Structural Properties of $Mg_xCa_{1-x}O$ (x = 0.0, 0.25 , 0.50, 0.75 and 1.0) : An *Ab-Initio* Study

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ABSTRACT

Structural properties of $Mg_xCa_{1-x}O$ ternary alloy have been calculated by employing the ab-initio periodic linear combination of atomic orbitals (LCAO) method utilizing CRYSTAL06 code. The correlation and exchange potential is treated by the generalized-gradient approximation (GGA) proposed by Perdew–Burke–Ernzerhof (PBE) and Becke's ansatz respectively. The calculated ground state properties such as lattice constants, bulk modulus, and pressure derivative of bulk modulus are in good agreement with earlier investigations. The study observes that as the concentration of magnesium increases the lattice constant decreases where as the bulk modulus increases.

Keywords: MgCaO, LCAO method, Structural Properties, PBE, GGA.

1. INTRODUCTION

The wide band gap CaO and MgO have been focused in many experimental and theoretical investigations because they are major minerals of the earth's mantle. These oxides are used in many technological applications ranging from catalysis to microelectronics [1].

CaO exhibits high mechanical and radiation resistance, and it has wide energy band gap (7.1 eV) with a high dielectric constant (11.8) [2]. CaO is used in bio-medical applications by incorporating in TiN-based films [3] and diamond-like carbon [4]. CaO is also used in biosensors [4]. It can play an important role in the field of spintronics. MgO is one of the most fundamental materials for industrial sciences due to its wide band gap (~7.833eV) [2], high dielectric constant, and ability to form ternary crystalline phases. It is used in numerous applications, such as medicine, as an insulator in industrial cables. Furthermore, MgO is used as an insulator in devices that exhibit the tunnel magneto-resistance effect. Several theoretical and experimental studies on structural properties of MgO and CaO have been reported [5-18].

In alkaline earth oxides, MgO and CaO have been extensively investigated, whereas $Mg_xCa_{1-x}O$ have received less attention. Using FP-LAPW method in combination with LDA, Miloua et al. [19]

have investigated the ground state properties and the stability of $Ca_{1-x}Mg_xO$ mixed oxides. Recently, structural phase transition and ground state properties of $Mg_{1-x}Ca_xO$ have been investigated by Srivastava et al. [20] using first-principles DFT and charge transfer interaction potential (CTIP) approach. Enhancing the scientific knowledge about the compounds of this kind is important to understand the behaviour of ternary compounds and it is also essential for manufacturing of the materials reproducibly, effectively and economically. In the present paper, we report the structural properties of the $Mg_xCa_{1-x}O$ (x=0.0, 0.25, 0.50, 0.75, 1.0) using LCAO method as implemented in CRYSTAL06 code [21]. An outline of this paper is as follows: The computational methods used in this study are described in section 2. In section 3, our main calculated results on structural and properties $Mg_xCa_{1-x}O$ are discussed. Finally, the last Section 4 summarizes the results of this investigation.

2. COMPUTATIONAL DETAILS

The first-principles LCAO method is used to study the structural properties of $Mg_xCa_{1-x}O$. The *ab-initio* periodic LCAO calculations are performed wherein one solves the Kohn-Sham equations self-consistently under the DFT [22]. There are a few fundamental schemes exist for constructing the Hamiltonian for the periodic solids. HF [23] approximation and the DFT [22] are the well-known approaches among these schemes. The CRYSTAL06 code [21] provides a platform to calculate structural and electronic properties of periodic systems with Gaussian basis employing HF, DFT and the hybrid schemes. In this method, each crystalline orbital $\psi_i(\mathbf{r},\mathbf{k})$ is a linear combination of Bloch functions $\varphi_\mu(\mathbf{r},\mathbf{k})$ defined in terms of local functions $\varphi_\mu(\mathbf{r})$, normally referred as atomic orbitals. The local functions are expressed as linear combination of certain number of individually normalized Gaussian-type functions. For Mg, Ca and O, the local functions were constructed from the Gaussian type basis sets [24]. The Kohn-Sham Hamiltonian was constructed while considering the exchange scheme of Becke [25] and PBE [26] correlation scheme. In order to calculate the structural properties of $Mg_xCa_{1-x}O$ (x = 0.00, 0.25, 0.50, 0.75, 1.00), the optimization was performed by minimizing the total energy with respect to the cell volume for each composition. The evaluated results are compared with the available results. The self consistent calculations are performed considering 165 **k** points in the irreducible Brillouin zone with sufficient tolerances. To achieve self consistency, 45% mixing of successive cycles is considered and self consistency is achieved within 15 cycles.

