Blue-Shift and Enhanced Photoluminescence in BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ Nanophosphor under VUV Excitation for PDPs Application

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ABSTRACT

In this report, five systems of varied diameters viz. 62 nm, 85 nm, 115 nm, 160 nm and 450 nm of BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ nanorods are prepared by solution combustion approach and with annealing at different temperature in reduced atmosphere (N$_2$ + H$_2$). An intense broad blue photoluminescence (PL), corresponding to the electronic transition of Eu$^{2+}$ from the 4f$^6$ 5d excited state to the 4f$^7$ ground state, is observed. The blue-shift and enhanced photoluminescence is also observed, and found to be highly dependent on the size of diameter of BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ nanostructures. The change in decay time and color-coordinates with change in size of diameter of BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ nanostructure have been analysed and thoroughly discussed.

Keywords: Quantum Confinement Effect, Nanophosphor, PDPs

1. Introduction

Recently, plasma display panels (PDPs) have been used for large screen television at home and for a public information display. However, luminescent properties such as intensity and efficiency of the resulting PDPs are still inferior to those of traditional cathode-ray tube display [1-4]. To overcome these drawbacks, optimization of phosphors used in PDPs becomes necessary. Red, blue and green phosphors used in PDPs are key materials to improve the performance of PDPs such as brightness, cost-effectiveness and stability. BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ (BAM) is an important blue-emitting phosphor for plasma display panel (PDP) because it can efficiently absorb the vacuum ultraviolet (VUV) light coming from the resonance radiation line of Xe atoms (147 nm) and from the excited state of molecular Xe (172 nm). BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ is an insulating host material with a wide band gap of 6.4 eV. Recently, nanocrystals composed of wide band gap insulator have attracted a lot of attention, since several interesting results have been observed in semiconductor nanocrystal [5-8]. Therefore, it is interesting to study whether a similar behaviour can be observed for wide band gap insulators. It is well known that size-dependent quantum confinement has significant effects on both radiative and non-radiative electronic transitions in nanocrystals. The principal consequences of quantum confinement are an increase in the band gap energy, and an associated increased probability of radiative transitions. Confinement of carriers in real space causes their wavefunctions to spread out in momentum space, increasing the probability of radiative processes due to greater wavefunction overlap [9-11]. B. Mercier et al. [12] observed the quantum confinement effect on the wide band gap of a material such as Gd$_2$O$_3$ (5.4 eV), however the observed effect was quite weak. Recently, Guiling Ning et al. [13] succeeded in reducing the size of BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ phosphor (particle size ~ 400 nm) and observed the increase in the intensity due to quantum size effect of nano-scale phosphor, but they failed to study optical properties with further reduction of particle size. In this paper, a novel solution combustion approach to synthesize BAM nanophosphors has been reported. Our primary aim is to explore and study the photoluminescence property of BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ nanoparticles with reduction of particle size under quantum confinement effect. The synthesized BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ nanoparticles have enhanced photoluminescence property which has a technological importance in plasma display panels (PDPs).
2. Experimental Details

A novel solution combustion approach has been adapted for the synthesis of BaMgAl<sub>10</sub>O<sub>17</sub>:Eu<sup>2+</sup> nanoparticles [14]. The typical of preparation is given below. Eu<sup>2+</sup> doped BaMgAl<sub>10</sub>O<sub>17</sub> nanophosphor powders with the composition of Ba<sub>1-x</sub>MgAl<sub>10</sub>O<sub>17</sub>:xEu<sup>2+</sup> (x = 0.35) were prepared from the starting precursor Ba(NO<sub>3</sub>)<sub>2</sub> (99.9%), Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99.9%), Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (99.9%) and Eu(NO<sub>3</sub>)<sub>3</sub> (99.99%). A stoichiometric amount of these above nitrates were dissolved in deionized water, then the required amount of urea as combustible fuel was added and stirred well to obtain homogeneously mixed solution. The container containing the above prepared solution was introduced into a muffle furnace maintained at 400 ± 5°C. After 15 min, the solution boils and undergoes dehydration followed by decomposition with liberating a large amount of gases such as CO<sub>2</sub>, NH<sub>3</sub>, etc., then the mixture swells and burning instantaneously with bright flame. At last, white colored product was obtained within 2-5 min. To investigate the effect of variation of size on the optical properties, the BaMgAl<sub>10</sub>O<sub>17</sub>:Eu<sup>2+</sup> phosphor obtained by solution combustion approach were further annealed at 600°C, 800°C, 1000°C and 1200°C for 4 h in reducing (N<sub>2</sub> + H<sub>2</sub>) atmosphere. As prepared BaMgAl<sub>10</sub>O<sub>17</sub>:Eu<sup>2+</sup> powder by solution combustion approach and annealed in reducing atmosphere at 600°C, 800°C, 1000°C and 1200°C were henceforth termed as BAM-1, BAM-2, BAM-3, BAM-4 and BAM-5, respectively.

