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Luminescent properties and thermal stability of $BaMgAl_{10}O_{17}$:Eu^{2+} synthesized by sol–gel route

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Abstract

$BaMgAl_{10}O_{17}$:Eu^{2+}(BAM) phosphor particles were prepared by sol–gel processes. The effect of the firing temperature and the Eu^{2+} concentration on the distribution of Eu^{2+} among different sites was firstly investigated through the changes of excitation spectra with changing firing temperature and Eu^{2+} concentration. The mechanism underlying was elucidated. The stability of BAM could be improved by increasing the firing temperature and Eu^{2+} concentration.

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Keywords: BAM; Sol–gel processes; Sites; Stability; Luminescence

1. Introduction

Phosphors are widely used in plasma display panels (PDPs), field emission displays (FEDs), and fluorescence lamps (FLs), etc. [1,2]. $BaMgAl_{10}O_{17}$ is an excellent matrix for phosphors because of its chemical stability. For example, the $BaMgAl_{10}O_{17}$:Eu^{2+}(BAM) as an efficient blue emission phosphor has been used in FLs because it has a deep blue color and a short decay time [3]. It is well known that in FL manufacturing, BAM, which spreads on the insides of a glass tub, is heated at 700–750 °C in air. The PDP manufacturing process also heats phosphor at 500–600 °C to make phosphor layers. These heat-treatments result in the luminance decrease [4]. This is a critical problem in manufacturing of FLs and PDPs. Unlike the other red and green phosphors, only the BAM phosphor shows a considerable decrease in luminescence after heating process [5]. So, the deterioration of its luminescence upon heating is one of the most significant shortcomings in application. The stability of BAM should be improved in order to improve the performance of FL and PDP.

The structure of $BaMgAl_{10}O_{17}$, or β-alumina, consists of two spinel blocks ($MgAl_{10}O_{16}$) separated by one mirror plane (BaO) [6]. When Eu^{2+} is substituted into the host lattice, it can have been three possible locations: Beevers-Ross (BR), anti-Beevers-Ross (a-BR), and mid-oxygen (mO) sites in the mirror plane [7]. Peak fitting results show that the primary emission center is assigned to Eu^{2+} on the normal Ba site (the BR site in the cation layer), while the second center is assigned to Eu^{2+} on the a-BR site. The third center has been assigned alternatively to Eu^{2+} in the spinel block, to Eu^{2+} on the mid-oxygen sites in the cation layer, or to Eu^{2+} associated with defect center in the lattice, But it is not populated in the fresh samples [7]. On the mechanism of the deterioration, much research has been conducted. In the literature, luminance deterioration is usually attributed to the oxidation of $BaMgAl_{10}O_{17}$:Eu^{2+} phosphor and the changes of the environments surrounding the europium ion [3–5]. They indicated that by oxidation, $BaMgAl_{10}O_{17}$:Eu^{2+} was converted into a mixture of two compounds $BaMgAl_{10}O_{17}$ and Eu (III) $MgAl_{11}O_{19}$. This deactivated the Eu^{2+} luminescent center and decreased the Eu^{2+} emission. The important thing that should be noted is that the Eu^{3+} no longer prefers to substitute for the Ba^{2+}, as the Eu^{2+} does. Instead it would prefer to substitute for an aluminum ion in the Al (2) positions, that is, a tetrahedral

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site. The computer simulation results show that Eu^{2+} prefers to occupy the BR site in the cation layer while Eu^{3+} prefers the Al (2) tetrahedral position in the spinel block [18]. Recently, some other opinions were demonstrated, such as generation of a lattice vacancy [8], migration of Eu^{2+} to the spinel block [9], intercalating water molecules into the host lattice [10], and the transfer of the electron from the divalent europium ions to adsorbed oxygen ions [11]. To the best of our knowledge, there was no report on the influence of the annealing temperature and the Eu^{2+} concentration on the distribution of Eu^{2+} among different sites and its luminescence properties.

In this work $BaMgAl_{10}O_{17}:Eu^{2+}$ is synthesized by sol–gel route. The influence of the annealing temperature and the Eu^{2+} concentration on the distribution of Eu^{2+} among different sites was investigated. The stability of BAM is improved by increasing firing temperature and Eu^{2+} concentration.

2. Experimental

Eu_2O_3 (A·R), $Al(NO_3)\cdot 9H_2O$ (A·R), $Ba(NO_3)_2$ (G·R), $Mg(NO_3)_2\cdot 6H_2O$ (A·R), and $C_6H_8O_7\cdot H_2O$ (A·R) were used as starting materials. Europium nitrate solution was obtained by dissolving analytical grade Eu_2O_3 in dilute nitric acid. Then a stoichiometric amount of metal nitrates were dissolved in distilled water. Subsequently, a weighed quantity of citric acid ($C_6H_8O_7\cdot H_2O$) was added to the nitrate solution. The mole ratio of citric acid to the total concentration of metal ions was adjusted to 1.5. After mixing, homogenous colorless solution was obtained. 3 h later, the 30% ammonia was added to the solution and the pH was adjusted to 5–6. The water was slowly evaporated off from solution at 110 °C and a dark metal citrate suspension was formed at first. Further heating 1 h result in dark colored amorphous citrate gels with high viscosity, which were then calcined at 700 °C for 2 h in air to remove organic residues. The calcined powder was, respectively, heated at 1250, 1350 and 1450 °C for 2 h under a reducing atmosphere (CO). In another experiment, the calcined powder was annealed at 1350 °C in air, and then heated in reducing atmosphere, respectively, at 600, 700, 750, 800, 900, 1000, 1100, and 1300 °C.

