

Pressure Induced Structural Phase Transition and Elastic Properties of Lutetium Chalcogenides (LuX, X: S, Se and Te)

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Abstract

We have investigated, the cohesive energies, pressure-volume relationship, phase transition pressure (Pt) and elastic constants for lutetium chalcogenides (LuX, X: S, Se, Te), using an interionic potential theory with modified ionic charge which includes Coulomb screening effect due to f-electrons. These compounds undergo structural phase transition from NaCl (B1) to CsCl (B2) structure at high pressure (ranges from 10 to 60 GPa). The B1 (NaCl) phase is found to be lower in energy than the B2 (CsCl) phase and more stable at zero pressure.

Keywords: Rare earth chalcogenides; high pressure; elastic properties; equations-of-state; phase transition.

1. Introduction

In the recent years the study of structural phase transformation and mechanical properties of binary rare earth (RE) monochalcogenides and mononictides due to their intricate electronic structures and their diverse and unusual properties, in respect of structural and phonon properties [1,2] have received considerable attention. These compounds possess partially filled f-electron orbital. The f-electrons in the rare-earth ion are highly delocalized and under pressure they interact strongly with the conduction band and p states of the neighbouring anion. In this regard many theoretical [3,4] as well as experimental [5-7] researches have been carried out to understand the role of f-electrons particularly under pressure. The yttrium and lutetium chalcogenides are especially well suited for a study of influence of the electron concentration upon superconductivity. At ambient condition, the chalcogenides of lutetium (LuX, X: S, Se, Te) crystallize in six-fold coordinated NaCl-type (B1) structure with space group symmetry $Fm\bar{3}m$ (225). They are expected to undergo pressure-induced first order phase transition to eight-fold coordinated CsCl-type (B2) structure with space group symmetry $Pm\bar{3}m$ (221), as is observed in many other heavier RE-chalcogenides. The crystal structure and the superconducting behaviour in the NaCl-phase in LuX compounds have been studied experimentally [8]. However no experimental work on the structural phase transformation and elastic properties on these compounds has been reported in the literature. Recently, the structural properties of lutetium chalcogenide have been studied by Seddik, et al. [9] using full-potential augmented plane wave plus local orbitals (FP-APW+lo) method. These authors have predicted B1-B2 structural phase transition in the pressure range from 12 to 52 GPa, and also reported the calculated values of elastic properties for these LuX compounds.

Earlier studies on the high pressure behaviour of RE-monochalcogenides (REX) reveal [10] that some of the Sm-X compounds are semiconductors (except SmO) with a large band gap [11], and do not show any structural phase transition but SmTe shows structural phase transformation followed by valence change [10]. High pressure phase for SmO has not been determined so far. EuO is the only compound amongst the chalcogenides of Eu, which shows a valence transition at \approx 30 GPa followed by NaCl- to CsCl-type transition around 40 GPa [11-14]. Heathman et al. [12] further extended the range of investigation upto 63 GPa using energy dispersive X-ray diffraction (EDXRD) and

synchrotron radiation and showed that no transformation of Eu²⁺ and Eu³⁺ occurs at the pressure region of 28 to 40 GPa and obtained a smooth compression curve until 47 GPa. The Yb monochalcogenides (Yb-S, -Se, -Te) undergo only valence transformation continuously with pressure, because of a change in the valence state from 2+ to 3+ as observed by Jayaraman et al [10]; YbO synthesised and studied upto little bit high pressure of 35 GPa by Werner et al. [15]. Who obtained similar results as that of the other Yb-chalcogenides. Bihan et al [16] performed x-ray diffraction measurements under pressure on uranium compounds with different pressure-transmitting media. US shows a phase transformation from its ambient NaCl-phase to CsCl type structure around 80 GPa in a silicone oil pressure medium [16]. Gerward et al [17] have documented high-pressure structures, transition pressures and compressibilities for UX monochalcogenides. USe and UTe also transform from B1 to B2 phase at around 20 and 9 GPa [18], respectively.

