Chapter 6

Structural and electronic properties of $\text{Mg}_x\text{Ca}_{1-x}\text{O}$
6.1 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 (~7.833 eV) [2], high dielectric constant, and ability to form ternary crystalline phases. It is formed by an ionic bond between one magnesium and one oxygen atom. It is used in numerous applications, such as medicine, where it is used for relief for heart burn and sore stomach, as an antacid, magnesium supplement and as a short-term laxative. Other known applications cover its use 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 electronic and structural properties of MgO and CaO have been reported [5-35]. Pantelides et al [5] reported an ab-intio study of the electronic properties of MgO using HF method. They predicted the indirect band gap in MgO. The electronic band structures of MgO and CaO have been investigated by Daude et al [6] using the tight-binding and pseudopotential methods. Kaneko et al [7,8] suggested that CaO is an indirect-band-gap material with the lowest gap at the X point. The high pressure behavior on structural and electronic properties of MgO has been investigated by Chang and Cohen [9] using PP method within the LDA. Causa et al [10] investigated the electronic structure and stability of different crystalline phase of MgO using the HF theory. The calculations were carried out for B1, B2 and B81 (inverse NiAs) structures in terms of Mulliken
population, charge density distribution, electron momentum distribution, anisotropy and band structure. The structural properties of B1 and B2 phases of alkaline earth oxides including MgO and CaO have been investigated by Habas et al [11] using the periodic ab-initio LCAO method. They employed HF and DFT schemes. The electronic structure of the oxides and sulfides of Mg, Ca and Sr have been investigated by Pandey et al [12] using self-consistent HF method including correlation. They predicted that these materials except MgS show direct band gap. Cortona et al [13] calculated the structural properties of MgO and CaO using DFT. Jaffe et al [14] predicted the high pressure phase transition in ZnO and MgO using LCAO method. They have used two different approximations in the exchange-correlation functional i.e. the LDA as parameterized by VWN and the GGA of PBE96. Oganav et al [15] studied the lattice dynamics, dielectric and thermodynamic properties for the B1 and B2 phase of MgO using density functional perturbation theory as employed within the ABINIT code. The bonding in MgO and CaO has been studied by Israel et al [16] using maximum entropy method. The electronic structures of MgO and CaO have been performed by Baltache et al [17] using FP-LAPW method. They have used LDA for exchange and correlation potentials. Alfe et al [18] reported the B1-B2 phase transition in MgO using diffuse monte-carlo (DMC) calculations. Medeiros et al [19] have performed a theoretical study on structural parameters of CaO using ABINIT code. They have used both LDA and GGA schemes. The ground state properties of CaO have been investigated by Deng et al [20] using ab-initio PW-PP method as implemented in CASTEP code. The electronic and optical properties of CaO have been investigated by Albuquerque and Vasconcelos [21] using LDA and GGA. Schleife et al [22] investigated these properties of MgO in B1, B2, B3 and B4 phases. They have used ab-initio pseudopotential method based on DFT, generalized gradient corrections to exchange and correlation and projector augmented wave (PAW) as employed in VASP code. The electronic structure and phase stability of MgO, ZnO, CdO and related alloys also have been investigated by the Zhu et al [23] using LAPW method. The structural parameters of MgO in the B1 and B2
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phases have been investigated by Gueddim et al [24] using the FP-LAPW. They observed structural phase transition from B1 to B2 at 611.12 GPa. The electronic structure and optical properties of the B1 and B2 phase of MgO at structural phase transition have been investigated by Liu et al [25] using PW-PP density functional method within the GGA. The electronic structure of MgO has been investigated by Labidi et al [26] using FP-LAPW method. The structural and electronic properties of CaO have been investigated by Ghebouli et al [27] using the DFT as embodied in CASTEP code. Experimentally, the structural properties of CaO and MgO have been investigated by Pichet et al [28] and Y. Fei [29] respectively.

