

High pressure phase transition and elastic properties of ytterbium compounds YbX (X=O, S, Se and Te)

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We have investigated structural stability, high pressure structural behaviour, elastic and thermo-physical properties of ytterbium compounds YbX (X=O, S, Se, Te) using an improved interaction potential model (IIPM). This model incorporates long range coulomb interaction, three body interaction, polarizability effect and short range overlap repulsive interactions extended up to second nearest neighbours. The ytterbium compounds show iso-structural phase transition under pressure. YbX are predicted to exhibit a phase transition from NaCl to CsCl-type structure at high pressure. To our knowledge this is the first theoretical prediction of structural, elastic and thermo physical properties of these compounds and still awaits experimental confirmations. Due to unavailability of experimental and theoretical data on these compounds we have compared our results with other compounds MX (M=Eu, Ce) which belong to group of same structure (B1) and show same transition (B1-B2) under pressure.

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1. Introduction

The ytterbium compounds YbX (X=O, S, Se, Te) attract much attention due to the intricate electronic properties relating to the highly correlated f electrons. A variety of phenomena like heavy fermions [1, 2], mixed valence [3], kondo-behavior [4, 5], electronic and optical properties are encountered. In recent past frequent attempts have been made to understand the electronic properties of rare earth compounds [6]. These technologically important materials are semi conducting if the rare earth (Yb) ion is in divalent state and metallic if trivalent [7-9]. The rare-earth compounds exhibit several physical and chemical properties due to the presence of f-electron. Under pressure, the nature of f-electrons changed from localized to itinerant, leading to significant changes in their structural, physical and chemical properties. The effect of pressure on materials can broadly be classified into two categories, (i) the lattice compression and (ii) the electronic structure change. As the inter-atomic distance decreases, the overlap of outer electronic orbitals increases leading to an increase in the energy band widths. The shift in energy bands leads to inter-band electron and valence transition [10, 11].

The valence of rare earth compounds continues to be a vivid research area [12]. The occurrence of iso-structural phase transitions upon compression or anomalous pressure-volume curves are distinct features of valence transformations. These ytterbium compounds crystallize in the simple NaCl (rock salt) structure with a semiconducting behaviour [13, 14]. Considerable theoretical and few experimental studies of ytterbium

compounds have been published during the last few decades. Jayaraman et al [15] studied the pressure-volume relationship in EuSe, EuS, YbSe and YbS, using high pressure x-ray diffraction techniques up to nearly 300 kbar. They obtained strong evidence of the occurrence of a pressure-induced valence change in the Yb compounds. EuSe and EuS show no evidence of an electronic transition, but they undergo NaCl-CsCl transition. Svane et al [13] studied the electronic structure of rare earth chalcogenides and pnictides with the ab-initio self-interaction corrected local-spin-density approximation (SIC-LSD). This approach allows both an atomic-like description of the rare earth f-electrons and an itinerant description of other electronic degrees of freedom. Chatterjee et al [16] studied the pressure-volume relationship in YbTe by using high pressure x-ray diffraction up to 300 kbar. This relationship is anomalous in the region 150-190 kbar indicating a continuous electronic collapse with pressure. Earlier studies on Sm, Eu, and Yb- chalcogenides show that some chalcogenides of Sm and Eu exhibit a valence transition followed by NaCl to CsCl-type transition at high pressure. Recently Srivastava et al [17] reported that oxides of Sm, Eu and Yb undergo NaCl to CsCl structural phase transition at high pressure. In addition, the cerium chalcogenides (CeS, CeSe and CeTe) undergo structural phase transition from NaCl to the CsCl phase at 24.3 GPa, 20 GPa and 8±1GPa respectively [13, 18].

It is clear from above description that a lot of work has been done on Ce and Eu chalcogenides but very little work is available in Yb chalcogenides. However, the structural and elastic studies on alkaline earth [19], rare

earth chalcogenides [20-22] and other compounds [23] have further increased the scope of future theoretical and accurate experimental investigations of crystallographic phase transition from B1 to B2 phase. The successful modelling for the study of RE compounds should be based on experimental inputs for good results. The ab initio calculations have successfully studied electronic, magnetic and structural properties of binary compounds. As these calculations demand large CPU time and memories the potential models based on interatomic interactions are still important for simulations of B1-B2 transitions. Moreover the phenomenological models have successfully studied phase transition phenomena and structural analysis in many compounds [24-26].

The phenomenological models have been found to be successful in giving the unified description of the lattice dynamic, static, elastic, optic, dielectric and photo-elastic properties of ionic [19-22] and semiconducting crystals [23]. In the present model the three body interactions (TBI) or charge transfer effects (CTE) owe their origin to the quantum mechanical foundation and also to the phenomenological approach in terms of the transfer or exchange of charge between the overlapping electron shells of the adjacent ionic solids. The need to include TBI (CTE) has already been emphasized by many workers like Sims et al [27]; Rao et al [28] and Froyen et al [29]. As their results were based on two body potentials, they remarked that the results could be improved by including the effect of non-rigidity of ions in the model. Also two body potentials cannot explain Cauchy violations ($C_{12} \neq C_{44}$). The deviation from the Cauchy relation $\delta = C_{12} - C_{44}$ is a measure of the contribution from the non-central many body force. Our present model is able to explain the Cauchy violation.

