

Study of Structural Phase Transition of Complex Metal Halide $Cu_xRb_{1-x}Br$ at High Pressure

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Date of Submission: 01-10-2020

Date of Acceptance: 19-10-2020

ABSTRACT: Our work envisages the theoretical investigations of the effect of high pressure on the phase transition of mixed metal halides $Cu_xRb_{1-x}Br$ for the different values of x . The current work uses the principle of two body potential model consisting of the long range Coulomb's attractive electrostatic forces, van der Waal's forces and short range repulsive forces. This model has been used to determine the phase transition pressure, Gibb's free energy and volume collapses as a function of pressure for Zinc-Blende and Rock Salt. The methodology of the current investigating work aims to determine the stability of complex metal halides crystal structures.

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

I. INTRODUCTION

Experimentally several investigators [1-15] observed that both AgI and CuI undergo a first order transition from Tetragonal to Rock salt structure on addition of pressure.

However, very few theoretical attempts have been made to explain the structural properties of an intermediate phase transition of the complex 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 halides using a suitable inter-ionic interaction energy model.

Several workers[16-31] 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 can vary from 0 to 1 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. METHODOLOGY & 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

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

$$U_{BT}(r) = -\frac{\alpha'_M z^2 e^2}{r'} - \frac{C}{r^6} - \frac{D}{r^8} + n'b\beta_{ij} \exp\left(\frac{r_i+r_j-r'_{ij}}{\rho}\right) + n'_1 b\beta_{ij} \exp\left[\frac{2r_i-Kr'_{ij}}{\rho}\right] + n'_1 b\beta_{ij} \exp\left[\frac{2r_j-Kr'_{ij}}{\rho}\right] - \frac{C'}{r'^6} - \frac{D'}{r'^8}$$

(3)

Where $\alpha_M(\alpha'_M)$ are the Madelung constants for ZnS and tetragonal structure. (n, n') and (n_1, n'_1) 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 dipole-quadrupole(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 according to the equation

$$a(A_x B_{1-x} C) = xa(AC) + (1-x)a(BC) \quad (4)$$

β_{ij} are Pauling coefficients defined as

$$\beta_{ij} = 1 + \frac{Z_i}{n_i} + \frac{Z_j}{n_j} \quad (5)$$

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

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

$$\left.\frac{d^2U(r)}{dr^2}\right|_{r=r_0} = 9Kr_0 B_0 \quad (6)$$

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 system is stable when the values of Gibb's Free energy G is minimum. The expression for G is given as

$$G = U + PV - TS \quad (7)$$

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

$$G_{B3} = U_{B3}(r) + PV_{B3}(r) \quad (8)$$

$$G_{BT} = U_{BT}(r) + PV_{BT}(r) \quad (9)$$

where U_{B3} and U_{BT} are the lattice energy for ZnS and tetragonal structures.

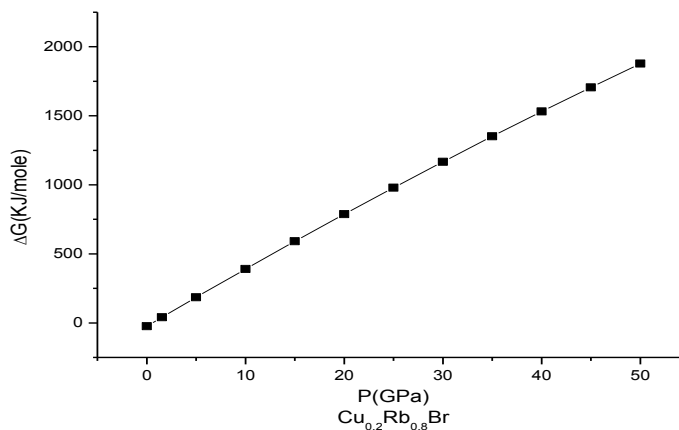
The volumes for the two phases are given by

