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Theoretical Investigation of Structural Phase Transition of Mixed Thorium Chalcogenides (ThS_xSe_{1-x}) under High Pressure and High Temperature

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ABSTRACT: We have theoretically investigated the phase transition pressure and volume collapse in the rare earth mixed compound ThS_xSe_{1-x} ($0 \leq x \leq 1$) using a realistic interaction potential model with polarization (RIPPM). This model consists of coulomb interaction, three body interaction, electronic polarizability and short range overlap repulsive interactions including temperature effects. Moreover, the phase transition pressures of mixed ThS_xSe_{1-x} crystal at high temperatures including the three-body interaction are done for the first time. We have calculated the phase transition pressure and volume collapses by using the Vegards Law from this approach and they are in good agreement with the experimental and other available data.

Keywords: Phase Transition, three body interaction, electronic polarizability, rare earth compound and volume collapses.

I. INTRODUCTION

The chalcogenides of rare earth (RE) have drawn the considered attention of theoretical and experimental researchers because of their diverse structural, magnetic and vibrational properties. These compounds possess partially filled f-electrons which are responsible for their anomalous behaviour. Shirotani *et.al* [1] used X-ray diffraction technique to predict the high pressure structural properties of these compounds. Among rare earth compounds the thorium chalcogenides show valence fluctuation due to hybridization of the unstable f-band and form a very important closed shell ionic system and possess high density, good thermal conductivity. The thorium monochalcogenides (ThX; X=S, Se, Te) crystallize in rocksalt structure (B_1) except ThTe which crystallize in CsCl-type (B_2) structure [2]. The thorium atom is positioned at (0,0,0) and the chalcogen atom at (1/2,1/2,1/2). At high pressure it was observed that ThS and ThSe have been found to undergo a first-order phase transition from the sixfold-coordinated rocksalt structure to eightfold coordinated CsCl-type structure.

The elastic properties of Thorium compounds (ThS and ThSe) using Born-Mayer repulsive potentials and the long- and short-range interaction approach under high temperature had been reported by Raju [3]. The structural phase transition for ThS and ThSe from B_1 to B_2 phases appear at 23-33 and 15 GPa respectively are shown by using the X-ray diffraction measurements [4, 5]. Anayas *et. al* [2] have analysed the phonon spectra of thorium chalcogenides and pnictides using the rigid ion and breathing shell models.

In the present paper we have studied the structural properties of present compounds by using a realistic interaction potential model with polarization (RIPPM). This model consists of coulomb interaction, three body interaction, electronic polarizability and short range overlap repulsive interactions including temperature effects. We have found that the results obtained from this approach are in fair agreement with available experimental and other data generated by applying Vegards law to experimental values available for end point materials.

II. METHOD OF COMPUTATION

The application of pressure causes a change in volume of the crystal, which leads to an increased charge transfer (three body interaction effects) [6] due to deformation of the overlapping electron shells of the adjacent ions. This interaction becomes more important to consider due to the decrease in inter-ionic spacing of the lattice crystal when pressure gets increased and when ions experience sufficient overlap. Besides, enhance in overlap energy, the transferred charge due to the overlap in electron shells, modifies the ionic charge which in turn modifies the Coulomb energy.

In order to obtain 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 it is equivalent to lattice energy, S is the vibrational entropy at absolute temperature T, pressure P and volume V.

The Gibbs free energy for rock salt (B_1, real) and CsCl (B_2, hypothetical) structure at 0K can be stated by:

$$G_{B_1}(r) = U_{B_1}(r) + PV_{B_1} - TS_1 \quad \ldots(1)$$

$$G_{B_2}(r') = U_{B_2}(r') + PV_{B_2} - TS_2 \quad \ldots(2)$$

The first terms in the energies in Eqns. (1) and (2) are lattice energies for B_1 and B_2 structures. The expressions of lattice energies are as follows:

$$U_{B_1}(r) = \left[\frac{-(\alpha_m z^2 e^2)}{r}\right] - \left[\frac{(12\alpha_m z e^2 f(r))}{r}\right] + \frac{\alpha_e e^2}{r^4} + 6\beta_{ij}\exp\left(\frac{r_i + r_j - r}{\rho}\right) \quad \ldots(3)$$

$$U_{B_2}(r') = \left[\frac{-(\alpha_m z^2 e^2)}{r'}\right] - \left[\frac{(16\alpha'_m z e^2 f(r'))}{r'}\right] + \frac{\alpha_e e^2}{r'^4} + 8\beta_{ij}\exp\left(\frac{r_i + r_j - r'}{\rho}\right) \quad \ldots(4)$$

where β_{ij} is the Pauling coefficient, $r_i(r_j)$ is the ionic radii of i(j) ions, $\rho(b)$ are range (hardness) parameters and α_e is electronic polarizability. The first terms in equations (3) and (4) are long-range Coulomb energy, second terms are three body interaction forces for B_1 and B_2 phases, third term is electronic polarizability [7] and last term is short range overlap repulsion represented by Hafemeister and Flygare approach [8].

with $V_{B_1} = 2.00r^3$ and $V_{B_2} = 1.54r'^3$ as the unit cell volumes for B_1 and B_2 phases, respectively.

