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Analysis of Structural Phase Stability of Strontium Sulphide under High Pressure

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Abstract

A three body interaction potential ($TBIPZ_{pe}$) model is developed to study the structural phase stability of SrS having NaCl (B_1) structure at room temperature. This model consists of long range Columbic, three body interaction forces, short range overlap forces operative up to next nearest neighbors and zero point energy effects. We have reported the phase transition pressure, volume collapse and second order elastic constants and found results well agreed with available experimental data.

Keywords: Phase transition, second order elastic constants, three body forces and zero point energy.

Introduction

The chalcogenides of strontium SrX (X = S, Se, Te) crystallize in the rock salt structure at normal temperature and forms a much closed shell ionic system with other alkaline earth chalcogenides. The majority of the compounds of strontium undergo a structural phase transition from the NaCl structure having coordination number 6 transforms to CsCl structure having coordination number 8 at a high pressure. Hence, in phase changes from NaCl to CsCl the coordination number changes from 6 to 8[1]. These chalcogenides are technologically important because of their applications in the area of luminescent devices, radiation dosimetry, fast high resolution, optically stimulated luminescence imaging and infrared sensitive devices[2-5].

SrS was found to undergo the structural phase transition by X-ray diffraction experiment at 18 GPa[4]. The structural phase transition and elastic constants of SrS are also reported by Khenata et al.[6]. B.Y.Thakore et al.[7] found the structural phase transition of SrS at 17.95 GPa by using plane wave pseudopotential density functional theory.

The electronic band structure and optical property of SrS are mainly discussed in other literatures[8-10]. In the present article, an effort has been devoted to develop an improved potential model, which has three-body interaction potential ($TBIPZ_{pe}$) and zero point energy effects. Due to this, our result shows a reasonable agreement with the available experimental data. The incorporation of zero point energy effects seems essential as it is the ground state energy of the compound which is the lowest energy a compound may acquire. It is well known that at T=0K the energy of a compound cannot be zero but ½ ($h\nu$). This term**,** produces a very less effect, as far as Gibbs free energy is concerned, yet cannot be neglected completely.

Material and Methods

Pressure on materials causes a variation in volume which leads to an increased charge transfer (three body interaction effects)[11] due to deformation of the overlapping electron shells of the adjacent ions. This interaction becomes more important to consider because ions experience sufficient overlap due to the decrease in inter-ionic spacing of the lattice crystal when pressure gets increased. Besides, increase in overlap energy, the charge is transferred due to the overlap in electron shells, changes the ionic charge which in turn alters the coulomb energy by a factor

$$\left[1+\left(\frac{2n}{z}\right)\mathrm{f}(\mathrm{r})\right]$$

where n and z are respectively the number of electrons in outermost shell and ionic charge of the compound. The $f(r)$ is the TBI parameter and it depends on the nearest neighbor distance (r)[12] as

$$f(r) = f_0 e^{-r/p} \quad (1)$$

Where f_0 is a constant and ρ is the range parameter. To achieve the stability for a crystal structure, the effect of TBI has been incorporated in the Gibbs free energy (G=U+PV-TS). Here U is the internal energy at T=0K, S is the entropy, pressure P and volume V. The Gibbs free energy for rock salt (B_1) and CsCl (B_2) structure at 0K can be stated by:

$$G_{B_1}(r) = U_{B_1}(r) + PV_{B_1} \quad (2)$$

$$G_{B_2}(r') = U_{B_2}(r') + PV_{B_2} \quad (3)$$

The first terms in the energies in equation (2) and (3) are lattice energies for B_1 and B_2 structures. Their expressions are:

$$U_{B_1} = \frac{-\alpha_m e^2 z^2}{r} - \frac{(12\alpha_m e^2 zf(r))}{r} + 6b\beta_{ij}\exp(\frac{r_i + r_j - r}{\rho}) + 6b\beta_{ii}\exp(\frac{2r_i - 1.414r}{\rho}) + 6b\beta_{jj}\exp(\frac{2r_j - 1.414r}{\rho}) + (0.5)h\left\langle w^2\right\rangle^{1/2}_{B_1} \quad (4)$$

$$U_{B_2} = \frac{-\alpha' m e^2 z^2}{r'} - \frac{(16\alpha' m e^2 zf(r'))}{r'} + 8b\beta_{ij}\exp(\frac{r_i + r_j - r'}{\rho}) + 3b\beta_{ii}\exp(\frac{2r_i - 1.154r'}{\rho}) + 3b\beta_{jj}\exp(\frac{2r_j - 1.154r'}{\rho}) + (0.5)h\left\langle w^2\right\rangle^{1/2}_{B_2} \quad (5)$$

β_{ij} is the Pauling coefficient, $r_i(r_j)$ is the ionic radii of i(j) ions, ρ and b are range and hardness parameters respectively.