We are motivated by the above-mentioned success of the TBP model in [23] semiconductors and divalent metal oxides [19], we thought it significant to apply an improved interaction potential model for the prediction of phase-transition pressures and associated volume collapses in rare-earth chalcogenides. As mentioned earlier, the present chalcogenides are showing iso-structure phase transition, it would also be showing structural NaCl to CsCl type at high-pressure phase transition. Cerium and europium chalcogenides undergo firstly isostuctural phase transition than they transform B1 to B2-type structural phase transition. Also the density functional theory (DFT) with local spin density (LSD) study which is appropriate for solid state properties, generally fails for f electron systems. This creates a need of theoretical study and approach suitable for Yb compounds. We are taking the effect of polarization for the first time in our model for YbX compounds to improve our results. This effect was applied by Kumar et al [30] in diatomic molecules of alkali

halides. As YbX show similar crystal structure as alkali halides (NaCl) we have included polarizability effect on the same lines. In addition, the elastic and thermo physical properties have also been discussed successfully.

To best of our knowledge, there is no theoretical and experimental reports on the structural phase transition on these compounds are available in the literature. Moreover, the elastic constants and their pressure derivatives of the investigated compounds have not been calculated and measured yet. Due to these reasons mentioned above, it motivated us to perform these calculations using an IIPM model. As no experimental data is available in present compounds, to know the authenticity of our study we have compared our results with other compound EuX and CeX which belong to group of same structure (B1) which show B1-B2 transition under pressure.

In the present article, we have developed an improved interaction potential model (IIPM) which incorporates proper crystal interactions viz., long range coulomb interaction, three body interaction, modified by polarizability effect and short range overlap repulsive interactions extended up to second nearest neighbours to study structural, elastic and thermo physical properties of ytterbium chalcogenides and oxide. We describe the improved modified potential model along with method of calculations in section 2, in section 3 the results and discussion for structural phase transition, elastic and thermo-physical properties were presented. Finally, a conclusion is given in section 4.

2. Improved interaction potential model and method of calculations

Hydrostatic pressure on materials causes a decrease in their volume, and consequently leads to a deformation of the overlapping electron shell (of a charge transfer). These transferred (or exchanged) charges appearing in the overlap region of adjacent ions interact with all other charges (or ions) of the lattice via Coulomb's law, and give rise to many body interactions [24]. The most significant contributions of many body interactions are three body interactions (TBI). The effects of these TBI are incorporated in the Gibbs free energy ($G=U+PV$) at $T=0K$ through the lattice energy, U . Here, V is the unit cell volume at pressure P . Thus, the Gibbs free energy for NaCl (B1) and CsCl (B2) structures' can be written as:

$$G_{B1}(r) = U_{B1}(r) + PV_{B1}(r) \quad (1)$$

$$G_{B2}(r') = U_{B2}(r') + PV_{B2}(r') \quad (2)$$

$$U_{B1}(r) = \frac{-\alpha_M Z^2 e^2}{r} - \frac{12\alpha_M Z e^2 f(r)}{r} - \frac{e^2(\alpha_1 + \alpha_2)}{2r^4} + 6b\beta_y \exp[(r_i + r_j - r)/\rho] + 6b\beta_z \exp[(2r_i - 1.414r)/\rho] + 6b\beta_j \exp[(2r_j - 1.414r)/\rho] \quad (3)$$

$$U_{B2}(r) = \frac{-\alpha'_M Z^2 e^2}{r'} - \frac{16 \alpha'_M Z e^2 f(r)}{r'} - \frac{e^2 (\alpha_1 + \alpha_2)}{2r'^4} + 8b\beta_{ij} \exp[(r_i + r_j - r')/\rho] + 3b\beta_{ii} \exp[(2r_i - 1.154r')/\rho] + 3b\beta_{jj} \exp[(2r_j - 1.154r')/\rho] \quad (4)$$

With $U_{B1}(r)$ and $U_{B2}(r')$ as the lattice energies for NaCl and CsCl structures, α_M and α'_M as Madelung constants for NaCl and CsCl structures respectively. e as charge of electron and r and r' as interionic separation for NaCl (CsCl). β_{ij} is Pauling coefficient defined as $\beta_{ij} = 1 + (Z_i/n_i) + (Z_j/n_j)$ with $Z_i(Z_j)$ and $n_i(n_j)$ as the valence and the number of electrons of the $i(j)$ th ion, b is hardness parameter while ρ is range parameter. Here, the first term is the long range Coulomb attraction, second term is the long range three body or charge transfer interactions, third term is the polarizability interaction, and the rest of the terms are the short range overlap repulsive interactions extended up to second neighbor ions given by Hafemeister and Flygare (Hf) [25].

The rare earth ytterbium chalcogenides generally show an iso-structural transition involving valence transition. Polarization effects have been included in the

cohesive energy given by eqs (3)-(4). Kumar et al [30] applied this effect in alkali halide compounds with B1 (NaCl) structure. We have included this effect in our potential model and applied it to study ytterbium compounds. In case of pure ionic compounds, there is some degree of covalent character. When two oppositely charged ions brought together, the positive ion attracts the outermost electrons of the negative ion. This results in distortion of electron clouds around the anion towards the cation. This distortion of electron cloud of the negative ion by the positive ion is called polarization.

