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Electronic Properties of $Mg_xCa_{1-x}O$ (x = 0.0, 0.25, 0.50, 0.75 and 1.0): A First Principles Study.

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ABSTRACT

Electronic band structures, densities of states, Compton profiles of $Mg_xCa_{1-x}O$ ternary alloy have been calculated by employing the linear combination of atomic orbitals (LCAO) method utilizing CRYSTAL code. The correlation and exchange potential is treated by the generalized-gradient approximation (GGA) given by Perdew–Burke–Ernzerhof (PBE) and Becke's ansatz respectively. Results obtained are in good agreement with earlier investigations. The study observes that band gap increases with the concentration of magnesium. Nature of bonding in the isovalent $Mg_xCa_{1-x}O$ compounds is also compared and it was found that MgO is more covalent.
Keywords: MgCaO, LCAO method, electronic band structure, Compton profile.

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INTRODUCTION

In alkaline earth oxides, MgO and CaO have been extensively investigated [1-14] whereas $Mg_xCa_{1-x}O$ have received less attention. The $Ca_{1-x}Mg_xO$ films can be used as dielectrics due to outstanding properties large band gap and compatibility of lattice with SiC [15]. Doman et al. [16] observed a severe immiscibility in the production of CaO-MgO solid solution with the help of bulk techniques. However, the metastable phase of MgCaO films can be formed by the molecular beam epitaxy (MBE) method. Hlad et al. [17] have prepared MgCaO films by rf plasma assisted MBE and capped with Sc_2O_3. They concluded that these films can be used as dielectric layer in high electron mobility transistors (HEMTs). $Mg_{1-x}Ca_xO$ solid solution films on ZnO layers have been grown by Nishii et al. [18] using pulsed laser deposition method. They have characterized these films by X-ray diffraction method and mentioned that both lattice parameters and diffraction intensities increases by increasing CaO composition. A potential model was developed by Tepesch et al. [19] for computing the phase diagrams of MgO and CaO solid solution.

Enhancing the scientific knowledge about the compounds of this kind is important to analyze the trend of ternary compounds and it is also necessary for developing materials. To have a deep knowledge of the nature of these alloys, the results of first principles calculations of CaO and MgO compounds and their ternary alloys $Mg_xCa_{1-x}O$ in rocksalt structure is presented. The present paper presents, the electronic properties of the $Mg_xCa_{1-x}O$ (x=0.0, 0.25, 0.50, 0.75, 1.0) using LCAO method as employed in CRYSTAL06 [20] code. The electronic properties are calculated on the previously calculated lattice constants [14]. These properties are studied in terms of band gap, densities of states, anisotropies in momentum densities and nature of bonding.

An outline of this paper is as follows: in section 2, the computational methods used in this study is described. In section 3, results on electronic properties $Mg_xCa_{1-x}O$ are discussed. Finally, the last section 4 summarizes the results of this investigation.

COMPUTATIONAL DETAILS

The first-principles LCAO method as embodied in CRYSTAL06 [20] code is applied to investigate the electronic parameters of $Mg_xCa_{1-x}O$. There are few basic schemes for building the Hamiltonian for, among which DFT [21] and HF [22] are the well-known and suitable approaches. For Mg, Ca and O, the local functions were constructed using the Gaussian type basis sets [23]. For constructing the Kohn-Sham Hamiltonian the exchange and correlation scheme of Becke [24] and PBE [25] respectively were employed. 165 **k** points in the irreducible Brillouin zone were used to perform the self-consistent calculations. The self-consistency is achieved within 15 cycles, with 45% mixing of successive cycles.

RESULTS AND DISCUSSION

Electronic properties

Table 1"Direct and indirect band gap energy (in eV) for $Mg_xCa_{1-x}O$ at various x compositions.					
$Mg_xCa_{1-x}O$	Present		Experimental	Other calculations	
x	Direct	Indirect		Direct	Indirect
0.0	6.68	6.64	7.1 [1]	7.74 [2], 5.02 [3], 4.79 [4], 4.81 [5], 4.5 [6], 5.2 [7], 5.40 [8]	10.8 [2], 3.46 [3], 3.7 [7], 4.3 [8]
0.25	6.82	7.85	-	-	-
0.5	7.57	8.28	-	-	-
0.75	7.92	9.79	-	-	-
1.0	8.05	11.62	7.83 [2]	8.21 [2], 5.05 [3], 4.8 [7], 7.76 [10], 4.5 [11],	8.96 [3]

