Band Gap Narrowing of Mg$_{1-x}$Cu$_x$O Nanostructured Materials

Nurhanna Badar$^{1*}$, Norlida Kamarulzaman$^{1,2}$, Nor Fadilah Chayed$^{1,3}$, Kelimah Elong$^{1,3}$ and Ri Hanum Yahaya Subban$^{1,2}$

$^1$Centre for Nanomaterials Research, Institute of Science, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
$^2$School of Physics and Material Studies, Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor Malaysia
$^3$School of Chemistry and Environment, Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor Malaysia

* nurhanna_1903@yahoo.com

Abstract. The band gap energies of MgO nanostructured can be tuned to a suitable value needed for various applications by substitution with dopant element. The study on doped compounds is to investigate band gap changes in the new materials. In this work, MgO and its doped materials Mg$_{1-x}$Cu$_x$O ($x = 0.02, 0.04, 0.06$) were synthesized using a combustion method. The phase and purity of materials were studied using X-Ray diffraction (XRD). The morphology and crystallites size of the materials were examined by a Field Emission Scanning Electron Microscope (FESEM). It was found that the synthesis route using triethanolamine for the combustion synthesis is suitable in obtaining pure and single phase MgO and Mg$_{1-x}$Cu$_x$O nanostructured. The presence of doped element, Cu in the MgO had caused changes in morphologies and crystallite size of the materials. The band gap energy of the materials was measured using a UV-Vis NIR spectrophotometer. The absorption edges of Mg$_{1-x}$Cu$_x$O were observed to shift to the right with respect to those of MgO as the Cu content increases, implying that band gap narrowing occurred in the materials.

1. Introduction

MgO is a useful and attractive oxide that is widely used in many research areas for investigation of their potential applications. MgO can act as a buffer layer in superconducting and ferroelectric materials due to its thermodynamically stable and wide band gap material (7.8 eV) [1]. It is also used as a protective layer of dielectrics in plasma display panels due to its high density, good transparency and good discharge characteristics with high secondary emission electrons [2-3]. It is also applied as a humidity sensor due to highly adsorptive properties for polar gaseous [4].

The properties of MgO nanomaterials can be very different from the micron sized crystals of conventional materials. It can exhibit novel and unique properties when the crystal dimensions of the materials are reduced to the nano scale [5-8]. One of the leading and important properties that are intimately connected with their functionalities is their band gap energy. Band gaps play a fundamental role in electrical and optical properties of materials. It is therefore important that the band gap values are measured because the values can later affect the application that the materials are intended for.
One way of changing the functional properties of materials is by doping. Doping the metal oxides will extend the range of band gaps of the materials which may have wider uses for different applications. Our work is focused on substitutional doping of Mg$_{1-x}$Cu$_x$O (x=0.02, 0.04, 0.06) whereby some Mg are replaced by Cu at a particular site in the crystal lattice using the combustion method and studying their characteristics. This method has the advantage of being simple, effective and low-cost for obtaining nanopowder metal oxides. The reaction time is also considerably shorter.

2. Experimental Details

MgO and its doped materials, Mg$_{1-x}$Cu$_x$O (x = 0.02, 0.04, 0.06) were synthesized using a self-propagating combustion (SPC) method. Magnesium nitrate hexahydrate, Mg(NO$_3$)$_2$.6H$_2$O and copper II nitrate trihydrate, Cu(NO$_3$)$_2$.3H$_2$O were used as the starting materials. They were dissolved in ultra pure deionised water from TKA Labtower (EDI:15-10 MΩcm) followed by addition of triethanolamine, (C$_2$H$_8$N$_2$O$_3$, 98%) as the combustant. The mixture was then slowly heated at a temperature of 200 °C until combustion occurs. The precursors were then annealed at 900 °C for 24 hours. The materials were ground using an agate mortar until fine powders were obtained. The phase identification was carried out using X-Ray Diffraction (XRD) via the Pan Analytical X’Pert Pro System. The morphology and crystallite size of the samples were examined by a Field Emission Scanning Electron Microscopy (JEOL JSM-7600F). Elemental analysis was done using the energy dispersive X-Ray spectroscopy (EDS), OXFORD INCA X-MAC 51, XMX 0021. The band gap energies of the samples were measured using a Ultraviolet-Visible-Near Infrared (UV-Vis-NIR) spectrophotometer (Perkin-Elmer Lambda 950) using a reflection geometry.

