Effect of Temperature on Structural Properties of Rare Erath Chalcogenides

Purvee Bhardwaj
High pressure Research Lab., Department of Physics, Barkatullah University, Bhopal-462026, India

Sadhna Singh
High pressure Research Lab., Department of Physics, Barkatullah University, Bhopal-462026, India.

The research is financed by Asian Development Bank. No. 2006-A171(Sponsoring information)

Abstract

In this study, the calculated results of the structural properties of ThX (X=S and Se) rare earth chalcogenides in rocksalt structure (B1) are presented. The Realistic Interaction Potential Approach (RIPA) model has been developed and used. A sudden collapse in volume has been occurred at phase transition pressures. At compressed volumes, these compounds are found in CsCl phase. Phase transition pressures have been reported at room and high temperature range 0-1000K. The phase transition pressures and associated volume collapses obtained from present potential model show a generally better agreement with available experimental and others results.

Keywords: Phase transition, High pressure, Crystal structure, Elastic properties.

1. Introduction

The rare-earth materials have attracted great attention both theoretically and experimentally because of their structural, magnetic, optical and electronic properties. Due to this reason new researchers have been focused on understanding their physical properties and practical application. These rare earth compounds provide an elementary explanation of their physical properties and also forming a wide range of magnetic structures [1-6]. Among these compounds the thorium monochalcoginides form a very important closed shell ionic system. Thorium compounds show valence fluctuation due to hybridization of the unstable f-band. They have paid attention because of their high density, good thermal conductivity. They have interesting applications in nuclear material for reactor composites and high strengths structures. The thorium monochalcoginides (ThX; X=S and Se) crystallize in NaCl-type structure (B1) at ambient conditions with space group F*m*3m (225). The thorium atom is positioned at (0;0;0) and the chalcogen atom at (1/2,1/2,1/2). At high pressure the most of these compounds have been found to undergo a first-order phase transition from the sixfold-coordinated NaCl structure to eightfold coordinated CsCl-type structure (B2) with the P*m*3*m* space group.

The X-ray diffraction measurements show that the structural phase transformation form B1 to B2 phases appear at 23-33 and 15 GPa for ThS and ThSe respectively [7,8]. Comparative aspects of the high-pressure behaviour of ThX, CeX and PuX compounds [9]. The Debye temperature of thorium compound has been reported by Thakur [10]. The structural and elastic properties of thorium chalcogenides at high pressure have been investigated using a suitable inter-ionic potential by Aynyas et al. [11]. The anharmonic elastic properties of thorium chalcogenides (ThS and ThSe) having NaCl-type structure under high temperature (100–1000 K) using Born-Mayer repulsive potentials and the long- and short-range interaction approach have been studied by Raju et al. [12]. The pressure induced phase transition and thermo-elastic properties of Th-chalcogenides have been investigated by means of two different models (i) modified charge-transfer potential model which consists of Coulomb and Coulomb screening due to delocalization of f-electron of the rare-earth atom and modified by covalency and zero-point energy effects and repulsive interactions, and (ii) charge transfer model which excludes covalency and zero-point energy effects in the previous model by Gupta et al. [13].

Seeing that thorium compounds are less reported in the literature, we have studied the structural properties using the Realistic Interaction Potential Approach (RIPA) model. The theoretical calculations are performed at zero temperature while experiments are carried out at room temperature and not at T=0K. This fact causes discrepancy in comparability of theoretical results with experimental data. For obtaining better comparability of theoretical results we have taken account of the room temperature in pressure induced theoretical calculations. The main aspire of the present paper is to study the structural properties at room and high temperatures.

2. Potential Model and Method of Calculation

Pressure causes a change in the volume of the crystal, and consequently it alters the charges distribution of the electron shells. As a result of this, a deformation of the overlapping electron shells of the adjacent ions takes place which leads to an increased charge transfer (or three body interaction (TBI) [14]). The f (r) is the TBI parameter and is dependent on the largest neighbour distance (r) as

$$f(r) = f_0 \exp(-r/\rho) \qquad (1)$$

Here, f_0 is a constant.