$\left\langle w^2\right\rangle^{1/2}$ is known as the mean square frequency related to Debye temperature θ_D as

$$\left\langle w^2\right\rangle^{1/2} = k(\theta_D)/h \quad (6)$$

Here Θ_D can be expressed by Blackman's formula[12].

$$\theta_D = \frac{h}{k}\sqrt{\frac{5rB_T}{\mu}} \quad (7)$$

where B_T and μ are the bulk modulus and reduced mass of the compounds. The first term in equations (4) and (5) are long-range Columbic, second terms are three body interaction forces for B_1 and B_2 phases, third terms are the short range overlap repulsion for (i, j) ions, fourth and fifth terms are overlap repulsive term extended up to next nearest neighbor ions within Hafemeister and Flygare approach[13] and the last term is zero point energy[12].

Here, V_{B1} (=2.00 r^3) and V_{B2} (=1.54 r^3) represent the unit cell volumes for B_1 and B_2 phases, respectively. The Gibbs free energy is equivalent to enthalpy at 0K.The relative stability condition of the two phases may be expressed as $\Delta G = G_{B2} \sim G_{B1}$, where G_{B1} and G_{B2} are the Gibbs free energies for rock salt (B_1) and CsCl (B_2) structure. The pressure at which $\Delta G \rightarrow 0$ is the phase transition pressure P_t which is associated with a sudden collapse in volume. This shows that the phase transition is of first order.

To understand the elastic properties, we have to calculate the second order elastic constants (SOECs), (C_{11}, C_{12} and C_{44}) at room temperature 0 K. For calculating the value of SOECs we have to determine the value of three model parameters (b, ρ, f(r)) namely hardness, range and three body force parameter. The values of b, ρ and f(r) have been determined by solving the equilibrium conditions using the measured values of the equilibrium inter-ionic separation (r).

$$\frac{dU}{dr} = 0 \text{ and } \frac{d^2U}{dr^2} = 9kB_T r$$

Here, B_T is isothermal bulk modulus and k=2 for B_1 phase.

Results and Discussion

The relative stability of the two phases were obtained by minimizing the lattice energies in both real and hypothetical phases at different pressures corresponding to equilibrium inter-ionic separation r(r') using the model parameters as listed in table-1. The phase transition pressure and volume collapse are listed in table-2. The second order elastic constants are listed in table-3. The calculated value of phase transition pressure (P_t= 17.97 GPa) is in reasonable agreement with experimental value (P_t= 18 GPa). The variation of ΔG with pressure for SrS is shown in figure-1.

Table-1
Input data and model parameters

Input parameters		Model parameters		
r	**B_T (GPa)**	**b(×10^{-12}ergs)**	**ρ(Å)**	**f(r)**
3.012	58[a]	10.7592	0.475	-0.049972

[a]Ref. [4]

Table-2
Calculated transition pressure and volume collapse

Transition	Transition Pressure (GPa)	Volume collapse (%)
B_1-B_2	17.97 (present)	11.1 (present)
	18 (exp)[a]	11.4 (exp)[b]
	18.3 (other)[c]	10.8 (other)[d]

[a]Ref. [4] , [b]Ref. [14] ,[c]Ref. [15], [d]Ref. [16]

Table-3
Calculated elastic constants

Elastic constants (GPa)	Present	Others
C_{11}	132.9	113.9[a]
C_{12}	25.7	19.4[a]
C_{44}	38.95	30.3[a]

[a]Ref. [17]

The values of relative volume change (Vp/Vo) associated with various compressions have been obtained and plotted against pressure in figure-2 for SrS. The calculated value of volume collapse is in good agreement with other theoretical values. We have plotted the variation of elastic constant with pressure in figure-3. The calculated values of, C_{11}, C_{12} and C_{44} is in good agreement with other theoretical values.