3. Results and Discussions

Figure 1(a) shows the colour of the MgO and Mg$_{1-x}$Cu$_x$O powders. It is observed that the pure MgO is white and those with low Cu substitutions are greenish in colour. With the increase of Cu content up to 6 %, it is observed that a brown powder is obtained. This colour observation in the Cu substituted samples suggests that the synthetic route has successfully yielded pure, polycrystalline Mg$_{1-x}$Cu$_x$O materials. Figure 1(b) shows the XRD patterns of the synthesized MgO and Mg$_{1-x}$Cu$_x$O (x = 0.02, 0.04, 0.06) materials. All the patterns are indexed according to the cubic crystal structure of MgO with space group Fm-3m (ICDD 01-089-7746).

Results revealed that all samples are pure with no presence of impurity or other phases. This means that the Cu$^{2+}$ ions have been successfully substituted into the MgO lattice. Therefore, the synthesis route using triethanolamine for the combustion synthesis is suitable in obtaining pure and single phase substitutionally doped Mg$_{1-x}$Cu$_x$O materials. Figure 1(c) shows the (200) peaks of the MgO and Mg$_{1-x}$Cu$_x$O stacked together for peak shift studies. It is observed that there are shifts in the 20 angle of the (200) peak to the left with increasing Cu content implying that the cell parameters and cell volume have also increased. If Cu has been substituted in the crystal lattice, it is expected that the cell constants should increase along with the cell volume because the ionic radius of Cu is larger than that of Mg (ionic radius of Mg$^{2+}$ = 0.86 Å and Cu$^{2+}$ = 0.87 Å for coordination number 6[9]).

Morphological images of all samples are shown in Figure 2. It can be seen that the MgO sample has the smallest crystallites of between 10 to 80 nm. Once Cu substitution is done on MgO, the crystallite size increases. The morphology of the MgO crystallites look cubic or cuboid in shape and this is also true for the lowest Cu content material. For Cu content in Mg$_{1-x}$Cu$_x$O of x > 0.02, the shape of the crystals become more irregular, consisting of mixtures of rounded, triangular and polyhedral shapes. The higher Cu content samples also show more agglomeration where the crystals seem to be joined together by strong grain boundaries.

Table 1 shows the average crystallite size for all samples and it is evident that Cu substituted samples have larger crystals. The larger crystallite size of the Mg$_{1-x}$Cu$_x$O samples implies that the crystal growth rate of the doped materials at 900 °C is faster compared to that of pure MgO. Therefore, at the calcination temperature of 900 °C, the crystals for the doped compounds grow more rapidly due
to more thermal energy being available of crystal formation and growth. This explains the observed larger crystal size of the Mg$_{1-x}$Cu$_x$O samples compared to the pure MgO.

Figure 1. (a) MgO and Mg$_{1-x}$Cu$_x$O powders, (b) XRD patterns of MgO (M), Mg$_{0.98}$Cu$_{0.02}$O (C2), Mg$_{0.96}$Cu$_{0.04}$O (C4) and Mg$_{0.94}$Cu$_{0.06}$O (C6) samples and (c) XRD (200) peak showing shifts for MgO and Mg$_{1-x}$Cu$_x$O samples.

Figure 2. SEM images for (a) MgO, (b) Mg$_{0.98}$Cu$_{0.02}$O, (c) Mg$_{0.96}$Cu$_{0.04}$O and (d) Mg$_{0.94}$Cu$_{0.06}$O samples.
Table 1. The crystallite size of all samples.

| Sample ID | Crystallite Size Range (nm) | Average Crystallite Size (nm) |
|-----------|-----------------------------|-------------------------------|
| M         | 10 – 80                     | 54                            |
| C2        | 30 – 100                    | 83                            |
| C4        | 30 – 200                    | 135                           |
| C6        | 30 – 300                    | 184                           |

EDX spectra are shown in Figure 3 and the elemental composition is listed in Table 2. The elemental content from the EDX measurements of the synthesised compounds show close stoichiometry to the calculated synthesised samples within experimental error. This once again supports the evidence of successful Cu substitution in the MgO samples. Therefore, the EDX results support the findings of the elements content of the synthesised materials.