Although the first principles calculations can predict the electronic properties of a wide class of rare earth compounds satisfactorily, but these methods involve very large computing time and large memory space. Secondly, most of *ab initio* theories do not include the effect of van der Waals interaction between the ions, which plays important role in bonding properties of such class of compounds. In view of these facts we decided to use this phenomenological model. The interionic potential theories have been found quite accurate to explain the structural phase transition, elastic and phonon properties of rare earth chalcogenide and pnictide compounds [19-22]. It is well known that the electronic configuration in rare-earth atom hybridize between $4f^n 5d^m$ and $4f^{n-1} 5d^{m+1}$ states, even at ambient condition. The interionic potential in these theories considers Coulomb screening effect on the atomic core due to the hybridization of *f*-electrons of rare earth atom phenomenologically through a charge parameter Z_m . The aim of the present paper is to use the interionic potential theory, as referred above [19], to calculate self-consistently, the high pressure structural and elastic and properties of lutetium chalcogenide compounds and compare them with available theoretical and experimental data to judge the suitability of the potential. Besides this, such a study will, essentially guide the experimental workers to initiate to bring out in depth understanding of the physics of this group of unexplored RE compounds.

The organization of the paper is as follows: the method of calculation of structural phase transition pressure and expressions for elastic properties derived from the model potential will be given in section 2, while in Section 3 we present potentially interesting results on the structural and elastic properties of lutetium chalcogenides, and compare them with available theoretical results [9].

2. Method of Calculation

2.1 Cohesive energy and phase transition pressure

The inter-ionic potential for the lutetium chalcogenides (LuX) in the framework of the rigid ion model is expressed as [19, 20].

$$U(r) = \sum_{ij} Z_m^2 e^2 / r_{ij} + \sum_{ij} b \beta_{ij} \exp[(r_i + r_j - r_{ij}) / \rho_{ij}] + \sum_{ij} C_{ij} r_{ij}^{-6} + \sum_{ij} D_{ij} r_{ij}^{-8} \quad (1)$$

which includes long range Coulomb Potential (first term), Hafemeister and Flygare form of short range repulsive (second term) and van der Waals multipole interactions (third and fourth terms). $Z_m e$ is the modified ionic charge due to Coulomb screening effect. The range and hardness parameters ρ and b in short-range part of the crystal energy are determined from the knowledge of lattice parameters, bulk modulus and the equilibrium condition

$$\left. \frac{dU(r)}{dr} \right|_{r=r_0} = 0 \quad (2)$$

where r_0 is the equilibrium lattice constant. The input constants and model parameters for LuX compounds are presented in Table 1. Since, no experimental data on bulk modulus (B_T) is available; we have used the theoretical values of B_T reported in Ref [9] for the determination of model parameters. Thermodynamically a phase transition is said to occur when changes in the structural details of the phase are caused by a variation of the free energy. The LuX compounds transform from their initial NaCl to CsCl structure under pressure. The stability of a particular structure is decided by the minima of the Gibbs free energy, given by

$$G = U + PV - TS \quad (3)$$

where U is the internal energy (Eq. (1)), which at 0 K corresponding to cohesive energy, S is the vibrational entropy at absolute temperature (T), pressure (P), volume (V). The Gibbs free energies $G_{B_1}(r)$ for NaCl (B_1) and $G_{B_2}(r)$ for CsCl (B_2) phase become equal at the phase transition pressure P_t at temperature 0 K. Such a theoretical approach has been found to predict most of the crystal properties of rare earth [19, 20] and transition metal mono-nitrides compounds [21-22] satisfactorily.

2.2 Mechanical properties

In the present paper, we have also calculated the second order elastic constants (SOEC) from the following expressions derived from the interionic potential (Eq.1) [20] by the method of the homogeneous deformation as follows:

$$C_{11} = \alpha[-5.112Z_m^2 + A_1 + \frac{1}{2}(A_2 + B_2)] \quad (4)$$

$$C_{12} = \alpha[0.226Z_m^2 - B_1 + \frac{1}{4}(A_2 - 5B_2)] \quad (5)$$

$$C_{44} = \alpha[2.556Z_m^2 + B_1 + \frac{1}{4}(A_2 + 3B_2)] \quad (6)$$

Here, $\alpha = e^2 / 4r_0^4$, $A_1 = A_{12}$, $B_1 = B_{12}$, $A_2 = (A_{11} + A_{22})$ and $B_2 = (B_{11} + B_{22})$, and are expressed as : $A_{ij} = 2V / e^2 (d^2 \Phi_{ij}(r) / dr^2)$ and $B_{ij} = 2V / e^2 (1 / r_{ij} (d \Phi_{ij}(r) / dr))$ where $\Phi_{ij}(r)$ is the short-range potential in Eq. (1) comprising of the last three terms and V is the unit cell volume. The bulk modulus is derived from elastic constants as

$$B_0 = \frac{1}{3}(C_{11} + 2C_{12}) \quad (7)$$

2. Results and discussion

3.1 Structural properties

The input crystal properties and calculated model parameters for the interionic potential model of lutetium chalcogenides are given in Table 1. We present the calculated properties on lattice constants, cohesive energies, structural phase transition pressures and relative volume change for these materials for initial NaCl- and final CsCl-type structures in Table 2. We have also compared our calculated results with the available theoretical [9] and experimental [8] data. It is seen from Table 1 that our calculated values of model parameters for interionic potential follow a systematic trend of variation for lutetium chalcogenides. The modified ionic charge parameter Z_m^2 is derived from the values of bulk modulus (B_T). It is clear from Table 2 that the calculated values of equilibrium lattice parameters in NaCl-type structure are in good agreement with available experimental [8] and theoretical [9] results. We have computed total energies in

