The Malaysian Journal of
ANALYTICAL
SCIENCES ISSN 1394-2506

EFFECTS OF LITHIUM DOPANT ON SIZE AND MORPHOLOGY OF MAGNESIUM OXIDE NANOPOWDERS

(Kesan-Kesan Litium Sebagai Pendopan Keatas Saiz dan Morfologi Serbuk Nano Magnesium Oksida)

Mohd Sufri Mastuli[1,2]*, Siti Nur Hazlinda Hasbu[1], Noraziahwati Ibrahim[1], Mohd Azizi Nawawi[1]

[1]*School of Chemistry and Environmental Studies, Faculty of Applied Sciences,*
Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
[2]*Centre for Nanomaterials Research,*
Institute of Science, Level 3 Block C,
Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

**Corresponding author: mohdsufri@salam.uitm.edu.my*

Abstract

Lithium doped of magnesium oxide powders have been synthesized using the sol-gel method with magnesium acetate tetrahydrate, oxalic acid dihydrate and lithium acetate dihydrate used as the starting materials. The dried sol-gel products were calcined at 950 °C for 36 h to form the Li doped-MgO samples. The calcined samples were characterized using X-Ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). The present work is investigated the effect of lithium ion on the band gap energy of studied samples. The band gap energies were obtained from a Tauc plot that drawn based on absorption edge of each sample that measured using a UV-Vis spectrophotometer. It is found that the doped and undoped MgO samples showed a slightly different in their band gap energies. The lithium ion that present in the MgO as a dopant affects the crystallite size and morphology of the final products. Our study shows that the lithium dopant can modified optical properties of the metal oxide which to be beneficial in some industrial applications.

Keyword: Magnesium oxide, doping, sol-gel method, band gap energy

Abstrak

Magnesium oksida yang didopkan dengan litium telah disintesis menggunakan kaedah sol-gel dengan magnesium asetat tetrahidrat, asid oksalik dihidrat dan litium asetat dihidrat sebagai bahan pemula. Produk-produk sol-gel yang kering telah dipanaskan pada 950°C selama 36 jam untuk pembentukan sampel-sampel MgO yang didopkan dengan Li. Sampel-sampel yang telah dipanaskan dianalisis menggunakan X-Ray pembelauan (XRD) dan bidang pelepasan elektron imbasan mikroskop (FESEM). Kerja terkini ini adalah mengkaji kesan ion litium keatas tenaga jurang jalur untuk bahan-bahan yang diuji kaji. Tenaga jurang jalur telah diperolehi daripada plot Tauc berdasarkan di pinggir penyerapan sampel yang diukur menggunakan UV-Vis spektrofotometer. Didapati bahawa MgO dengan dan tanpa pendopan ion litium menunjukkan sedikit perbezaan dalam jalur tenaga jurang mereka. Kehadiran litium didalam magnesium oksida sebagai pendopan juga memberikan kesan kepada saiz kristalit dan morfologi serbuk tersebut. Kajian ini menunjukkan bahawa ion litium boleh mengubahsuai sifat-sifat optik oksida logam yang memberikan kebaikan kepada beberapa aplikasi industri.

Kata kunci: Magnesium oksida, pendopan, kaedah sol-gel, jalur jurang tenaga

Introduction

Magnesium oxide (MgO) is a versatile metal oxide having numerous applications in many fields such as catalysis [1], toxic waste remediation [2], refractory materials [3], antimicrobial materials [4] and electrochemical biosensor [5]. It is widely accepted that the properties of MgO is depend strongly on the synthesis methods and the processing conditions. Many efforts have been devoted to synthesize MgO nanostructures using various methods such as precipitation [6], sol-gel [7], chemical vapour deposition [8], combustion [9] and many other methods. The properties of MgO are further improved when it used as nanosized particles compared to bulk MgO. Therefore, the formation of MgO nanostructures with small crystallite size of less than 100 nm and well-defined morphology is a key issue on the nanomaterial research. The crystallite size and morphology of the nanomaterials can be tuned by introducing a secondary metal into crystal structure of metal oxide that can be done *via* doping either interstitial or substitution [10]. This may alter the properties of the materials. The aim of this study is to synthesize MgO and $Li_{0.2}Mg_{0.9}O$ samples using the sol-gel method and studying the effects of Li^+ ions on their properties.

