

Blue luminescence from Bi doped MgAl₂O₄ prepared by the combustion method

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Abstract. Magnesium aluminate (MgAl₂O₄) has received special attention as a technologically important material because of its attractive properties, such as mechanical strength, chemical inertness, a wideband gap, relatively low density, high melting point, high thermal shock resistance, low thermal expansion coefficient, resistance to neutron irradiation and low dielectric loss. It has also been used as a phosphor host activated by a variety of transition metal and lanthanide ions. As an alternative to such ions, luminescence can often be obtained from the ns² type ions such as Tl⁺, Pb²⁺, Bi³⁺ and Sb³⁺. For Bi³⁺ the luminescence is attributed to the electron transition between the 6s² ground state and the 6s¹6p¹ excited states. A simple combustion method was employed for the preparation of Bi doped MgAl₂O₄ nanocrystals using metal nitrates as precursors and urea as a fuel in a preheated furnace at 520°C. The samples thus obtained were characterized by x-ray diffraction, UV-visible spectroscopy, scanning electron microscopy and photoluminescence spectroscopy. For an excitation wavelength of 335 nm, the Bi³⁺ doped MgAl₂O₄ produced a blue emission band centred near 400 nm, indicating that Bi³⁺ ions were successfully incorporated in the lattice. Maximum blue emission was obtained for the sample doped with 0.5 mol% Bi. The results indicate that doping MgAl₂O₄ with Bi ions may be an attractive alternative to doping it with Ce ions, which give broad blue-green luminescence in this host but requires reducing at a high temperature (1400°C) to convert non-luminescent Ce⁴⁺ ions to the luminescent Ce³⁺ charge state.

1. Introduction

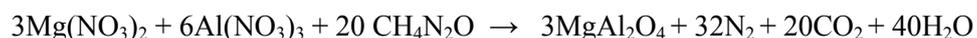
Phosphor materials are widely applied in lighting, displays, lasers and scintillators, and it is necessary that the phosphor host exhibits good optical, mechanical and thermal properties. Magnesium aluminate (MgAl₂O₄), corresponding to the mineral spinel, is considered to be an optically inert medium and its chemical and thermal stability increases its attractiveness as a host for luminescent ions [1]. Rare-earth ions are often used as activators for phosphor materials, especially in the trivalent charge state where luminescence is generally due to f-f electron transitions [2,3]. However, metallic impurities with an outer ns² configuration ground state such as Tl⁺, Pb²⁺, Bi³⁺ and Sb³⁺ ions may also be excellent luminescence activators [4]. Bi atoms have an electronic configuration [Xe]4f¹⁴5d¹⁰6s²p³ and Bi³⁺ ions, with outermost 6s² electrons, have been widely used as activators for various host materials including oxides, phosphates, aluminates and borates [5]. The 6s² ground state has a single energy level ¹S₀ while the 6s¹6p¹ excited configuration has energy levels ³P₀, ³P₁, ³P₂ and ¹P₁ in order of increasing energy. Electron transitions between the ¹S₀ ground state and the ³P₁ levels are spin forbidden, but optical absorption can occur to the high energy ¹P₁ level. However, spin-orbit coupling between the

1P_1 and 3P_1 levels makes the lower energy transitions $^1S_0 \leftrightarrow ^3P_1$ possible and the luminescence from Bi^{3+} activated phosphors is usually attributed to this transition. In some materials the $^1P_1 \rightarrow ^1S_0$ emission is also observed [6]. The outer electron orbitals of Bi^{3+} are not shielded (as in the case of the 4f energy levels of trivalent lanthanide ions) so the broad luminescence band shows a strong dependence on the composition and crystal structure of the host lattice and the emission wavelength is tuneable from the ultraviolet, through blue to green [7].