In alkaline earth oxides, MgO and CaO have been extensively investigated, whereas $\text{Mg}_x\text{Ca}_{1-x}\text{O}$ have received less attention. The $\text{Ca}_{1-x}\text{Mg}_x\text{O}$ films can be used as dielectrics due to favourable properties such as high dielectric constant, wide band gap and lattice compatibility with SiC [36]. Stodika et al [36] used $\text{Mg}_{0.75}\text{Ca}_{0.25}\text{O}$ solid solution in SiC MOS applications. Doman et al [37] observed a severe immiscibility in the synthesis of CaO-MgO solid solution by using bulk techniques. However, the metastable phase of MgCaO films can be formed by the molecular beam epitaxy (MBE) method. Hlad et al [38] have prepared MgCaO films by rf plasma assisted MBE and capped with $\text{Sc}_2\text{O}_3$. They concluded that these films can be used as surface passivation layers and gate dielectrics on GaN-based high electron mobility transistors (HEMTs). $\text{Mg}_{1-x}\text{Ca}_x\text{O}$ solid solution films on ZnO layers have been grown by Nishii et al [39] using pulsed laser deposition method. They have characterized these films by X-ray diffraction mapping technique and concluded that both lattice parameters and diffraction intensities increases with the increasing CaO composition. A potential model was developed by Tepesch et al [40] to compute the phase diagrams of MgO and CaO solid solution. Using FP-LAPW method in combination with LDA, Miloua et al [41] have investigated the ground state properties and the stability of $\text{Ca}_{1-x}\text{Mg}_x\text{O}$ mixed oxides. Recently, structural phase transition and ground state properties of Mg$_1$. 
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$\gamma$-Ca$_x$O have been investigated by Srivastava et al [42] using first-principles DFT and charge transfer interaction potential (CTIP) approach.

It is well established that the physical properties of a material like energy band gap, lattice constant, and bulk modulus can be varied by the addition of another material of known properties. Hence, we have done alloying of Ca-MgO to make Mg$_x$Ca$_{1-x}$O. 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 work, the structural and electronic properties of Mg$_x$Ca$_{1-x}$O ($x=0.0, 0.25, 0.50, 0.75, 1.0$) have been reported using LCAO method. These properties are studied in terms of lattice constant, bulk modulus, pressure derivative of bulk modulus, band gap, densities of states, anisotropies in momentum densities and nature of bonding. Therefore, the present study can be considered as a step ahead in the direction of understanding the structural and electronic parameters of this compound.

An outline of this chapter is as follows: A brief description of computational details is given in Section 6.2 and the results are discussed in Section 6.3. The last Section 6.4 summarizes the results of this investigation.

6.2 Computational details

The first-principles LCAO method is used to study the structural and electronic properties of Mg$_x$Ca$_{1-x}$O. The \textit{ab-initio} periodic LCAO calculations are performed wherein one solves the Kohn-Sham equations self-consistently under the DFT [44]. There are a few fundamental schemes exist for constructing the Hamiltonian for the periodic solids. HF [45] approximation and the DFT [44] are the well-known approaches among these schemes. The CRYSTAL06 code [43] 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 $\varphi_n(\mathbf{r},\mathbf{k})$ defined in terms of local
functions $\varphi_\mu(r)$, 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 [46]. The Kohn-Sham Hamiltonian was constructed while considering the exchange scheme of Becke [47] and PBE [48] correlation scheme. In order to calculate the structural properties of $\text{Mg}_x\text{Ca}_{1-x}\text{O}$ ($x = 0.0, 0.25, 0.50, 0.75, 1.0$), the optimization was performed by minimizing the total energy with respect to the cell volume for each composition. Then calculated lattice constants were used to investigate the electronic properties. 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.

6.3 Results and Discussion

6.3.1 Structural properties

The total energies of the B1 and B2 phases of CaO and MgO compounds 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 6.1 and 6.2. 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 and MgO, the total energy have also been calculated as a function of cell volume and fitted to the third order Birch-Murnaghan equation of state [49,50]. Using this equation, we calculated the ground state properties such as the lattice constants ($a$), bulk modulus, pressure derivative of bulk modulus. The calculated structural parameters of CaO and MgO in B1 and B2 phases are listed in Table 6.1. Since B1 is a stable phase for CaO and MgO, so the structural properties of $\text{Mg}_x\text{Ca}_{1-x}\text{O}$ for the compositions $x= 0.25, 0.5, 0.75$ are computed in B1 phase. The variation of
Figure 6.1 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).
Figure 6.2 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).
### Table 6.1
Calculated and experimental lattice parameter (a), bulk modulus (B₀) and its pressure derivatives (B₀’) for CaO and MgO.