Materials and Methods

All the chemicals were analytical grade and directly used as received without further purification. Both MgO and $Li_{0.2}Mg_{0.9}O$ were synthesized using the sol-gel method with magnesium acetate tetrahydrate, $Mg(CH_3COO)_2.4H_2O$ (Merck, 99.5 % purity); oxalic acid dihydrate, $C_2H_2O_4.2H_2O$ (Merck, > 98 % purity); lithium acetate dihydrate, $LiCH_3COO.2H_2O$ (Merck, 99.9 %) and absolute ethanol, C_2H_5OH (J. Kollin Chemical, 99.9 % purity) used as the starting materials. For MgO, magnesium acetate tetrahydrate was dissolved in ethanol under constant stirring. Then, pH of the solution was adjusted to pH 5 using 1 M of oxalic acid. The mixture solution was continuously stirred until formed a thick white gel. The sol-gel product was left overnight for further gelation process before drying in an oven at 100 ºC for 24 h. The steps above were repeated for the $Li_{0.2}Mg_{0.9}O$ sample with lithium acetate dihydrate was added during the sol-gel reaction. Later on, the dried solids were ground using mortar and pestle to produce fine powder precursors. Each precursor was annealed at 950 ºC for 36 h to form the respective samples.

The two synthesized samples were systematically characterized using various instruments. The XRD patterns of MgO and $Li_{0.2}Mg_{0.9}O$ were obtained by X-Ray diffraction (XRD: PANalytical X'Pert Pro MPD) with CuK_α radiation. The Bragg-Brentano optical configuration was used during the data collection. The size and morphology of the samples were examined using field emission scanning electron microscopy (FESEM: JEOL JSM-7600F). The band gap energies for both samples were measured using UV-Vis-NIR spectrophotometer (Perkin Elmer Lambda 950 UV-Vis-NIR).

Results and Discussion

The XRD patterns for MgO and $Li_{0.2}Mg_{0.9}O$ are shown in Figure 1. All the diffraction peaks are indexed according to ICDD 01-0178-0430 reference number showing a face-centered cubic phase of periclase MgO with space group Fm-3m. These XRD peaks are assigned to (111), (200), (220), (311), and (222) crystal planes. The XRD pattern of lithium-doped MgO is isostructural to the XRD pattern of MgO. However, all the XRD peaks for $Li_{0.2}Mg_{0.9}O$ are slightly shifted to the right due to the presence of Li^+ ions. Figure 2 shows the shifting of (200) peaks and this is true with the other peaks as well. The lithium ion can be said to have been successfully introduced into the cubic crystal structure of MgO. In addition, the sharp and intense XRD peaks are clearly observable for both samples that reflect higher crystallinity. The XRD results also suggest that the obtained samples are also pure and single phase with no impurities present. The doped sample is expected to have a larger crystallite size as compared to the undoped sample and this agrees with its FWHM (full width at half maximum) value that can be obtained from the XRD peak broadening. The smaller FWHM value corresponds to the larger crystallite size, and vice versa. The FWHM values for the (200) peak of MgO and $Li_{0.2}Mg_{0.9}O$ are 0.1506° and 0.1004° respectively. Thus, the crystallite size of MgO is smaller than the $Li_{0.2}Mg_{0.9}O$ crystals. This observation is in a good agreement with the FESEM micrographs for both samples.