Spinel powders have been prepared by solid-state reaction [2], precipitation [8], hydrothermal synthesis [3] and sol-gel synthesis [9]. Alternatively, synthesis via the combustion method [10] occurs via a highly exothermic redox reaction between metal nitrates and an organic fuel and this technique can produce a homogenous product in a short amount of time without using expensive high temperature furnaces. This method has been used to prepare novel $\text{MgAl}_2\text{O}_4:\text{Bi}$ nanocrystalline phosphor powders in order to study their optical properties.

2. Experimental

MgAl_2O_4 was prepared by combustion synthesis using magnesium nitrate $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and aluminium nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as precursors and urea $\text{CH}_4\text{N}_2\text{O}$ as the fuel according to the reaction



where the waters of crystallization of the nitrates have been omitted for simplicity. Either 5 or 10 mmol of aluminium nitrate was added to stoichiometric amounts of the other reactants in about 3 or 6 ml of distilled water, which was stirred vigorously for 30 min to obtain a homogeneous transparent solution. The transparent solution of reagents was transferred into a porcelain crucible which was placed in a muffle furnace maintained at 520°C . Within a few minutes the water boiled off and the sample ignited as the exothermic combustion reaction occurred, giving off copious quantities of gas and heating the material to well above the furnace temperature. After the reaction the foamy white product was removed from the furnace and, after cooling to room temperature, it was crushed into powder using a pestle and mortar. Doping of samples with Bi ions was achieved by replacing an appropriate amount of aluminium nitrate with the same amount of bismuth nitrate $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. In spinel the Al^{3+} ions occupying octahedral sites and the Mg^{2+} ions in tetrahedral sites are both small (effective ionic radii of 53 and 58.5 pm respectively [11]) compared to 6-coordinated Bi^{3+} ions (103 pm [12]). Although the Mg^{2+} ion is the larger of the two, the Al^{3+} ion has the same valence as Bi^{3+} and occupies the octahedral site with higher coordination number (6). From these considerations it appears that Bi^{3+} ions would not easily substitute the host cations, nor if it did which site it would prefer. However, lanthanide ions are also large and since it has been suggested that Eu^{3+} ions occupy the Al^{3+} ions sites in spinel [13], that is the assumption made here. However, it has also been reported that Eu^{3+} ions may occupy the Mg^{2+} sites in spinel [14].

X-ray diffraction (XRD) measurements were made using a Bruker D8 Advance diffractometer (40 kV, 40 mA) with Cu $K\alpha$ x-rays (154.06 pm). Scanning electron microscope (SEM) images of the particle morphology were obtained using a Shimadzu SSX-550 instrument. Diffuse reflection spectra were measured using a Lambda 950 UV-Vis spectrophotometer (with spectralon as a reference material) and photoluminescence (PL) properties were measured using a Cary-Eclipse fluorescence spectrophotometer and a 325 nm He-Cd laser.

3. Results and discussion

3.1. Structure

The XRD pattern of pure MgAl_2O_4 shown in figure 1 matches the standard JCPDS card no. 74-1132 well. The main peak of the cubic structure, corresponding to the crystal plane with Miller indices $\{311\}$, is centred at $2\theta = 36.86^\circ$.