The crystal structure of BaMgAl<sub>10</sub>O<sub>17</sub>:Eu<sup>2+</sup> nanocrystals was characterized by X-ray diffraction (XRD, Rigaku D/Max -2200 H/PC, Cu Kα radiation). The VUV photoluminescence study was carried out on McPherson spectrometer. The excitation spectra study was carried out on a Perkin Elmer LS 55 spectrometer. The field emission-scanning electron microscopy (FE-SEM) images were taken on Quanta 200 FEG (FEI Company, Eindhoven, The Netherlands). Quanta 200 FEG fitted with an energy dispersive x-ray spectroscopy (EDS; Genesis 2000, EDAX), was used for elemental analysis.

3. Result and Discussion

The crystallographic phase purity of BaMgAl<sub>10</sub>O<sub>17</sub>:Eu<sup>2+</sup> nanophosphor synthesized by solution combustion approach was confirmed by X-ray diffraction (XRD). Figure 1 shows the XRD pattern of BAM nanophosphor synthesized by solution combustion method. Barium magnesiuim aluminate BaMgAl<sub>10</sub>O<sub>17</sub> (BAM) is classified into β-alumina structure with a space group P 6<sub>3</sub>/mmc [15]. The BaMgAl<sub>10</sub>O<sub>17</sub> phase obtained by solution combustion method shows good agreement with Joint Committee on Powder Diffraction Standards card No. 26-0163 [16].

Moreover, the broadening of major diffraction peaks indicates nanocrystalline nature of particles present in powder. No additional diffraction peaks are observed in XRD pattern, this indicate that obtained BaMgAl<sub>10</sub>O<sub>17</sub>:Eu<sup>2+</sup> powder synthesized by combustion approach at 400°C has pure phase. No change in phase purity of crystal structure of BaMgAl<sub>10</sub>O<sub>17</sub>:Eu<sup>2+</sup> nanoparticles annealed at different temperature have been also observed.

Figure 2 shows the field emission-scanning electron microscopy (FE-SEM) images of BaMgAl<sub>10</sub>O<sub>17</sub>:Eu<sup>2+</sup> phosphor powder synthesized by solution combustion method: (a) as prepared (BAM-1), (b) annealed at 600°C (BAM-2), (c) annealed at 800°C (BAM-3), (d) annealed at 1000°C (BAM-4), and (e) annealed at 1200°C (BAM-5). From Figure 2(a), it is clear that as prepared BaMgAl<sub>10</sub>O<sub>17</sub>:Eu<sup>2+</sup> has nonorods in structure with diameter ~ 62 nm and length ~ 300-600 nm. The change in diameter of BaMgAl<sub>10</sub>O<sub>17</sub> nanorods with annealing temperature, can be seen in Figure 2 and Table 1.

The spectrum obtained during Energy Dispersive X-ray Analysis (EDX) study is used to know the presence of europium in BaMgAl<sub>10</sub>O<sub>17</sub>. Figure 3 shows the EDX spectrum of BaMgAl<sub>10</sub>O<sub>17</sub>:Eu<sup>2+</sup> nanophosphor particles synthesized by solution combustion method. The EDX spectrum of BaMgAl<sub>10</sub>O<sub>17</sub>:Eu<sup>2+</sup> nanostructure shows the presence of barium, magnesium, aluminium, oxygen and europium. The EDX spectrum confirms the doping of europium in BaMgAl<sub>10</sub>O<sub>17</sub> nanonanostructures.