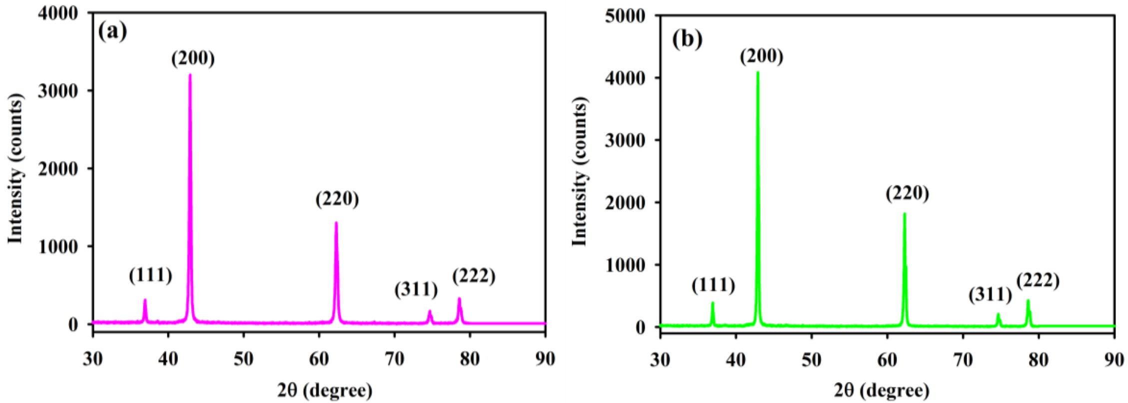

Figure 1: XRD patterns of (a) MgO and (b) $Li_{0.2}Mg_{0.9}O$

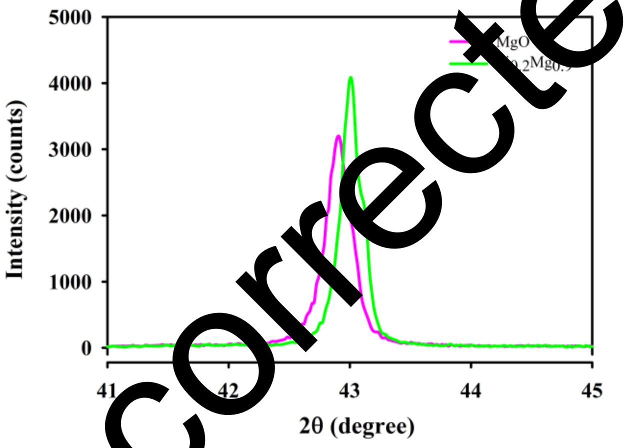

Figure 2: Shifting of (200) peak for both samples

Figure 3 shows the FESEM micrographs for the studied samples. As can be seen, the crystallite size for MgO and $Li_{0.2}Mg_{0.9}O$ are different to each other in which the doped sample exhibited larger crystallites although the annealing temperature and annealing time are identical as for the undoped sample. The MgO sample has crystallite size of average 30 nm which is smaller than of $Li_{0.2}Mg_{0.9}O$ sample which has an average crystallite size of more than 100 nm. The morphology of MgO is cubic crystal while that of $Li_{0.2}Mg_{0.9}O$ is of mixed cube and sphere shaped. These results show that the addition of lithium ion causes the crystal defect in the sample.

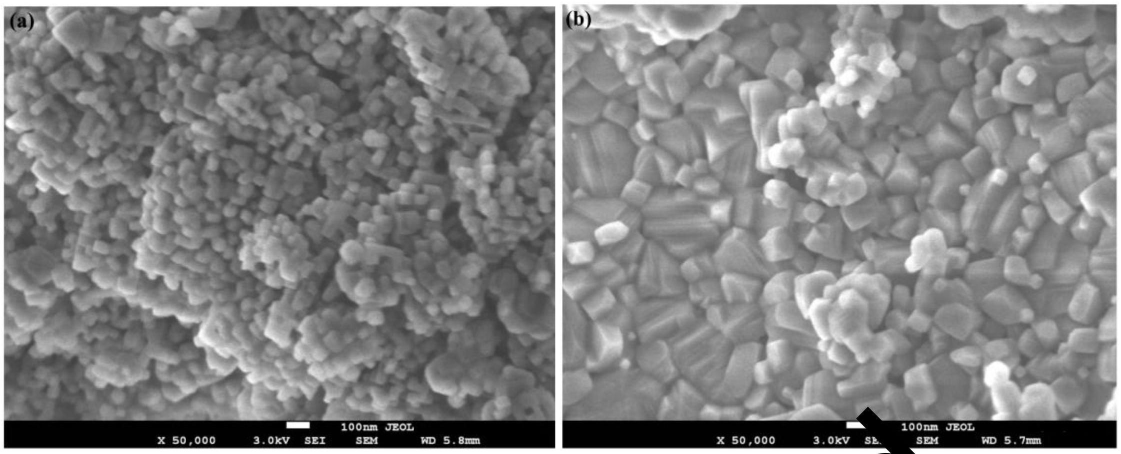

Figure 3: FESEM micrographs of (a) MgO and (b) Li$_{0.2}$Mg$_{0.9}$O

The UV-Vis spectra for MgO and Li$_{0.2}$Mg$_{0.9}$O are shown in Figure 4. It can be seen that the absorption edge for the MgO appeared at a higher wavelength compared to the Li$_{0.2}$Mg$_{0.9}$O. This reveals that the MgO should have larger band gap energy than the Li$_{0.2}$Mg$_{0.9}$O. The band gap energies for both samples were estimated using a Tauc equation as shown in Equation (1) [11].

$$\alpha h\upsilon = C(h\upsilon - E_g)^n \tag{1}$$

where, α is the absorption coefficient at a certain value of wavelength (λ), h is the Planck's constant, υ is the frequency of light, C is the proportionality constant, n is the nature of transition and E_g is the band gap energy. MgO is considered as a direct band gap material, thus, its n has the value of ½ indicating the allowed direct transition mode, resulting in Equation (2).