The effect of TBI is introduced in the expressions of Gibbs free energy (G = U+PV-TS), in order to obtain the stability condition for a crystal structure. Here, U is the internal energy, which at T=0K is equivalent to the lattice energy, P is the pressure, V is the volume and S is the entropy.

The Gibbs free energies for rock-salt (NaCl, B1) and cesium-chloride (CsCl, B2) structures at room temperature T=300K are given by:

$$G_{B_1} = U_{B_1}(r) + P(2.0r^3) - TS_1 \qquad (2)$$

$$G_{B_2} = U_{B_2}(r') + P(1.54r'^3) - TS_2 \qquad (3)$$

With V_{B1} ($=2.00r^3$) and V_{B2} ($=1.54r'^3$) as unit cell volumes S_1 and S_2 are the entropies for B_1 and B_2 phases respectively. In fact the condition for a transition is that the difference in free energy between two phases should approach to zero.

$$\Delta G = \Delta H - T\Delta S$$

The first terms in (2) and (3) are lattice energies for B_1 and B_2 structures and they are expressed as:

$$\begin{aligned} U_{B_1}(r) = {} & \frac{-\alpha_m z^2 e^2}{r} - \frac{(12\alpha_m z e^2 f\ (r))}{r} - [\frac{C}{r^6} + \frac{D}{r^8}] \\ & + 6b\beta_{ij}\exp[(r_i + r_j - r)/\rho + 6b\beta_{ii}\exp[(2r_i - 1.414r)/\rho] \\ & + 6b\beta_{jj}\exp[(2r_j - 1.414r)/\rho] \qquad (4) \end{aligned}$$

$$\begin{aligned} U_{B2}(r') = {} & \frac{-\alpha'_m z^2 e^2}{r'} - \frac{(16\alpha'_m z e^2 f(r'))}{r'} - [\frac{C'}{r'^6} + \frac{D'}{r'^8}] \\ & + 8b\beta_{ij}\exp[(r_i + r_j - r')/\rho] + 3b\beta_{ii}\exp[(2r_i - 1.154r')/\rho] \\ & + 3b\beta_{jj}\exp[(2r_j - 1.154r')/\rho] \qquad (5) \end{aligned}$$

With α_m and α'_m as the Madelung constants for NaCl and CsCl structures respectively. C (C') and D (D') are the overall van der Waals (vdW) 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. S_1 and S_2 are the entropies for NaCl (CsCl) structure.

The first term in Eqs.(5) and (6) are long range Coulomb energy, second terms are three body interactions corresponding to the nearest neighbour separation r(r') for B1 (B2) phases, third terms are vdW (van der Waals) interaction, fourth, terms are the energy due to the overlap repulsion represented by Born-Mayer potential for (i,j) ions, fifth and sixth terms are the overlap repulsive term extended up to the second neighbour ions by using Hafemeister and Flygare (HF) type potential. Now the entropy differences in the last term of Eqs. (2) and (3) can be calculated from the relation used by our earlier work [15-17]

$$S_1 - S_2 = \int_1^2 \left[\frac{C_1 - C_2}{T} \right] \qquad (6)$$

here, 1 and 2 stands for the B1 and B2 phases, C_1 and C_2 are the specific heats of the two phases at constant pressure and their values can be calculated by the knowledge of Gruneisen parameter (γ) and linear isothermal temperature coefficients

$$C_i = \frac{\{\beta V_i B\}_i}{\gamma_i} \qquad (7)$$

here, Gruneisen parameter (γ) can be calculated by well known formula as follows [15-17]

$$\gamma = -r_0 / 6\left[U'''(r_0) / U''(r_0)\right] = -r_0 / 6\rho \qquad (8)$$

The three model parameters b (hardness), ρ (range) and f(r) (three body force parameter) have been derived from equilibrium condition:

$$\left[\frac{dU}{dr}\right]_{r=r_0} = 0 \qquad (9)$$

and the bulk modulus

$$B = \frac{1}{9kr_0}\left[\frac{d^2U}{dr^2}\right]_{r=r_0} \qquad (10)$$

Where k is the crystal structure dependent constant and r_0 is the lattice constant.

3. Results and Discussion

At first we estimate the input crystal parameters and then calculate the model parameters of the present thorium compounds. These input [7] and output parameters have been given in Table-1.