![Figure 3](image_url)

**Figure 3.** EDX Spectrum for (a) Mg$_{0.98}$Cu$_{0.02}$O, (b) Mg$_{0.96}$Cu$_{0.04}$O and (c) Mg$_{0.94}$Cu$_{0.06}$O samples.

Table 2. Stoichiometry of Mg$_{1-x}$Cu$_x$O samples from EDX.

| Sample ID | Atomic % of Synthesized Mg | Atomic % of Synthesized Cu | Atomic % Mg ± 0.01 | Atomic % Cu ± 0.01 | Synthesized Stoichiometry | Stoichiometry from EDX SEM |
|-----------|---------------------------|----------------------------|--------------------|-------------------|--------------------------|----------------------------|
| C2        | 98.00                     | 2.00                       | 98.07              | 1.93              | Mg$_{0.98}$Cu$_{0.02}$O   | Mg$_{0.9819}$Cu$_{0.0193}$O |
| C4        | 96.00                     | 4.00                       | 96.09              | 3.91              | Mg$_{0.96}$Cu$_{0.04}$O   | Mg$_{0.9609}$Cu$_{0.0391}$O |
| C6        | 94.00                     | 6.00                       | 94.12              | 5.88              | Mg$_{0.94}$Cu$_{0.06}$O   | Mg$_{0.9412}$Cu$_{0.0588}$O |

The band gap energies of all samples are obtained by UV-Visible spectroscopy where the reflection spectra are shown in Figure 4(a). The reflectance spectra are observed in the wavelength range of between 180 nm to 1780 nm. It is immediately noticeable that the presence of Cu in the MgO lattice modifies the UV-Visible spectrum of materials. New absorption edges in the 890 nm to 1200 nm region are observed. The band energies of all samples are calculated using the well-known Tauc relation [10] as shown in equation (1) below,
\[(\alpha h \nu) = A(h \nu - E_g)^x\]  

(1)

where \(\alpha\) is the absorption coefficient of the material at a certain value of wavelength \(\lambda\), \(h\) is Planck's constant, \(A\) is the proportionality constant, \(\nu\) is the frequency of light, \(E_g\) is the band energy and \(x = \frac{1}{2}\) (for direct transition mode materials) [11]. The band energies of the materials are obtained at the intersection of the linear extrapolation part of the graphs of \((\alpha h \nu)^2\) versus \(h \nu\) with the abscissa. The band energies of all the materials are obtained from the Tauc plots shown in Figure 4(b) and 4(c) for different absorption edges and listed in Table 3.

For the MgO sample, the UV-Visible spectra shown in Figure 4(a) show the absorption edges marked as 1, which corresponds to the band gap energy of the material. Band gap is the electronic transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). As can be seen in Table 3, the band gap energy of the MgO nanomaterials, which is 5.80 eV, is lower than the standard value of around 7.8 eV for bulk MgO [12-13]. However, the band gap energy of the nano MgO agrees with findings from other researchers for nanoscale MgO [5,14]. The reduced band gap of the nano MgO can be explained by the small crystal size of the MgO powders (10 to 80 nm). When crystal size decreases to the nano scale, it is believed that the band structure of this material is modified such that the valence band maximum or highest occupied molecular orbital (HOMO) is shifted upwards towards the conduction band. Thus, the band gap of nano MgO is narrower compared to that of bulk MgO [8].