$$V_{B3} = 3.08 * r^3 \quad (10)$$

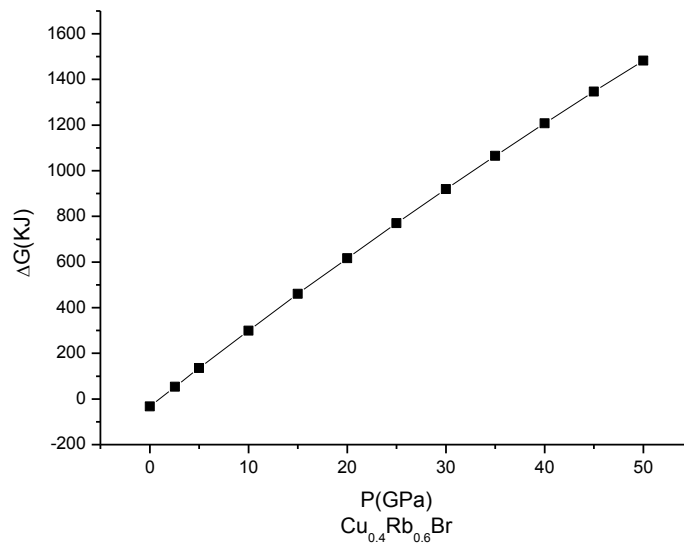
$$V_{BT} = 2.00 * r'^3 \quad (11)$$

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

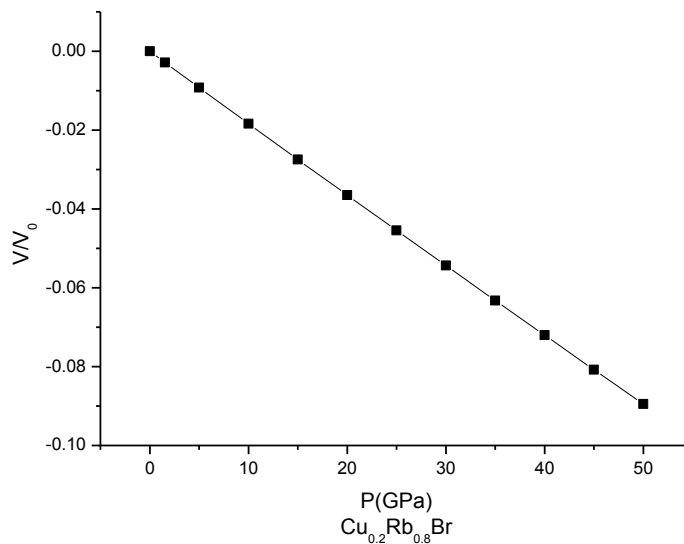
III. GRAPHS



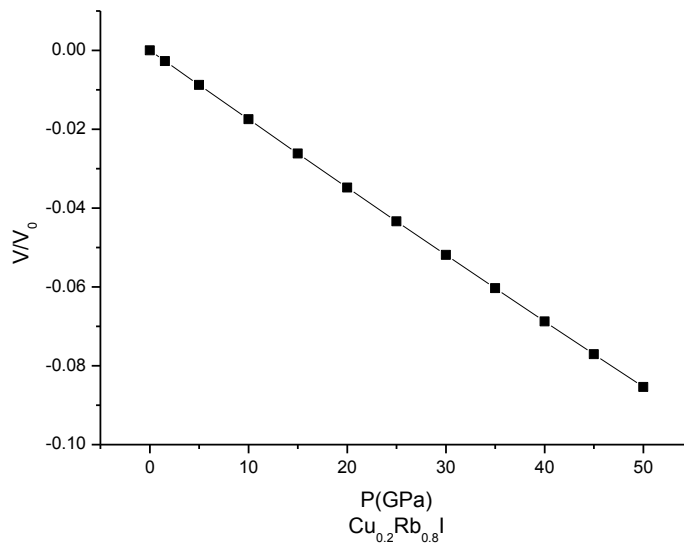
Variation of Gibb's energy with pressure(GPa) for $Cu_{0.2}Rb_{0.8}Br$



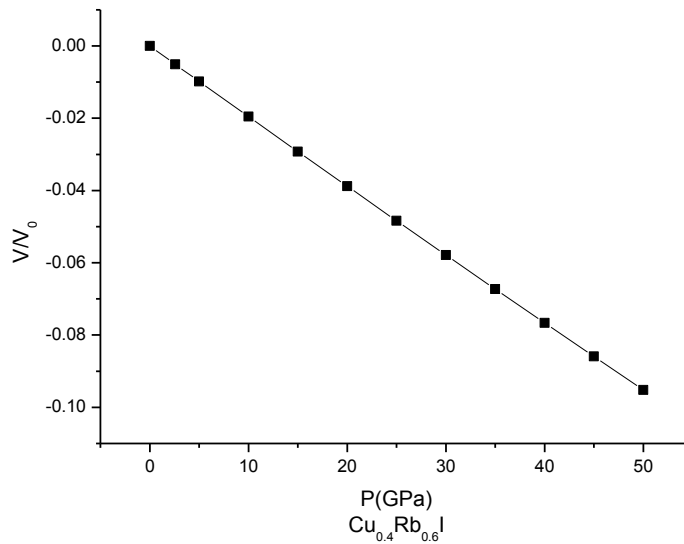
Variation of Gibb's energy with pressure(GPa) for Cu_{0.4}Rb_{0.6}Br