3. RESULTS AND DISCUSSION

3.1. Structural properties

The total energies of the B1 and B2 phases of CaO and MgO over a set of volumes are computed using LCAO method. The variations of the total energy versus volume for both compounds in B1

and B2 phases are given in Figures 1 and 2. From these Figures, it is evident that B1 phase is the energetically favourable for both compounds because its energy is significantly lower than B2 phase. For CaO, the total energy has also been calculated as a function of cell volume and fitted to the third order Birch-Murnaghan equation of state [27,28]. Using this equation, we calculated the ground state properties such as the lattice constants (a), bulk modulus, pressure derivative of bulk modulus. For MgO, data are taken from our earlier calculations [18]. The calculated structural parameters of CaO and MgO in B1 and B2 phases are listed in Table 1. Since B1 is a stable phase for CaO and MgO, so the structural properties of $Mg_xCa_{1-x}O$ for the compositions x= 0.25, 0.5, 0.75 are computed in B1 phase. The variation of total energy versus volume curves for $Mg_xCa_{1-x}O$ (x=0.25, 0.50, 0.75) are given in Figures 3-5. The calculated structural parameters for B1 phase of $Mg_xCa_{1-x}O$ (x=0.25, 0.50 and 0.75) are listed in Table 2 along with previous results. Our computed values of lattice constant for $Mg_xCa_{1-x}O$ (x=0.25, 0.5 and 0.75) are in good agreement with the results of Milaua et al. [19]. The variations of lattice constant and bulk modulus of $Mg_xCa_{1-x}O$ as a function of x are shown in Figures 6 and 7 respectively. Figure 6 depicts that the present LCAO values show similar trend with the values of Vegard's law [29]. The disagreement in the region of lower x values may be the large mismatch of lattice constants of MgO and CaO. From Figure 7, it is clear that the compressibility decreases with the increasing x. Hence, CaO is more compressible than MgO.

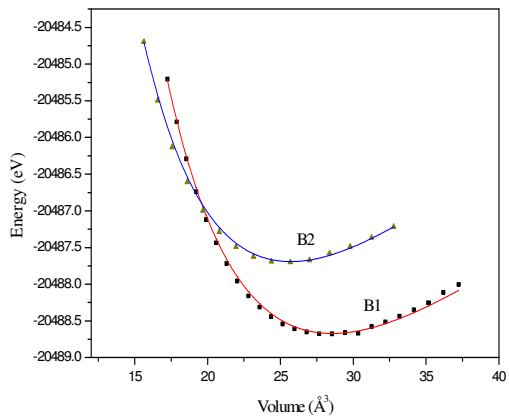

Fig. 1 First-principles energy volume curves for B1 and B2 phases of CaO. The scattered points show calculated energies and the solid lines show the fitted E(V) curves according to Birch-Murnaghan equation of state (EOS).

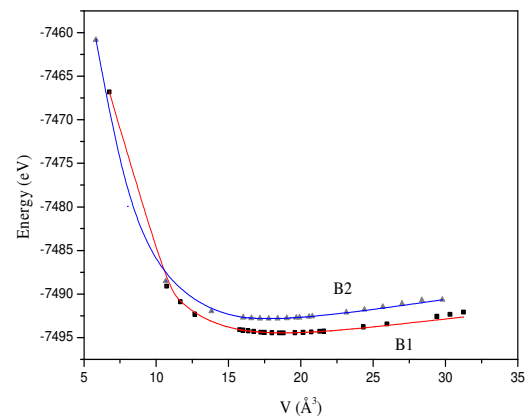

Fig. 1 First-principles energy volume curves for B1 and B2 phases of MgO. The scattered points show calculated energies and the solid lines show the fitted E(V) curves according to Birch-Murnaghan equation of state (EOS).

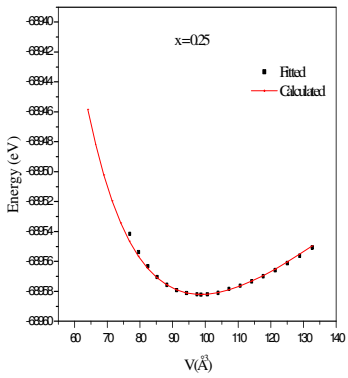

Fig. 3 First-principles energy volume curves for B1 structure of $Mg_{0.25}Ca_{0.75}O$.

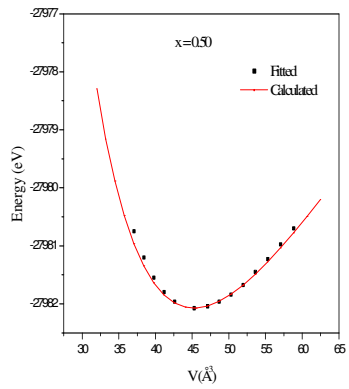

Fig. 4 First-principles energy volume curves for B1 structure of $Mg_{0.50}Ca_{0.50}O$.

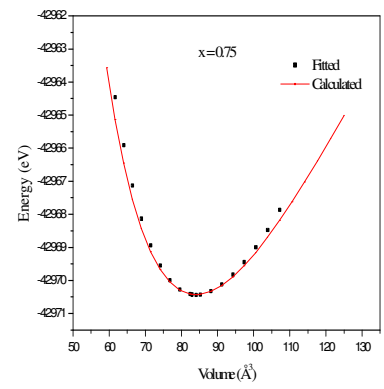

Fig. 5 First-principles energy volume curves for B1 structure of $Mg_{0.75}Ca_{0.25}O$.

