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Preparation of a novel red $KBaGd(MoO_4)_3:Eu^{3+}$ phosphor by sol-gel method and its luminescent properties

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ABSTRACT

For the first time, $KBaGd(MoO_4)_3:Eu^{3+}$ phosphors were synthesized by sol-gel method and its structure, morphology and luminescent properties were characterized by means of X-ray diffraction (XRD), scanning electron microscope (SEM), excitation and luminescent spectra. The results show that shape and the particle size distribution of samples synthesized by sol-gel method were more regular and narrower than those synthesized by solid state method. Under the excitation of near UV light (395 nm), an intensive red emission band around 617 nm corresponding to the transition of $^5D_0 \rightarrow {}^7F_2$ was observed. The effects of the dose of citric acid, pH value of precursor solution and concentration of Eu^{3+} ions on the morphology and luminescent properties of the samples were also analyzed. The phosphors show the highest emission intensity as the molar ratio of citric acid to metal ions (C:M) was 2:1, and the optimum concentration of Eu^{3+} was $x = 0.8$. The thermal stability of the $KBaGd_{0.2}(MoO_4)_3:0.8Eu^{3+}$ phosphor was investigated in the framework of crossover mechanism, and the activation energy was determined to be 0.264eV. Lastly, a red LED was fabricated using the as-synthesized phosphor and its luminescent performances were investigated.

1. Introduction

The invention of white lighting-emitting diodes (LEDs) has brought a revolution to the illumination technology because of its inherent merits, such as high luminous efficiency, energy-saving, long lifetime, compact size, high reliability and environmental protection [1–4]. As a new generation of illuminant source, LEDs are replacing the traditional incandescent and fluorescent lamps and widely applied to various fields [3]. At present, the combination of a blue LED chip (InGaN) with yellow phosphor ($YAG:Ce^{3+}$) is still the most popular method for the production of white LED products, as white lights can be simply obtained by a suitable mixture of blue and yellow emission [1–3]. However, due to the lack of red light component, white LED products produced by such method usually have low rendering index Ra (~80) and high color temperature (~7000) [2–4]. As a result, a suitable amount of red phosphor should be added to improve the Ra of the light and the red phosphors of $(Ca, Sr)AlSiN_3:Eu^{2+}$ and $(Ca-Ba)_2Si_5N_8:Eu^{2+}$ are widely used for this purpose [5,6]. However, the large overlap between the broad emission and absorption bands of these compounds leads to a serious reabsorption effect and thus decreases the luminescent efficiency [5,6]. Besides, the severe synthesis condition and complicated synthesis technique are also not encouraging for their applications. Consequently, it still makes sense to explore new red emitting phosphors with high luminescent efficiency, low cost and low-demanding synthesis condition.

Beside Eu^{2+} ions, the trivalent europium (Eu^{3+}) ion is also frequently investigated for the development of red emitting phosphors, since it can give rise to an intense red emission around 615 nm via the $^5D_0 \rightarrow {}^7F_2$ transition. Besides, Eu^{3+} doped phosphors can be easily synthesized in air, which reduces the production cost with respect to Eu^{2+} activated red phosphors. As a consequence, many kinds of Eu^{3+} doped systems, including borate, phosphates, silicates, molybdates and tungstates, etc, have been investigated as potential red emitting phosphors [1–8]. Among the above mentioned hosts, molybdate based materials have aroused particular attention as promising host for Eu^{3+}-activated luminescent phosphors, because of their excellent properties, such as excellent chemical stability, moderate synthesis conditions, low cost and pollution-free features [1–3]. Furthermore, molybdate based phosphors can be synthesized by a variety of methods and thus provide us a good case to investigate the relations among luminescent property, morphology and synthesis method. Consequently, in the last decades, besides the conventional scheelite-type molybdates $AB(MoO_4)_2$ (A = Li, Na, K; B= Y, La, Gd) [2,9–11] and ferroelectric molybdates $Re_2(MoO_4)_3$ (Re= Y, La, Gd) [1], some new molybdates like

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$Li_3Ba_2Re_3(MoO_4)_8$ (Re = Y, Gd, La) [2,5,12], $BaGd_2(MoO_4)_4$ [13], and $CsGd(MoO_4)_2$ [14] have also been explored as potential host for luminescent materials.

