Ultraviolet and Violet-Blue Emission of Zn doped MgO/Mg(OH)₂ Particles Prepared by One Step Spray Pyrolysis Method

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Abstract: Spherical particles of Zn doped MgO were prepared by one-step spray pyrolysis method. The crystalline nature and particle size of the samples were characterized by X-ray diffraction analysis (XRD). The morphology of samples was studied by scanning electron microscope (SEM) and the presence of Zn in the sample was confirmed by energy dispersive X-ray analysis (EDX). The optical properties of the samples were investigated using photoluminescence spectroscopy (PL) analysis to obtain excitation and emission spectra of the samples. Results indicated that the doped MgO particles exhibited a cubic structure without hexagonal wurtzite structure as the Zn concentrations were increased. Spherical shape and porous particles are found with increasing of doping concentration. The optical band gap of MgO altered with the addition of doping concentration. A considerable redshift of about ~0.08 – 0.13 eV in the excitation spectra of 2.22 eV emission band was revealed in Zn doped MgO samples. It was highlighted that Zn doped MgO prepared by the spray pyrolysis generated emission at UV-Vis wavelength required for many applications.

Keywords: MgO, Mg(OH)₂, spray pyrolysis, luminescence, spherical particles

1. Introduction

The engineering of luminescence materials attracts many researchers to obtain UV-Vis light emission required for many applications, e.g. light-emitting diodes [1–6]. In addition, Magnesium Oxide (MgO) is an important material used in wide range of applications, such as catalysis, toxic waste remediation, paint, superconducting products, anti-bacterial, and biosensing [7]. In the case of MgO applied for the anti-bacterial applications, Zn is doped into MgO [8,9]. Recently, MgO has considered as a potential luminescence material since efforts on doping MgO with Fe, Eu, Cd, Dy [10–13] successfully reported able to generate an emitted visible light required for many industrial applications. The presence of various defect generates intermediate energy levels in MgO materials considered responsible for generating a broadband emission in the visible region.
Considerable interests have been put on binary oxides of Mg and Zn since they can be tailored to achieve any band gap in the range 3.37-7.2 eV [14]. The ionic radius of Mg$^{2+}$ (0.72 Å) is quite similar to that of Zn$^{2+}$ (0.74 Å). MgO is an insulator material that has a band gap of about 7.2 eV, meanwhile, ZnO is a semiconductor material that has a band gap of about 3.37 eV. MgO is doped by Zn to obtain a luminescence material with any band gap between their band gaps and shift the emitted light in the visible region. Sharma et al. [15] have reported the synthesis of Zn doped MgO with a different Zn$^{2+}$ ratio that could emit light in UV and Blue region. Recently, Vasanthi et al. [6] reported that Zn doped MgO nanoparticles generated a bright bluish green emission (450 nm to 570 nm) when excited with near UV light (330 nm to 380 nm). However, emission of luminescence materials does not only depend on the doping materials, but also on the size, size distribution and also morphology of the particles. Generally, reported Zn doped MgO particles were irregular morphology and various particle size distribution ranges depend on how these materials were prepared. Despite, the proper doping materials on MgO, the exploration of the synthesis method is essential to enhance the doped MgO luminescence properties.

There are many methods that can be used to synthesize doped MgO such as sol-gel [16], wet chemical reaction method [9], extractive-pyrolytic method [17], combustion [18–20], thermal evaporation method [21]. The liquid-phase route can indeed produce un-agglomerated particles, but with low crystallinity. Meanwhile, solid-state routes can produce high crystalline materials but have constraints in controlling agglomeration, particle size distribution, and particle shape. Obtaining homogenous composition, desired morphology and uniform particle size are interesting by introducing a modification of the conventional process [22]. Spray pyrolysis is one of the prospective methods offered many advantageous, such as producing particles with controlled particle size and size distributions, spherical-shaped, high crystallinity and high purity. Spray pyrolysis is a method adopted for making a submicrometer-sized powder up to nanometers. In spray pyrolysis, crystal structure, morphology, and luminescence properties particles are affected by the concentration of the solution precursor, the flow rate of the gas carrier, the frequency of atomizer and processing temperatures [23].

In this current work, we report the Zn doped MgO/Mg(OH)$_2$ particles obtained through a spray pyrolysis method aims to produce spherical particles, uniform particle size distribution and emitted light at UV-Vis region. The crystal structure, morphology, and the luminescence properties were investigated as the Zn dopant concentration increases.