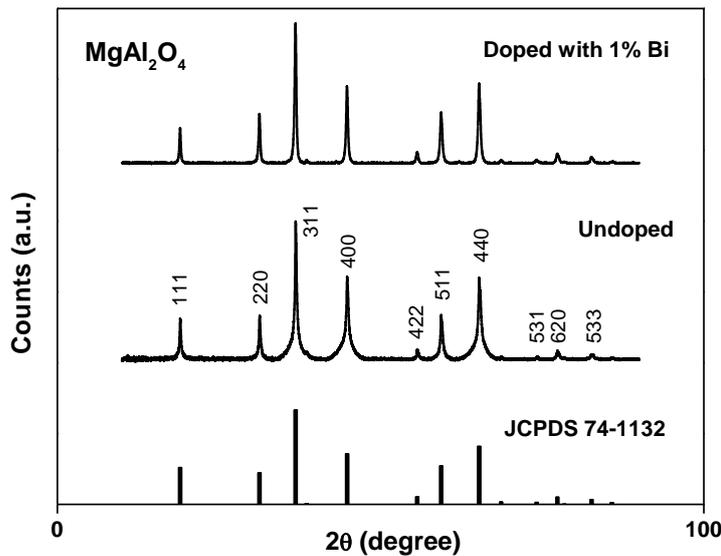


Figure 1. X-ray diffraction patterns of MgAl_2O_4 prepared by the combustion method, pure and doped with Bi.

The peaks are not Gaussian in shape, but are superimposed on a broad base (amorphous halo), indicating that the material between the crystallites is in a disordered state. For the sample doped with 1 mol% Bi no extra peaks are observed, nor was a shift of the peak positions detected. However, the peaks are now sharper, so the addition of a small amount of Bi has produced samples with better crystallinity. Bismuth oxide has a much lower melting point (817°C) compared to Mg and Al oxides ($> 2000^\circ\text{C}$). Since the temperature during synthesis is estimated to be near 1500°C [15], the addition of Bi may act like a flux, thereby improving the crystallinity. The average crystallite size D was estimated from the full-width at half-maximum β of the diffraction peaks at angle θ by using the Scherrer equation $D = \frac{0.9\lambda}{\beta \cos \theta}$ where λ is the x-ray wavelength and was about 25 nm for both the pure and doped samples. This value is approximate only, considering the non-Gaussian peak shape for the undoped sample and possible impurity or strain broadening of the peaks in the doped sample.

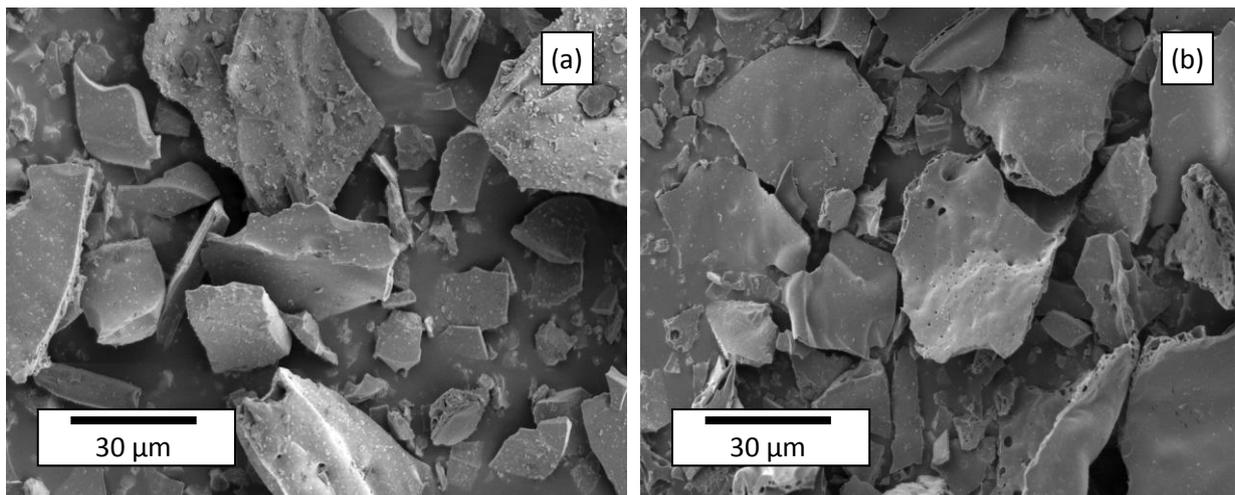


Figure 2. SEM images of MgAl_2O_4 powders obtained by the combustion method (a) undoped and (b) doped with 0.5 mol% Bi.