More recently, a new kind of triple molybdate compound $KBaRe(MoO_4)_3$ (Re = Y, Gd), which belongs to the monoclinic system with space group *C*2/*c*, have emerged as promising laser materials [15–17]. In previous papers, Yu et al. have reported the growth and spectroscopic properties of Yb^{3+} and Nd^{3+}-doped $KBaRe(MoO_4)_3$ crystals, and demonstrated their potential applications in solid-state lasers [15–17]. However, to the best of our knowledge, very few reports were devoted to the investigation of these compounds as host material for luminous phosphors. Not long ago, Wang et al. have reported the structure and luminescent properties, including the diffuse reflectance spectra, excitation and emission spectra, life decay curves, and the thermal stability of a stoichiometric phosphor $KBaEu(MoO_4)_3$ [18]. However, in our view, the potential application of the $KBaRe(MoO_4)_3$ system in LEDs cannot be exactly evaluated from the luminescent performance of $KBaEu(MoO_4)_3$ phosphor since the concentration quenching effect was not taken into consideration with such a high Eu^{3+} concentration that may degrade the luminescent property. Furthermore, in their paper, the $KBaEu(MoO_4)_3$ phosphor was prepared by a conventional solid state reaction method at 900 °C for a long time of 24 h. The high sintering temperature and long holding time may lead to serious aggregation and irregular shape of particles, which were also unfavorable to the luminescent properties [1]. Based on the above considerations, in the present study, we have synthesized a series of $KBaGd(MoO_4)_3:Eu^{3+}$ phosphors with different Eu^{3+} doping concentrations by sol-gel method and investigated the effects of experimental conditions, including the amount of citric acid and pH value, on the morphology and luminescent properties of the prepared phosphors. Furthermore, the exciting and emission spectral, luminescence decay curves, quantum yield, as well as thermal stability of the phosphors were also analyzed in detail. Finally, to fully access their potential for white LEDs applications, a red LED was fabricated using the as-synthesized phosphor and its luminescent performances were investigated as a function of filament currents.

2. Experimental procedures

2.1. Sample preparation

$KBaGd_{1-x}(MoO_4)_3:xEu^{3+}$ (KBGM:xEu^{3+} for short) (x = 0.5–1.0) phosphors were prepared using sol-gel method with raw materials of KNO_3 (AR), $Ba(NO_3)_2$ (AR), Gd_2O_3 (99.999%), Eu_2O_3 (99.99%), $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (AR), HNO_3(AR) and $NH_3{\cdot}H_2O$ (AR). The detailed experimental process is similar to that in Refs. [1,2]. Firstly, Gd_2O_3 and Eu_2O_3 were dissolved in diluted HNO_3, and the excess HNO_3 was removed under heating. Simultaneously, a stoichiometric amount of KNO_3 and $Ba(NO_3)_2$ was dissolved in deionized water and then added to the above solution. Subsequently, different amounts of citric acid (citric acid/metal ion = 1:1, 2:1, 3:1, 4:1, 5:1) were dissolved in deionized water and then dropped into the above mixture solution and stirred for 1 h to obtain a homogeneously mixed metal citrate solution. At the end, a stoichiometric amount of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ solution was slowly dropped into the metal citrate solution, and then the pH value of the solution was adjusted to 4–9 b y adding proper amount of $NH_3{\cdot}H_2O$ under stirring. After being stirred for a few minutes, the final solution was dried at a constant temperature of 80 °C in water bath to form a yellow transparent gel, and the transparent gel was further dried at 120 °C in an oven until it transformed into a black dried gel. Finally, the dried gel was calcined at different temperatures for 5 h in muffle furnace and the final products were obtained. For comparison, KBGM:0.5Eu^{3+} phosphor was also synthesized by conventional solid-state reaction method at 800 °C for 10 h.