The values of the model parameters, viz b , ρ and $f(r)$ have been computed from the

$$[dU(r)/dr]_{r=r_0} = 0 \quad (5)$$

and

$$B_T = \frac{e^2}{12r'^4} \left[-4.66Z(Z + 12f(r)) + (A_1 + A_2) - 2(B_1 + B_2) + 27.9612Zrf'(r) \right] \quad (6)$$

knowledge of the lattice parameter, bulk modulus and equilibrium conditions [31-33] using the self-consistent method:

2.1 Phase transition properties

The structural phase stability is determined by calculating the Gibb's free energy difference ($G=U+PV-TS$) for both phases. As, the stable phase is associated with minimum free energy of the crystal, we have minimized the lattice energies in both the real and the hypothetical phases at ambient conditions corresponding to equilibrium inter-ionic separation r (r') using the IIPM model

parameters listed in Table 1. We have plotted the values of Gibbs free energy difference ΔG against the pressure (P) as shown in fig 1 for all YbX ($X=O, S, Te$). It is clear from the fig 1 that the values of ΔG at zero pressure are positive for all YbX compounds, which conforms that these compounds stabilize in B1 structure at zero pressure. The YbX ($X=O, S, Te$) compounds are predicted to exhibit a pressure induced structural transformation from low pressure B1 (NaCl) to high pressure B2 (CsCl) phase. The phase transition pressure (P_t) is the pressure at which ΔG approaches zero.

Table 1 Input data r_0 in (\AA), B_T in (GP a) and model parameters b in (10^{-12} ergs), ρ in (\AA) for Ytterbium chalcogenides

Compound	input data		model	parameter	
	r_0	B_T	b	ρ	$f(r)$
YbO	2.43 ^a	130 ^a	0.5757	0.260	-0.0082
YbS	2.84 ^b	72 ^b	15.0605	0.186	-0.0063
YbSe	2.965 ^b	61 ^b	9.8130	0.250	0.0046
YbTe	3.18 ^b	46 ^b	12.0828	0.248	-0.0069

^a Ref [17], ^b Ref [15]

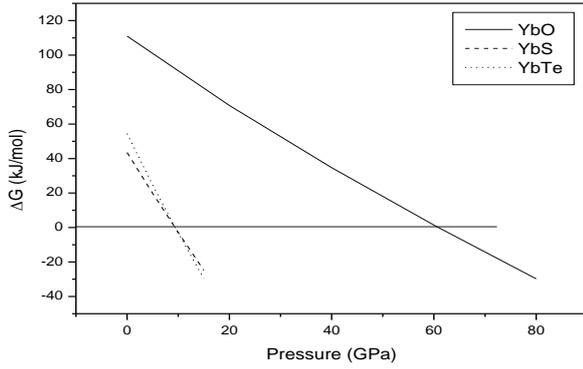


Fig 1 Variation of Gibbs free energy difference with pressure for YbX.

$$C_{12} = \left(\frac{e^2}{4r^4}\right)[0.226Z(Z + 12f(r)) - B_1 + \frac{A_2 - 5B_2}{4} + 9.3204Z(af'(r_0))] \quad (8)$$

$$C_{44} = \left(\frac{e^2}{4r^4}\right)[1.391Z(Z + 12f(r)) + \frac{A_2 - B_2}{4}] \quad (9)$$

The knowledge of elastic constants is important for the stability of compounds and for the stability of compound many stability criteria are available. Vukcevic et al. [34] followed the Born high pressure stability criterion for ionic crystal according to which the stable phase of a crystal is one in which the shear elastic constant C_{44} is small and positive. The elastic energy density must be a positive definite function of strain. In order to fulfill the above criterion the principle minor (Eigen values) of the elastic constant matrix should all be positive [35]. Thus, the stability of NaCl type structure in terms of elastic constants should satisfy the following conditions:

$$B_T = (C_{11} + 2C_{12})/3 > 0, C_{44} > 0 \text{ and } C_S = (C_{11} - C_{12})/2 > 0 \quad (10)$$

The study of elastic constants and their combinations is important to understand the elastic properties. It also gives valuable information about the mechanical and dynamical properties, such as inter atomic potentials operating in solids. In particular, they provide information on the stability and stiffness of materials. We have computed the second order elastic constants (SOECs) and their combinations as reported in Table 2 (i). The shear (C_S) and stiffness constant (C_L) of a cubic crystal are given by [23]:

$$C_S = \frac{C_{11} - C_{12}}{2} \quad (11)$$

$$C_L = \frac{C_{11} + C_{12} + 2C_{44}}{2} \quad (12)$$

Kleinman parameter is a combination of elastic constants and is given by expression [36]:

2.2 Elastic properties

The knowledge of elastic constants of solids provides a link between the mechanical and dynamical behaviors of crystals, nature of the forces operating in the solids, stability and stiffness of materials. The present model (IIPM) described above for the NaCl phase contains three model parameters (b , ρ and $f(r)$), which are used to determine the second order elastic constants (SOECs) whose expressions are as follows:

$$C_{11} = \left(\frac{e^2}{4r^4}\right)[-5.112Z(Z + 12f(r)) + A_1 + \frac{A_2 + B_2}{2} + 9.3204Z(af'(r_0))] \quad (7)$$

$$\xi = \frac{C_{11} + 8C_{12}}{7C_{11} + 2C_{12}} \quad (13)$$

This describes the relative positions of the cation and anion sub-lattice under volume conserving strain distortions for which positions have not fixed by Symmetry. Harrison [36] defines the internal displacement parameter slightly differently from Kleinman. However, the physical meanings of the ζ are depended to each other. Instead of a uni-axial strain, a pure shear strain applied to the crystal. The total energy is a contribution of bond stretching term and bond bending term. The ζ is derived in terms of crystals elastic parameters, C_{11} and C_{12} . According to Harrison the range of ζ is from -1/2 to 1. $\zeta = -1/2$, when there is no energy cost associated with bond stretching and if $\zeta = 1$ when there is no energy cost for bond bending. We have computed the values of ζ , reported them in Table 2 (ii), and compared them with compounds with similar structure (EuX and CeX).