Table 1 Ionic radii of anions r_+ , cations r_- and lattice constants r_0 (Å), Bulk modulus B_T (GPa), modified ionic charge parameter Z_m^2 , hardness parameter b (J) and range parameter ρ (Å) for lutetium chalcogenides.

Solids	Input data			Model Parameters			
	r_+ (Å)	r_- (Å)	r_0 (Å)	B_T (GPa)	Z_m^2	b ($\times 10^{-19}$ J)	ρ (Å)
LuS	1.25	1.40	2.677 ^a	108.10 ^b	1.82	1.097	0.301
LuSe	1.25	1.55	2.786 ^a	89.29 ^b	1.66	0.705	0.280
LuTe	1.25	1.64	2.976 ^a	69.07 ^b	1.54	0.751	0.266

^a) Ref. [8], ^b) Ref. [9]

Table 2 Cohesive and phase transition properties for lutetium chalcogenides.

Solids		Equil. separation (Å)	inter-ionic Cohesive Energy (KJ/mole)		ΔU (KJ/mole)	P_t (GPa)	$\Delta V(P_t)/V(0)$ %	
			$R_1(B_1)$	$R_2(B_2)$	$U_1(B_1)$			$U_2(B_2)$
LuS	Pres.	2.680	2.82	-2702.7	-2612.8	89.91	51	5.78
	Expt.	2.677 ^a					--	--
	Th.	2.684 ^b					51.41 ^b	4.31 ^b
LuSe	Pres.	2.790	2.92	-2147.7	-2090.5	57.2	21	9.16
	Expt.	2.786 ^a					--	--
	Th.	2.81 ^b					22.15 ^b	4.59 ^b
LuTe	Pres.	2.980	3.11	-1793.3	-1750.6	42.7	11	10.05
	Expt.	2.976 ^a					--	--
	Th.	3.011 ^b					12.32 ^b	5.67 ^b

^a) Ref. [8], ^b) Ref. [9]

B_1 and B_2 phases upon compressions. It is found that the stable phase of lutetium chalcogenides at ambient condition is B_1 for which the energy is minimum as compared to B_2 phase. In addition we have also calculated the total energies of these LuX compounds in their BCT phase (not presented here) which reveal that $B_1 \rightarrow$ BCT transition is not favourable, as is seen in the lighter REX compounds [19]. The structural phase transition pressure of these compounds are listed in Table 2 and compared with the available theoretical values [9].

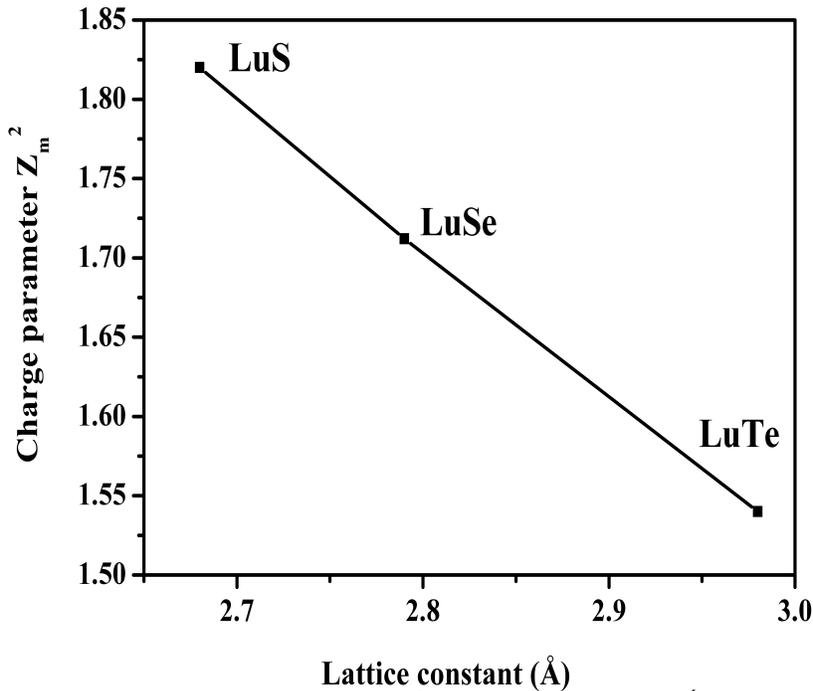


Figure 1 Variation of modified ionic charge parameter Z_m^2 with lattice constant r_0 (Å) for lutetium chalcogenides.