Figure 4 shows the photoluminescence spectra of BaMgAl<sub>10</sub>O<sub>17</sub>:Eu<sup>2+</sup> nanorods of different diameter D, viz. 62 nm, 85 nm, 115 nm, 160 nm and 450 nm under VUV (147 nm) excitation. The emission spectra shows the blue
Figure 2. FE-SEM image of BaMgAl\(_{10}\)O\(_{17}\):Eu\(^{2+}\) (BAM) blue PDP nanoporphor synthesized by solution combustion method: (a) as prepared (BAM-1); (b) annealed at 600\(^{\circ}\)C (BAM-2); (c) annealed at 800\(^{\circ}\)C (BAM-3); (d) annealed at 1000\(^{\circ}\)C (BAM-4); (e) annealed at 1200\(^{\circ}\)C (BAM-5)

Figure 3. EDX spectrum of BaMgAl\(_{10}\)O\(_{17}\):Eu\(^{2+}\) nanostructure synthesized by solution combustion method
Table 1. The mean grain size (diameter) D (estimated by FE-SEM, the standard deviation is given in brackets), emission energy (eV), decay time \( \tau \) (\( \mu \) s), color-coordinates and relative intensity (%)

<table>
<thead>
<tr>
<th>Samples</th>
<th>D (nm)</th>
<th>Emission Peak Position (eV)</th>
<th>Decay time ( \tau ) (( \mu )s)</th>
<th>Color-coordinate</th>
<th>Relative Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAM-1</td>
<td>62 (±4)</td>
<td>2.775</td>
<td>1.07</td>
<td>0.1387</td>
<td>100</td>
</tr>
<tr>
<td>BAM-2</td>
<td>85 (±6)</td>
<td>2.744</td>
<td>2.91</td>
<td>0.1377</td>
<td>87</td>
</tr>
<tr>
<td>BAM-3</td>
<td>115 (±8)</td>
<td>2.719</td>
<td>4.33</td>
<td>0.1356</td>
<td>73</td>
</tr>
<tr>
<td>BAM-4</td>
<td>160 (±20)</td>
<td>2.702</td>
<td>4.75</td>
<td>0.1351</td>
<td>69</td>
</tr>
<tr>
<td>BAM-5</td>
<td>450 (±26)</td>
<td>2.670</td>
<td>2.46</td>
<td>0.1289</td>
<td>96</td>
</tr>
</tbody>
</table>

emission in the region 400-510 nm with strongest peak at ~ 450 nm, corresponding to the electronic transition of Eu\(^{2+}\) from the 4\(f^{6}5d\) excited state to the 4\(f^7\) ground state [17]. It can also be clearly seen from the Figure 4 that with the reduction in size of diameter of BaMg\(_{10}\)Al\(_{10}\)O\(_{17}\):Eu\(^{2+}\) nanostructure there is blue-shift in emission peak position as well as change in intensity of luminescence under 147 nm excitation. There are many reports on the blue-shift effect in the luminescence spectra of semiconductor nanocrystals [18-19]. However, few reports are available on nano-sized rare earth doped insulating luminescent material. The mechanism of luminescence in the semiconductor is the recombination of electron in the conduction band and holes in the valence band. A larger band gap is necessary for quantum confinement to cause the blue-shift in the luminescence. However, the luminescence in BaMgAl\(_{10}\)O\(_{17}\):Eu\(^{2+}\) is due to the transition between energy levels of Eu\(^{2+}\) atoms as the luminescence center. Therefore, a different interpretation is required to explain the blue-shift in the luminescence spectra of the BaMgAl\(_{10}\)O\(_{17}\):Eu\(^{2+}\) nanorods.