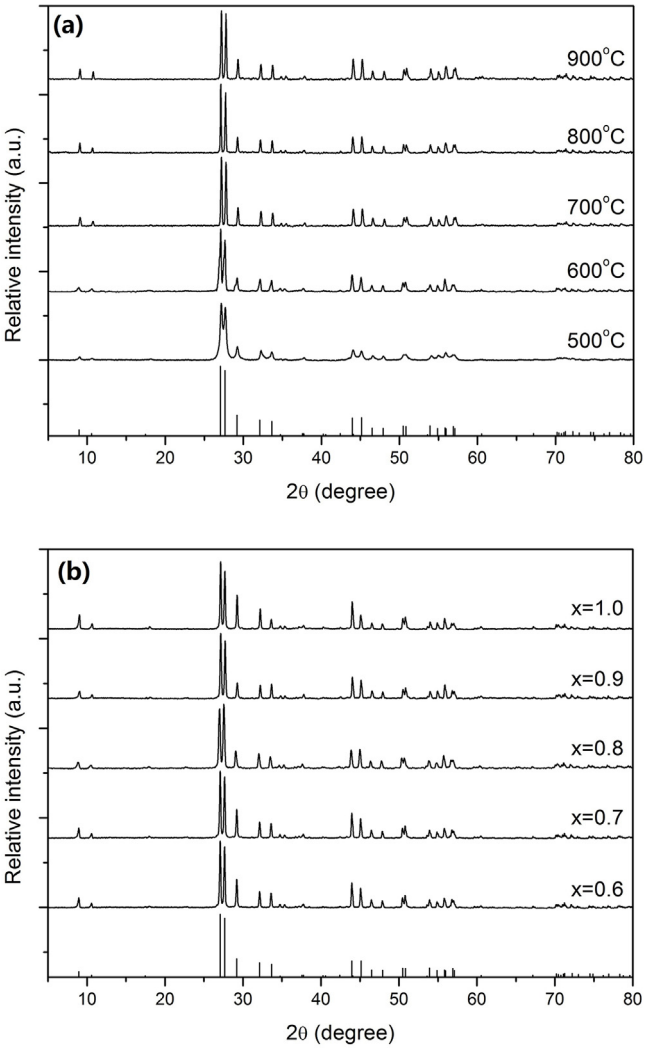

Fig. 1. (A) The XRD patterns of KBGM:0.5Eu^{3+} phosphors synthesized at different temperatures; (b) The XRD patterns of KBGM:xEu^{3+} (x = 0.6–1.0) phosphors.

2.2. Characterizations

The powder X-ray diffraction (XRD) data of the samples were collected at room temperature using the Bruker D8 Advance X-ray diffractometer equipped with a CuKα radiation (λ = 1.5406 Å). The FT-IR spectra of the samples were recorded using a Nicolet 5700 FT-IR spectrometer. The morphology of the samples was characterized using a Hitachi SU8010 field-emission scanning electron microscope (SEM). The excitation and emission spectra were recorded using the Hitachi F-4600 fluorescence spectrophotometer with a xenon lamp as excitation source. The decay curves of the phosphors were recorded using an Edinburgh Instruments FLS920 spectrophotometer.

3. Results and discussion

3.1. Structure and morphology

The crystal structure of the KBGM:0.5Eu^{3+} phosphors synthesized at different calcination temperature was characterized by XRD. When the as-synthesized gel is calcined at 500 °C, the diffraction peaks of the sample (Fig. 1a) are in agreement with the standard data of KBGM (ICSD#186560) and no impurity peaks are observed, indicating that the materials start to crystallize. As the calcination temperature increases,