Table-1 Input parameters and generated model parameters for ThS and ThSe.

Solid	**Input Parameters**		**Model Parameters**		
	r_0 (Å)	**B (GPa)**	**b(10^{-12} ergs)**	**ρ(Å)**	**f (r)**
ThS	2.842^a	145.0^a	18.9654	0.262	0.01041
ThSe	2.945^a	125.0^a	15.3712	0.213	0.01098

a-ref [7]

The present compounds are stable in rock-salt (NaCl) structure and at high pressure they transform to body centred caesium (CsCl) structure. The structural properties of these thorium compounds have been calculated using the technique of minimization. At a particular pressure the Gibbs free energy difference ΔG approaches zero (ΔG→0). This is called phase transition pressure (P_t). At this phase transition pressure these compounds undergo a (B1-B2) transition associated with a sudden collapse in volume showing a first order phase transition. We have plotted the Gibbs free energy difference ΔG with pressure in Fig. 1 and 2 at different temperatures for ThS and ThSe respectively.

The computed values of phase transition pressure and volume collapse are tabulated in Table-2 along with the experimental [8] and theoretical results [7,11,13,18]. The present calculated value of phase transition pressure is 25.0 GPa and 14.2 GPa respectively for ThS and ThSe which is in better agreement with experimental value 23-33 GPa [7] and 15 GPa [8] than others theoretical values, 24.78 GPa [13], 23.98 GPa [13], 19.20 GPa [11] and 100.0 GPa [18] for ThS and 14.0 GPa [13], 13.0 GPa [13] and 15.20 GPa [11] for ThSe. For studying the temperature behaviour of phase transition pressure we have computed the values of phase transition pressure at the temperature range 0-900K. This variation has been plotted in Fig. 3 for ThS and ThSe respectively. It is apparent from this figure that when we increase temperature the phase transition pressures decrease for the present compounds.