The electronic band structures for B1 phase of $Mg_xCa_{1-x}O$ (x=0.0, 0.25, 0.50 and 0.75) calculated at the equilibrium lattice constant [14] are shown in Figures I-V. 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 [3,12,13]. The calculated results of band gaps are given in Table I. The results are compared with previous experimental and other theoretical results for two end point members of $Mg_xCa_{1-x}O$ solid solution. It is evident that both direct (Γ-Γ) and indirect (Γ-X) gap increases as the concentration of Mg increases.
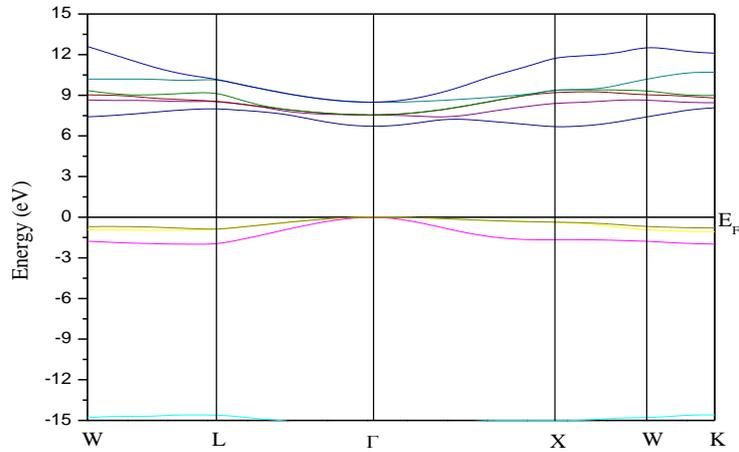

Figure I: Energy band structure of CaO for B1 phase.
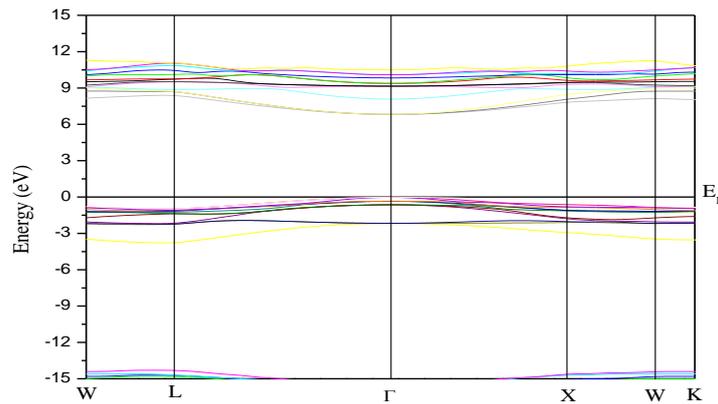
Figure II: Energy band structure of $Mg_{0.25}Ca_{0.75}O$ for B1 phase.
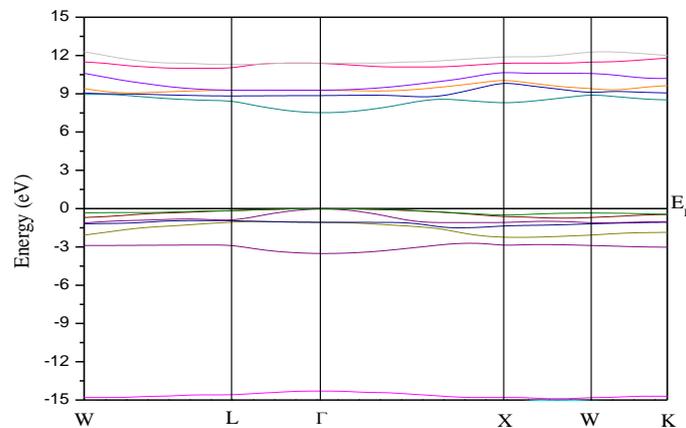
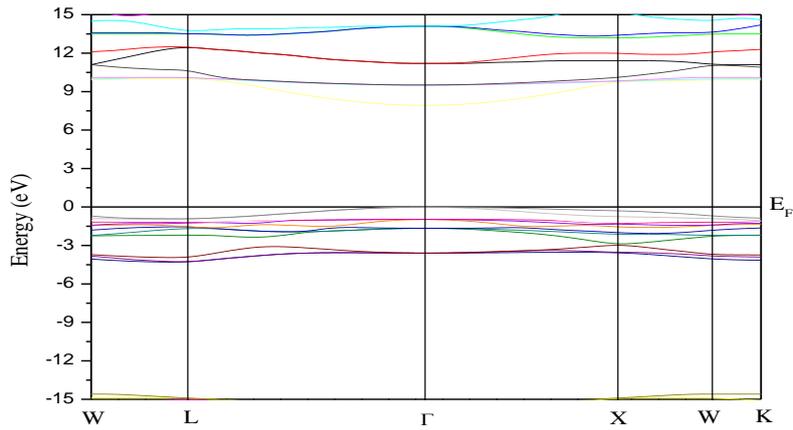**Figure III: Energy band structure of B1 phase of $Mg_{0.50}Ca_{0.50}O$.**

