DOS Calculation Analysis of New Transparent Conductor Mg(OH)2-C

Takahiro Murakami, Takamitsu Honjo and Toshiro Kuji

Department of Applied Chemistry, School of Engineering, Tokai University, Hiratsuka 259-1292, Japan

In this paper, the new transparent conductive material, Mg(OH)2-C is analyzed by an ab initio quantum chemical calculation based on the density of states (DOS) with DV-Xz calculation. In this study the calculation of DOS for Mg(OH)2 by DV-Xz calculation with Mg(OH)2 cluster model was carried out first to assure the validity of our calculation. Next, it was hypothesized that Mg(OH)2-C is modeled with MgOHOC cluster as well as the Mg(OH)2 cluster. The expected behavior of the MgOHOC DOS well agrees with the experimental results for Mg(OH)2-C, and the hypothesized MgOHOC model well explained the characteristics of the Mg(OH)2-C. Moreover, replacing a part of the H atoms with C atoms in some of nonconductive hydroxide materials yields conductivity as well as our MgOHOC, because the reason of the MgOHOC conductivity appearance is the one by the replacements from the OH bond to the OC bond and the characteristics of Mg atom doesn’t especially take the part of the conductivity appearance. [doi:10.2320/matertrans.M2011046]

(Received February 2, 2011; Accepted May 16, 2011; Published July 6, 2011)

Keywords: hydroxide materials, magnesium (Mg), brucite (Mg(OH)2), carbon (C), transparent conductive films, ab initio quantum chemical calculations (DV-Xz)

1. Introduction

Transparent conductors are essential materials for flat display and solar cell technology. Tin doped Indium oxide, ITO has been widely used as a key material for liquid crystal display technologies because of its high transparency and electric conductivity. Recently, however, high cost of Indium due to the scarcity (Clarke number is $10^{-5}$) and the toxicities of indium oxides have been strongly pointed out so that alternative transparent conductive materials have been actively studied over the last two decades.1-4)

The conventional transparent conductive materials are based upon metal oxides without exception. It is well known that the metal oxides are more and less semiconductor due to the deviation from the stoichiometry.

Recently, Kondoh’s group reported very interesting results on the colored transparent for Mg-C compounds,5) The structure of compounds was identified to be amorphous. On the other hand, the new transparent conductive material developed in our group, Mg(OH)2-C, was prepared by the sputtering Mg and C, and post-reaction of the Mg-C film with moisture in the air.6-9) The transmittance of the visible ray was 90% in the average. The electric resistivity of the film was on the order of $10^{-3}$ Ωcm.9) Experimental details have been shown in previously reports.6-8) The lattice symmetry of Mg(OH)2-C was identified to be Mg(OH)2 structure (P-3m1) with slightly elongated c-axis compared with hexagonal Mg(OH)2.7) The mineral name is brucite. It is believed that the new material is the first non-oxide type transparent conductor. Therefore, in this paper, understanding the density of states (DOS) of the unit-cell of Mg(OH)2-C by using DV-Xz molecular orbital calculations (electronic state calculations) must be very much important.10) The DV-Xz method is an ab initio quantum chemical calculation and the cluster discrete-variational Xz method based on the Hatree-Fock-Slater self-consistent approximation,11) and suitable for the examination of electronic state of a random impurity atom in small crystallites or thin films because the method does not use the plane wave approximation which specializes in uniformity.

2. The computation Model and Calculation Methods

The basic crystal structure of Mg(OH)2 is hexagonal close-packed (hcp), and the lattice geometry data has been reported by F. Pascale et al.12) or Joint Committee of Powder Diffraction Standards (JCPDS) data.13) The crystal is composed of Mg layers, and the hydroxyl ligand (OH) bonds are parallel to the c-axis of the hexagon Mg(OH)2 structure and the OH ligands which bond with the upper and lower Mg layer respectively are opposite and alternately arranged. The unit-cell of Mg(OH)2 is shown in Fig. 1(a) and the lattice geometry distances are defined as follows.

\[
\begin{align*}
\alpha &= 0.31500 \text{ nm}, \\
\beta &= 0.47700 \text{ nm}, \\
R_{OH} &= 0.09583 \text{ nm}, \\
R_{OMg} &= 0.10499 \text{ nm}, \\
\end{align*}
\]

where $\alpha$ and $\beta$ are the $a$- and $c$-axis in the Mg(OH)2 unit-cell, respectively. And $R_{OH}$ and $R_{OMg}$ describe the distances from the O atom to the H atom and to the Mg layer, respectively. Here it should be noted that the film thickness and the crystallite diameter of the transparent conductive film are about 1000 nm and 5 nm, respectively.10) Thus, the thickness and the diameter should influence the electronic state. It is concluded that the calculation results of cluster models must be expected to be very much strongly influenced by surface effects, such as surface dangling bond. Therefore, Fig. 2 shows the defined cluster model of Mg(OH)2 under consideration of the basic crystal model used for the DOS analysis of Mg(OH)2-C. As shown in Fig. 2, in our calculation the one unit-cell shown in Fig. 1(a) is located in the center of the Mg(OH)2 cluster model in order to prevent the strong surface effects from the calculation results. The surface region on the colored transparent for Mg-C compounds.5) The structure of compounds was identified to be amorphous.6-9) The transmittance of the visible ray.6-9) The transmittance of the visible ray.