In Fig. 1 we have plotted the modified ionic charge parameter Z_m^2 with lattice constant of LuX. The magnitude of the modified ionic charge parameter Z_m^2 decreases linearly from LuS to LuTe. This fact emphasizes that the delocalization of f electrons increases as one goes across in this series. The large value of Z_m^2 in LuS indicates that the effect of f -electron screening in this compound is quite small as compared to LuSe and LuTe, and indicates the ionic character of the bonds in these compounds. The slope of the graph between Z_m^2 and lattice constant is found to be negative and in accordance with the decreasing magnitude of bulk modulus B_T . Two other short-range parameters b and ρ follow systematic trend of variation (see Table 1). The equation of states for LuX compounds are presented in Figs. 2(a)-(c). In the case of LuS, we have predicted a transition pressure of 51 GPa with volume collapse of 5.8%. Since there is no experimental data, therefore, we have compared our results with those reported by Seddik et al. [9]. For similar phase transition in LuSe and LuTe, our calculated values of transition pressure are 21 and 11 GPa with volume collapse of 9.2%, 7.95% respectively. Our results compare well with other theoretical work [9], who have found B_1 to B_2 transition pressure as 51.42, 22.15 and 12.32 GPa for LuS, LuSe and LuTe, respectively. It is noteworthy that there is a transfer of electrons from chalcogen s and p -like states to the Lu f -like states continuously under pressure, which must be responsible for the observed structural transformation. However, it can be noticed from Table 2. that the percentage of relative volume change at P_T , in our case are larger, as compared to ref. [9].

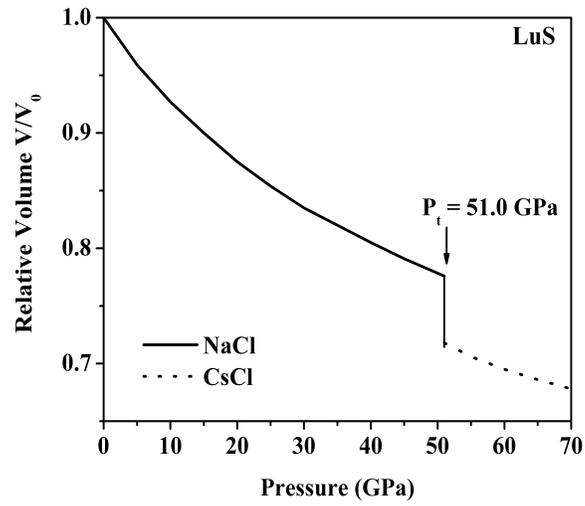


Figure 2 (a)

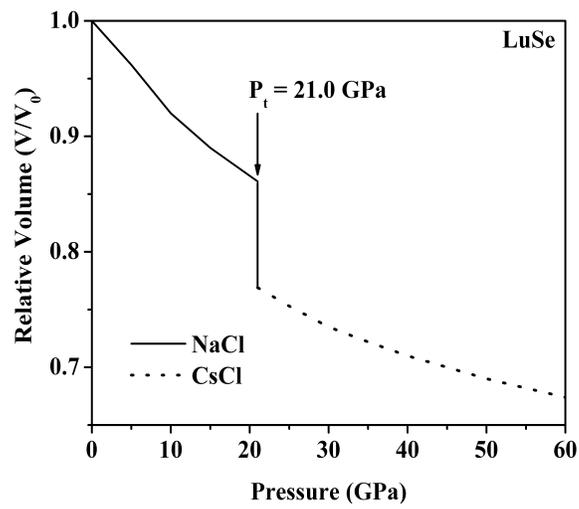


Figure 2 (b)

