

Luminescent Properties of the $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+},\text{M}^{3+}$ (M = Nd, Er) Phosphor in the VUV Region

Junying Zhang,^{*,†} Zhongtai Zhang,[†] Zilong Tang,[†] Ye Tao,[‡] and Xin Long[‡]

State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, P.R.China, and Beijing Synchrotron Radiation Laboratory, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, P.R.China

Received December 28, 2001. Revised Manuscript Received April 25, 2002

$\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphor powder was synthesized using a sol–gel process. Doping Er^{3+} and Nd^{3+} in the phosphor can increase the luminescent intensity of the phosphor in the VUV region. The $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphor crystallizes completely when the dried gel is calcined at 1300 °C. The $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ can absorb the VUV efficiently, and Er^{3+} and Nd^{3+} ions have great effects on the luminescent properties of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphor by forming positive charged defects. When a suitable amount of Er^{3+} or Nd^{3+} ion is doped in the phosphor, the excitation intensity in the VUV region especially at about 172 nm increases and the luminescent intensity excited by VUV also increases.

1. Introduction

$\text{BaMgAl}_{10}\text{O}_{17}$ is an excellent matrix for phosphors because of its chemical stability. $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$, as an efficient blue emission phosphor, has been used in fluorescent lights (FL), and recently, it has been widely applied in plasma display panels (PDPs).^{1–5}

AC color PDPs are one of the most promising candidates for large flat panel displays. As the main blue-emitting phosphor used for PDPs, with an ideal emission peak, the luminescent efficiency of the $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphor is not high enough in the VUV region.^{1,2} Luminescent efficiency of the phosphors should be increased in order to improve the performance of PDPs. One way is to obtain fine particles without milling or grinding, and another way is to dope other elements to increase the ability of the phosphor to absorb ultraviolet (UV) and vacuum ultraviolet (VUV) excitation.^{2–3}

Through a sol–gel process, it is possible to synthesize phosphors with small particle size. It is easy to control the composition and homogeneity.^{6–10} The active precursors result in low calcination temperatures and minimize the potential for cross contamination. Many

researchers have done work to synthesize phosphors by sol–gel processing, but most of the starting materials employed have been ester or alcohol based, which are volatile and harmful to the environment.^{11–13}

This paper reports the $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphor synthesized by a simple sol–gel process with Er^{3+} and Nd^{3+} doping. A suitable amount of Er^{3+} and Nd^{3+} help the $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphor absorb the excitation energy in the VUV region, and thus, the luminescent intensity increases.

2. Experimental Section

The starting materials were Eu_2O_3 , Nd_2O_3 , Er_2O_3 (99.99%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (AR), BaCO_3 (AR), $\text{Mg}(\text{OH})_2 \cdot 4\text{MgCO}_3 \cdot 6\text{H}_2\text{O}$ (AR), and citric acid (AR), and KI (AR) was added to balance the electric charge. Figure 1 is the flow scheme for the process of preparing the $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+},\text{M}^{3+}$ phosphor by the sol–gel method.

X-ray diffraction patterns were obtained with a Rigaku D/MaxIIIB X-ray diffraction meter (XRD) using $\text{Cu K}\alpha$ radiation. The excitation and emission spectra of the phosphor powders in the UV region were recorded using a Hitachi 850 spectrophotometer. The excitation and emission spectra of the phosphor in the VUV region were obtained using synchrotron radiation from the BSRF storage ring at Institute of High Energy Physics (Academy of Chinese Sciences, China). The electron energy of the storage ring is 2 GeV, and the beam current is about 100 mA with a lifetime of approximately 40 h. Excitation spectra were corrected for spectral distribution of the light source and the instrumental response by using sodium salicylate as a standard.

The positron lifetime was measured by using the ORTEC fast–slow coincidence lifetime spectrometer with a time resolution of 270 ps as measured with the ^{22}Na radioisotope. After subtracting background and source contributions, the lifetime

* To whom correspondence should be addressed. E-mail: zjy99@ mails.tsinghua.edu.cn.

† Tsinghua University.

‡ Chinese Academy of Sciences.