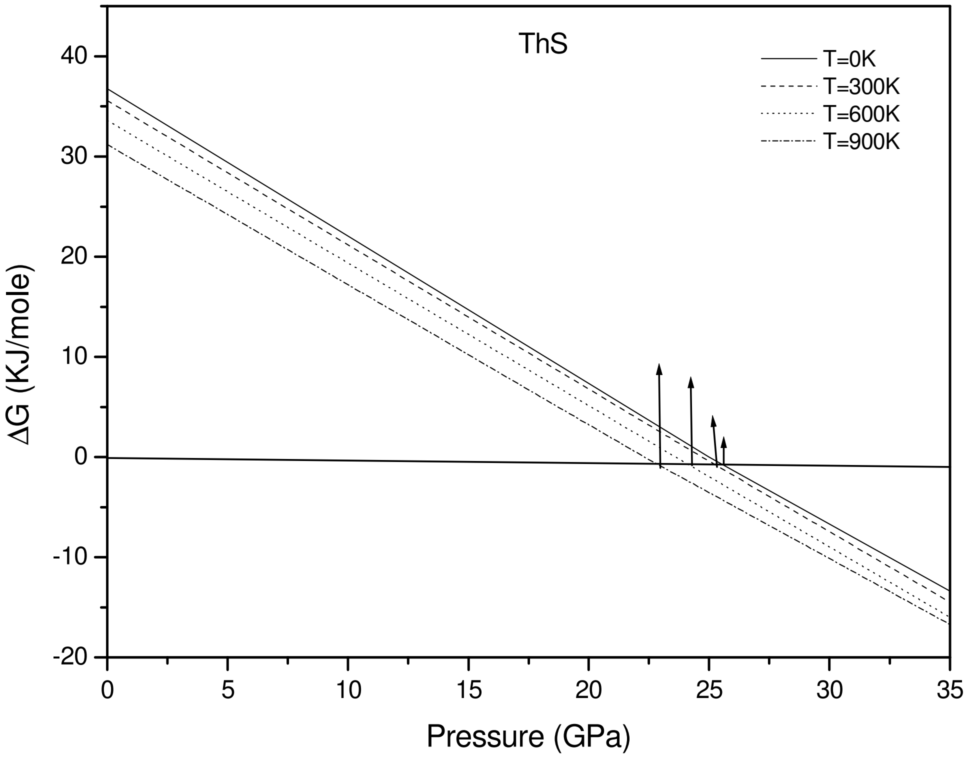

Fig: 1 Variation of ΔG (KJ/mole) with pressure for ThS at different temperatures

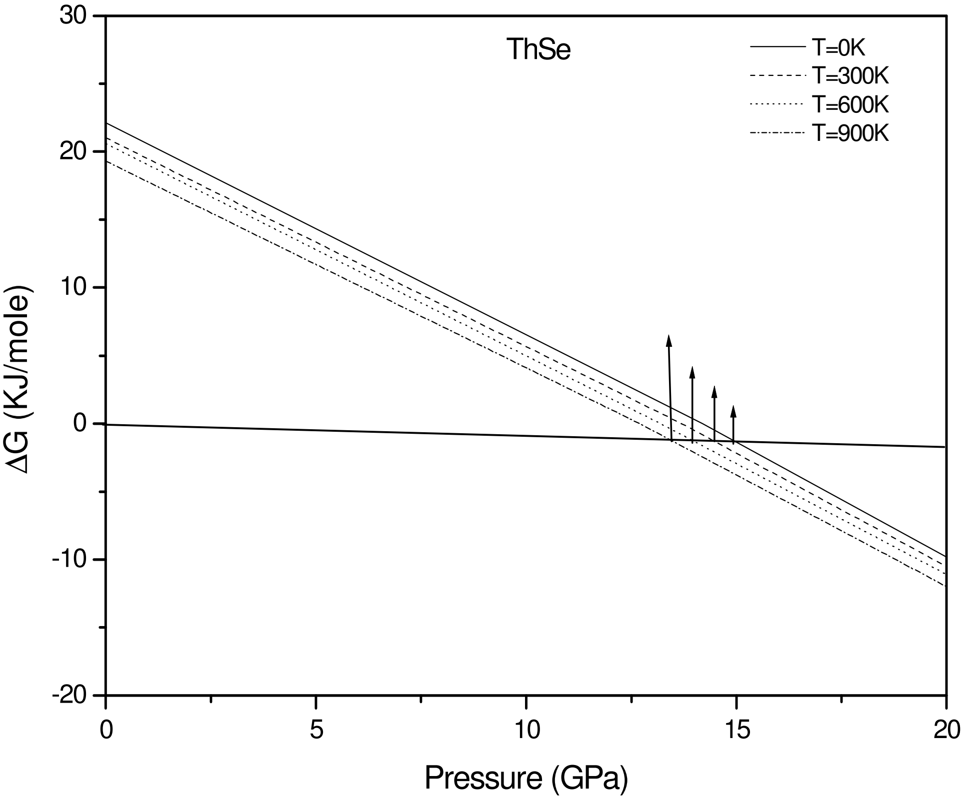

Fig: 2 Variation of ΔG (KJ/mole) with pressure for ThSe at different temperatures.