$$(\alpha h\upsilon)^2 = C'(h\upsilon - E_g) \tag{2}$$

From Equation (2), the plot of $(\alpha h\upsilon)^2$ against hυ would gives the value of band gap energy. This plot is also known as a Tauc plot. The Tauc plot is evaluated such that the linear part when extrapolated will give the band gap, E_g, as shown in Figure 5. The band gap energies for the MgO and Li$_{0.2}$Mg$_{0.9}$O are found to be 6.38 eV and 6.35 eV respectively. These energies are lower than the band gap energy of bulk MgO (7.8 eV) [12]. The reduced in band gap for the MgO nanostructures have been reported by other researchers [13-15] and our results are consistent with theirs. The lower band energy for the nanosized MgO is attributed to the reduced of crystallite size. As the crystallite is scaled down to nano size, its surface area-to-volume (SAV) ratio is increased [16]. The higher SAV ratio would affect the electron binding energy of the material because the number of core atoms in nanosized crystallites seems less than they in micron crystals. This affects the energy levels of the nanocrystals resulting in widening of the bands. When the number of core atoms in a crystallite is much reduced from micron sized crystals, the fraction of atoms at the surface becomes larger. This results in higher average binding energy of the smaller crystallites.

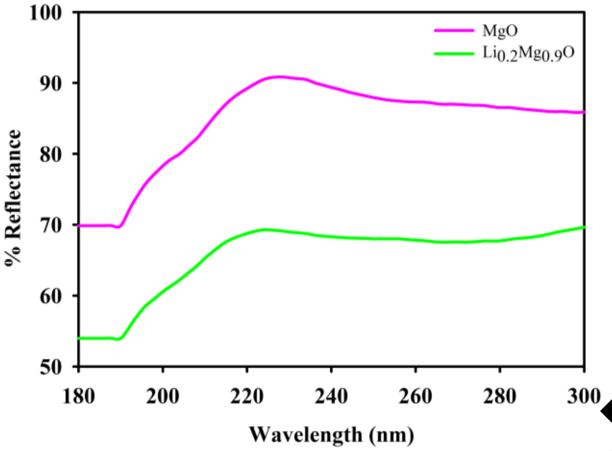

Figure 4: UV-Vis spectra of the samples

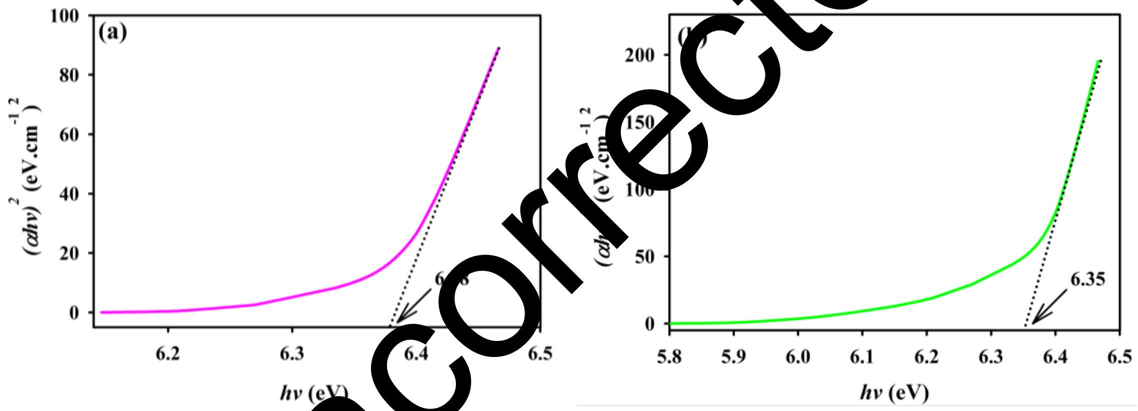

Figure 5: Tauc plots of (a) MgO and (b) $Li_{0.2}Mg_{0.9}O$

Conclusion

The pure and single phase of MgO and $Li_{0.2}Mg_{0.9}O$ were obtained *via* the sol-gel process. The presence of the lithium ion affects the crystallite size and morphology for both samples. The used of lithium as a dopant has been demonstrated as an important way in tuning the energy levels of the target material.

Acknowledgement

Authors would like to thank the Ministry of Higher Education, Malaysia for supporting this work through the Fundamental Research Grant Scheme (600-RMI/ST/FRGS 5/3/Fst(200/2010)).

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