The bulk modulus can be derived from elastic constants. We know that the hardness and strength of materials are related to their elastic module, such as young's modulus Y , bulk modulus B_T , and the shear modulus G . In general, the larger the modulus, harder the material is.

$$B_T = \frac{C_{11} + 2C_{12}}{3} \quad (14)$$

$$G_V = \frac{(2C_S + 3C_{44})}{5} \quad (15)$$

$$G_R = 15\left(\frac{6}{C_S} + \frac{9}{C_{44}}\right)^{-1} \quad (16)$$

The Voigt shear modulus G_V and G_R Reuss shear

modulus are using energy consideration. Hill [37] proved that the Voigt and Reuss equations represent upper and lower limits of the true polycrystalline constants and recommended that a practical estimate of the shear modulus was the arithmetic value of the extremes. Hence, the Shear modulus for cubic system is given as

$$G = \frac{G_V + G_R}{2} \quad (17)$$

The Young's modulus and Poisson's ratios are also important properties of solids. The Young's modulus defined as the ratio of stress to strain. It used to provide a measure of the stiffness of the solid. The present values of Young's modulus increase from Te to S which points out that the stiffness of the materials also increases from Te to S. The expression for Young's modulus is as follows:

$$Y = C_{11} - \frac{2(C_{12})^2}{C_{11} + C_{12}} \quad (18)$$

The Poisson's ratio of a material influences the speed of propagation and reflection of stress waves. As the Poisson's ratio is an important property to know the hardness of compounds. We have calculated the Poisson ratio (σ) of present compounds. The expression of σ given as:

$$\sigma = \frac{C_{12}}{C_{11} + C_{12}} \quad (19)$$

$$\frac{dB}{dp} = -(3\Omega)^{-1} [13.980Z(Z + 12f(r)) + C_1 - 3A_1 + C_2 - 3A_2 - 167.7648Zaf'(r) + 41.9420Za^2 f''(r)] \quad (21)$$

$$\frac{dS}{dp} = -(2\Omega)^{-1} [23.682Z(Z + 12f(r)) + C_1 + \frac{C_2 + 6A_2 - 6B_2}{4} - 50.0752Zaf'(r) + 13.9808Za^2 f''(r)] \quad (22)$$

$$\frac{dC_{44}}{dp} = -(\Omega)^{-1} [-11.389Z(Z + 12f(r)) + A_1 - 3B_1 + \frac{C_2 + 2A_2 - 10B_2}{4} + 44.6528Zaf'(r)] \quad (23)$$

$$\Omega = -2.330 Z (Z+12f(r) + A_1+A_2+21.9612Zaf'(r))$$

The values of A_i , B_i and C_i have been evaluated from the knowledge [33] of b , ρ and polarization effect.

2.3 Third-order elastic constants

A quantitative measure of vibrational anharmonicity can be obtained from the TOEC; although a complete set

$$C_{111} = \left(\frac{e^2}{4r^4}\right) [37.563Z(Z + 12f(r)) + C_1 - 3A_1 + \frac{C_2 - 3A_2 - 9B_2}{4} + 89.304Z(rf') + 13.981Za^2 f''(r_0)] \quad (24)$$

$$C_{112} = \left(\frac{e^2}{4r^4}\right) [-4.836Z(Z + 12f(r)) + \frac{C_2 - 3A_2 + 3B_2}{8} + 18.64Z(af'(r_0)) + 4.66Za^2 f''(r_0)] \quad (25)$$

The Poisson's ratio has two limits, it must be greater than -1 and less than or equal to .5

We know that even the cubic crystal, which is isotropic structure, has anisotropy because of a fourth rank tensor property of elasticity. The elastic anisotropy factor (A) of a cubic crystal defined as [38]

$$A = \frac{2C_{44} + C_{12}}{C_{11}} - 1 \quad (20)$$

We have calculated anisotropy parameter of Yb compounds. For an isotropic crystal, the value of A is 1. Any value smaller or larger than 1, indicates the presence of anisotropy.

The Cauchy relation $C_{12}-C_{44}=2P$ (P; pressure) is valid only when all interatomic forces are central under static lattice conditions. At zero pressure, our calculations give negative values of $C_{12}-C_{44}$, showing violation of the Cauchy relation.

The study of pressure dependency of the second-order elastic constants (SOECs) for ytterbium compounds is also important. As this area is unexplored for Yb compounds and no experimental and theoretical, data on the pressure-dependence of elastic constants are available.

Using model parameters (b , ρ and $f(r)$), pressure derivatives of second order elastic constants (SOECs) have also been computed, whose expressions are as follows:

of TOECs can only be determined by measurement of the effects of uni-axial as well as hydrostatic pressure on ultrasonic wave velocity.

