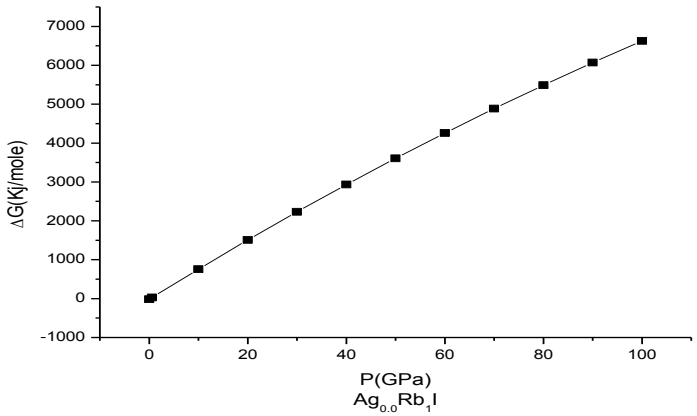
The volumes for the two phases are given by

$$V_{B3} = 3.08 * r^3 \quad (9)$$

$$V_{BT} = 2.00 * r'^3 \quad (10)$$

r(r') are the interionic separation for the compounds in their respective phases.

III. GRAPHS



Variation of Gibb's energy with pressure(GPa) for $Ag_{0.0}Rb_1I$

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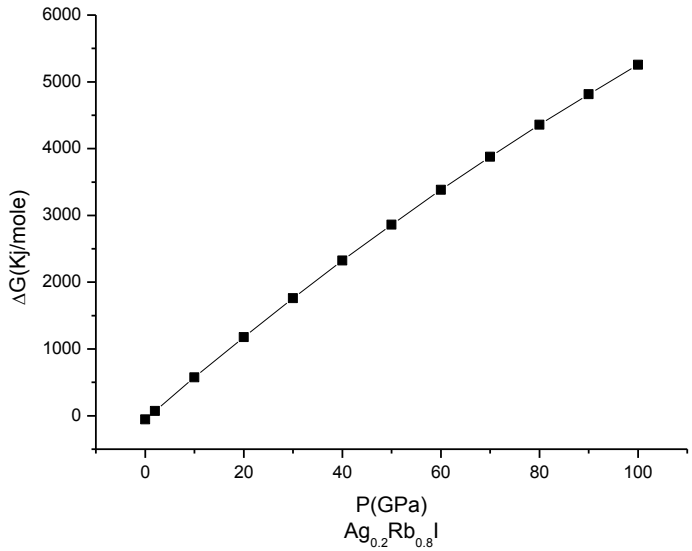
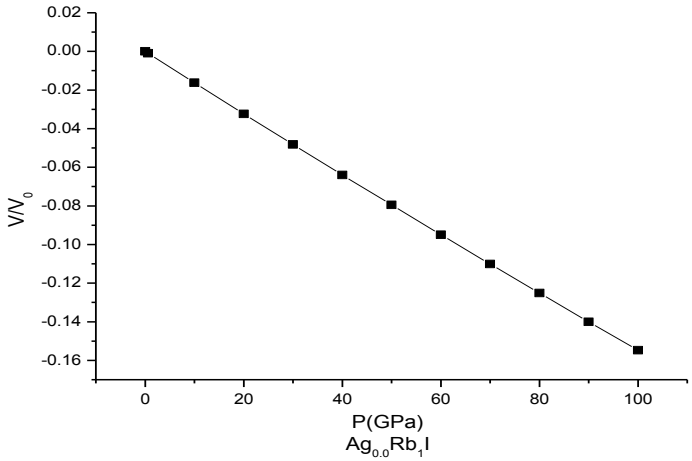
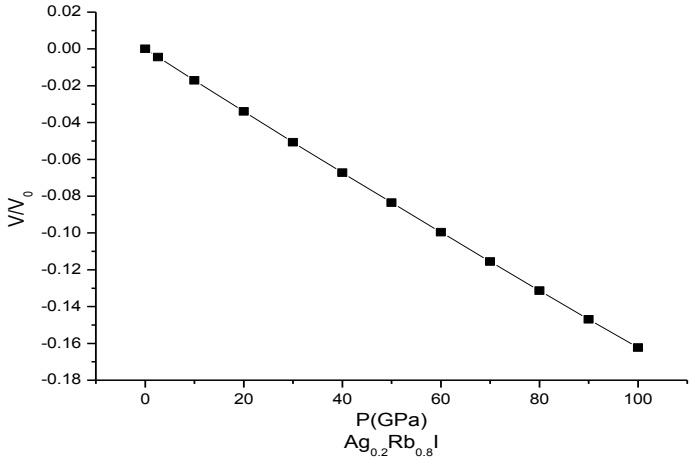


Variation of Gibb's energy with pressure(GPa) for $Ag_{0.2}Rb_{0.8}I$





IV. RESULT & CONCLUSION

The Gibb's free energy and volume collapses for the system under consideration have been determined for concentration =0 and 0.2. The two body potential model has come out quite successful in predicting the phase transition pressure for complex crystal under consideration. The transition pressures are found to be 5.58GPa for x=0 and 3.63GPa for x=0.2

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