Figure 5 shows the excitation spectra of BaMgAl\(_{10}\)O\(_{17}\):Eu\(^{2+}\) nanostructures at 450 nm emission peak. The excitation spectrum consists of a broad band with a maximum ~ 328 nm with two shoulders at 270 nm and 380 nm, respectively, which are due to the transitions from the ground state 8\(S^\frac{7}{2}\) of Eu\(^{2+}\) with 4\(f^7\) configuration to the different crystal field splitting components of the Eu\(^{2+}\) with (4\(f^6\)5\(d\)) configuration in the excited states [20]. Recently, S. Zhang et al. [21] reported that when the BaMgAl\(_{10}\)O\(_{17}\):Eu\(^{2+}\) phosphor is excited at wavelength 147 nm, the excitation energy is first absorbed by the host and then transferred to Eu\(^{2+}\) ions. In this case, the emission efficiency of Eu\(^{2+}\) ions therefore depends strongly on the host. The change in the particle size will significantly affect the emission intensity of Eu\(^{2+}\) ions in the indirect excitation. From excitation spectra, it is clear that there is also blue-shift in the broad band corresponding to 4\(f^6\)5\(d\) → 4\(f^7\) transition of Eu\(^{2+}\) ions in BaMgAl\(_{10}\)O\(_{17}\):Eu\(^{2+}\) nanostructure host with decrease in size. Here, it is noticeable that the BaMgAl\(_{10}\)O\(_{17}\):Eu\(^{2+}\) nanostructure with diameter 450 nm has little greater intensity as compare to nanostructure with diameter size 160 nm, and also deviates from the trend of decrease in PL intensity with increase of size, while the trends of decrease of PLE intensity with increase in size is maintained in PLE spectra. This can be explained as: the BaMgAl\(_{10}\)O\(_{17}\):Eu\(^{2+}\) nanostructure with
diameter 450 nm have low PLE intensity and also due to larger size it has low surface defects as compare to smaller diameter sized nanostructure. The surface defects in nanostructures play an important role in influencing the luminescence properties. The surface defects, mainly responsible for non-radiative transitions, quench the PL intensity. Here, in case of BaMgAl10O17:Eu2+ nanostructure with diameter size 450 nm, the abrupt increase in PL intensity with lower PLE intensity is mainly due to decrease in surface states which are responsible for non-radiative transition. It is also noticeable that the deviation in PL intensity does not support the degradation in PL intensity due to annealing temperature. Therefore the observed change in PL and PLE intensity is mainly due to change in size of diameter of BaMgAl10O17:Eu2+ nanostructures. The observed blue-shift in PLE and consequently PL is related to change in position of energy levels of 4f⁶5d¹ → 4f⁷ transition of Eu²⁺ ions in BaMgAl10O17:Eu²⁺ nanostructure host. It is already observed that the energy states associated with the luminescent center are influenced by the host lattice material. The degree to which they are influenced depends also on the size and shape of nanostructures [22,23]. Recently, Y. Lin et al. [24] reported preparation of the ultrafine SrAl₂O₄:Eu,Dy needle-like phosphor and its optical properties. This group observed that the optical absorption edge shifts to the blue as the phosphor particle size decreases. They explained that it may be associated with the quantum size effect of the nanometer phosphor, which increased the kinetic energy of the electrons and resulted in a larger band gap, and thus required higher energy to excite the luminescent powders. Simultaneously they observed that the emission maximum shifted to shorter wavelength, they explained that it may be caused by the prepared technology, which resulted in some changes of the crystal field around Eu²⁺. Although the 4f electrons of Eu²⁺ are not sensitive to lattice environment due to the shielding function of the electrons in the inner shell, the 5d electron may couple strongly to the lattice. Consequently, the mixed states of 4f and 5d will be split by the crystal field, which may lead to the blue-shift of its emission peak. In our case, the blue-shift in the emission band may be attributed to the changes of the crystal field around Eu²⁺ arising from the nanosized particles. Since the excited 4f⁶5d¹ configuration of Eu²⁺ ion is extremely sensitive to the change in the lattice environment in contrast to the shielded 4f⁷ ground configurations, the 5d electron may couple strongly with the lattice. Therefore, the mixed states of 4f and 5d will be influenced strongly by the crystal field. On the other hand, the particles with nanometer size make the surface energy increase significantly, which causes the change of the crystal field around the local environment of Eu²⁺. These reasons lead to the blue-shift of PLE and PL emission peak in BaMgAl₁₀O₁₇:Eu²⁺ nanophosphor with decrease in particle size. Table 1 contains information about change in emission peak position, decay time, color coordinate and relative intensity with change in diameter of BaMgAl₁₀O₁₇:Eu²⁺ nanostructure.