The expressions for TOECs [32] are

$$C_{123} = \left(\frac{e^2}{4r^4}\right)[2.717Z(Z + 12f(r)) + 16.692Z(af'(r_0))] \quad (26)$$

$$C_{144} = \left(\frac{e^2}{4r^4}\right)[2.717Z(Z + 12f(r)) + 5.564Z(af'(r_0))] \quad (27)$$

$$C_{166} = \left(\frac{e^2}{4r^4}\right)[-7.165Z(Z + 12f(r)) - 2(B_1 + B_2) + \frac{C_2 - 3A_2 + 3B_2}{8} + 5.564Z(af'(r_0))] \quad (28)$$

$$C_{456} = \left(\frac{e^2}{4r^4}\right)[1.5522Z(Z + 12f(r)) - (B_1 + B_2)] \quad (29)$$

2.4 Thermo-physical properties

The thermo physical properties provide us the interesting information about the substances. We have calculated thermo physical properties of ytterbium compounds and listed them in Table 5. The Debye characteristic temperature (θ_D) reflects its structure stability, the bonds strength between its separate elements, structure defects availability and its density [19]. We have also computed molecular force constant (f), infrared absorption frequency (ν_0), Gruneisen parameter (γ) and ratio of volume expansion coefficient (α_v) to specific heat (C_v) at constant volume which are directly derived from the cohesive energy $U(r)$. Their expressions [33, 38] are given below.

In terms of molecular force constants

$$f = \frac{1}{3} \left[U_{kk'}^{SR}(r) + \frac{1}{2} U_{kk'}^{SR}(r) \right]_{r=r_0} \quad (30)$$

With $U_{kk'}^{SR}(r)$ as the short range nearest neighbor ($k \neq k'$) part of $U(r)$ given by the last three terms in "equation (3)". This force constant f leads to the infrared absorption frequency with the knowledge of the reduced mass (μ) of ytterbium chalcogenides:

$$\nu_0 = \frac{1}{2\pi} \left(\frac{f}{\mu}\right)^{1/2} \quad (31)$$

This frequency gives us the Debye temperature:

$$\theta_D = \frac{h\nu_0}{k} \quad (32)$$

with h and k as the Planck and Boltzmann constants respectively.

The value of the Gruneisen parameter (γ), has been calculated from the relation:

$$\gamma = -\frac{r_0}{6} \left[\frac{U'''(r)}{U''(r)} \right]_{r=r_0} \quad (33)$$

We have calculated the ratio of the volume expansion coefficient (α_v) to specific heat (C_v) from the expression:

$$\frac{\alpha_v}{C_v} = - \left[\frac{U'''(r)}{2rU''(r)} \right]_{r=r_0} \quad (34)$$

The thermal expansion coefficient (α_v) can be calculated with the knowledge of specific heat (C_v).

3. Results and discussion

Stability of a particular structure is always decided by minima of energy. Therefore, we have minimized Gibb's free energies given by eqs. (1)-(2) for interionic separations r and r' . The Gibb's free energy differences ΔG of B1 and B2 phases have been plotted in Fig. 1 and their associated volume changes V_p/V_0 have been plotted in Fig 2. It is clear from fig 1 that ΔG is positive at zero pressure for YbX showing the stability of B1 structure.

It is seen from Fig. 1 that YbX compounds undergo a (B1-B2) transition associated with a sudden collapse in volume showing the occurrence of first order phase transition. ΔG becomes negative beyond phase transition pressure (P_t) predicting thereby that the high-pressure phase B2 is now thermodynamically and mechanically stable as compared to B1 phase. The value of P_t computed by us is in good agreement with that obtained in earlier work [17] available only for YbO. As the phase transition pressures of YbX have not been measured yet, to know the comparable range we have compared our results of YbO with EuO, that of YbS with EuS and CeS and lastly results of YbTe have been compared with the results of EuTe and CeTe. EuX and CeX belong to the same structure B1 and under pressure, they also show B1-B2 transition. It is clear from Table 2(i) and fig 1 that our values of phase transition pressures for YbO (61.10 GPa), YbS (9.4 GPa), YbSe (≤ 60 GPa) and YbTe (9.3 GPa) are in comparable range of phase transition pressures measured and predicted by others for other rare earth compounds YbO (61 GPa theo.) [17], EuO (40 GPa expt.) [15], CeS (24.3 GPa theo.) [13], EuS (21.5 expt.) [41], CeSe (20 GPa theo.) [39], EuSe (14.5 GPa expt.) [15], CeTe (8 \pm 1 GPa theo.) [39] and EuTe (11 GPa expt.) [15]. Fig 2 shows a sudden collapse in volume associated with phase transition pressures showing the occurrence of first order phase transition except YbSe which is not showing any sign of transition till 100 GPa (up to 40 GPa is seen in fig 2). Also the values of volume collapses associated with phase

transition pressure are 9.15 % for YbO, 15.51 % for YbS and 8.92 % for YbTe and they are near to other rare earth compounds 6.5 % for EuO [15], 12.50 % for EuS [41], 7.0 % for CeS [13] and 11.6 % for EuTe [15] and 8.5 % for CeTe [42]. It is clear from Table 2 (i) that these volume collapses are in comparable range with experimental and others values of EuX and CeX.