The SEM image in figure 2(a) shows the morphology of the undoped MgAl_2O_4 particles produced with the combustion process after grinding the foamy product with a mortar and pestle. The particle size varies up to several tens of microns and depends on the amount of grinding, but it is evident that

large flat, plate-like particles occur. This is characteristic of material made by combustion synthesis due to the large amount of gas that evolves during the reaction. The variation in thickness of the plates is due to the non-uniform distribution of temperature and mass flow in the combustion flame. Figure 2(b) shows that the sample doped with 0.5 mol% Bi, which has a similar morphology as the undoped sample. These SEM images show several pores in the particles which are formed by the escaping gases during the combustion reaction. These particles are much larger than the crystallite size estimated from the XRD results, indicating that the particles consist of smaller crystallites.

3.2. Optical properties

UV-Vis diffuse reflection spectroscopy was used to study the absorption characteristics of MgAl_2O_4 and the effects of Bi dopant measured with the Lambda 950 UV-Vis spectrophotometer at room temperature. Figure 3(a) compares the diffuse reflectance spectra of the different samples. For the undoped host (as-prepared) the reflectance remains high even for very short wavelengths, and the host only begins to absorb below 300 nm. The reflectivity R can be transformed into a value proportional to the absorption using the Kubelka-Munk function $K = (1 - R)^2 / (2R)$, and the Tauc plot of $(K\hbar\nu)^n$ against $\hbar\nu$ (with $n = 2$, applicable for a direct bandgap material) is given in Figure 3(b), from which the optical bandgap is estimated to be about 5.85 eV. When 1 mol% Bi is incorporated in the as-prepared material the reflectance spectrum changes dramatically, with absorption occurring at much longer wavelengths.

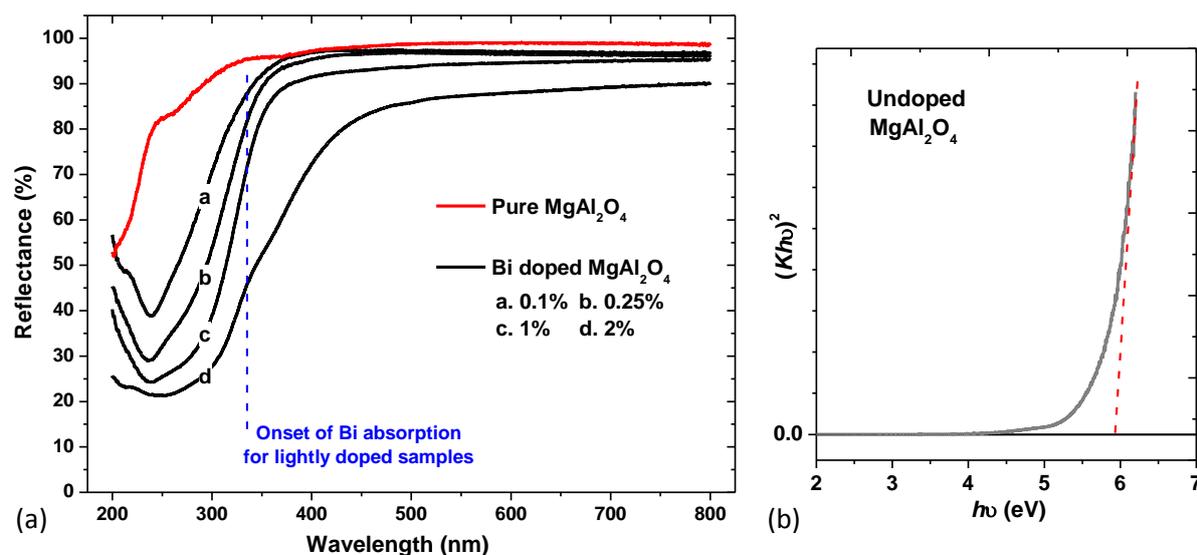


Figure 3. (a) Diffuse reflectance spectra of MgAl_2O_4 samples. (b) Estimate of the direct optical bandgap of undoped MgAl_2O_4 host using Kubelka-Munk function.