The colorimetric coordinate (x, y) for BAM:Eu²⁺ nanophosphor were calculated using equidistant wavelength method [25]. Table 1 summarizes the comparison of CIE colorimetric coordinates for BaMgAl₁₀O₁₇ nanostructure with variation of diameter size of nanostructure.

To study the decay behaviours of Eu²⁺ luminescence in BaMgAl₁₀O₁₇ nanostructures with varied diameter size, fluorescence decay curve for the 4f⁶⁵d¹ → 4f⁷ transition of the Eu²⁺ were studied [26]. Figure 6 shows the fluorescence decay curve of BaMgAl₁₀O₁₇ nanostructure of diameter size 62 nm. The decay curve can be well fitted by double exponential equation: I (t) = I₀ + A exp (-t/τ₁) + B exp (-t/τ₂), where I and I₀ is the luminescence intensity, A and B are constants, t is the time, τ₁ and τ₂ are the decay time for the exponential component, respectively. It is found that the life time of BaMgAl₁₀O₁₇ nanostructure is varied as a function of diameter size of nanostructure. Table 1 summarizes the change in decay time of BaMgAl₁₀O₁₇:Eu²⁺ nanostructure with variation in diameter size. From table I, it is clear that the life time varies with the diameter size of BaMgAl₁₀O₁₇:Eu²⁺ nanorods and decay rate decreases with increase in diameter size. The PL intensity of the 4f⁶⁵d¹ → 4f⁷ transition is strongly related to the decay time of a particular transition. The decrease in decay rate trend is continue to diameter size 62 nm, 85 nm, 115 nm and then 160 nm, however the trend of decrease of decay rate with increase of size deviates in case of BaMgAl₁₀O₁₇:Eu²⁺ nanostructure with diameter size 450 nm. The increment in decay rate at diameter size 450 nm in case of BaMgAl₁₀O₁₇:Eu²⁺ nanorods is due to decrease in surface states, responsible for non-radiative transition, with increase of size. In general, the photoluminescence (PL) decay rate is a sum of
the radiative and non-radiative decay rates:
\[
\frac{1}{\tau_{PL}} = \frac{1}{\tau_R} + \frac{1}{\tau_{NR}}
\]
where \(\tau_{PL}\), \(\tau_R\), and \(\tau_{NR}\) are the photoluminescence, radiative and non-radiative decay time constants, respectively. Therefore, the origin of the decrease in PL decay rate versus size may be radiative and non-radiative. The possibility may be invoked for the non-radiative process in origin is surface states, responsible for non-radiative decay, which changes as surface-to-volume ratio varies with size. Other possibility for radiative in origin, may be considered for the size dependence as quantum confinement effect may lead to size dependent oscillator strength. The quantum confinement effect in nanoparticles predicts a decreased radiative decay rate as the size increases [27]. As PL and PLE spectra are dependent on the size of diameter of BAM nanostructures indicating that the quantum confinement effect as well as surface effect both is responsible for change in decay rate. These finding provide glimpse for detailed study of quantum confinement effect for rare earth doped wide band gap insulating material for enhancement of emission intensity, emission energy, improvement in color-coordinates and decay time etc. for better results of phosphor in LEDs and PDPs.

4. Conclusions

In summary, we have successfully synthesized BaMgAl\(_{10}\)O\(_{17}\):Eu\(^{2+}\) nanorods with variation in size of diameter of nanostructure by solution combustion approach and annealing at different temperature under reducing atmosphere (H\(_2\) + N\(_2\)). Enhanced blue photoluminescence emission and blue-shift is observed under 147 nm excitation, and found to be highly dependent on the size of diameter of BaMgAl\(_{10}\)O\(_{17}\):Eu\(^{2+}\) nanostructures. Decreased radiative decay rate with increase in the diameter size of BaMgAl\(_{10}\)O\(_{17}\):Eu\(^{2+}\) is also observed.

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REFERENCES


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