<table>
<thead>
<tr>
<th></th>
<th>Present</th>
<th>Experimental</th>
<th>Other Calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CaO</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>4.85</td>
<td>4.81[28]</td>
<td>4.83 [11], 4.86 [11], 4.76 [13], 4.84 [13], 4.81 [16], 4.72 [17], 4.714 [28], 4.71 [41], 4.953 [42], 4.92 [42]</td>
</tr>
<tr>
<td><strong>B₀ (GPa)</strong></td>
<td>110.10</td>
<td>116.1[30], 110 [29]</td>
<td>128 [17], 129 [28], 127 [41], 106.47 [42], 135 [42]</td>
</tr>
<tr>
<td><strong>B₀’</strong></td>
<td>3.91</td>
<td>4.26</td>
<td>4.11 [17], 4.47 [28], 3.62 [42]</td>
</tr>
<tr>
<td>B2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>2.95</td>
<td>-</td>
<td>2.94 [11], 2.855 [17], 2.969 [42]</td>
</tr>
<tr>
<td><strong>B₀ (GPa)</strong></td>
<td>115</td>
<td>-</td>
<td>132.8 [17], 104.66 [42]</td>
</tr>
<tr>
<td><strong>B₀’</strong></td>
<td>3.67</td>
<td>-</td>
<td>4.37 [17], 4.34 [42]</td>
</tr>
<tr>
<td><strong>MgO</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>B₀ (GPa)</strong></td>
<td>178.9</td>
<td>178.0 [51], 160.0 [29]</td>
<td>183.0 [18], 148.6 [22], 174.0 [23], 145.68 [24], 157.40 [25]</td>
</tr>
<tr>
<td><strong>B₀’</strong></td>
<td>4.455</td>
<td>4.15 [29]</td>
<td>4.30 [18], 4.24 [22], 4.23 [24], 4.16 [25]</td>
</tr>
<tr>
<td>B2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>2.610</td>
<td>-</td>
<td>2.661 [14], 2.656 [22], 4.227 [24]</td>
</tr>
<tr>
<td><strong>B₀ (GPa)</strong></td>
<td>205.0</td>
<td>-</td>
<td>152.60 [14], 140.30 [22], 134.33 [24]</td>
</tr>
<tr>
<td><strong>B₀’</strong></td>
<td>4.05</td>
<td>-</td>
<td>3.39 [14], 4.10 [22], 4.24 [24]</td>
</tr>
</tbody>
</table>
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total energy versus volume curves for Mg\textsubscript{x}Ca\textsubscript{1-x}O (x=0.25, 0.50, 0.75) are given in Figures 6.3-6.5. The calculated structural parameters for B1 phase of Mg\textsubscript{x}Ca\textsubscript{1-x}O (x=0.25, 0.50 and 0.75) are listed in Table 6.2 along with previous results. Our computed values of lattice constant for Mg\textsubscript{x}Ca\textsubscript{1-x}O (x=0.25, 0.5 and 0.75) are in good agreement with the results of Milaua et al [41]. The variations of lattice constant and bulk modulus of Mg\textsubscript{x}Ca\textsubscript{1-x}O as a function of x are shown in Figures 6.6 and 6.7 respectively. Figure 6.6 depicts that the present LCAO values show similar trend with the values of Vegard's law [52]. The disagreement in the region of lower x values may be the large mismatch of lattice constants of MgO and CaO. From Figure 6.7, it is clear that the compressibility decreases with the increasing x. Hence, CaO is more compressible than MgO.

