

PHASE TRANSITION OF CeO₂ UNDER HIGH PRESSURE

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***Abstract-** The Pressure induced structural phase transition of Ceria (CeO₂) has been investigated using an effective interionic interaction potential. The present potential had been found to reproduce well the experimentally observed phase fluorite to orthorhombic transition pressure and associated volume collapses and elastic constants of CeO₂ is in good agreement with their corresponding experimental data (31.5 GPa). We have also reported the elastic properties of CeO₂ in both phases.*

***KeyWord-** Gibbs Free Energy, High Pressure, Phase Transition, Relative Volume Collapse. PACS Code- 64.70.Kb., 62.20.Dc.*

I INTRODUCTION

Cerium dioxide (CeO₂) is one of the extensively studied dioxides because of its technological applications and theoretical implications [1]. The pressure-induced transition of CeO₂ has been the subject of some recent studies [2] because it can be related to the systematic of the high-pressure behaviour of the fluorite type ceria [3]. At ambient pressure and temperature Ceria (CeO₂) has fluorite symmetry and its electronic structure of it is characterized by unoccupied 4f states of Ce⁴⁺ (4f⁰) [4]. Under high pressure behaviour of pure Ceria revealed the presence of its transformation to orthorhombic (PbCl₂) type structure [5-7].

In the present paper we have investigated the high pressure structural phase transition (phase transition pressure, relative volume collapse), cohesive energy and elastic properties of Ceria from fluorite lattice (B_F) (*Fm3m*) space group to orthorhombic (B_O)

(*Pnam*) space group using inter-ionic potential model. Major part of the cohesion in these potential is contributed by long range (L-R) Coulomb interactions, (*Pnam*) space group using inter-ionic potential model. Major part of the cohesion in these potential is contributed by long range (L-R) Coulomb interactions, which are counter balanced by short range (S-R)

overlap repulsion. Surveys of literature, shows that, many experimental results are being available, but no theoretical attentions have been made to explain the structural properties of CeO₂ for their description. Motivated from this fact we thought it pertinent to apply an effective interionic potential which have been successfully applied to describe the superionic solids [8-10] and binary semiconductors. The consequent formulation of effective interionic potential has been described in section II. The application of present potential to predict the phase transition pressure and elastic constants are presented and discussed in the next section.

II THEORY AND FORMULATION

The stability of a lattice is attained at the minimum Gibbs free energy for a particular lattice spacing *r*, given as:

$$G = U + PV - TS \quad (1)$$

Here, U is the internal energy, which at 0K corresponds to the cohesive energy, S is the vibrational entropy at absolute temperature T and V is the volume at pressure P. At sufficient low temperature nearly zero (T=0K) one can ignore entropy term (TS), thus Gibbs free energy for Fluorite (B_F) and Orthorhombic (B_O) structures are expressed as:

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

$$G_{B_O}(r') = U_{B_O}(r') + PV_{B_O}(r') \quad (3)$$

with lattice energies (U) defined as:

$$U_{B_F}(r) = -\frac{\alpha_M e^2 Z^2}{r} + b \sum_{ij} \beta_{ij} \exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right) \quad (4)$$

$$U_{B_O}(r') = -\frac{\alpha'_M e^2 Z^2}{r'} + b \sum_{ij} \beta_{ij} \exp\left(\frac{r_i + r_j - r'_{ij}}{\rho}\right) \quad (5)$$

Here, first term represents the Coulomb attraction corresponding to nearest neighbor separations *r* (*r'*) and Madelung constant α_M (α'_M) for Fluorite (Orthorhombic) structure and Ze is the ionic charge. The second term is the Hafemeister-Flgyare (HF) type repulsive interaction operative upto the second neighbor ions. β_{ij} is the Pauling coefficients with *r_i* (*r_j*) as the

ionic radii of the cations (anions); ρ , b are the range and hardness model parameters determined by the equilibrium condition

$$\left. \frac{dU(r)}{dr} \right|_{r=r_0} = 0 \text{ and } B = \frac{1}{9Kr_0^3} \left[\frac{d^2U(r)}{dr^2} \right]_{r=r_0} \quad (6)$$

where, B is bulk modulus, r is the nearest interionic separation; r_0 is the equilibrium separation i.e. $r = r_0$ and K as the crystal structure constant. The pressure variations of C_{11} , C_{12} , C_{44} and B have been computed using the expression given elsewhere [8] for both phases is listed in table.