Table 1: Calculated and experimental lattice parameter (a), bulk modulus (B_0) and its pressure derivatives (B_0') for CaO and MgO.

		Present	Experimental	Other Calculations
CaO				
B1	a (Å)	4.85	4.81[16]	4.83 [5], 4.86 [5], 4.76 [6], 4.84 [6], 4.81 [7], 4.72 [8], 4.71 [19], 4.953 [20], 4.92 [20]
	B_0 (GPa)	110.10	116.1[17], 110 [16]	128 [8], 127 [19], 106.47 [20], 135 [20]
	B_o'	3.91	4.26 [16]	4.11 [8], 3.62 [20]
B2	a (Å)	2.95	-	2.94 [5], 2.855 [8], 2.969 [20]
	B_0 (GPa)	115	-	132.8 [8], 104.66 [20]
	B_o'	3.67	-	4.37 [8], 4.34 [20]
MgO				
B1	a (Å)	4.22 [18]	4.213 [16]	4.098 [11], 4.254 [12], 4.185 [13], 4.259 [14], 4.215 [15]
	B_0 (GPa)	178.9 [18]	178.0 [51], 160.0 [16]	183.0 [11], 148.6 [12], 174.0 [13], 145.68 [14], 157.40 [15]
	B_o'	4.455	4.15 [16]	4.30 [11], 4.24 [12], 4.23 [14], 4.16 [15]

		[18]		
B2	a (Å)	2.610 [18]	-	2.661 [10], 2.656 [12], 4.227 [14]
	B_0 (GPa)	205.0 [18]	-	152.60 [10], 140.30 [12], 134.33 [14]
	$B_o^{'}$	4.05 [18]	-	3.39 [10], 4.10 [12], 4.24 [14]

Table 2 Calculated lattice parameter (a), bulk modulus (B_0) and its pressure derivatives ($B_0^{'}$) for $Mg_xCa_{1-x}O$ (x=0.25, 0.5 and 0.75).

		x= 0.25	x = 0.50	x= 0.75
a (Å)				
	Present	4.62	4.49	4.38
	Vegards Law	4.69	4.53	4.38
	Experimental	-	-	-
	Other calculations			
	WIEN2K code [19]	4..61	4.49	4.35
	SIESTA code [20]	4.812	4.65	4.48
	Charge transfer interaction potential (CTIP) approach [20]	4.82	4.7	4.58
B_0 (GPa)				
	Present	150	165	170
	Experimental	-	-	-
	Other calculations			
	WIEN2K code [19]	135.84	144.41	157.12
	SIESTA code [20]	118.76	131.15	134.53
	Charge transfer interaction potential (CTIP) approach [20]	156.78	178.70	200.27
B_0'				
	Present	4.4	4.5	4.01
	Experimental	-	-	-
	Other calculations			
	SIESTA code [20]	3.64	3.54	3.77

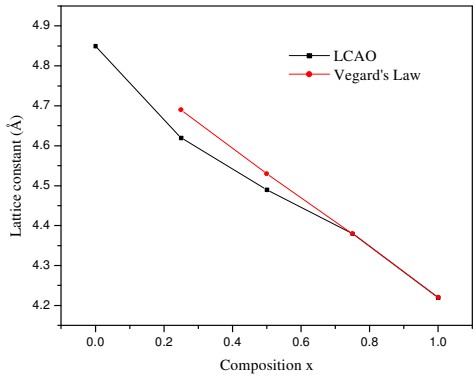

Fig. 6 Calculated lattice constants for $Mg_xCa_{1-x}O$ as a function of x

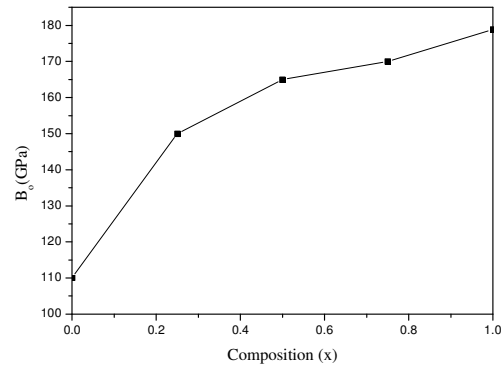

Fig. 7 Calculated bulk modulus as a function of composition (x).

4. CONCLUSIONS

The LCAO method is used to explore the structural properties of $Mg_xCa_{1-x}O$. The main results are summarized as follows:

(i) The total energy calculations show that the stable phase for binary compounds i.e MgO and CaO is B1.

(ii) As the concentration of magnesium increases the lattice constant decreases where as the bulk modulus increases.

The present results for the MgCaO are only predictions and may serve as the input to the other theoretical and experimental investigations.

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