Figure IV: Energy band structure of Mg$_{0.75}$Ca$_{0.25}$O for B1 phase.
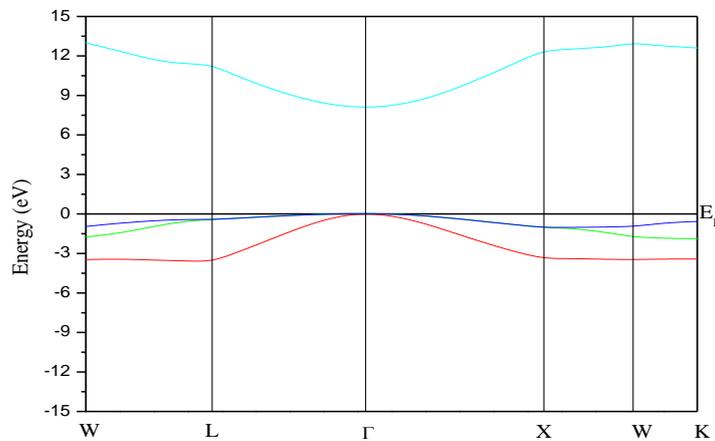

Figure V: Energy band structure of MgO for B1 phase.

The densities of states (DOS) have also been shown in Figures V-X for Mg$_x$Ca$_{1-x}$O at x=0.0, 0.25, 0.50, 0.75 and 1.0 respectively. From Figures V-X, it is clear that as the concentration of magnesium increases the conduction band minima shifts in high energy region. The calculated band gaps from the DOS are in close proximity with those calculated from the electronic band structures.
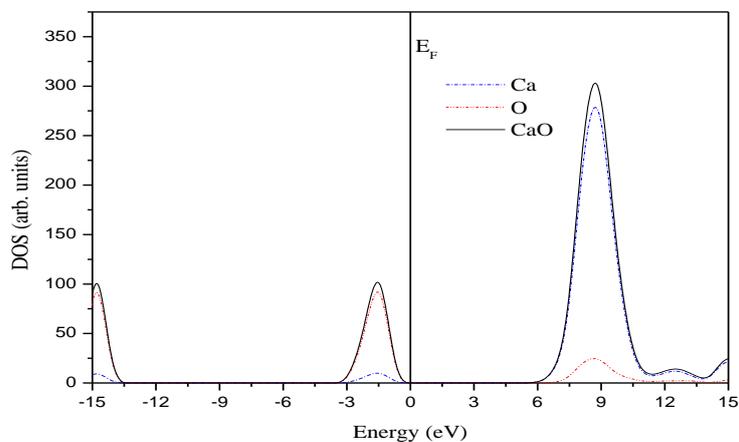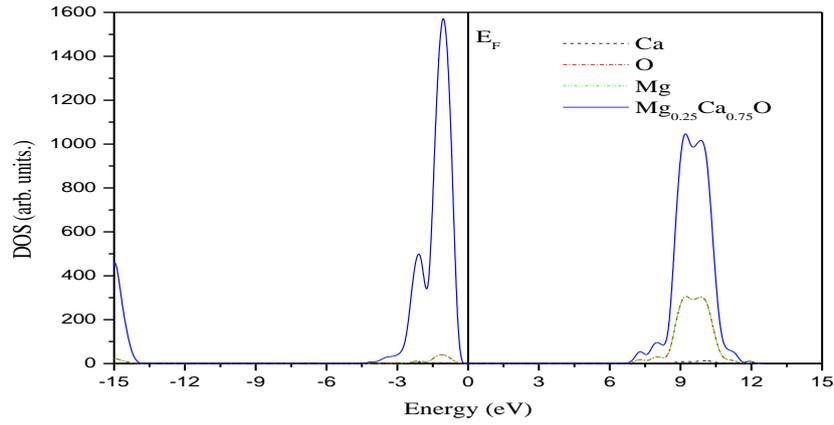

Figure VI: Density of states of B1 phase of CaO.