- (1) Smets, S. M. J. *Mater. Chem. Phys.* **1989**, *16*, 283.
- (2) Ronda, C. R. *J. Lumin.* **1997**, *72–74*, 49.
- (3) Ronda, C. R. *J. Alloys Compd.* **1995**, *225*, 534.
- (4) Kim, C. H.; Kwon, I.-E.; Cicillini, C. H.; et al. *J. Alloys Compd.* **2000**, *311*, 33.
- (5) Serra, O. A.; Cicillini, S. A.; Ishiki, R. R. *J. Alloys Compd.* **2000**, *303–304*, 316.
- (6) Matthews, R. B.; Swanson, M. L. *Am. Ceram. Soc. Bull.* **1979**, *58*, 223.
- (7) Jo, K. H.; Yoon, K. H. *Mater. Res. Bull.* **1989**, *24*, 1.
- (8) Komarneni, P. S.; Bhalla, A. *J. Mater. Res.* **1988**, *3*, 810.
- (9) Mulder, C. A.; Van Leeuwen-Stienstra, M. G.; Van Lierop, J. G.; et al. *J. Non-Cryst. Solids* **1985**, *82*, 148.
- (10) Lee, M. H.; Park, Y. H.; Yang, C. K. *J. Am. Ceram. Soc.* **1987**, *70*, c.35.

- (11) Ruan, S. K.; Zhou, J. G.; Zhong, A. M.; et al. *J. Alloys Compd.* **1998**, *275–277*, 72.
- (12) Park, C. H.; Park, S. J.; Yu, B. Y.; et al. *J. Mater. Sci. Lett.* **2000**, *19*, 335.
- (13) Ravichandran, D.; Roy, R.; White, W. B.; et al. *J. Mater. Res.* **1997**, *12*, 819.

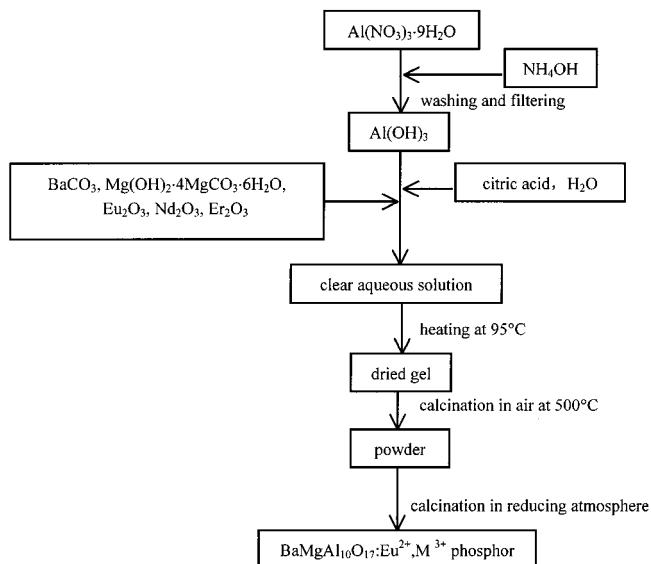


Figure 1. Synthesis procedure of the $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+},\text{M}^{3+}$ phosphor.

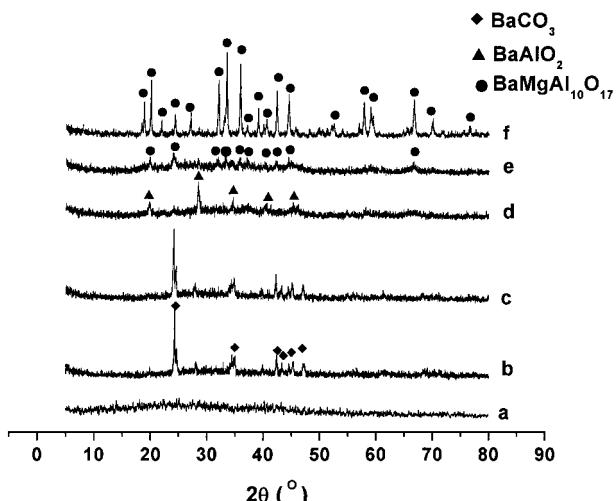


Figure 2. XRD patterns of the powder calcined at different temperatures. (a) Dried gel, (b) 500 °C, (c) 600 °C, (d) 900 °C, (e) 1200 °C, and (f) 1300 °C.

spectra were analyzed in two lifetime components by using the program PATFIT-88.