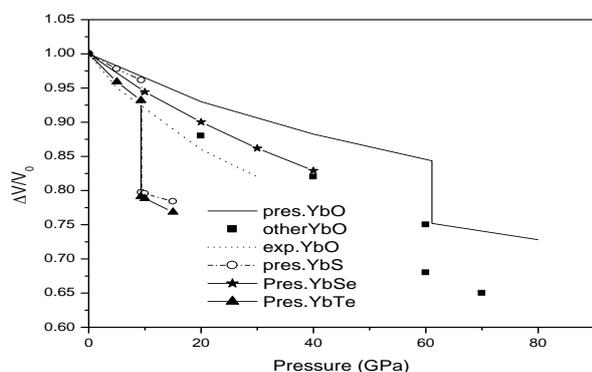


Fig 2 Variation of relative volume change with pressure for YbX.

The elastic properties define the properties of material that undergoes stress, deforms and then recovers and returns to its original shape after stress ceases. To study the elastic behavior of these compounds, we have computed SOECs and their combinations (C_L and C_S) by using eqs (7)-(12) and they are reported in Table 2 (i). Our present values of SOECs and their combination follow the same trend as other rare earth chalcogenides. The study of SOECs under pressure is important as C_{11} represents elasticity in length and C_{12} and C_{44} are shape related elastic constants. C_{11} represents a measure of resistance to deformation by a stress applied on (1, 0, 0) plane with polarization in the direction $\langle 1, 0, 0 \rangle$. C_{44} represents the measure of resistance to deformation with respect to a shearing stress applied across the (1, 0, 0) plane with polarization in the $\langle 0, 1, 0 \rangle$ direction. The experimental values of elastic constants (SOECs) for ytterbium compounds are not available at present. Future experimental measurements will however, testify all calculated results. Our values of elastic constants satisfy all the stability condition of equation (10) and hence we may state that these compounds are stable against elastic deformation.

Table 2 (i) Calculated values of phase transition pressure and elastic module and their combinations (in GPa) for Ytterbium chalcogenides at ambient condition. For comparison, results of others theoretical [a, f] and experimental results [b, c, d, e, g, h] for EuX and CeX are included.

Compound	P_t	$\Delta V/V_0$ (%)	C_{11}	C_{12}	C_{44}	C_S	C_L	Ref.
YbO	61.10	9.15	203.14	93.27	122.39	54.93	270.59	Present
	60 ^a	6.8 ^a	284 ^a	54 ^a	54 ^a	-	-	Other's
	40 ^b	6.5 ^b	192.6 ^c	42.5 ^c	54.2±13 ^c	74 ^c	171 ^c	Expt. [EuO]
YbS	9.4	15.51	177.90	19.16	49.24	79.37	147.77	Present
	21.5 ^d	12.5 ^d	115±1 ^d	36±2 ^d	26±1 ^d	39.5 ^d	101 ^d	Expt. [EuS]
	24.3 ^e	7.0 ^e	156.28 ^f	40.0 ^f	40.14 ^f	-	-	Other's [CeS]
YbSe	-	-	158.72	12.31	49.40	73.20	134.92	Present
	14.5 ^b	12.8 ^b	116.6 ^g	12 ^g	22.8 ^g	43.45 ^g	66.45 ^g	Expt. [EuSe]
	20 ^h	9.0 ^h	154.48 ^f	31.97 ^f	32.01 ^f	-	-	Other's [CeSe]
YbTe	9.3	8.92	104.66	16.66	33.42	44.00	94.08	Present
	11 ^b	11.6 ^b	93.6 ^g	6.7 ^g	16.3 ^g	52 ^g	86.8 ^g	Expt. [EuTe]
	8±1 ^h	8.5 ^f	137.98 ^f	22.31 ^f	22.28 ^f	-	-	Other's [CeTe]

^a Ref[17], ^b Ref [15], ^c Ref [40], ^d Ref [41], ^e Ref [13], ^f Ref [42], ^g Ref [43], ^h[39].

The values of Kleinman parameter ξ given in Table 2 (ii) are well in range given by Harrison (-0.5 to 1) for all YbX compounds. They are also in range of other EuX and CeX compounds. The values of Kleinman parameter ξ could not be compared due to unavailability of experimental values however, we have calculated from experimental elastic values and compared with them. The calculated values of Y and G in general decrease with increase of anion size (S-Te).

As we know that, the Poisson ratio (σ) is an important property to know the hardness of compounds. This ratio deals with the way stretching or compressing an object in one direction causes it to compress or stretch in the other direction. The usual range of σ is from 0.5 to -1. The calculated values of Poisson ratio for Yb compounds given in Table 2 (ii) are in above limit. Anisotropy values as reported in Table 2 (ii) show that these compounds are anisotropic and have values other than 1.

The value of Cauchy's discrepancy at zero pressure is

given by $\delta = C_{12} - C_{44}$ in Table 2(ii). The values of δ are compared with EuX and CeX compounds and they are showing similar trend. The deviation from the Cauchy violation $C_{12} - C_{44} = 2P$ is a measure of the contribution from the non-central many body force. Our present model is able to explain the Cauchy violation.