6.3.2 Electronic properties

The electronic band structures for B1 phase of Mg\textsubscript{x}Ca\textsubscript{1-x}O (x=0.0, 0.25, 0.50 and 0.75) calculated at the equilibrium lattice constant are shown in Figures 6.8-6.12. The different symmetry points considered in the Brillouin zone are W (0.5, 0.25, 0.75), L (0.5, 0.5, 0.5), Γ (0.0, 0.0, 0.0), X (0.5, 0.0, 0.0), W (0.5, 0.25, 0.75) and K (0.375, 0.375, 0.75). Figures reveal that as the concentration of magnesium is increased the band gaps are observed to change from indirect to direct. For x = 0.25, 0.5, 0.75 and 1.0, direct band gaps are observed along the highly symmetric direction (i.e Γ). Thus, CaO has an indirect band gap and other alloys have direct band gaps. This is consistent with earlier investigations [7,8,17]. The calculated results of band gaps are given in Table 6.3. The results are compared with previous experimental and other theoretical results for two end point members of Mg\textsubscript{x}Ca\textsubscript{1-x}O solid solution. It is evident that both direct (Γ-Γ) and indirect (Γ-X) gap increases as the concentration of Mg increases. The densities of states (DOS) have also been shown in Figures 6.13-6.17 for Mg\textsubscript{x}Ca\textsubscript{1-x}O at x=0.0, 0.25, 0.50, 0.75 and 1.0 respectively. From Figures 6.13-6.17, it is clear that as the concentration of magnesium increases the conduction band minima shifts in high energy region.
Figure 6.3 First-principles energy volume curves for B1 structure of Mg$_{0.25}$Ca$_{0.75}$O calculated using the DFT-PBE scheme.
Figure 6.4 First-principles energy volume curves for B1 structure of Mg$_{0.50}$Ca$_{0.50}$O calculated using the DFT-PBE scheme.
Figure 6.5 First-principles energy volume curves for B1 structure of Mg$_{0.75}$Ca$_{0.25}$O calculated using the DFT-PBE scheme.
Table 6.2
Calculated lattice parameter (a), bulk modulus ($B_0$) and its pressure derivatives ($B_0'$) for Mg$_x$Ca$_{1-x}$O (x=0.25, 0.5 and 0.75).

<table>
<thead>
<tr>
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<th>x = 0.25</th>
<th>x = 0.50</th>
<th>x = 0.75</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Present</td>
<td>4.62</td>
<td>4.49</td>
<td>4.38</td>
</tr>
<tr>
<td>Vegards Law</td>
<td>4.69</td>
<td>4.53</td>
<td>4.38</td>
</tr>
<tr>
<td>Experimental</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Other calculations</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WIEN2K code [41]</td>
<td>4.61</td>
<td>4.49</td>
<td>4.35</td>
</tr>
<tr>
<td>SIESTA code [42]</td>
<td>4.812</td>
<td>4.65</td>
<td>4.48</td>
</tr>
<tr>
<td>Charge transfer interaction potential (CTIP) approach [42]</td>
<td>4.82</td>
<td>4.7</td>
<td>4.58</td>
</tr>
<tr>
<td>$B_0$ (GPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Present</td>
<td>150</td>
<td>165</td>
<td>170</td>
</tr>
<tr>
<td>Experimental</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Other calculations</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WIEN2K code [41]</td>
<td>135.84</td>
<td>144.41</td>
<td>157.12</td>
</tr>
<tr>
<td>SIESTA code [42]</td>
<td>118.76</td>
<td>131.15</td>
<td>134.53</td>
</tr>
<tr>
<td>Charge transfer interaction potential (CTIP) approach [42]</td>
<td>156.78</td>
<td>178.70</td>
<td>200.27</td>
</tr>
<tr>
<td>$B_0'$</td>
<td></td>
<td></td>
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<tr>
<td>Present</td>
<td>4.4</td>
<td>4.5</td>
<td>4.01</td>
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<tr>
<td>Experimental</td>
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<td>-</td>
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<td>Other calculations</td>
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<td></td>
</tr>
<tr>
<td>SIESTA code [42]</td>
<td>3.64</td>
<td>3.54</td>
<td>3.77</td>
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Figure 6.6 Calculated lattice constants for $\text{Mg}_x\text{Ca}_{1-x}\text{O}$ as a function of $x$. 
Figure 6.7 Calculated bulk modulus as a function of composition (x).
Figure 6.8 Energy band structure of B1 phase of CaO.
Figure 6.9 Energy band structure of B1 phase of Mg$_{0.25}$Ca$_{0.75}$O.
Figure 6.10 Energy band structure of B1 phase of $\text{Mg}_{0.50}\text{Ca}_{0.50}\text{O}$. 
Figure 6.11 Energy band structure of B1 phase of Mg$_{0.75}$Ca$_{0.25}$O.
Figure 6.12 Energy band structure of B1 phase of MgO.
Table 6.3
Direct and indirect band gap energy (in eV) for Mg$_x$Ca$_{1-x}$O at various x compositions.