Now the entropy differences in the last terms of equations (1) and (2) can be calculated from the relation used by Shanker *et al.* [9].

$$S_1 - S_2 = \int_1^2 \left[\frac{(C_1 - C_2)}{T}\right] dT \quad \ldots(5)$$

Here 1 and 2 stand for B_1 and B_2 phases, C_1 and C_2 are the specific heats of two phases at constant pressure. Their values can be calculated by the relation

$$C_i = \frac{\beta V_i B_T}{\gamma_i} \quad \ldots(6)$$

here, B_T, γ and β are the bulk modulus, the Gruneisen parameter and linear isothermal temperature coefficient respectively. We can calculate the Gruneisen parameter (γ) by well known formula [10] as

$$\gamma = \frac{-r_0}{6}\left[\frac{U'''(r)}{U''(r)}\right]$$

Here, U'''(r) and U''(r) are the third and second derivatives of lattice energy.

To calculate the value of lattice energies, one has to determine the value of three model parameters (b, ρ, f(r)) namely hardness ,range and three body force parameter. Their values have been determined by solving the equilibrium conditions using the measured values of the equilibrium inter-ionic separation (r).

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

Here, k = 2 for B_1 Phase.

According to the virtual crystal approximation, the mixes crystals are generally regarded as an array of average ions whose masses, force constants and effective charges are considered to scale linearly with concentration. The calculated data on lattice constants versus concentration vary linearly hence they follow Vegards law.

$$a(ThS_xSe_{1-x}) = a(x)AB + a(1-x)AC \quad \ldots(7)$$

The values of these model parameters are the same for end point members (AB-ThS) and (AC-ThSe). We have calculated the model parameters (b, ρ, F(r)) by using the Vegards law.

III. RESULTS AND DISCUSSION

We know that the stable phase is associated with minimum free energy of the crystal. In order to obtain structural phase transition, we have applied the condition of the relative stability of the two phases. It is 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 . It may be expressed as $\Delta G = G_{B_2} - G_{B_1}$, where G_{B_1} and G_{B_2} are the Gibbs free energies for rock salt (B_1, real) and CsCl (B_2, hypothetical) structure. The phase transition pressure P_t is the pressure at which $\Delta G \rightarrow 0$, shows a sudden collapse in volume showing that the phase transition is of first order.

The input parameters and model parameters for both compounds are listed in table 1. In order to study the temperature behaviour of phase transition pressure we have computed the values of phase transition pressure at the temperature range 0-600K for both compounds. The phase transition pressure and volume collapse for present compounds are listed in Table 2.

Table 1: Input parameters and model parameters.

Compounds	**Input parameters**			**Model parameters**		
	r(□)	**B_T (GPa)**	**α_e (□^{3})**	**b (10^{-12}erg)**	**ρ(□)**	**f(**
ThS	2.842[a]	145 [a]	5.448 [b]	16.1086	0.2425	-0.00608
ThSe	2.945 [a]	125 [a]	8.087 [b]	14.0829	0.2111	-0.02571

a-ref. [4], b-ref. [2]

Table 2: Calculated transition pressure and volume collapse.

Compounds	Temperature (K)	Transition Pressure (GPa)			Volume collapse (%)		
		present	exp	other	present	exp	other
ThS	0	24.32	23-33[a]	25.26[b]	13.30	-	11.5[c]
	300	22.5	-	-	13.45	-	-
	600	18.4	-	-	13.75	-	-
ThSe	0	19.75	15-20[d]	23.20[d]	9.6	9.1[d]	9.5[c]
	300	17.45	-	-	9.85	-	-
	600	15.02	-	-	10.15	-	-

a-ref. [4], b-ref. [11], c- ref. [12], d-ref. [13]

The calculated values of phase transition pressures for ThS and ThSe are 24.32 GPa and 19.75 GPa are found to be in reasonable agreement with experimental values. The variations of ΔG with pressure for present compounds are shown in fig. 1 and 2.

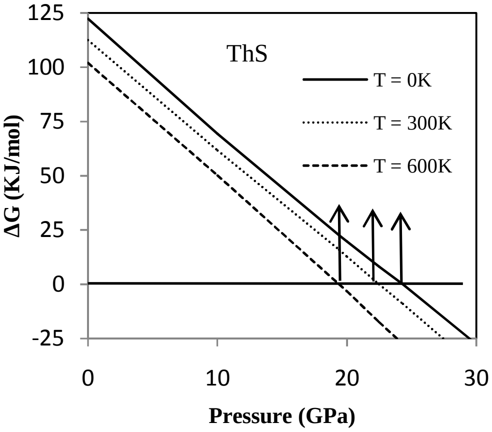

Fig. 1. Variation of Gibbs free energy with pressure for ThS.