3. Results and Discussion

In the process of heating at 95 °C, the volume of the aqueous solution was slowly reduced, and then a transparent sol formed. Further heating led to dehydration and caused the condensation reaction between $-\text{COOH}$ groups with the concurrent formation of water. When most of the excess water was removed, the sol turned into a transparent gel.

The dried gel was calcined at 500 °C in air for 3 h and calcined again at different temperatures in reducing atmosphere. X-ray diffraction patterns for the powder calcined at different temperatures are shown in Figure 2. At low temperature, the main crystal is BaCO_3 , whereas the compounds of aluminum and magnesium are amorphous so that they are not observed by X-ray diffraction. At 900 °C, BaCO_3 almost disappears and BaAl_2O_4 forms while some remnants of the compounds of aluminum and magnesium are still amorphous. At

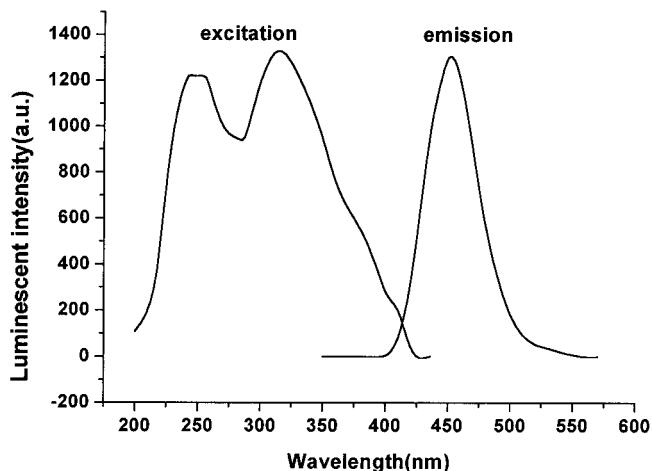


Figure 3. Excitation and emission spectra of the $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphor in the UV region.

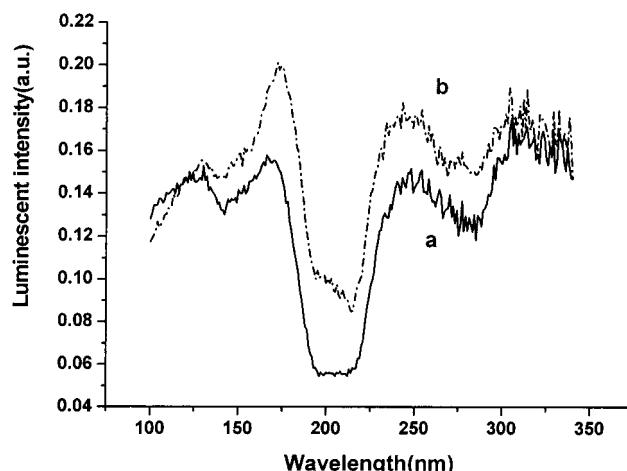


Figure 4. Excitation spectra of phosphors in VUV region. (a) $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}_{0.10}^{2+}$ and (b) $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}_{0.10}^{2+},\text{Er}_{0.10}^{3+}$.

1200 °C, patterns of $\text{BaMgAl}_{10}\text{O}_{17}$ appear, whereas BaAl_2O_4 almost disappears completely, but the crystallinity of $\text{BaMgAl}_{10}\text{O}_{17}$ is still very low. With the temperature increasing up to 1300 °C, $\text{BaMgAl}_{10}\text{O}_{17}$ crystallizes completely.

Figure 3 shows the excitation and emission spectra of the $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphor in the UV region. The excitation spectrum of the blue fluorescence ($\lambda = 450$ nm) shows two wide bands with their peaks at about 230 and 310 nm, respectively, which are due to the crystal field splitting of the Eu^{2+} d orbitals. The emission spectrum excited by 310 or 230 nm UV consists of a wide band with a peak at about 450 nm, which corresponds to 4f–5d transition of Eu^{2+} ions.¹⁴

Use of phosphors in PDPs requires efficient excitation in the VUV region, especially near the Xe resonance line (147 nm) and the Xe_2 molecular emission band (172 nm). Figure 4a shows the excitation spectrum of the $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}_{0.10}^{2+}$ phosphor by monitoring the blue emission at 450 nm. The shape of the excitation in the UV region is similar with that in Figure 3. The two bands in the VUV region with peaks at about 123 and 166 nm correspond to the band-to-band excitation of the host crystal; that is, the electrons are promoted from

(14) Blasse, G.; Geiabmaier, B. C. *Luminescent Materials* Springer-Verlag: Berlin, 1994.