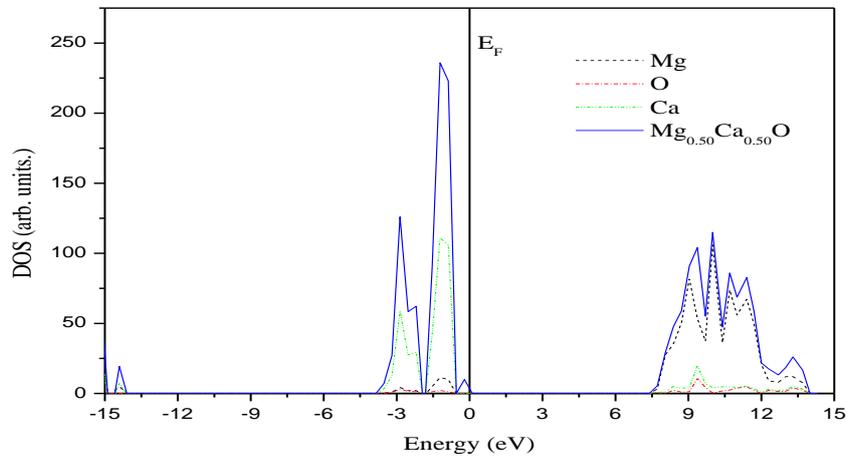Figure VII: Density of states of Mg$_{0.25}$Ca$_{0.75}$O for B1 phase.

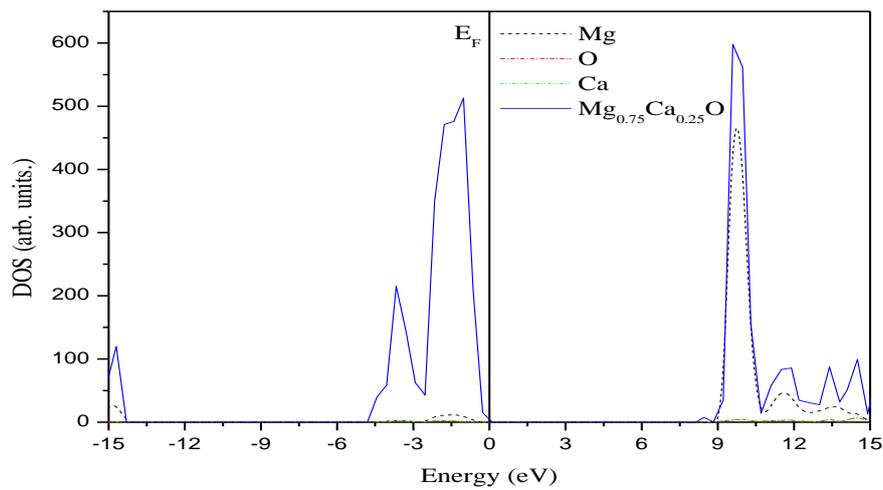Figure VIII: Density of states of Mg$_{0.50}$Ca$_{0.50}$O for B1 phase.

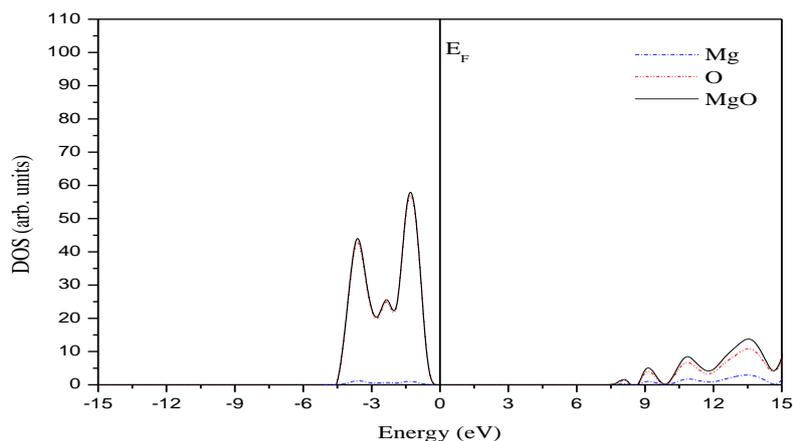Figure IX: Density of states of Mg$_{0.75}$Ca$_{0.25}$O for B1 phase.