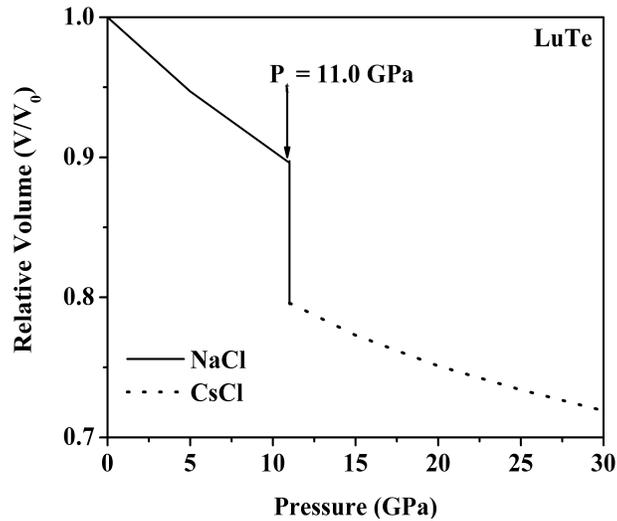


Figure 2 (c)

Figure 2 The equation of state (a)-(c) for LuS, LuSe and LuTe respectively, solid line represents B_1 phase and dotted line represents B_2 phase.

The similar calculated values of phase transition pressure obtained in both ref. [9] and the present calculations; suggest that the interactions between Lu and X atoms are predominantly ionic in nature. However, since in the present we use so often short-range potential for the repulsive interactions, which the *ab initio* theory does not, our calculated values of volume change at phase transition are large as compared to those in ref [9]. Such a discrepancy is therefore can be understood as the difference in methods theoretical approach.

3.2 Elastic properties

The elastic constants are important parameters that describe the response to an applied macroscopic stress. Elastic properties of a solid are especially important because they are related to various fundamental solid-state phenomena. The elastic constants of solids provide a link between the mechanical and dynamical behavior of crystals, and give important information concerning the nature of the forces operating in solids. In particular, they provide information on the stability and stiffness of materials. Since the forces and the elastic constants are functions of the first and second order derivatives of the interionic potential, their calculation will provide a further check on an accuracy of the calculated values of forces in solids. We have calculated the elastic constants of LuX compounds at normal as well as at high pressure by using the methodology discussed in Section 2. In the case of cubic system, there are only three independent SOEC namely C_{11} , C_{12} and C_{44} . Since we use two-body interaction potential between the species, the calculated values of C_{12} and C_{44} are equal. The calculated values of SOEC are tabulated in Table 3 and compared with other theoretical values [9]. One can see, however, from Table 3 that the elastic constants decrease in magnitude as we go from -S to -Te in the series of lutetium chalcogenides which is also the same reported in ref. [9]. However, in our case the magnitudes of C_{11} are significantly smaller as compared to ref. [9]. Moreover we have predicted $C_{12} = C_{44}$ from our calculations, since we have used a two body interaction potential to predict the elastic constants, and this is an obvious outcome.

Table 3 Calculated second order elastic constants (GPa) for lutetium chalcogenides.

<i>Solids</i>		C_{11}	C_{12}	C_{44}
		(in GPa)	(in GPa)	(in GPa)
LuS	Present	199.07	53.25	53.25
	Theory	280.74 ^b	21.78 ^b	147.8 ^b
LuSe	Present	181.56	37.44	37.44
	Theory	235.29 ^b	16.29 ^b	109.2 ^b
LuTe	Present	151.40	24.79	24.79
	Theory	189.34 ^b	8.94 ^b	95.9 ^b

^b)Ref. [9]

The Cauchy discrepancy, i.e. $C_{12} \neq C_{44}$ can be explained only by incorporating many body interactions, which is beyond the scope of present work, a quantitative comparison of the values of elastic constants can not be made at present particularly in the absence of any experimental data. The stability of these chalcogenides can also be defined in terms of the SOEC to the criteria [23, 24] using the following relation:

$$C_{11} - C_{12} > 0, C_{44} > 0$$

We have found that in the NaCl-type structure; these criteria are satisfied, indicating that this phase is elastically stable.

4. Conclusion

A two-body inter-ionic potential is formulated to analyze the structural as well as elastic properties of lutetium chalcogenides. We identify the structural phase transformation from NaCl- to CsCl-type structure through pressure-volume relationship. From our calculated results it can be emphasized that the present approach predicts the structural and elastic properties at high pressure consistently, in terms of the effect of f -electron Coulomb screening through the modified ionic-charge parameter. An immediate consequence of our model is the Born criterion for crystal structure stability depicted by the elastic constants. The elastic constants of these compounds are calculated and they display a linear dependence with lattice constant. Our calculated high pressure transition pressures are in good agreement with the available theoretical results. From this model, the nature of inter-atomic forces can be predicted as mostly ionic.

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