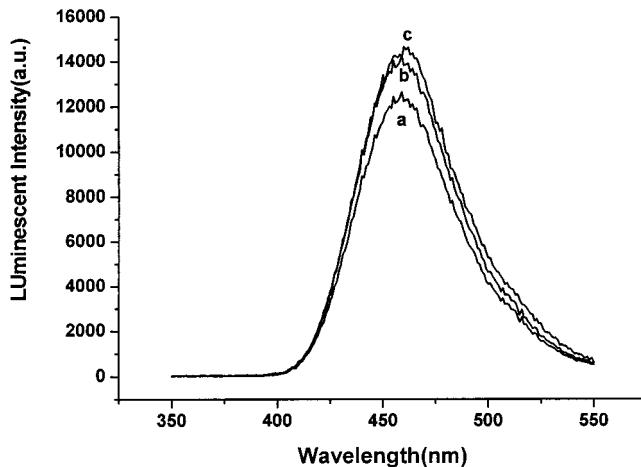


Figure 5. Emission spectra of phosphors excited by 172 nm VUV. (a) $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}_{0.10}^{2+}$, (b) $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}_{0.10}^{2+},\text{Nd}_{0.03}^{3+}$, and (c) $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}_{0.10}^{2+},\text{Er}_{0.10}^{3+}$.

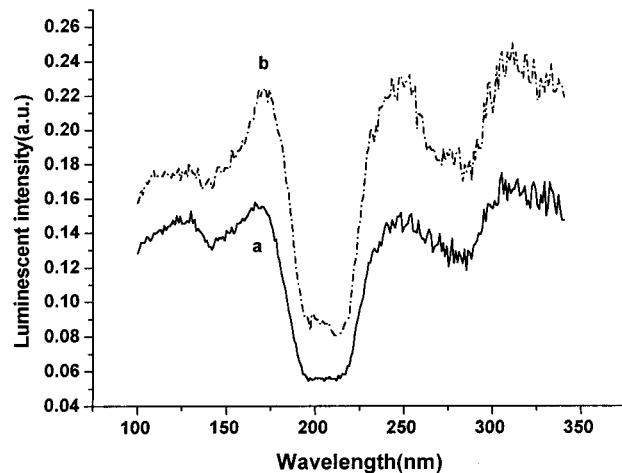


Figure 6. Excitation spectra of phosphors in VUV region. (a) $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}_{0.10}^{2+}$ and (b) $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}_{0.10}^{2+},\text{Nd}_{0.03}^{3+}$.

the valence band to the electron band. The emission spectra in Figure 5 excited by 147 and 172 nm VUV consist of a wide band with a peak at about 450 nm, which corresponds to the 4f–5d transition of Eu^{2+} ions. The excitation energy absorbed by the host lattice is transferred to Eu^{3+} in contrast with that in the UV region in which the excitation energy is absorbed by Eu^{2+} ions themselves.

When Er^{3+} is doped in the $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}_{0.10}^{2+}$ phosphor, the shape of the excitation and emission spectra remains, but the excitation intensity at about 166 nm increases in comparison with that at about 123 nm as indicated in Figure 4, and the peak position shifts to about 172 nm. This is a very useful result because xenon plasma has a strong emission band with a peak at 172 nm, and the shift of the peak can improve the luminescent intensity of the phosphor for PDPs. The luminescent intensity excited by VUV increases with the amount of Er^{3+} increasing as shown in Figure 5 which gives the luminescent spectra of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}_{0.10}^{2+},\text{Er}_x^{3+}$ phosphor when x is changed. When a suitable amount of Er^{3+} is doped in the phosphor, the luminescent intensity becomes maximum. When the Nd^{3+} ion is doped in the $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}_{0.10}^{2+}$ phosphor, the same result is obtained. The excitation intensity at about 166 nm increases in comparison with that at