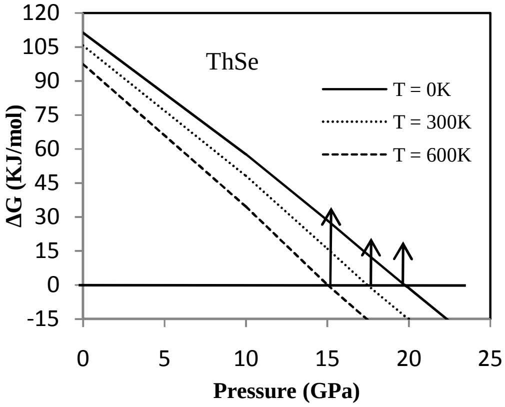

Fig. 2. Variation of Gibbs free energy with pressure for ThSe.

The values of relative volume change (V(p)/V(o)) associated with various compressions have been obtained and plotted against pressure in fig. 3 for ThS and ThSe. The calculated value of volume collapse is in good agreement with the experimental and other theoretical values.

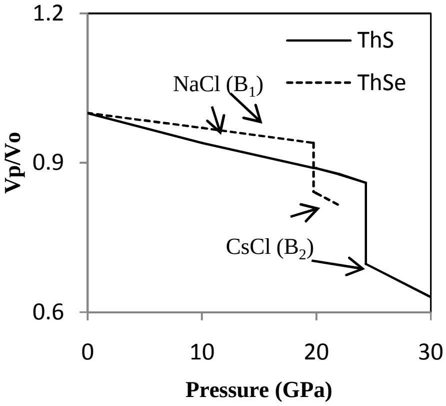

Fig. 3. Variation of Vp/Vo with pressure for ThS and ThSe.

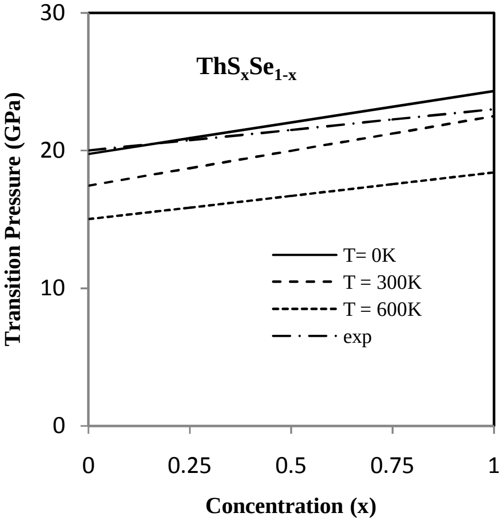

Fig. 4. Variation of transition pressure with concentration (x).

We have also computed the transition pressures and volume collapses of both compounds at different concentration (x) in the temperature range 0-600K and listed in table 3. We have plotted the variation of ΔG and volume collapse with concentration at temperature range 0-600K for ThS and ThSe are shown in fig.4 and 5.

Table 3: Calculated transition pressure and volume collapse for ThS_xSe_{1-x} ($0 \leq x \leq 1$).

Crystal	Transition Pressure (GPa) at			Volume collapse (%) at		
	T = 0K	T = 300K	T = 600K	T = 0K	T = 300K	T = 600K
ThSe	19.75	17.45	15.02	9.6	9.85	10.15
$ThS_{25}Se_{75}$	20.98	18.71	15.85	10.52	10.75	11.05
$ThS_{50}Se_{50}$	22.03	19.97	16.71	11.45	11.65	11.95
$ThS_{75}Se_{25}$	23.17	21.23	17.55	12.37	12.55	12.85
ThS	24.32	22.50	18.40	13.30	13.45	13.75

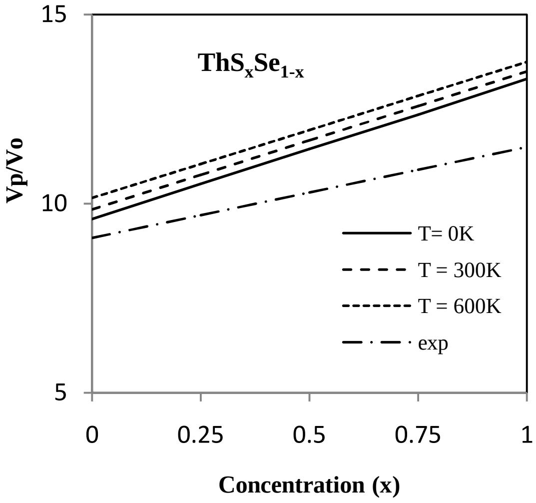

Fig. 5. Variation of Vp/Vo with concentration (x).

CONCLUSION

Finally, we can conclude that the realistic interaction potential with polarizability effect (RIPPM) model successfully predicts 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 rocksalt structure (B_1) at ambient conditions and under pressure transform to the CsCl-type structure (B2).

The calculated B_1 to B_2 phase transition pressures and volume collapse suit well with available experimental and theoretical results.

2. The temperature variation of phase transition pressures show the same behaviour as reported previously.
3. The ThS_xSe_{1-x} transforms from NaCl to CsCl structure at high pressure and high temperature.

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