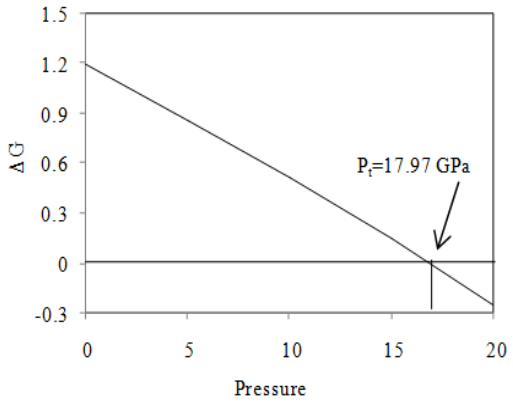

Figure-1
Variation of Gibb's free energy with pressure

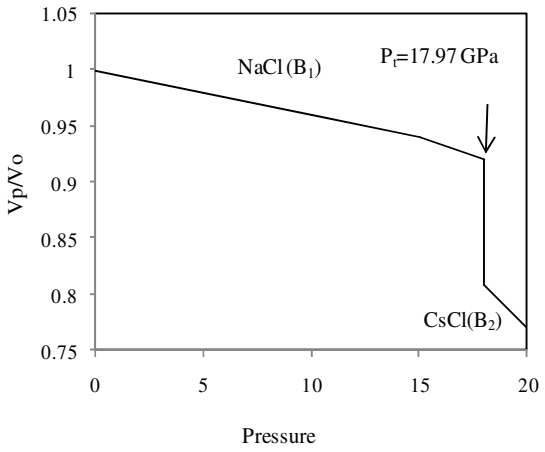

Figure-2
Variation of Vp/V$_0$ with pressure

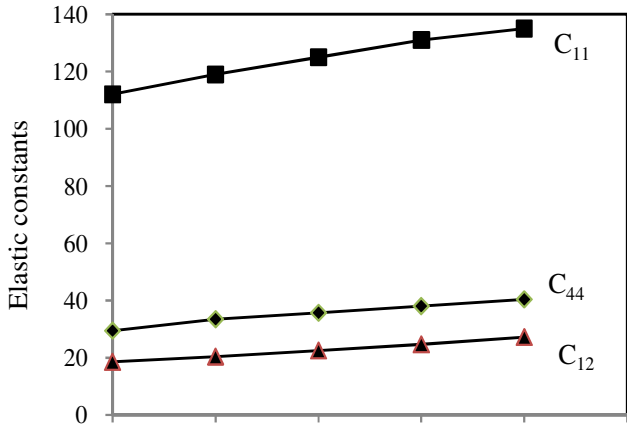

Figure-3
Variation of SOECs with pressure

Conclusion

Finally, we can conclude that the three body interaction potential (TBIPZ$_{pe}$) model has yielded more precise predictions of the structural, elastic and phase transition of SrS from NaCl to CsCl structure.

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References

1. Bhardwaj P. and Singh S., Investigation of SrS under High pressure including the role of temperature, *Measurement*, **46,** 1161-1168 **(2013)**

2. Khenata R., Baltache H., Rerat M., Driz M., Sahnoun M., Bouhafs B., Abbar B., Structural, electronic, elastic and high pressure properties of some alkaline earth chalcogenides: An ab-initio study, *Physica B*., **371**, 12-19 **(2006)**

3. Zimmer H.G., Winze H. and Syassen K., High-pressure phase transitions in CaTe and SrTe, *Phys. Rev.B,* **32** 4066-4070 **(1985)**

4. Syassen K., Pressure induced structural transition in SrS, *Phys. Stat. Sol. (a),* **91,** 11 **(1985)**

5. Chakrabati A., Role of NiAs phase in pressure induced phase transitions in IIA-VI chalcogenides, *Phys. Rev B,* **62**, 1806-1814 **(2000)**

6. Khenata R, Baltyache H., Rerat M. Driz M., Sahnoun M., Bouhafs B., Abbar B, First principle study of structural, electronic and elastic properties of SrS, SrSe and SrTe under pressure, *Physica B,* **339**, 208-215, **(2003)**

7. Thakore B.Y., Vahora A.Y., Khambholja S.G., Bhatt N.K. and Rani A.R., Pressure induced structural phase transition in SrS, *Journal of Physics: Conference series*, **377**, 012064 **(2012)**

8. Pandey R., Jaffe J.E. and Barry Kunj, Ab-initio band structure calculations for alkaline earth oxides and sulphides, *Phys. Rev. B,* **43**, 9228 **(1991)**

9. Stepanyuk V.S., Band structure calculation and optical properties, *Phys. Stat. Sol.,* **155,** 215 **(1989)**

10. Ching W.Y., Gan F. and Haung M.Z., Band theory of linear and non linear susceptibilities of some binary ionic insulators, *Phys. Rev. B,* **52,** 1595 **(1995)**

11. Singh R. K., Many body interactions in binary ionic solids, *Phys. Rep. (Netherlands),* **85,** 259-401 **(1982)**

12. Singh R.K., Neb D.K. and Sanyal S.P., Many body interactions in rare-gas solid mixtures, *J. Phys. C,* **16,** 3409-3423 **(1983)**

13. Hafemeister D.W. and Flygare W.H., Outer-shell overlap integrals as a function of distance for halogen-halogen, halogen-alkali, and alkali-alkali ions in the alkali halides lattices, *J. Chem. Phys*., **43** 795-800 **(1992)**

14. Ross M. and McMohan A.K., Systematics of the s→d and p→d electronic transition at high pressure for the elements I through La, *Phys. Rev. B,* **26,** 4088 **(1982)**

15. Kholiya K. and Gupta B.R.K, Theoretical investigation of phase transition properties in strontium chalcogenides using potential model, *Phase Transitions,* **81,** 403 **(2008)**

16. XiaO-Cui Y., H. Ai-Min, Y Jie, H Yong-Hao, P Gang, G Chun-Xiao and Z Guang-Tian, Chin Theoretical prediction for structural stabilities and optical properties of SrS, SrSe and SrTe under high pressure, *Phys. Lett*., **25,** 1807 **(2008)**

17. Chang Yan, IU Lai-Yu, JIA ou-He and GOU Qing-Quan, First-principle calculations for transition phase and elastic properties of SrS, *Commun Theor. Phys*., **49,** 1611 **(2008)**