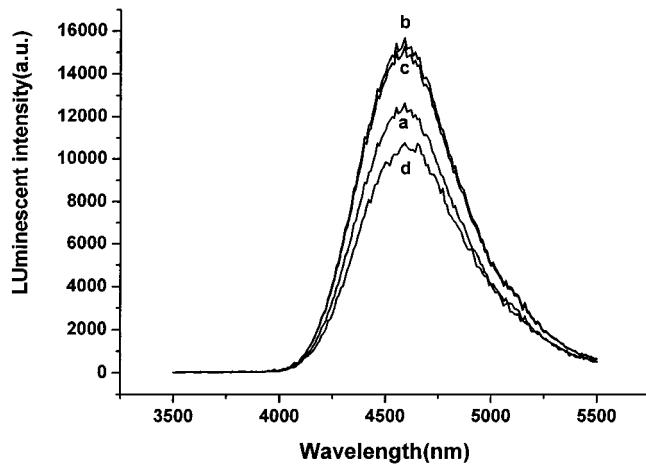


Figure 7. Emission spectra of phosphors excited by 172 nm VUV. (a) $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}_{0.10}^{2+}$, (b) $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}_{0.10}^{2+},\text{Nd}_{0.03}^{3+}$, (c) $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}_{0.10}^{2+},\text{Nd}_{0.06}^{3+}$, and (d) $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}_{0.10}^{2+},\text{Nd}_{0.10}^{3+}$.

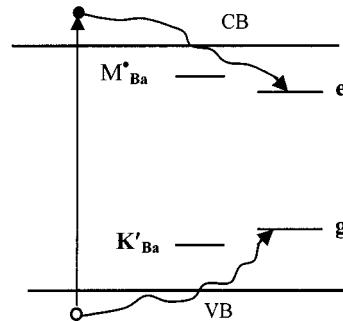


Figure 8. Energy levels of the $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+},\text{M}^{3+}$ ($\text{M} = \text{Nd}, \text{Er}$) phosphor.

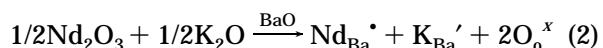
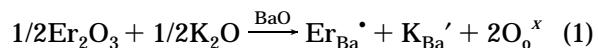
Table 1. Positron Annihilation Lifetimes of the $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}_{0.10}^{2+},\text{M}^{3+}$ ($\text{M} = \text{Er}, \text{Nd}$) Phosphor

| sample | τ_1 | τ_2 | I_1 | I_2 |
|---|----------|----------|-------|-------|
| $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}_{0.10}^{2+}$ | 261.8 | 420.5 | 68.86 | 30.31 |
| $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}_{0.10}^{2+},\text{Er}_{0.10}^{3+}$ | 238.5 | 389.3 | 59.33 | 39.90 |
| $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}_{0.10}^{2+},\text{Nd}_{0.03}^{3+}$ | 201.8 | 341.4 | 43.47 | 55.16 |

about 123 nm as indicated in Figure 6, and the peak position shifts to about 172 nm when suitable amount of Nd^{3+} is doped. The maximum luminescent intensity is obtained when a suitable amount of Nd^{3+} is doped and the intensity decreases again when the amount of Nd^{3+} further increases.

The positron annihilation lifetime of the $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+},\text{M}^{3+}$ ($\text{M} = \text{Er}, \text{Nd}$) phosphor is shown in Table 1. From Table 1, it can be seen that, when Er^{3+} and Nd^{3+} ions are doped in the $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphor, τ_2 decreases and the corresponding intensity I_2 increases. τ_1 is a weighted average of the lifetime of free positrons, and τ_2 contributes from positron annihilation in defects. So the amount of positive charged defects increases when Er^{3+} and Nd^{3+} ions are doped in the $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphor.

When Er^{3+} and Nd^{3+} ions are doped in the $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphor, defects form as follows:



As shown in Figure 8, the energy levels of $\text{Er}_{\text{Ba}}\cdot$ and $\text{Nd}_{\text{Ba}}\cdot$ are close to the conduction band of the host, and the holes are captured from the conduction band. The energy level of K_{Ba}' is close to the valence band, and the electrons are captured from the valence band. As a result, when Er^{3+} and Nd^{3+} ions are doped in the phosphor with K^+ as a charge compensator, the holes in the valence band and the electrons in the conduction

band increase. The possibility for the excited state of Eu^{2+} to capture electrons and the ground state to capture the holes increases too, so that the luminescent intensity increases. When too large of an amount of Er^{3+} and Nd^{3+} ions is doped in the phosphor, the defects will associate. As a result, the luminescent intensity decreases again.

CM011744U