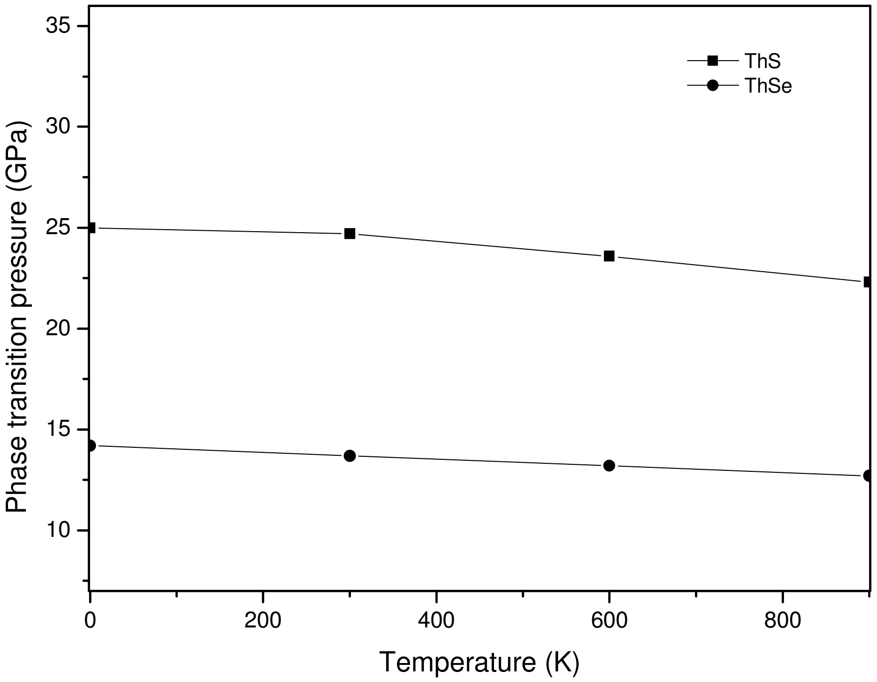

Fig: 3 Variation of phase transition pressure with temperature range 0-900K for ThS and ThSe.

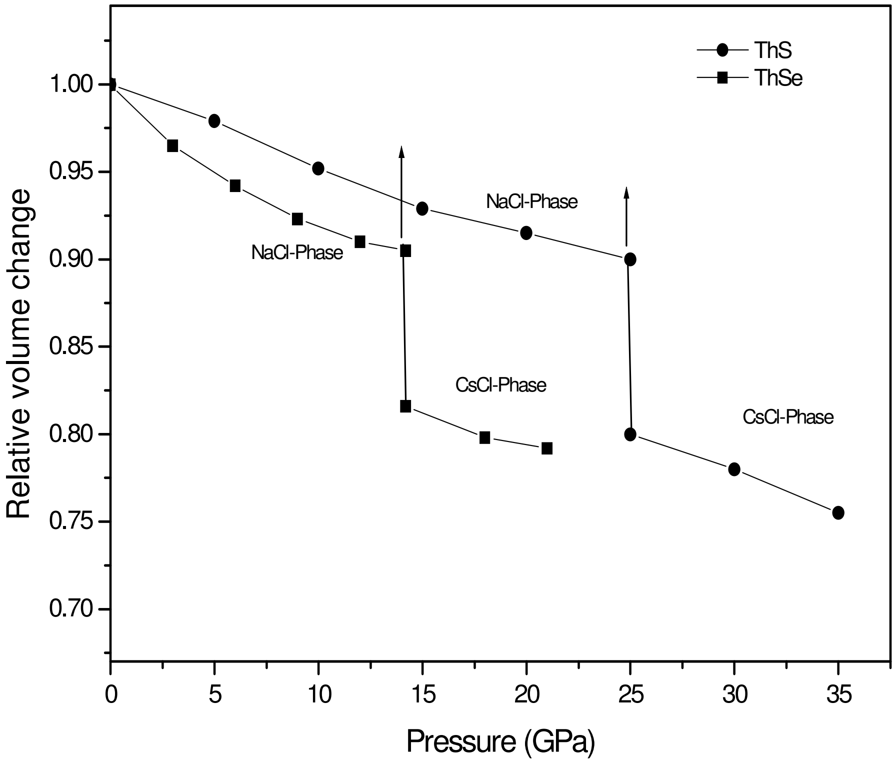

Fig: 4 Volume change with pressure, solid circles and solid squares represent for ThS and ThSe respectively.

Table-2 Phase transition and volume change of plutonium pnictides.

Solid	Phase Transition Pressure (GPa)			Volume Collapse %		
	Present	Expt.	Others	Present	Expt.	Others
PuAs	35.5	35-38[a]	35.0[b]	8.7	9.0[a]	8.6[b]
PuSb	21.0	20[a],40[a]	20.8[b]	7.2	4.0[a], 9.0[a]	6.9[b]

a-ref [2], b-ref [11]

Table-3 Calculated values of second order elastic constants (SOEC's) (in GPa), bulk modulus (in GPa), and pressure derivative of bulk modulus of plutonium pnictides.