*Corresponding author, E-mail: tkuji@wing.ncc.u-tokai.ac.jp
extend to the horizontal Mg layer and the surface effect is strongly reflected on the calculation results, which should be not neglected for calculation. We basically consider the center unit-cell for our calculation.

In this study, we hypothesize the unit-cell model of Mg(OH)$_2$-C as shown in Fig. 1(b) and the crystal model is called MgOHOC. In Fig. 1(b), the O atoms bonding with C and H are described O* and O**, respectively and the Mg atoms bonding with O* and O** are described Mg* and Mg**, respectively. The distance between the O* and the C is described $R_{OC}$. We hypothesize $R_{OC} = 0.11500$ nm, which is the same degree of Ni(CO)$_4$, because Ni(CO)$_4$ is an example of a carbon monoxide ligand in a metal. It was reported that the lattice symmetry of Mg(OH)$_2$-C was identified to be Mg(OH)$_2$ structure (P-3m1), and the example model of Mg(OH)$_2$-C lattice was like Fig. 1(b). Thus, the hypothesized unit-cell model is made from exchanging one H in the unit-cell of Mg(OH)$_2$ with C. And then, the MgOHOC cluster model was constructed as follows. The hypothesized MgOHOC cluster model is made by replacing the center unit-cell (Fig. 1(a)) of Mg(OH)$_2$ cluster model (Fig. 2) with the MgOHOC unit-cell model (Fig. 1(b)). The new transparent conductive material, Mg(OH)$_2$-C film, was prepared with a less amount of C than that of Mg and then it is thought that the crystal structure of Mg(OH)$_2$-C film is composed dominantly of the Mg(OH)$_2$ unit-cell (Fig. 1(a)) and partially of the assumed MgOHOC unit-cell (Fig. 1(b)).

We use the Madelung potential of the point charge model in the DV-Xα electronic state calculations because of suppressing the surface effect in the calculation results. The Madelung potential is the electro-static potential of ions outside the cluster. And the used number of the charge points is 260 positions of Mg and 492 positions of OH, although the charge points on the boundary side are made a half to keep the symmetry. We applied the ionic charge values for each element under agreement as self-consistency. The each charge value in the position of Mg, O and H is +1.40, −1.12 and +0.42, respectively. These given values are certainly good agreements with the charge quantities of the calculation results shown in Table 1.

3. Results and Discussions

Figures 3(a) and (b)–(d) show the partially DOS (PDOS) of the Mg(OH)$_2$ unit-cell (Fig. 1(a)) and the MgOHOC unit-cell (Fig. 1(b)) in the cluster model (Fig. 2), respectively. The calculated band gap ($E_g$) shown in Fig. 3(a) is about 1.1 aJ (7 eV) (1 eV = 1.60218 × 10⁻¹⁹ J = 0.160218 aJ), and well agrees with the experimental value of $E_g$ shown in Fig. 4. This $E_g$ indicates the characteristic of transparent insulator as Mg(OH)$_2$, because the $E_g$ is much more than the wide-gap semiconductor $E_g$, i.e. 0.4 aJ (2.2 eV) and the highest visible photon energy, i.e. 0.5 aJ (3.2 eV). This implies that the PDOS in Fig. 3(a) represents the typical enough as the DOS of Mg(OH)$_2$. The calculated results of the MgOHOC cluster model could be good enough to analysis MgOHOC material as well as the calculated results of the Mg(OH)$_2$ cluster model is good enough to analysis Mg(OH)$_2$ crystal. Figures 3(b), (c), and (d) are almost equivalent although $Δc$ changes. Thus, slightly elongating the c-axis like the experimental fact hardly influences the MgOHOC DOS. The calculated band gaps of MgOHOC with $Δc = 0.000$ nm (Fig. 3(b)), 0.005 nm (Fig. 3(c)) and 0.010 nm (Fig. 3(d)) are especially same as 1.0 aJ (6 eV), because the states in the band gaps are thought to be the impurity energy levels derived from the C atom. The MgOHOC $E_g$ indicates the transparent characteristic as well as Mg(OH)$_2$-C. Then, in the comparison between the Mg(OH)$_2$ and MgOHOC, the MgOHOC $E_g$ becomes small and about 0.2 aJ (1 eV) from the
Mg(OH)$_2$. This value well agrees with the experimental value of $E_G$ changing.\(^9,15\) Next, the impurity energy level was paid to attention. The impurity DOS peak at 0.0 eV in Figs. 3(b)–(d) has the two electronic orbital states where one electron enters, and the energy level difference between the two electronic orbital states is under 0.1 eV (0.5 eV). Thus the impurity DOS peak can generate the both of electron and hole carrier so that it is difficult to distinguish whether the majority carrier is electron or hole. Moreover, the impurity DOS peak corresponding to the insertion of carbon atoms in Mg(OH)$_2$ lattice is almost in the middle of the band gap. Therefore it could be estimated that the carriers can move around the impurity-energy-level network generated by many C atoms. In this case, the material is very unique and to be applied to even quantum devices, for instance, quantum computer or communication.