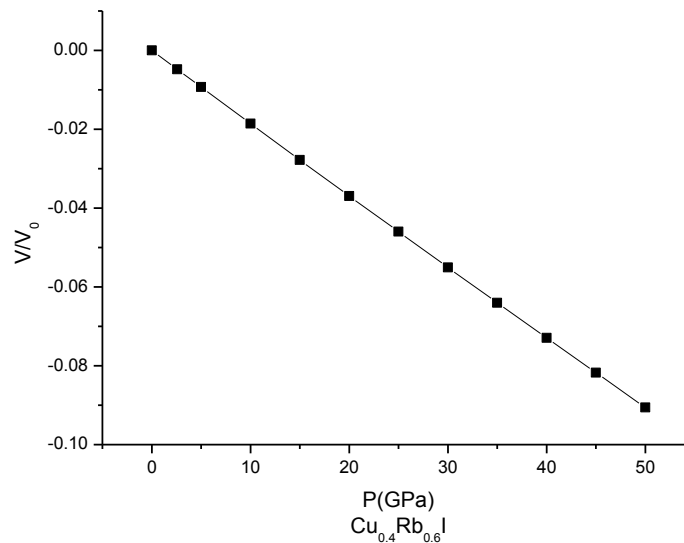
Graph of Volume versus Pressure(GPa)of Cu_{0.2}Rb_{0.8}Br for ZnS Structure



Graph of Volume versus Pressure(GPa)of Cu_{0.2}Rb_{0.8}I for tetragonal Structure



Graph of Volume versus Pressure(GPa)of Cu_{0.4}Rb_{0.6}I for ZnS Structure



Graph of Volume versus Pressure(GPa)of $\text{Cu}_{0.4}\text{Rb}_{0.6}\text{I}$ for Tetragonal Structure

IV. RESULT & CONCLUSION

The Gibb's free energy and volume collapses for the system under consideration have been determined for concentration =0.2 and 0.4. The two body potential model has come out quite successful in predicting the phase transition pressure for complex crystal under consideration. The phase transition pressure for the complex compound under consideration has been found to be 1.55 GPa for $x=0.2$ and 2.56 GPa for $x=0.4$. The current study establishes the stability of composite crystals in ZnS structure.

REFERENCES

- [1]. R. B. Jacobs , Phys. Rev. 54, 468 (1938)
- [2]. M. Born and J. B. Mayor, Z. Phys, 75, 1, (1932)
- [3]. J.E. Mayer: J.chem. phys.1(1933)327.
- [4]. D.W. Lynch: J.phys. chem.solids 28(1967)
- [5]. L. Bottger and A.L.Geddes: J.chem.phys 46(1969) 300
- [6]. K. Singh and H.N.Gupta : Proc. Roy. Soc(Lond) A349(1976)289
- [7]. R.K. Singh, and H.N.Gupta :and S.P Sanyal:2.Nuovo. Cimento 60B (1980)89
- [8]. K.S.Upadhyaya and P.S.Mahesh.phys.Status Solidi (b) 59(1973)279.
- [9]. R.K.Singh : current trend in lattice dynamic (IPA Publication, India
- [10]. G.Herzberg: Atomic spectra and Atomic structure (Van nostrand New York 1954) P. 219
- [11]. M.Born and K.Huang :Dynamical theory of Crystal.lattice (Clarendon Press , oxford ;1954)
- [12]. M. P. Tosi, Solid physics(Academic Newyork) Vol. 16 (1964)
- [13]. A.I.Cohen, M.L.Gordon phys rev b14 4593 (1976)
- [14]. J.E. Mayer: J.chem. phys.1(1933)327.
- [15]. M.F.C Ladd and W.H.Lee: Trans. FradaySoc.54(1958)34
- [16]. K.P.Thakur: J.Inog.Nucl.chem.38(1976)1433
- [17]. R.K. Singh and H.N.Gupta : Proc. Roy. Soc(Lond) A349(1976)289
- [18]. K.P.Thakur: J.Inog.Nucl.chem.38(1976)1433
- [19]. P.O.Lowdin: Ark.Mat .Fys(sweden)35A (1947) 30.
- [20]. R.K.Singh and V.V.S.Nirwal: phys Rev.B20 (1979)53 79.
- [21]. R.K. Singh and P.Khare :Proc.Nucl.phys .status Solidi (b)103 (1981)337.
- [22]. D.W.Hafemeister and W.H. Flygare: J.chem.phys.47(1967)1428
- [23]. A.DTandon and B.Yatis : j.phys C5 (1972) 1589
- [24]. M.I.Petrashen.L.V.Avrenkov and N.N.Kristofel: opt.spectrose 9(1960)
- [25]. C.kittle: Introduction to the solid state Phys(Wiley Eastern. Limited New ,Delhi 1976) P.75
- [26]. O Brafman ,M cardona and Z vardney phys rev. B 15 1081(1977)
- [27]. S.P.Sanyal;IT Nuovo cement 60b (1980) 89



- [28]. R.K. Singh and KP Singh phys. status solidi
B 78 (1976)677
- [29]. V.C. Jain and Jai Shankar pramana 13 (1979)
31
- [30]. D.W. Hafemeister and J.D.Zaraht j.chem.
phys. phys 47 (1967) 1428
- [31]. LW Stock, J.Phys.Chem. B25, 441, 31
(1956)