2. Materials and Methods

2.1. Preparation of samples

The sample was prepared using precursors of magnesium nitrate hexahydrate-Mg(NO$_3$)$_2\cdot$6H$_2$O and zinc acetate dihydrate-Zn(CH$_3$COO)$_2\cdot$2H$_2$O with purity 99.99% (Cica Reagent, Kanto Chemical Co., Inc.) as a starting material with distilled water as a solvent. The precursor with a molarity of 0.05 M and vary in Zn precursor compositions 1%, 3%, and 5%, consequently. The diluted precursor was then atomized by ultrasonic atomizer (1.7 MHz) to produce droplets. Air was used as a carrier gas with flow rates 5 L/min to flow droplets toward the furnace controlled at a temperature processing of 700°C. The wire plate type of electrostatic precipitator was used to capture the produced particles.

2.2. Characterization

The samples were characterized by X’pert PANalytical diffractometer (CuKα, λ=1.5406 Å) in the range of 2θ from 10° to 90° with a step scan of 0.03° to analyze properties of the crystal structure. The morphology of the samples was characterized by SEM-EDX (JSM-6510LA) with an accelerated voltage of 20 KV. The samples were scanned with a magnification of 10,000x. The photoluminescence properties were examined by spectrofluorophotometer (Perkin Elmer LS 55).

3. Results and Discussion

3.1. Structure of Crystals

Figure 1 showed the results of XRD analysis of doped MgO at various Zn$^{2+}$ dopants. It was observed that the diffraction peak intensity position at 2θ about 42.70° corresponds to dominant orientation, i.e.,
With the increased of Zn$^{2+}$ dopants, the (2 0 0) diffraction peak appeared less dominant. On the contrary, two diffraction peaks related to Mg(OH)$_2$ phase were identified and exhibited with higher intensities as the increasing of Zn$^{2+}$ ion dopants. The entire peaks on the result of XRD spectra were related to the rock-salt structure of MgO (JCPDS 45-0946) and hexagonal crystal structure of Mg(OH)$_2$ (JCPDS 44-1482). The observed relationship between the degree of Mg(OH)$_2$ dominant peaks and the increment of Zn$^{2+}$ dopants may be explained in terms of migration of molecules onto the nucleation process. Mg(OH)$_2$ was expected to have a lower energy configuration during nucleation rather than MgO. The Zn$^{2+}$ dopant could move to substitute Mg$^{2+}$ in the sites, thus the Mg(OH)$_2$ phase occurred while the substitution process lowered the energy configuration.

Furthermore, another factor that affects the presence of Mg(OH)$_2$ phase was the temperature decomposition of both precursors. The zinc acetate dihydrate- Zn(CH$_3$COO)$_2$.2H$_2$O decomposed at 237°C while the precursor magnesium nitrate hexahydrate- Mg(NO$_3$)$_2$.6H$_2$O decomposed at 400°C. The precursor magnesium nitrate hexahydrate-Mg(NO$_3$)$_2$.6H$_2$O has a higher decomposition temperature than zinc acetate dihydrate-Zn(CH$_3$COO)$_2$ precursors. Therefore, the magnesium precursor needs longer residence time to completely decomposed. The lower evaporation rate of the droplets compared to the residence time in the furnace caused incomplete decomposition of the material.

![X-ray diffraction patterns for doped MgO at different Zn dopants](image)

**Figure 1.** X-ray diffraction patterns for doped MgO at different Zn dopants: (a) Zn 0%; (b) Zn 1%; (c) Zn 3%; (d) Zn 5%; JCPDS cards correlated to identified phases were shown above.

The Scherrer's formula, $D = \frac{0.89\lambda}{\beta\cos\theta}$ (where $D$ is the average crystallite size, $\lambda$ is the X-ray wavelength of CuKα, $\beta$ is FWHM of diffraction peaks, and $\theta$ is the Bragg angle) is used to determine the size of the crystal. The average crystallite sizes of the samples were taken from the highest crystal orientation, i.e. (2 0 0), plane.

