Pressure Effect on Structural, Electronic and Optical Properties of Zinc Blend MgO Solid Solution

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Abstract- First principles total energy calculations were carried out to investigate structural, electronic and optical properties of zinc-blend (ZB) MgO solid solution. Firstly, we have calculated lattice parameters a₀(A°), bulk modulus B in GPa and pressure derivative B'(GPa). The direct and indirect band-gap energies were calculated for this material. Total and partial densities of states are depicted in Fig. 2. Secondly, we have examined the pressure effects on the electronic properties. We have varied the pressure from hydrostatic pressure to 350 GPa. Linear coefficients α and β of band gaps are calculated. Finally, the optical properties were investigated under hydrostatic pressure and under a pressure of 300 GPa, where the refractive index n, the optical conductivity in (1/Ω cm), the real part ε₁ and imaginary part ε₂ of the dielectric function are presented. Results obtained are discussed and compared with other available theoretical and experimental results.

Keywords- Wide Gap Semiconductors; FP-LAPW; MgO; Pressure Effect

INTRODUCTION

In recent years, intensive research effort has been devoted to the search of materials with semi conducting properties at room temperature and hydrostatic pressure.

Magnesium oxide (MgO) has long been the focus of geological research since it is an important material of the Earth’s lower mantle. It is also an important material for a wide range of technological applications, for example, due to its wide band gap, high dielectric constant, and ability to form solid solutions and ternary crystalline phases.

Being a possible candidate for applications in optoelectronic devices, ZnO has strongly re-attracted interest in the last years. Other Group-II metal oxides, like MgO and CdO, are discussed in the context of spintronics (together with transition metal oxides), alloys, or heterostructures. ZnO and MgO allow for the formation of new types of nanostructures, such as nanorods and tubes. A better fundamental understanding of the electronic structure of MgO oxide would undoubtedly be helpful for interpreting experimental results. Starting from a detailed investigation of the structural, electronic and optical properties of this material in the framework of density functional theory (DFT) using the Kohn-Sham (KS) approach, we present FP-lapw calculations of the structural parameter, bulk modulus, band structure, densities of states (DOS) and the refractive indices. Also the pressure effect on the band gaps and the refractive indices is investigated.

METHOD OF CALCULATION

First principal calculations of total energies and the electronic structure based on the scalar non-relativistic full-potential (FP) “Linearized augmented plane wave (LAPW)” method were carried out using the Wien2k code packages. This is very accurate and efficient scheme to solve the Kohn-Sham equations of density functional theory (DFT). While this method can use different schemes for the treatment of the effects of exchange and correlation, we here use, the local density approximation (LDA) following the Perdew-Wang implementation and Perdew–Burke–Ernzerhof generalized gradient approximation GGA. Basis functions, electron densities and potentials were expanded inside the muffin-tin spheres in combination with spherical harmonic functions with a cut-off ℓ_m=10, and in Fourier series in the interstitial region. Within this method a parameter which determines matrix size, Rmt×Kmax =7, was used with a value of 7, where R_m denotes the atomic sphere radius and K_max gives the magnitude of the K vector in the plane wave expansion.

For Mg we adopted a value of 1.7 and a value of 1.3 Bohr for oxygen O (1 Bohr = 0.529 Å), as the muffin tin MT radii. We have distinguished the Mg (1s² 2s² 2p⁶), O (1s² 2s² 2p⁴) inner-shell electrons from the valence electrons of Mg (3s2) and O (3s² 3p⁴) shells. For the irreducible wedge of the Brillouin zone, a mesh of 204 special k-points is used.

CALCULATIONS AND RESULTS

A. Structural Properties

The calculations were firstly carried out to determine the structural properties of ZB MgO, solid solution. The structural properties were obtained by a minimization of total energy as a function of the volume.
The bulk modulus and the pressure derivative were obtained by a non-linear fit of the total energy versus volume according to the Birch-Murnaghan equation of state [7]. In Table 1, we summarize the calculated structural properties (lattice constants, bulk modulus and the pressure derivative) of MgO solid solution together with available theoretical and experimental data from the literature. The analysis of our computed quantities shows a good agreement with theoretical and experiment [8-9] results.