In order to study the high-pressure elastic behavior of YbO, we have presented the variation of second order elastic constants with pressure as shown in fig 3. It is clear from fig 3 that in case of YbO, it is found that C_{11} is more

sensitive to the change of pressure compared to the other elastic constants; C_{12} and C_{44} are less sensitive to the change of pressure. A longitudinal strain produces a change in C_{11} and a transverse strain causes a change in shape without a change in volume. So C_{12} and C_{44} are shape related elastic constants. As pressure increases C_{11} and C_{12} of the B1 phase at zero temperature increase, but C_{44} decreases monotonically and this trend is seen in divalent metal oxides having same (B1) NaCl structure and showing same (B1-B2) transition under pressure [19].

Table 2 (ii) some structural G and Y (in GP a) and mechanical properties ξ , σ , A (dimensionless) for ytterbium chalcogenides. For comparison, results of others theoretical [a] and experimental results [b, c, d, e] for EuX and CeX are included.

Compound	ξ	G	Y	σ	A	$\delta = C_{11} - C_{44}$	Ref.
YbO	0.60	88.74	144.44	0.30	0.66	-29.12	Present
	-	-	-	0.26 ^a	0.47 ^a	-	Other's
	0.44 ^b	62 ^b	174.59 ^b	0.18 ^b	0.73 ^b	-11.7 ^b	Expt.[EuO]
YbS	0.25	59.67	174.17	0.1	-0.34	-30.08	Present
	0.47 ^c	31 ^c	97.83 ^c	0.23 ^c	0.65 ^c	-10 ^c	Expt.[EuS]
YbSe	0.22	58.96	156.94	0.07	-0.29	-37.09	Present
	0.22 ^d	27.16 ^d	92.73 ^d	0.18 ^d	0.37 ^d	-9.6 ^d	Expt.[EuSe]
	-	-	-	-	-0.009 ^e	-	Expt.[CeSe]
YbTe	0.31	37.31	100.08	0.14	-0.20	-16.76	Present
	0.25 ^d	34.48 ^d	113.75 ^d	0.09 ^d	0.43 ^d	-10.8 ^d	Expt.[EuTe]
	-	-	-	-	0.01 ^e	-	Expt.[CeTe]

^a Ref[17] ^b Ref [40], ^c Ref [41], ^d Ref [43], ^e Ref [18].

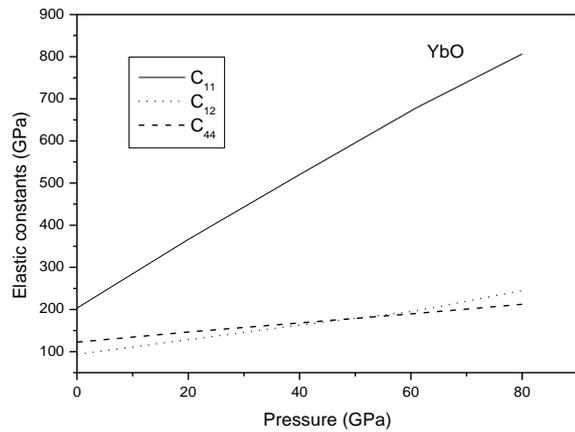


Fig. 3. Variation of SOECs with pressure for YbO.

To know the variation of elastic constants with lattice parameter, we have plotted C_{11} , C_{12} and C_{44} as a function of lattice constant for YbX compounds and compared them with the theoretical and experimental values of CeX and EuX compounds reported earlier [39, 40, 41, 42, 43] in Fig 4. We remark that the values of C_{12} and C_{44} in all the three ReX (Re=Ce, Yb, Eu) chalcogenides, vary linearly with increasing lattice constants, the variation of C_{11} for EuX and CeX is not smooth. In this fig we see that when we go from YbTe to YbO, a linear increase of the elastic constants corresponding to a decrease of the lattice parameter is seen. It is clear from the figure that whiles the

values of C_{11} deviate in EuO and YbO and for other chalcogens it is smooth. Future measurements will testify our calculated results. To study the anharmonic properties of these compounds, we have calculated the values of pressure derivatives of the SOECs and TOECs. The values of the pressure derivatives of the SOECs are reported in Table 3 and TOECs are reported in Table 4. It is clear from Table 3 that the values of first-order pressure derivatives of B_T , C_S and C_{44} are positive as found in most of the compounds with rock-salt structure.

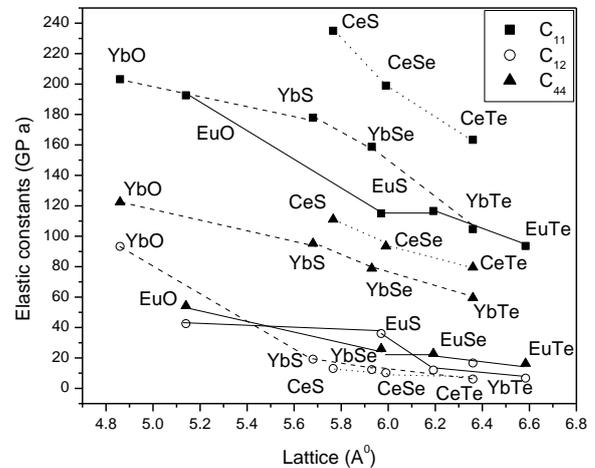


Fig. 4. Variation of the elastic constants: C_{11} , C_{12} , C_{44} , with lattice constants for Ytterbium.

