JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 6, June 2008, p. 1311 - 1314

Phase transition and elastic properties of calcium chalcogenides at high pressure

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We have investigated high pressure structural behavior and elastic properties of Calcium chalcogenides (CaX; X = S, Se, Te) by using a two body inter ionic potential approach with modified ionic charge (Z_m).The equation of state, phase transition pressure in NaCl (B_1) to CsCl (B_2) structural phase and associated volume collapse at transition pressure obtained from this approach and compared with recently measured energy dispersive X- ray data reveal good agreement with experimental results. We have also investigated bulk modulii, pressure derivatives, second and third order elastic constants at transition pressure which show predominantly ionic nature of these compounds. The variations of C_{11} and C_{44} with pressure are also presented.

(Received May 15, 2008; accepted June 4, 2008)

Keywords: Calcium chalcogenide, Phase transition, High pressure

1. Introduction

High pressure research on structural phase transformations has been approaching a stage of systematic study and understanding of a series of material with analogous physical and / or chemical properties. A survey of the literature reveals that in recent years most of the theoretical and experimental investigators have paid attention to the study of structural, optical and electrical properties at high pressure [1-7]. The pressure induced structural phase transition and insulator-metal transition are also of great theoretical interest. The study of phase transition and elastic behavior of alkaline earth chalcogenides (AEC) (AX ; A = Be, Mg, Ca, Sr, Ba; X = O, S ,Se, Te) have closed shell ionic system and crystallize in the NaCl type (B_1) structure at ambient condition except for the MgTe and the Beryllium Chalcogenides. An interesting feature in the electronic band structure of the AEC compounds is that there are no d electrons in the valence band. The band gaps in the AEC compounds range from about 2.5 to 6.0 eV. At high pressure, the AEC compounds first undergo a structural phase transition from sixfold co-ordinated NaCl (B_1) to eightfold co-ordinated CsCl (B_2) structural [8-16].

Recently, the high pressure structural phase transition and equations of state for CaX compounds have been measured by means of X-ray diffraction [6] techniques and it was found that they transform from NaCl (B_1) phase to the CsCl (B_2) structure at 40-42 GPa, 38 GPa and 33 GPa respectively for CaS, CaSe and CaTe. In the case of CaTe, Luo et al [6] observed an intermediate phase similar to the observed by Zupon et al [12] and Zimmer et al [4] and finally going to the B_2 phase at above 33 GPa. Most of the theoretical approaches predict that the metallization phenomenon through band overlap by using different methods of band structure calculation such as linear muffin tin orbital [LMTO] [17] and tight binding approximation [18]. These calculations have shown that overlap of bands at high pressure causes metallization in the AEC compounds. However, some of these theories failed to predict phase transition pressure, volume and cohesive prosperities even with a reasonable order of magnitude [18].

In the present paper, we have proposed a modified interionic potential model based on the two-body interaction potential approach [7] to describe successfully the equation of state, elastic and other high pressure properties of CaX; (X = S, Se, Te) compounds. This model has been quite successful in predicting the high pressure behavior of several rare-earth compounds [5,7]. In this approach, the lowering of d-like conduction band relative to the p-like valance band results in band overlap through modified charge transfer. This is common reason of metallization of these compounds under high pressures. The essentials of the present theory and methods are given in section 2. The results presented and discussion in section 3.

2. Method of calculation

The inter-atomic potential for the calcium chalcogenides in the framework of two-body interaction (rigid ion) model can be expressed as:

$$U(r) = \Sigma_{ij} Z^2 m\, e^2/r_{ij} + {}_s\Sigma_{ij}\, b\, ß_{ij} \exp[(r_i+r_j-r_{ij}) / \rho\,] + \Sigma_{ij} C_{ij} r_{ij}^{-6} + \Sigma_{ij} D_{ij} r_{ij}^{-8} \quad (1)$$

where $Z_m e$ is the modified ionic charge. In Eq. (1) the first term is the long range Coulomb energy, second term represent the short range repulsive energy, third and fourth

terms are the van der Waals multiple interactions. r_{ij} is the nearest neighbor separation between the ions, r_i and r_j are the ionic radii. The range and hardness parameters ρ and b in the short-range part of the crystal energy are determined from the knowledge of lattice parameters and bulk modulus. The parameters so have been obtained are presented in Table 1. along with the input parameters. Such a theoretical approach has been found to predict most of the crystal properties of rare-earth compounds [5,7] satisfactorily. In the present paper, we have also calculated the second order elastic constants ($SOEC_s$) from the following expressions, derived form the interionic potential (Eq.1)[3]

Table 1. Input data and model parameters of Calcium Chalcogenides.