| Table I Lattice Constants a, Bulk Modulus B, and Pressure Derivative of Bulk Modulus B' for ZB MgO Compound |
|-----------------|-----------------|-----------------|-----------------|
| MgO             | This work       | GGA             | LDA             |
| a(A)            | 4.68            | 4.53            | 4.19,4.21,4.25  |
|                 |                 |                 | 4.25,4.21       |
| b(GPa)          | 121.14          | 130.8           | 146,157.4,148.6 |
|                 |                 |                 | 151,160         |
| u (GPa)         | 4.21            | 4.34            | 4.16, 4.34      |
|                 |                 |                 | 4.20,4.15       |

aRefs.[9], bRefs.[8], cRefs.[16], dRefs.[17], eRefs.[18]

B. Electronic Properties

The calculations of the electronic band structure properties and density of states were carried out for MgO (ZB) structure at the equilibrium calculated lattice parameter. The band gaps calculated using the FP-LAPW method for MgO are listed in Table 2 for the high-symmetry points Γ, X and L in the Brillouin zone. All energies are with reference to the top of the valence band. The electronic structures of MgO with GGA and LDA approximations along symmetry lines are shown in Fig. 1. The results show that MgO is a wide and direct-gap semiconductor. The value of the direct gap is 5.25 eV and agrees well with values obtained in other works [10-11].

C. Density of States (DOS)

A very high degree of precision with the use of a fine k-points mesh in the first Brillouin zone (BZ) is required for the DOS calculations. In this paper, we have considered a K-mesh = 3500. For ZB MgO the total DOS spectrum presents three regions. One valence region VB1 below the top of the valence band (E_F) and two conduction bands CB1 and CB2 above Fermi level E_F. Fig. 2 The valence band region VB1 is dominated of O-2p with a low contribution of Mg-3s and the deeper orbital Mg-2p. The first region CB1 results from the contribution of O-2p and Mg-2p. For the conduction band CB2, we observe a high contribution of Mg 3s with a small contribution of O-3p.

The total valence charge densities of (ZB) MgO given in Fig. 3 show an obvious delocalisation of charges toward the bond center in spite of the slight transfer noticed around oxygen which reflects a strong covalent bond for this compound. The transfer from Mg to O reflects the small ionic contribution.

III. PRESSURE EFFECTS ON BAND GAPS

To understand, the pressure effects on electronic properties. We have varied the pressure from hydrostatic pressure to 350 GPa. Results are depicted in Fig. 4. It is clearly seen from this result that energies E (Γ→Γ) increase and E (Γ→X) decrease with increasing pressure A cross over between their curves is presented at P = 302.96 GPa, where a phase transition of MgO is observed. For E (Γ→L) a similarly increase is shown versus pressure variations. The direct gap character of MgO is changed at the pressure value of P = 302.96 GPa (316 GPa in other works). We summarize in Table 3 the results of our calculated linear
coefficients of band gaps by using a linear pressure dependent fit function:

\[ E(P) = E(0) + \alpha P + \beta P^2 \]  

Where \( E \) is in eV and the pressure \( P \) is in GPa.

\[ (1) \]

TABLE III PRESSURE COEFFICIENTS RELATED TO THE CALCULATED VALUES OF THE ENERGY GAPS FOR ZB MgO COMPOUND

<table>
<thead>
<tr>
<th>Transitions</th>
<th>This work</th>
<th>Other works</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma \rightarrow c )</td>
<td>( \alpha ) (meV/GPa)</td>
<td>7.59</td>
</tr>
<tr>
<td>( \Gamma \rightarrow c )</td>
<td>( \beta ) (meV/GPa²)</td>
<td>-0.003</td>
</tr>
<tr>
<td>( \Gamma \rightarrow \Gamma^* )</td>
<td>( \alpha ) (meV/GPa)</td>
<td>2.44</td>
</tr>
<tr>
<td>( \Gamma \rightarrow \Gamma^* )</td>
<td>( \beta ) (meV/GPa²)</td>
<td>-0.16</td>
</tr>
<tr>
<td>( \Gamma \rightarrow \Gamma^* )</td>
<td>( \alpha ) (meV/GPa)</td>
<td>6.09</td>
</tr>
<tr>
<td>( \Gamma \rightarrow \Gamma^* )</td>
<td>( \beta ) (meV/GPa²)</td>
<td>-0.13</td>
</tr>
</tbody>
</table>

The pressure coefficient is \( \alpha = 7.59 \) for direct energy gap and \( \alpha = 2.44 \) for indirect gap, this means that the variation of the direct band gap energy is more important in comparison with the indirect gap and the direct band gap character for MgO material will take a change in one pressure.