Chalcogenides, Cerium Chalcogenides and Europium chalcogenides:

■, ○ and ▲ with dot line represent the values of C_{11} , C_{12} and C_{44} respectively for Cerium Chalcogenides

■, ○ and ▲ with dash line represent the values of C_{11} , C_{12} and C_{44} respectively for Ytterbium Chalcogenides

■, ○ and ▲ with Solid line represent the values of C_{11} , C_{12} and C_{44} respectively for Europium Chalcogenides

It is seen from Table 4 that the C_{111} , C_{112} and C_{166} are negative for ytterbium chalcogenides while the values of

C_{123} , C_{144} and C_{456} are positive. The magnitude of the

Table 3. First-order pressure derivatives

Compound	dB_T/dP	dC_{44}/dp	dC_S/dp
YbO	8.403	7.007	1.403
YbS	11.282	12.946	0.155
YbSe	10.108	10.518	0.803
YbTe	10.070	10.913	0.434

Table 4. Third order elastic constants (GPa) of ytterbium chalcogenides.

Compound	C_{111}	C_{112}	C_{123}	C_{144}	C_{166}	C_{456}
YbO	-73.380	-6.090	2.160	1.850	-8.800	0.780
YbS	-85.904	-3.477	1.211	1.021	-2.768	0.466
YbSe	-56.253	-1.716	0.695	0.787	-2.959	0.539
YbTe	-44.851	-7.044	0.627	0.642	-7.024	0.325

TOECs decrease continuously as one goes from O to Te. A similar decrement occurs also if one goes from the lithium to rubidium salt in the alkali halide series. The experimental results of the pressure derivatives of SOECs and TOECs of these compounds are not available and hence, they are of only academic interest at present but these will certainly be useful for experimentalists in future.

We have also computed the thermo physical properties of these compounds, and they provide us important information about the substance. Molecular force constant (f), the ratio of thermal expansion

coefficient to specific heat ($\frac{\alpha_v}{C_v}$), Debye temperature (θ_D) and Gruneisen parameter (γ) of a crystal are material parameters. These properties involved in all physical phenomena where lattice vibrations play a role, such as thermal conductivity, superconductivity, specific heat and melting point and they reflect material's structural stability, the strength of bonds between its separated atoms and structural defects. In addition, Gruneisen parameter (γ) measures the anharmonicity of a crystal [33, 44]. The values of above parameters are reported in Table 5.

Table 5. The value of molecular force constants (f in 10^4) frequency (ν_0 in 10^{12} Hz), the ratio of thermal expansion coefficient to

specific heat ($\frac{\alpha_v}{C_v}$ in 10^3 J), Debye temperature (θ_D in K) and Gruneisen parameter (γ). For comparison, results of

experimental values [a] for EuO and EuS are included.

Compound	f	ν_0	α_v/C_v	θ_D	γ	Ref
YbO	2.681	5.227	0.560	523.990	1.104	Present
	-	-	-	-	1.57 ^a	Expt.[EuO]
YbS	2.251	3.574	1.120	444.640	3.013	Present
	-	-	-	-	1.93 ^a	Expt.[EuS]
YbSe	2.095	2.490	0.983	392.556	2.882	Present
YbTe	1.557	1.836	0.766	361.160	2.583	Present

^a Ref [45]

From this table we can see that the values of force constants (f) and frequency (ν_0) decreases from O to Te as the size of anion increases. In a similar manner, the Debye temperature increases in magnitude as a function of the chalcogen as one moves upward within period VI, i.e. from Te to S. We know that Debye temperature is also related to elastic constants and it decreases as the elastic constants decrease from YbO to YbTe. The calculated values of Gruneisen parameter (γ) for these compounds are almost of the same magnitude as that of EuO and EuS. Presently these values are of academic interest only as

measured data on them are not available. However, they follow the same trend as the other lanthanide chalcogenides follow.

4. Conclusions

In the present study, we have investigated for the first time, structural, elastic and thermophysical properties of ytterbium compounds YbX (X= O, S, Se, Te), using an improved interaction potential model (IIPM). The results are summarized as follows:

1. The ytterbium compounds crystallize in sixfold coordinated NaCl structure (B1) and under pressure transform to the eightfold coordinated CsCl structure (B2) (except YbSe, as studies have not confirmed it).

2. Our calculated phase transition pressure and volume collapses for YbO is in good agreement with the available other's theoretical data.

3. During the phase transition from NaCl to CsCl for YbX (X=O, S and Te) the volume discontinuity in pressure-volume phase diagram identifies the occurrence of the first order phase transition.

4. The calculation for second order elastic constants have been performed which have not been performed experimentally yet.

5. The calculated different combinations of second order elastic constants are in general in good agreement with the available other rare earth compounds such as EuX and CeX.

6. The four-ytterbium compounds show the high-pressure behavior, elastic and structural stability and thermo physical properties similar to the other rare earth compounds such as EuX and CeX. As to the best of our knowledge, these values have not yet been measured hence our results can serve as a prediction for future investigation.

Finally, to the best of our knowledge; the structural phase transition, elastic constants and their pressure dependence and thermo-physical properties have not been calculated and measured yet, so it is our aspiration that these calculations will inspire further experimental research on these compounds. Therefore, we can conclude that our present (IIPM) model is appropriate to study high-pressure phase transition, elastic behavior, thermo physical properties of ytterbium compounds and this model can be extended to study other lanthanide compounds, and this study is already in process in our group.

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