Solids	Input Data		Model Parameters		
	r_0 (Å)	B_0 (GPa)	Z_m^2	$b(10^{-19}$ J)	ρ
CaS	2.845	64	2.789	6.621	0.326
CaSe	2.958	51	2.586	4.694	0.340
CaTe	3.174	42	2.496	4.047	0.347

$$C_{11} = \alpha\ [\ -5.112\ Z_m^2 + A_1 + \tfrac{1}{2}\ (A_2 + B_2)\ ]$$
$$C_{12} = \alpha\ [\ 0.226\ Z_m^2 - B_1 + \tfrac{1}{4}\ (A_2 - 5B_2)\ ]$$
$$C_{44} = \alpha\ [\ 2.556\ Z_m^2 + B_1 + \tfrac{1}{4}\ (A_2 + 3B_2)]$$

with $\alpha = e^2/4r_o^4$, Here, $A_1 = A_{12}$, $B_1 = B_{12}$, $A_2 = (A_{11} + A_{22})$ and $B_2 = (B_{11} + B_{22})$,and are expressed as: $A_{ij} = 2V/e^2\ (d^2V_{ij}(r)\ /dr^2)$ and $B_{ij} = 2V/e^2\ (1/r_{ij}\ (dV_{ij}\ (r)\ /dr)$, where V_{ij} (r) is the short-range potential in Eq.(1) and Vis the unit cell volume. The expressions for the third order elastic constants ($TOEC_s$) can be derived as follows

$$C_{111} = \alpha\ [\ 37.556\ Z_m^2 + C_1 - 3A_1 + \tfrac{1}{4}\ (C_2 - 3A_2 - 9B_2)\ ]$$
$$C_{112} = C_{166} = \alpha\ [-4.786\ Z_m^2 + 1/8\ (C_2 - 3\ A_2 - 3B_2)\ ]$$
$$C_{123} = C_{144} = C_{456} = \alpha\ \ (2.717\ \ Z_m^2)$$

with $C_{1(2)} = A_1^2{}_{(2)} / B_{1(2)}$. The expressions for the pressure derivatives of second order elastic constants can be derived from the combination of $SOEC_s$ and $TOEC_s$ constants for NaCl structure using their standard relations [3].

3. Results and discussion

In the present paper, we have presented the structural and elastic properties of calcium chalcogenides CaX (X: S, Se, Te) at high pressure using modified inter-ionic potential discussed in section 2. In Fig.1, we have presented equation of state for CaS, CaSe and CaTe. For a better comparison of the present results with experimental data, we have presented in Table 2, the calculated values of cohesive energies, interatomic distance in B_1 and B_2 phases and phase transition pressure for these compounds along with the experimentally measured values. A look at Fig.1 and Table 2 show that the present theoretical results on structural phase transition pressure (P_t), equation of state and volume collapse for these compounds from the present modified inter-ionic model are generally in good agreement with experimental data [6]. The present theoretical high pressure studies show that they exhibit a NaCl (B_1) and transform to CsCl (B_2) type structure under pressure as revealed by x-ray diffraction studies [6]. We have also been able to show from present model calculation that phase transition pressures are 39.9 GPa, 38.5 GPa and 34.9 GPa for CaS, CaSe and CaTe with relative volume change 6.0%, 5.0% and 4.0% respectively which are similar to the experimental observations. This small volume collapse at the transformation in these compounds is related to the large ionic radius of chalcogen ion. Hence, the repulsive force between large ions in these compounds resists volume collapse at phase transition. It is also seen from the Table2, that the present model predicts the relative stability of the competitive structures as it satisfied the required criterion [21] for change in cohesive energy (ΔU) to be always to be positive. Hence, the positive values of ΔU reveal that the B_1 phase is most stable at ambient pressure for these compounds.

Table 2. Cohesive and Phase transition properties of Calcium Chalcogenides.