<table>
<thead>
<tr>
<th>Mg$<em>x$Ca$</em>{1-x}$O</th>
<th>Present</th>
<th>Experimental</th>
<th>Other calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>Direct</td>
<td>Indirect</td>
<td>Direct</td>
</tr>
<tr>
<td>0.0</td>
<td>6.68</td>
<td>6.64</td>
<td>7.1</td>
</tr>
<tr>
<td>0.25</td>
<td>6.82</td>
<td>7.85</td>
<td>-</td>
</tr>
<tr>
<td>0.5</td>
<td>7.57</td>
<td>8.28</td>
<td>-</td>
</tr>
<tr>
<td>0.75</td>
<td>7.92</td>
<td>9.79</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>8.05</td>
<td>11.62</td>
<td>7.83 [2]</td>
</tr>
</tbody>
</table>
Figure 6.13 Density of states of B1 phase of CaO.
Figure 6.14 Density of states of B1 phase of $\text{Mg}_{0.25}\text{Ca}_{0.75}\text{O}$. 
Figure 6.15 Density of states of B1 phase of Mg$_{0.50}$Ca$_{0.50}$O.
**Figure 6.16** Density of states of B1 phase of Mg$_{0.75}$Ca$_{0.25}$O.
Figure 6.17 Density of states of B1 phase of MgO.
The calculated band gaps from the DOS are in close proximity with those calculated from the electronic band structures.

The directional Compton profiles along the principal crystallographic directions, namely, [100], [110] and [111] have been computed using the DFT-LCAO method. The anisotropies [100]-[110], [100]-[111] and [110]-[111] for Mg$_x$Ca$_{1-x}$O are plotted in Figure 6.18 (a)-(e). The Figure 6.16 (a)-(c) depicts that all three anisotropies are positive in nature around $p_z=0$ and the anisotropy [100]-[111] direction is maximum. The Figures (a)-(c) also depicts that the anisotropy between [100] and [111] directions is larger than other anisotropies around $J(0)$. It indicates larger occupied states along the [100] direction in this region. The Figure 6.18 (d) depicts that [110]-[111] anisotropy becomes negative. Further, all anisotropies are negative in nature for $x=1.0$ composition. Thus, the Mg doping modifies the momentum densities.

According to Reed and Eisenberger [53], the EVED profiles offer a way to understand the nature of bonding in isovalent and isostructural compounds. The theoretical EVED profiles for Mg$_x$Ca$_{1-x}$O compounds have been calculated by DFT-PBE valence profiles. The Figure 6.19 shows that the EVED profile corresponding to $x=1.0$ i.e MgO is larger around the low momentum region as compared to other compositions. As a larger value around the low momentum region is attributed to a greater covalent character, it shows that MgO is more covalent and hence less ionic than CaO. The higher covalent character of MgO is well supported by the earlier reported ionicity factors $f_i$ [54,55]. It is also visible from Figure 6.19 that Mg$_x$Ca$_{1-x}$O shows strong covalent nature with increasing concentration of Mg.

### 6.4 Conclusions

The LCAO method is used to explore the electronic and structural properties of Mg$_x$Ca$_{1-x}$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.
Figure 6.18 Compton profile anisotropies obtained from unconvoluted directional Compton profiles for B1 phase of Mg$_x$Ca$_{1-x}$O (x=0.0, 0.25, 0.50, 0.75 and 1.0) using LCAO method.
Figure 6.19 The equal-valence-electron-density (EVED) profiles for B1 phase of \( \text{Mg}_x \text{Ca}_{1-x} \text{O} \). All profiles are normalized to 4.0 electrons.
(iii) The analysis of the electronic properties indicates that the calculated band gaps at equilibrium lattice constant for Mg$_x$Ca$_{1-x}$O in B1 phase increases as the concentration of magnesium increases.

(iv) EVED profiles reveal that MgO is more covalent as compared to others compounds.

(v) 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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