III RESULT AND DISCUSSION

The present effective interaction potential contains only two model parameters (ρ and b) which have been

evaluated by using input data taken from ref [5] are listed in Table 1.

Crystal	Input Data		Model Parameters	
	$r_0(\text{\AA})$	$B(\text{GPa})$	$\rho(\text{\AA})$	$b(10^{12}\text{erg})$
CeO ₂	2.703	230	0.297	0.242

Table 1:

We have followed the minimization techniques of cohesive energy at different pressure in order to obtain, the inter-ionic separations for fluorite and orthorhombic phases. The computed cohesive energy using the model parameters are reported in Table 2.

Crystal	U_{BF}	U_{BO}
CeO ₂	-289.313	-477.943

Table 2:

Our comments on the reliability of cohesive energy value for both the phases are restricted until the experimental data report on them. In an attempt to reveal the structural phase transition of CeO₂; we minimized the Gibbs free energies for both the phases. As pressure is increased, ΔG decreases to zero at phase transition pressure and becomes negative when pressure is further increased. The phase transition pressure and relative volume collapse evaluated is reported in Table 3 and plotted as a function of pressure in fig 1 and fig 2 respectively. Table 3:

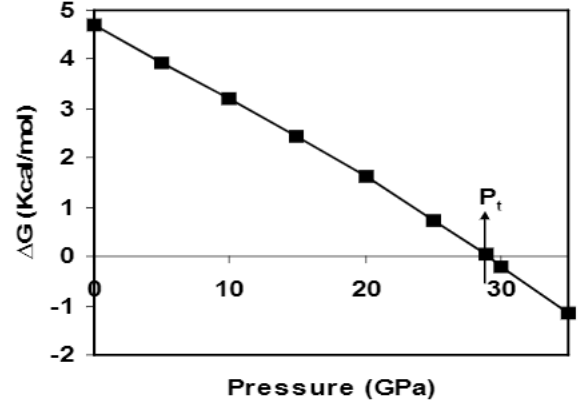


Figure 1: Change in Gibbs free energy from Fluorite → Orthorhombic structure.

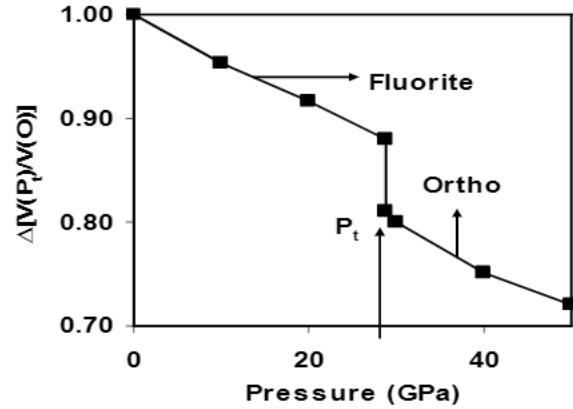


Figure 2: Volume Collapse as function of pressure (P) from Fluorite → Orthorhombic structure.

Crystal	$P_t(\text{GPa})$	$\Delta[V(P_t)/V(O)](\%)$
CeO ₂ Fluorite-	28.9	6.9
Ortho	(31.5 ^a , 22.3-6.5 ^b)	(7.5 ^{ab})

^a ref. [5-7], ^b ref. [11]

Table 3:

The phase transition pressure, at which ΔG approaches zero is known as phase transition pressure (P_t). Ambient pressures, CeO₂ crystallize on fluorite (B_F) structure and undergo a transition to orthorhombic (B_O) structure upon compression. The (-) sign shows the compression in CeO₂. The value of phase transition pressure and relative volume collapse are in satisfactorily agreement with the available experimental data.

In order to understand the high pressure elastic behaviour of CeO₂ we have calculated SOEC's and B for both the phases and reported them in Table 4. The accuracy of the bulk modulus is remarkably good.

CeO ₂	Fluorite	Orthorhombic
C_{11} (GPa)	289.98	333.88

C_{12} (GPa)	197.92	281.73
C_{44} (GPa)	123.6	219.51
B (GPa)	228.61 (230) ^a	299.11 (304) ^a

Table 4:

IV CONCLUSION

On the basis of overall achievement it may be concluded that the present effective interionic potential has evolved more realistic representation of interaction mechanism to describe the high pressure phase transition and elastic properties of CeO_2 .

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