Solids	Equilibrium lattice constants(Å)	Cohesive energy (KJ/mol)			Phase tran. pres. (P_t)	Rel. Vol. change%
		$R_1(B_1)$	$R_2(B_2)$	$U_1(B_1)$	U_2 (B_2)	GPa
CaS	Pre. 2.850 Exp. 2.845[a]	3.010	-2130.9	-2055.2	39.9 40[a], 42[b]	6.0 10.2[a], 6.1[b]
CaSe	Pre. 2.960 Exp. 2.958[a]	3.140	-1900.4	-1827.8	38.5 38[a]	5.0 7.7[a]
CaTe	Pre. 3.180 Exp. 3.174[a]	3.370	-1721.6	-1650.8	34.9 3[a]	4.0 4.6[a]

[a]Ref. [6] , [b]Ref. [19]

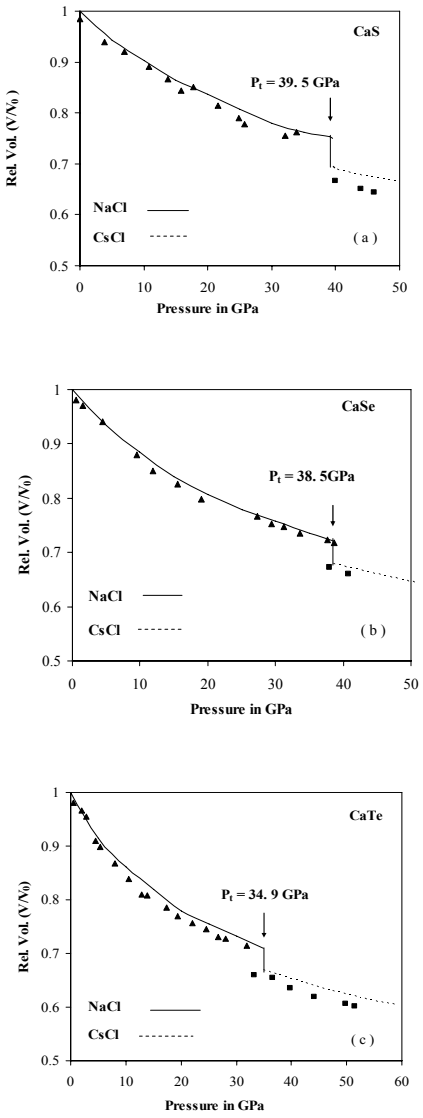

Fig. 1. Equation of state for (a) CaS, (b) CaSe, (c) CaTe. (▲, ■) experimental points are taken from ref [6].

Fig. 2 shows the variation of Ca- Ca and Ca-Se distance in CaSe with high pressure. The Ca-Se distance in the NaCl type structure is 2.960 (Å) at ambient pressure. This distance is slightly shorter than the sum of ionic radii of Ca^{+2} (0.99 Å) and Se^{-2} (1.98 Å) . The Ca- Se distance is much shorter than the sum of the atomic radius of Ca (1.94 Å) and the covalent radius of Se (1.16 Å), longer than the sum of the covalent radii of Ca (1.74 Å) and the Se (1.160 Å. Thus the chemical bond between Ca and Se atoms has the partly ionic nature. When the B_1 - B_2 transition occurs at around 38.5 GPa, the Ca -Se distance suddenly increases in the CsCl type structure .This almost agrees with the Ca- Se distance (2.960 Å) in the NaCl type structure at ambient pressure. On the other hand , the Ca-Ca distance in CaSe abruptly decreases if the B_1 – B_2 transition ocuures. The same analysis is done for other two compounds (CaS & CaTe) and found the similar variation in the interionic distances with increasing pressure.