The average crystallite size increased from 7.8 nm for undoped MgO (ZN0) to 17.98 nm for ZN5 as zinc concentration increased (Table 1). This increased in the crystallite size was correlated to the increase of lattice parameter of the samples [6] and might be due to the greater ionic radius of Zn$^{2+}$ ion (0.74 Å) than that of Mg$^{2+}$ ion (0.72 Å) [8,24].
Table 1. Structural parameters of Zn doped MgO.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Plane (111)</th>
<th>Plane (200)</th>
<th>Plane (111)</th>
<th>Plane (200)</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ (rad)</td>
<td>FWHM (rad)</td>
<td>Crystallite Size (nm)</td>
<td>θ (rad)</td>
<td>FWHM (rad)</td>
</tr>
<tr>
<td>ZN0</td>
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<td>0.0166</td>
<td>8.6281</td>
<td>0.3580</td>
</tr>
<tr>
<td>ZN1</td>
<td>0.5901</td>
<td>0.0097</td>
<td>14.8103</td>
<td>0.3580</td>
</tr>
<tr>
<td>ZN3</td>
<td>0.5879</td>
<td>0.0097</td>
<td>14.8054</td>
<td>0.3727</td>
</tr>
<tr>
<td>ZN5</td>
<td>0.5868</td>
<td>0.0069</td>
<td>20.7241</td>
<td>0.3768</td>
</tr>
</tbody>
</table>

3.2. Morphology of Particles

SEM was an important tool to investigate the texture, topography and surface features of materials. It is well established that particles produced by the spray pyrolysis method were spherical due to the well-known principle of one droplet-one particle (ODOP). The SEM images for the doped MgO showed that the morphologies depended on the dopants variation. It was also clear that the synthesized Zn doped MgO samples was dense, spherical and found uniformly in the submicron range (490-700 nm) as shown in Fig. 2.

For ZN0 sample (Fig. 2a), the spherical particles with an average diameter of 495 nm were observed unaggregated with a delicate surface of the grains. It was assumed that the precursor experienced homogeneous nucleation of the surface of the droplet when the solute reached the critical supersaturation. The crystallites were formed continuously from the surface to the droplets center lead to the formation of spherical particles shaped during volume precipitation.

The spherical aggregated grains were observed on the other samples with higher Zn dopants (Fig. 2b-d) but with more roughness and pores. This morphology was considered to be formed during the organics removal due to surface precipitation. In the presence of impurities (in this case i.e. Zn²⁺) the solute diffusion rate became slower than the solvent evaporation. Therefore, the solute concentration at the center of droplets would be less than at the surface caused the solid precipitation early occurred on the outer layer of the surface of the droplet. The droplets of magnesium nitrate hexahydrate-Mg(NO₃)₂.6H₂O possibly evaporated before approaching the critical supersaturation and resulted in surface precipitation. According to the particle size distribution histograms, the average particle size for ZN0, ZN1, ZN3, and ZN5 were ~495, 492, 524 and 710 nm, respectively. The most uniform distribution was found in Zn0 sample. Low coordinated surface segregated Zn²⁺-O²⁻ chains were produced by the doping of Zn²⁺ ions. These chains had a lower surface energy than Mg²⁺-O²⁻ surface ions that increased the nucleation rate and might initiate the secondary nucleation [6]. As a result of this process, larger particles were obtained in Zn doped samples [25]. As the doping concentration increased, the secondary nucleation rate became high and resulted in an increase of larger particle density. The elemental composition of the samples was analyzed using the EDX spectrum as shown in the Fig. 3. This confirmed the presence of Mg, Zn, and O without a trace of any other impurities.
Figure 2. SEM micrographs for doped MgO particles at different doping: (a) Zn 0%; (b) Zn 1%; (c) Zn 3%; (d) Zn 5%; Particle size distribution of each sample is shown on the right of SEM image.
Figure 3. EDX spectra of doped MgO at doping: (a) Zn 0%; (b) Zn 1%; (c) Zn 3%; (d) Zn 5%. These results confirmed the successful replacement of Mg$^{2+}$ ions by Zn$^{2+}$ ions in the MgO lattice.

3.3. Photoluminescence Spectra

Figure 4 showed the photoluminescence excitation (PLE) spectra for the samples. The excitation peaks were shifted to lower energy as the Zn dopants increases. It was assumed that the Zn$^{2+}$ ion has lowered the photonic band gap of MgO due to the band gap narrowing. The conduction band shifted to lower energy when the Zn dopant was introduced into MgO due to the hybridization of Zn 4s state with the Mg 3s and O 2s (conduction band). The bonding states between Zn and O shifted the conduction band toward lower energies thus reducing the band gap. The effect of this hybridization to the band gap was predicted using density functional theory (DFT) and GW calculation reported elsewhere [26].