Solid	C_{11}	C_{12}	C_{44}	B	dB/dP
PuAs	150	27	31	68	2.01
Others	152[a]	25[a]	25[a]	67[a]	-
Expt.	-	-	-	69[b]	-
PuSb	155	25	29	68.33	1.91
Others	158[a]	21[a]	21[a]	67[a]	-
Expt.	-	-	-	68[b]	-

a-ref [11], b- ref [12]

The structural phase transition associated with a sudden change in the arrangement of the atoms. The atoms are rearranged in new positions. The discontinuity in volume at the transition pressure is obtained from the phase diagram. We have also computed the relative volume changes V/V_0 at different pressures and plotted them against the pressure in Fig. 4 for ThS and ThSe. It is clearly seen from this figure that solid squares and solid circles represent the B1 and B2 phases for ThS and ThSe respectively. It is revealed from these figures that this NaCl to CsCl transition shows this is first order phase transition. The calculated values of relative volume change (%) are given in Table-2. Our values are 10.0% and 8.9% for ThS and ThSe respectively compared with experimental 9.0% [8] only available for ThSe and theoretical results 8.92% [13], 8.11% [13] and 11.50% [11] and 9.13% [13], 8.97% [13] and 9.50% [11]. Our results are in good agreement with available literature.

4. Conclusion

In conclusion, we can conclude that the Realistic Interaction Potential Approach (RIPA) model successfully investigates the phase transition and volume collapse of the present thorium compounds at high temperature and pressure. The main outcomes are as follows:

1. The present thorium compounds crystallize in six fold coordinated NaCl-type structure (B1) at ambient conditions and under pressure, they transform to the eightfold-coordinated CsCl-type structure (B2).
2. The calculated B1 to B2 phase transition pressures and volume collapse agree well with available experimental and theoretical results.
3. At the phase transition pressure, the discontinuity in volume identifies the occurrence of first order phase transition.
4. The temperature variation phase transition pressure show the same behaviour as reported previously.

ACKNOWLEDGEMENT

Authors are thankful to Department of Science & Technology (DST), New Delhi for the financial support to this work. One of the authors (PB) is grateful to Department of Science & Technology (DST), New Delhi for, awarding WOS-'A'(Grant no. SR/WOS-A/PS-17/2013).

References

1. L. Petit, R. Tyer, Z. Szotek, W.M. Temmerman, A. Svane, New J. Phys. 12 (2010) 113041.
2. G. Vaitheeswaran, L. Petit, A. Svane, V. Kanchana, M. Rajagopalan, J. Phys.: Condens. Matter 16 (2004) 4429.
3. J.M. Leger, Physica B. 190 (1993) 84.
4. J.S. Olsen, High Temp.-High Press. 20 (1988) 553.
5. M. De, P.K. Sinharoy, S.K. De, Phys. Lett. A 249 (1998) 147.
6. C.G. Duan, R.F. Sabirianov, W.N. Mei, P.A. Dowben, S.S. Jaswal, E.Y. Tsymbal., J. Phys.: Condens. Matter 19 (2007) 315220.

7. U. Benedict, J.C. Spirlet, L. Gerward, J.S. Olsen, J. Less-Com. Mat. 98 (1984) 301.
8. R.W.M. D'Eye, P.G. Sellman, J.R. Murray, J. Chem. Soc. (1952) 2555 (1954) 3760.
9. U. Benedict, Journal of Alloys and Compounds 223 (1995) 216-225.
10. K.P. Thakur, Aust. J. Phys. 30 (1977) 325.
11. M. Aynyas, N. Kaurav, S.P. Sanyal, J. Phys. Chem. Sol 63 (2002) 821.
12. K.M. Raju, Bulg. J. Phys. 37 (2010) 115–122.
13. D C Gupta and K C. Singh, Solid State Sciences 12 (2010) 1809-1815.
14. R. K Singh, Phys. Reports 85 (1982) 259.
15. P. Bhardwaj and S. Singh, phys. status solidi b, 249 (2012) pp. 38-49.
16. Purvee Bhardwaj and Sadhna Singh Current Applied Phys. 14 (2014) 496-507.
17. Purvee Bhardwaj and Sadhna Singh, J. of Material Science in Semiconductor Processing 31 (2015) 44-51.
18. V. Srivastava, S.P. Sanyal, High Press. Res. 23 (2003) 477.
19. L. Petit, A. Svane, W.M. Temmerman, Z. Szotek, Eur. Phys. J. B 25 (2002)139.