Figure X: Density of states of MgO for B1 phase.

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 $Mg_xCa_{1-x}O$ are plotted in Figure 11 (a)-(e). The Figure XI (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 XI (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 XI (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.
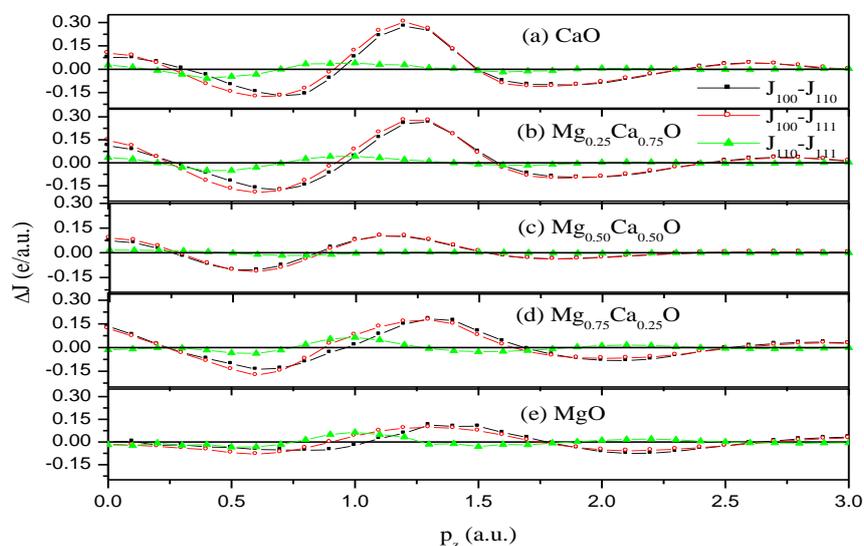

Figure XI: Compton profile anisotropies obtained from unconvoluted directional Compton profiles for B1 phase of $Mg_xCa_{1-x}O$ (x=0.0, 0.25, 0.50, 0.75 and 1.0) using LCAO method.

According to Reed and Eisenberger [26], the EVED profiles offer a way to understand the nature of bonding in isovalent and isostructural compounds. The theoretical EVED profiles for $Mg_xCa_{1-x}O$ compounds have been calculated by DFT-PBE valence profiles. The Figure XII 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 *fi* [27, 28]. It is also visible from Figure 12 that $Mg_xCa_{1-x}O$ shows strong covalent nature with increasing concentration of Mg.
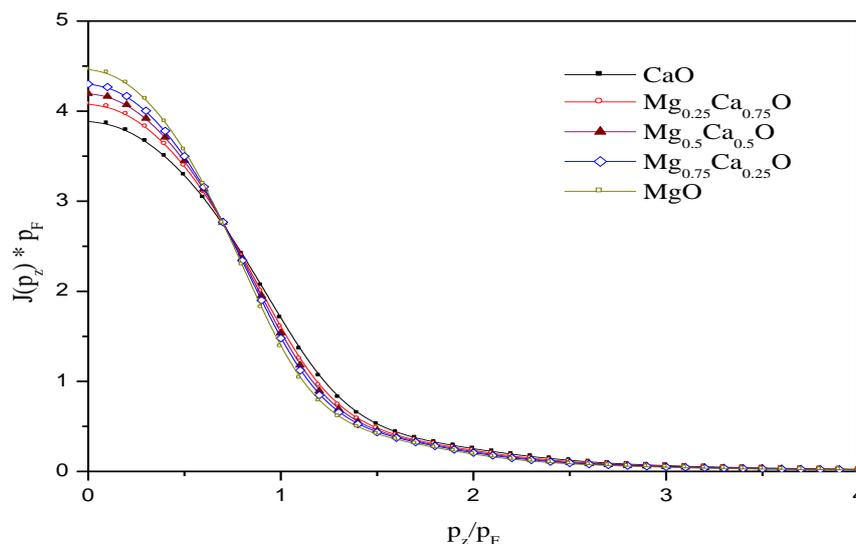
Figure XII: The equal-valence-electron-density (EVED) profiles for B1 phase of $Mg_xCa_{1-x}O$. All profiles are normalized to 4.0 electrons.

CONCLUSIONS

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

- The analysis of the electronic properties indicates that the calculated band gaps at equilibrium lattice constant for $Mg_xCa_{1-x}O$ in B1 phase increases as the concentration of magnesium increases.
- EVED profiles reveal that MgO is more covalent as compared to others compounds. 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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