In the same way, $Ba_{1-x}Eu_xMgAl_{10}O_{17}$ ($x = 0.01$, 0.05, 0.1, and 0.18) precursors were obtained. These precursors were calcined at 700 °C for 2 h in air, and then heated at 1350 °C for 2 h under a reducing atmosphere.

Finally, all the as-prepared samples are annealed at different temperatures for some time in air.

XRD studies were conducted on a Rigaku D/max-2000 X-ray powder diffractometer with Cu Kα radiation. The emission and excitation spectra at room temperature were measured with a Hitachi F-4500 fluorescence spectrometer.

3. Results and discussion

3.1. XRD and photoluminescence analysis

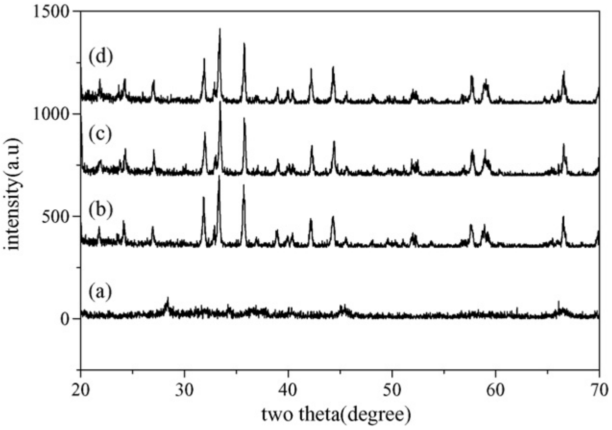

Fig. 1. XRD patterns of the $Ba_{0.9}Eu_{0.1}MgAl_{10}O_{17}$ sintered at different temperatures in reducing atmosphere. (a) 1150 °C, (b) 1250 °C, (c) 1350 °C, and (d) 1450 °C.

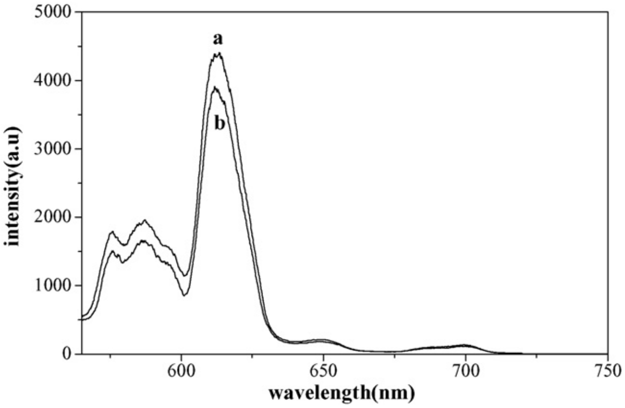

Fig. 2. Emission spectra of the precursors sintered at (a) 1050 °C, and (b) 1150 °C in reducing atmospheres under 254 nm excitation.

In order to understand the relationship between the luminescence characteristics and the crystallization behavior of BAM from amorphous citrate precursor, temperature-resolved X-ray diffraction patterns and photoluminescence (PL) spectra were measured, as represented in Fig. 1. The precursor fired at 1150 °C in reducing atmosphere only shows characteristic of a certain unknown phase (see Fig. 1(a)), correspondingly, its emission spectrum is shown in Fig. 2(b). The peaks observed are characteristics of the $^5D_0 \rightarrow {}^7F_{J(J=0\text{–}4)}$ transition of Eu^{3+}, no blue emission is observed yet. This indicates that this unknown phase obtained at 1150 °C is a certain Eu^{3+}-containing compound. When the temperature increases to 1250 °C, the characteristics of diffraction peaks of BAM appear without any other impurities (see Fig. 1(b)) and the red emission is no longer observed, but we observed the blue emission peaking at 450 nm as illustrated in the Fig. 3(c) Fig. 3 is the emission spectrum under 254 nm excitation, which consists of a wide band peaking at 450 nm (the blue emission), corresponding to 5d → 4f transitions of the Eu^{2+}. The

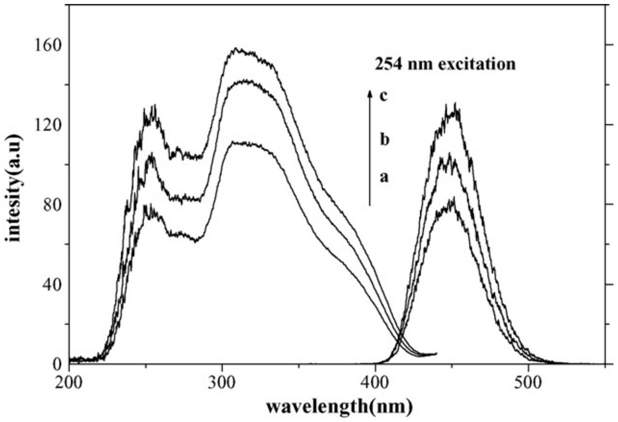

Fig. 3. Emission spectra under 254 nm excitation and excitation spectra monitoring the 450 nm emission of $Ba_{0.9}Eu_{0.1}MgAl_{10}O_{17}$ synthesized at (a) 1250 °C, (b) 1350 °C and (c) 1450 °C.

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