**Figure 4.** (a) UV-Visible reflectance spectra (b) Tauc plots of all samples for the absorption edges 1 (c) Tauc plots of all samples for the absorption edges 2.
Table 3. Band energies of samples M (MgO), C2 (Mg$_{0.98}$Cu$_{0.02}$O), C4 (Mg$_{0.96}$Cu$_{0.04}$O) and C6. (Mg$_{0.94}$Cu$_{0.06}$O).

| Sample                  | Absorption edge designation | Band energies ± 0.001 (eV) | Interpretation of the absorption edges |
|-------------------------|------------------------------|----------------------------|---------------------------------------|
| MgO (M)                 | 1                            | 5.800                      | Band gap (Mainly due to transition from valence band to conduction band of O 2p to the Mg 3s) |
| Mg$_{0.98}$Cu$_{0.02}$O (C2) | 1                            | 3.600                      | Band gap (Mainly due to transition from valence band to conduction band of O 2p to the Mg 3s / Cu 3d) |
| Mg$_{0.96}$Cu$_{0.04}$O (C4) | 1, 2                        | 3.500, 1.390              | Band gap (Mainly due to transition from valence band to conduction band of O 2p to the Mg 3s / Cu 3d) |
| Mg$_{0.94}$Cu$_{0.06}$O (C6) | 1, 2                        | 3.400, 1.370              | Band gap (Mainly due to transition from valence band to conduction band of O 2p to the Mg 3s / Cu 3d) |

The absorption edges of the copper substituted samples as shown in Figure 4(a) are observed to shift to the right as the Cu content increases, implying that band gap narrowing occurred in the materials. There are two absorption edges for the Cu containing samples instead of just one as observed for the MgO sample. The higher energy (marked as 1 in the spectra) is mainly believed to be due to the electronic transitions from the O 2p valence band to the conduction band of the Mg$_{1-x}$Cu$_x$O materials. The presence of Cu in the MgO crystal lattice produces additional energy bands due to the d orbital of the Cu atoms and resulting in the lower band gap energies of the Mg$_{1-x}$Cu$_x$O materials [15].

The effect of Cu substitution in MgO is quite dramatic as can be seen by the additional absorption edges (marked as 2) as shown in Figure 4(a) compared to that of the MgO spectrum. Even though the Cu content in the materials is low, as in sample C2, the consequence of the presence of the 3d transition metal on the MgO structure results in drastic modification of the orbital states of the electrons in the materials in the UV-Visible region. The absorption edges of the Mg$_{1-x}$Cu$_x$O materials is explained by the crystal field splitting due to the presence of Cu [15-16] in the crystal lattice. The presence of Cu 3d orbitals introduces colour centres that exhibit these absorption edges. Cu$^{2+}$ has a d$^9$ electronic configuration, and in the pure octahedral coordination, the Cu$^{2+}$ state is split into $^2T_{2g}$ ground state and $^2E_g$ excited state. Therefore, the optical transition that may give rise to the absorption edge 2 is mainly due to the d-d transition of Cu$^{2+}$ from the $^2T_{2g}$ level to the $^2E_g$ level [16]. These Cu$^{2+}$ d states create band states, thereby favoring electronic transition to these levels and resulting in electronic band transition of Mg$_{1-x}$Cu$_x$O. These very different spectra observed for the Cu substituted samples are another proof of the formation of new Mg$_{1-x}$Cu$_x$O compounds. These d-d transitions can also be proven by the color changes of the Mg$_{1-x}$Cu$_x$O materials compared to that of MgO, as shown earlier in Figure 1(a). Materials containing transition metals are usually coloured due to the partly filled d orbitals that undergo d-d transitions which can absorb wavelengths from visible light. The partly filled Cu$^{2+}$ d orbital must be involved in generating the colour in Mg$_{1-x}$Cu$_x$O materials.
4. Conclusion

Pure and single phase MgO and its doped materials, Mg$_{1-x}$Cu$_x$O ($x = 0.02$, 0.04, 0.06) have been successfully synthesised using a combustion synthesis method. Results show that the combustion method was suitable for the production of nanocrystallites. The substitution of Cu into MgO lattice affects the materials characteristics which included phase, morphology and crystallite size. The band gap energy of nanostructured MgO obtained in this work exhibits lower energies than the standard value of the bulk MgO. It is also immediately noticeable that the presence of substitutional Cu$^{2+}$ in the MgO lattice modifies the UV-Visible spectrum of the materials resulting in band gap narrowing. The observed electronic transitions are due to the presence of Cu in the crystal lattice which introduces colour centres responsible for the d-d transitions of Cu$^{2+}$. Therefore, it can be observed that other than adjusting the crystallite size, band gap tuning can also be done by doping of foreign metals into the host structure.

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