IV. OPTICAL PROPERTIES

This work is completed by calculations of optical properties, where the dielectric function \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \) (5) was investigated and used in the calculation of the refractive index. In Fig. 5 and 6 we present the real part \( \varepsilon_1 \) and the imaginary part \( \varepsilon_2 \) respectively, for ZB MgO. The imaginary part \( \varepsilon_2 \) shows two major peaks, the calculated peak positions give these peaks at 7.32 eV for the first peak and at 14.05 eV for the second one and correspond to the electronic transition \((\Gamma \rightarrow \Gamma_c)\) and \((\Gamma \rightarrow \Gamma_x)\) respectively. Minor peaks are shown at 12.9 eV and 16.83 eV and correspond to the interband transitions and a shoulder-like structure near 5.22 eV. Values obtained in this work agree well with experiment and other works.

The real part \( \varepsilon_1 \) calculated under hydrostatic pressure presents a series of peaks located at 3.67, 6.96, 10.63, 13.35, 13.92 eV. In the same time \( \varepsilon_1 \) presents only one major peak and located at 8.43 eV. The important bearing of the refractive index on the operation of an injection laser is its role in the confinement of the emitted radiation to the intermediate vicinity of an active region[13].

The refractive index \( n \) shown in Fig. 7 was computed as a function of the real part of the dielectric function, \( n = \sqrt{\varepsilon_1} \) [13].

The refractive index \( n \) is calculated under hydrostatic pressure and under a pressure of 300 GPa. Values obtained are 1.69 and 2.38 respectively. Curves in the Fig. 7 show that the high value of the refractive index is 2.02. This value is located at 6.96 eV. A cross over between curves is observed at 7.32 eV, the corresponding value of the refractive index is 1.74. In order to confirm our results, we have used the Moss model and Herve–Vandam model. Where:

\[ n = \left( \frac{K}{E_0} \right)^{1/2} \]
Moss\textsuperscript{[14]} with $k = 95$ and $E_0$ is the fundamental gap. And:

$$n = \left[ 1 + \left( \frac{A}{E_0 + B} \right)^2 \right]^{\frac{1}{2}}$$

Herve-Vandam\textsuperscript{[15]} with $A = 13.6$, $B = 3.4$ eV and $E_0$ is the fundamental gap.

Results obtained are summarized in and TABLE IV show that every model can be used in a range of energies. A good agreement is observed between our results and with other theoretical values. The small difference observed between values may be explained by the approximations used in every model.

<table>
<thead>
<tr>
<th>Model</th>
<th>Refractive index (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moss Model</td>
<td>1.7</td>
</tr>
<tr>
<td>Herve-Vandam Model</td>
<td>2.06</td>
</tr>
<tr>
<td>Ravinda Model</td>
<td>1.6</td>
</tr>
<tr>
<td>Other works</td>
<td>0.82</td>
</tr>
<tr>
<td>Hydrostatic pressure</td>
<td>1.7\textsuperscript{a}</td>
</tr>
<tr>
<td></td>
<td>1.81\textsuperscript{b}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Ref [1-2].\textsuperscript{b}Ref [16]

The optical conductivity in (1/Ω cm) is shown in Fig. 8. We observe and compare the optical conductivities under hydrostatic pressure and under a pressure of 300 GPa. The optical conductivity calculated under hydrostatic pressure presents some major peaks, they are located at 6.99, 9.77, 12.31, 12.82 eV. For the optical conductivity under 300 GPa, one ablated peak is observed and he is large of approximately 1.46 eV. The maximum values of the optical conductivities under hydrostatic pressure and 300 GPa are $3871.45$ and $4539.58$. These peaks are located at 12.31 and 8.53 eV respectively. From this result we can say that optical conductivity for MgO material is more important under 300 GPa in the energy range (7.35-9.25) eV.

![Fig. 8 Optical conductivities under hydrostatic pressure and under a pressure of 300GPa of ZB MgO in (1/Ω.cm)](image)

V. CONCLUSION

In this paper, we have carried out the structural, electronic and optical properties of MgO, compound. The calculated lattice constants, bulk modulus and band gap computed from FP-LAPW calculations are attested by a comparison with experimental data and theoretical available studies. The dielectric function, absorption spectrum and refractive index were obtained in a wide energy range between 0 and 20 eV; the calculated static dielectric constants $\varepsilon_1(0)$ of the ZB MgO phase at hydrostatic pressure and under a pressure of 300 GPa are 2.92 and 1.96 respectively, which are in accord with experimental data.

REFERENCES