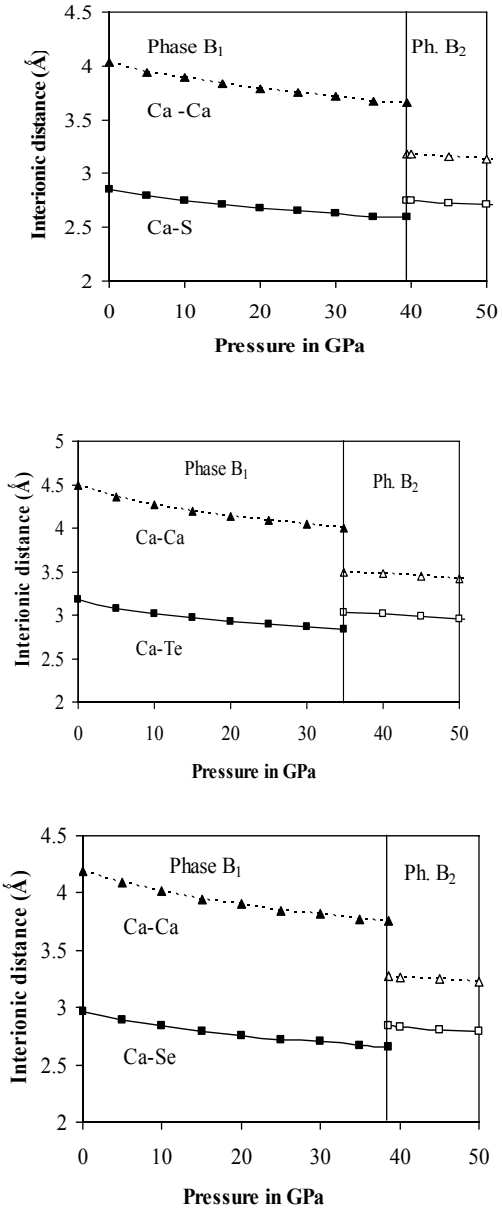

Fig. 2. Ca-Ca and Ca-X distance as a function pressure for CaS, CaSe and CaTe.

Table 3. Second and third order elastic constants of Calcium Chalcogenides in GPa.

Solids	C_{11}	C_{12}=C_{44}	C_{111}	C_{112}=C_{116}	C_{123}=C_{144}=C_{456}
CaS	122.74	36.78	-536.77	-187.24	66.70
CaSe	94.98	29.96	-414.86	-94.19	52.92
CaTe	74.46	22.71	-408.38	-68.59	38.54

Table 4. Bulk modulus (GPa) and pressure derivatives of Calcium Chalcogenides.

Solids		B_0	K_p	S_p	C_p
CaS	Present(Exp.)	64.59 (64[a])	4.56 (4.2[a])	4.2	-0.1527
CaSe	Present(Exp.)	50.76 (51[a])	4.60 (4.2[a])	4.36	-0.0708
CaTe	Present(Exp.)	39.07 (42[a])	4.81(4.3[a])	4.77	-0.0201

[a]Ref. [6]

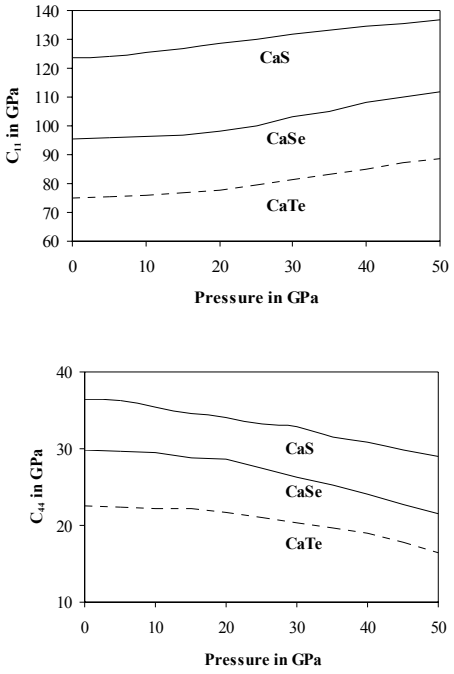

Fig. 3. Variations of C_{11},C_{44} with pressure.

In order to study of the high pressure elastic behavior of CaX compounds, we have calculated the pressure variation of second order elastic constants (SOECs) C_{11} and C_{44} shown in Fig. 3. We observed that C_{11} increases linearly with increase pressure but C_{44} decreases linearly, showing the reduction in resistance to shear as the phase transition is approached as shown in [15]. We have also reported second and third order elastic constants in Table 3, bulk modulus and pressure derivatives in Table 4 and compared with experimental data for bulk modulus only.

Acknowledgement

The authors are thankful to Madhya Pradesh Council of Science and Technology (MPCST) for financial support. One of author is thankful to CSIR, New Delhi.

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