Figure 4(a) shows the PL excitation and emission spectra (for excitation with the xenon lamp at 335 nm) for the $\text{MgAl}_2\text{O}_4:\text{Bi}$ (0.5 mol%) measured with the Cary-Eclipse fluorescence spectrophotometer, as well as the emission spectrum obtained when the sample is excited at 325 nm by a He-Cd laser. A single broad band of blue fluorescence emission was observed centred near 400 nm, which has an optimal excitation wavelength of 335 nm. This excitation wavelength corresponds to the onset of absorption in Bi doped MgAl_2O_4 samples as seen in Figure 3(a). The excitation and emission are attributed to $^1\text{S}_0 \leftrightarrow ^3\text{P}_1$ transitions of Bi^{3+} ions, with a Stokes shift of 0.60 eV. For comparison, in Bi doped Y_2O_3 two emission bands occur at 410 and 520 nm with Stokes shifts of 0.31 and 1.24 eV respectively, which are attributed to Bi^{3+} ions in two different host lattice sites [5]. The single emission band in our results (figure 4(a)) indicates that only one site occurs for Bi^{3+} ions in spinel. Shoulders on both the low and high wavelength sides of the emission peak observed using the Cary-Eclipse (but not the laser PL system) require further study. Figure 4(b) shows that the luminescence intensity is a

maximum for a Bi^{3+} doping concentration of 0.5 mol%. Above that concentration the luminescence intensity decreases. While such an effect is often attributed to concentration quenching, the optimal concentration is rather low. Instead, it is suggested that the large size of the Bi^{3+} ions limits the amount of Bi that can be successfully incorporated into the host and that excess amounts of dopant leads to defects or quenching centres which then limit the luminescence intensity.

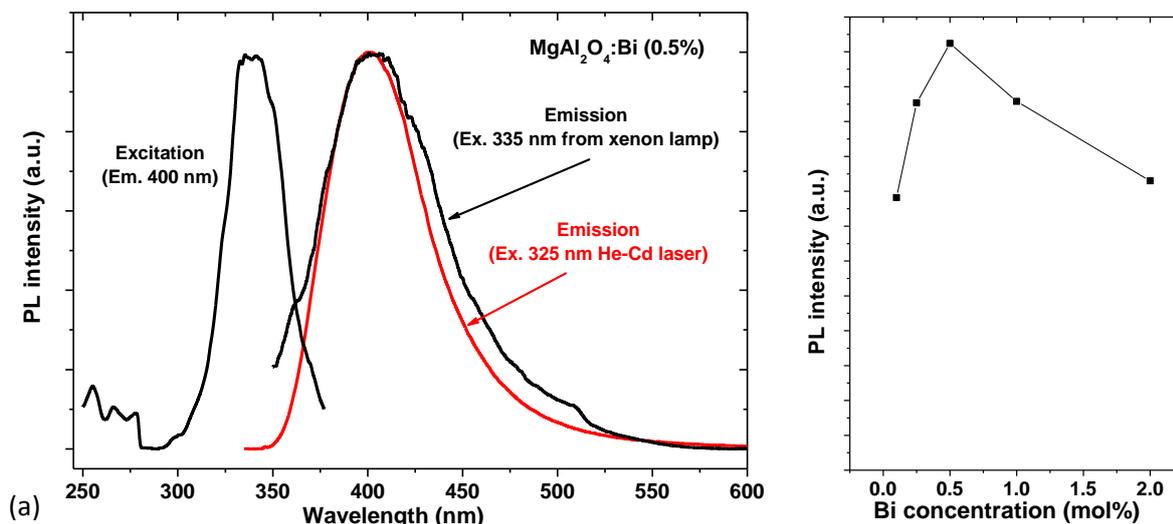


Figure 4. (a) Room temperature luminescence spectra of $\text{MgAl}_2\text{O}_4:\text{Bi}$ (0.5 mol%) measured with the Cary-Eclipse fluorescence spectrophotometer (using a xenon lamp) as well emission when excited by a He-Cd laser. (b) Luminescence peak intensity as a function of Bi doping concentration measured with the Cary-Eclipse fluorescence spectrophotometer for excitation wavelength of 335 nm.