Figure 4. Excitation spectrum of Zn doped MgO corresponding to emission at 3.22 eV (solid line) for: (a) Zn 0% (dashed line); (b) Zn 1% (dotted line); (c) Zn 3% (dash dotted line); (d) Zn 5% (short dashed line); the excitation spectra are red shifted due to the effect of band gap lowering.
Photoluminescence spectra of doped MgO were recorded upon excitation at 4.59 eV as shown in Fig. 5. The undoped MgO (ZN0) exhibited a broad emission band that was consisted of one dominant peak at 3.22 eV (Violet) and three peaks at 3.48 eV (UV), 3.08 eV (Violet), and 2.82 eV (Blue), respectively. The strongest ultraviolet luminescence (UVL) was shifted to 3.21 eV (ZN1), 3.20 (ZN3) and 3.16 (ZN5) as the Zn dopant concentration in samples increased. It can be seen that three remaining peaks were redshifted, in agreement with [26]. The redshift of about ~0.08 – 0.13 eV in the three observable excitation spectra might due to the size effect, occurrence of defects and mechanical stress from the bending of the MgO. This result showed that the luminescence intensities were not regularly increased as the Zn dopant increased. The reason for this behavior was possibly due to the particle morphology effect. The redshifts of the peak position of the three observable bands compared with those of the bulk undoped MgO might due to the nanosized effect, densities of defects and mechanical stress from the bending of the MgO.

Furthermore, more detail analysis about the origin of the observed peaks will be discussed as follows. The emission peak centered at 402 nm (3.08 eV, Violet Luminescence) was related to intrinsic defects namely oxygen vacancies, F-center/F’-centers/surface states, this value was in close agreement with reported results in ref. [27,28]. The energy levels of these intrinsic defects were found in the forbidden energy gap of MgO. Upon the dopant addition, oxygen atoms and ions were excited resulted in the creation of oxygen vacancies, and released electrons were trapped in the oxygen vacancies resulting in the creation of F centers. Thus, the origins of the ultraviolet luminescence (UVL) and Blue-Violet luminescence (BVL) can be also attributed to F’ and F centers.

Figure 5. Photoluminescence for Zn doped MgO particles. (a) Excitation spectrum of Zn 0% corresponding to emission at 3.22 eV (solid line); Emission spectra upon an excitation at 4.59 eV (270 nm) of doped MgO with dopants variation of: (b) Zn 0% (dashed line); (c) Zn 1% (dotted line); (d) Zn 3% (dash dotted line); (e) Zn 5% (short dashed line).

Figure 6 shows the photoluminescence spectra for Zn doped MgO upon excitation at 4.96 eV. The spectra were still dominated by the violet and blue emissions. The result showed that the blue spectrum was increasing in a significant way. Hence, our experiment reveals that increasing Zn concentration gives rise to the blue luminescence and retains the UV luminescence. Whereas, the emission intensity Zn5 samples were low compared to others and it may be due to lack of surface defects occurrence or also due to different morphologies. Therefore, the particle morphology plays an important role in photoluminescence emission.
Figure 6. Emission spectra upon an excitation at 4.96 eV (250 nm) of doped MgO with dopants variation of: (a) Zn 0% (dashed line); (b) Zn 1% (dotted line); (c) Zn 3% (dash-dotted line); (d) Zn 5% (short dashed line). The spectra are still dominated by two violet luminescence, but the Zn concentration gives rise to the blue luminescence (BL) significantly.

4. Conclusions

The Zn$^{2+}$ ion has been successfully incorporated into the MgO lattice using the spray-pyrolysis method without reducing gas atmosphere confirmed by the EDX spectrum. The powder XRD confirms the rock-salt cubic of MgO and hexagonal structure of Mg(OH)$_2$. The surface morphological studies confirm the formation of unaggregated and porous particles in the submicron range which has spherical and round-shape. Excitation of samples under 250 nm produced a broad emission in the violet-blue emission due to the lowering of band gap created by the doping. Their photoluminescence (PL) behavior associated with the F centers and/or new energy levels created below the conduction band due to Zinc incorporation, the excitation spectra of 3.22 eV emission band was observed in samples. A considerable redshift of about ~0.08 – 0.13 eV in the excitation spectra was revealed. It was predicted that the optical band gap of doped MgO was reduced as the concentration of Zn increased.

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