### Table 1. Effective ionic charge.

<table>
<thead>
<tr>
<th></th>
<th>Mg(OH)$_2$</th>
<th>MgOHOC</th>
<th>MgOHOC</th>
<th>MgOHOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$</td>
<td>+2</td>
<td>+1.40</td>
<td>+1.432</td>
<td>+1.448</td>
</tr>
<tr>
<td>Mg$^+$</td>
<td>+2</td>
<td>+1.40</td>
<td>+1.432</td>
<td>+1.448</td>
</tr>
<tr>
<td>O$^-$</td>
<td>−2</td>
<td>−1.12</td>
<td>−1.14</td>
<td>−1.129</td>
</tr>
<tr>
<td>H</td>
<td>+1</td>
<td>+0.42</td>
<td>+0.434</td>
<td>+0.437</td>
</tr>
<tr>
<td>C</td>
<td>−0.017</td>
<td>−0.026</td>
<td>−0.023</td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>−0.70</td>
<td>−0.710</td>
<td>−0.669</td>
<td>−0.682</td>
</tr>
<tr>
<td>OC</td>
<td>0.00</td>
<td>+0.011</td>
<td>+0.063</td>
<td>+0.026</td>
</tr>
</tbody>
</table>

The O$^-$ (Mg$^+$) atom is on the near side and the O$^{2-}$ (Mg$^{2+}$) atom is on the far side.

---

**Fig. 3** The PDOS in the Mg(OH)$_2$ model and the MgOHOC model. $D$ and $E_g$ indicate the density of states and the energy level, respectively. 1 eV is 0.160218 aJ. When the density of states was calculated, we used the Gaussian function whose full width at half maximum (FWHM) is 0.1 aJ (0.5 eV). $E_g = 0.0$ aJ is defined the HOMO. The each $E_g$ represents the band gap. In (b), (c), and (d), the states in the band gaps are thought to be the impurity energy levels. The green lines, the red lines, the gray lines and the black lines derive from Mg, O, H, and C in the center unit-cell, respectively. The blue dashed lines are the total density of Mg, O, H, and C. And the dot lines and the solid lines derive from the atom on the far and near side from the C atom, respectively. In Fig 2(b), the O/C$_3$ (Mg/C$_3$) atom is on the near side and the O/C$_3$/C$_3$ (Mg/C$_3$/C$_3$) atom is on the far side.
The hypothesized MgOHOC model is transparent semiconductor, although it is not clear whether the conductivity is yielded by a n(p) type semi-conductor or an impurity-energy-level network generated by many C atoms. The reason of the transparency is that the hypothesized MgOHOC model keeps sufficiently wide band gap for visible light to transmit. And the reason of the conductor is that the C atom generates the impurity energy level in the band gap of Mg(OH)$_2$. The expected behavior of the hypothesized MgOHOC model well agree with the experimental results for Mg(OH)$_2$-C, i.e. the characteristic of transparent conductor, the band gap reduction of about 0.2 eV (1 eV) and elongating the c-axis. From our discussions, it can be well explained that the hypothesized MgOHOC model is approximate for the Mg(OH)$_2$-C. Moreover, replacing a part of the H atoms with C atoms in some of nonconductive hydroxide materials yields conductivity as well as our MgOHOC, because the reason of the MgOHOC conductivity appearance is the one by the replacements from the OH bond to the OC bond and the characteristics of Mg atom doesn’t especially take the part of the conductivity appearance. And some of hydroxide materials replacing a part of the H atoms with C atoms might have so peculiar impurity-energy-level network. This could imply the potential application to electric devices or quantum devices, even if Mg(OH)$_2$-C doesn’t have the unique impurity-energy-level network.

Acknowledgments

Authors greatly acknowledge for valuable suggestions from Prof. M. Sato of Tokai University and Dr. J.-C. Crivello of National Center for Scientific Research (CNRS) in France as well as Prof. M. Morinaga, Dr. H. Yukawa and Dr. M. Yoshida of Nagoya University and Prof. T. Ishii of Kagawa University.

REFERENCES

1) The 166th Committee on Photonic and Electronic Oxide, and JSPS, Toumei-dou-denmaku no gijyutu (in Japanese), (Ohmsha Ltd., Tokyo, 2007).
13) JCPDS on No. 07-0239, Quality: 1.