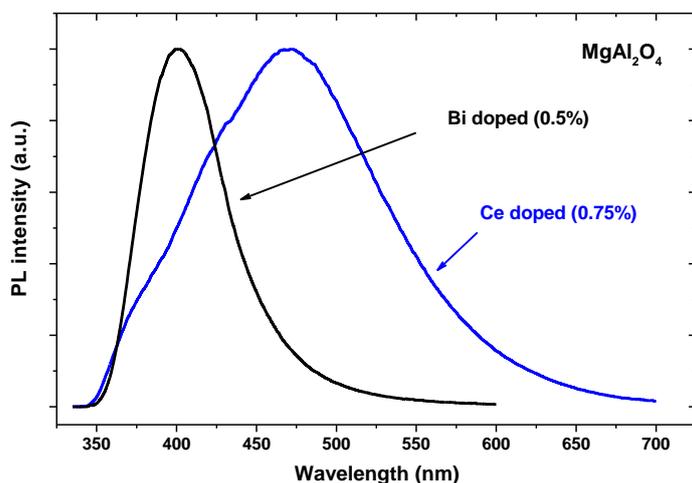


Figure 5. Comparison of the normalized emission spectra for Bi and Ce doped MgAl_2O_4 , both excited with a He-Cd laser at 325 nm.

Figure 5 compares the PL emission spectra of Bi (0.5 mol%) and Ce (0.75 mol%) doped MgAl_2O_4 , both excited by a He-Cd laser at 325 nm. The fluorescence of the Ce doped sample is a broad band centred near 470 nm and is attributed to the transition of electrons that have been excited to the 5d level returning to the $^2\text{F}_{7/2}$ and $^2\text{F}_{5/2}$ states of the 4f level, although the peaks corresponding to the two final states are not resolved. Ce is often used as a sensitizer for Tb ions in many phosphor hosts because it can be excited efficiently and also transfer energy to Tb as a result of an overlap of its emission spectrum with the f-f excitation bands of Tb. The Tb f-f excitation bands occur in almost the same position independent of the host, beginning near 380 nm and extending to shorter wavelengths.

This region is better overlapped by the Bi emission spectrum, suggesting that Bi may act as a good sensitizer for Tb. In addition, the Bi doped sample is more easily prepared, since it does not require annealing. The Ce doped sample had to be annealed in a reducing atmosphere of 4% H₂ in Ar at 1400°C for 2 h in order to convert non-luminescent Ce⁴⁺ ions to trivalent Ce³⁺ ions before emission was obtained. Bi therefore seems a strong candidate to replace Ce in Ce,Tb co-doped samples, and co-doping spinel with Bi and Tb will therefore be the focus of future work.

4. Conclusion

Nanocrystalline Bi doped MgAl₂O₄ has been successfully synthesized by the combustion method. A broad band of blue fluorescence emission centred at 400 nm was observed for excitation at 335 nm, which is attributed to the ³P₁ → ¹S₀ transition of Bi³⁺ ions. The emission intensity was measured as a function of Bi doping concentration, with the maximum occurring for 0.5 mol% of Bi doping. The results indicate that doping MgAl₂O₄ with Bi ions may be an attractive alternative to doping it with Ce ions, which give broad blue-green luminescence in this host but requires reducing at a high temperature (1400°C) to convert non-luminescent Ce⁴⁺ ions to the luminescent Ce³⁺ charge state. The emission of Bi also suggests that it may be act as a good sensitizer for Tb ions in MgAl₂O₄.

Acknowledgments

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