Optical properties of MAI$_{12}$O$_{19}$:Eu (M = Ca, Ba, Sr) nanophosphors

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ABSTRACT

The MAI$_{12}$O$_{19}$:Eu (M = Ca, Ba, Sr) phosphor were synthesized by combustion method and systematically characterized by photoluminescence excitation and emission spectra, concentration quenching, morphology and X-ray mapping with scanning electron microscopy. In SrAl$_{12}$O$_{19}$:Eu phosphor two PL emission peaks are observed at about 389 nm and another around 420 nm as well as BaAl$_{12}$O$_{19}$:Eu phosphor shows blue emission around 460 nm is observed in the blue region of the spectrum and CaAl$_{12}$O$_{19}$:Eu shows only red emission at 592 nm as well as 615nm. Both phosphors can be efficiently excited in the wavelength range of 250-425 nm, where the near UV (~320 nm) solid state excitation is matched. By combining MAI$_{12}$O$_{19}$:Eu (M = Ca, Ba, Sr) phosphor with near UV chops emitting intense blue green (Ba), yellow-red (Ca) and blue purple (Sr) LEDs white LEDs can be produced. Copyright © 2011 VBRI press.

Keywords: Phosphor; photoluminescence; SEM; X-ray diffraction, nanophosphors; LEDs.

Introduction

Rare-earth and non-rare-earth-doped inorganic phosphors are widely used in a variety of applications, such as lamp industry, radiation dosimetry, X-ray imaging, and colour display. In particular, the luminescent properties of europium-ion doped phosphors have been studied extensively for their applications in these areas [1, 2]. Eu$^{2+}$ activated phosphors MAI$_2$O$_4$ and MAI$_{19}$O$_{39}$ (M = Sr, Ba, Ca, Mg) are well known since the studies by Blasse and Brill [3] in the 1960s. Their researches lead to the conclusion that these compounds were adequate phosphorescent materials because of their high quantum efficiency in the visible region. The emission of Eu$^{3+}$ ions varies from blue to red depending on the host lattice due to crystal-field effects [2]. A completely new generation of persistent luminescent phosphors, Eu$^{3+}$ doped alkaline Earth
aluminates, MAI₂O₄:Eu²⁺ (M = Ca, Sr), has been developed to replace ZnS:Cu [4]. At present, complex aluminates [5] as well as other materials [6] are subject to investigation.

Up to date, very little literatures reported the synthesis of nanostructured MAI₂O₄ (M = Ca, Ba, Sr) by combustion method. Douy and Capron [7] prepared SrAlO₃ powders by spray-drying aqueous solutions of strontium and aluminium nitrates followed by heating the powders to decompose the nitrates. Chen et al. [8] synthesized Eu²⁺ and Dy³⁺ co-doped SrAlO₃ by a sol–gel process. In fact, BaAl₂O₄:Mn is known as a green-emitting phosphor for PDPs [9], and Pr- or Nd-doped SrAlO₃ crystals has been suggested as one of the potential material with good laser properties [10]. In this article, we reported the synthesis of nanostructured MAI₂O₄:Eu (M = Ca, Ba, Sr) phosphors via combustion root synthesis, using urea as fuel and the effect of the Ca Ba and Sr in MAI₂O₄ on PL properties was investigated.

Experimental

The (Ca,Ba,Sr)₃₋ₓAlₓO₉:Euₓ (x = 1%, 3% and 5%) phosphor doped with Eu ions were prepared through a low temperature initiated combustion process. The starting material were taken as aluminium nitrate [Al(NO₃)₃·9H₂O], Calcium nitrate [Ca(NO₃)₂·6H₂O]. Europium nitrate was prepared by dissolving europium oxide [Eu₂O₃] in nitric acid. All the reagents were of analytical grade from Merck with 99.99% purity were used without further purification. The correct amount of each excess urea [CO(NH₂)₂] were injected into the precursor solution or these compositions. The amount of metal nitrates (oxidizers) and urea (fuel) were calculated using the total oxidizing and reducing valencies of the components, which serve as the numerical coefficients so that the equivalence ratio is unity and the heat liberated during combustion is at a maximum. After stirring for about 15 min, precursor solution was transferred to a furnace preheated to 400℃ and 500℃, the porous products were obtained.

The phase composition and phase structure were characterized by X-ray diffraction (XRD) pattern using a PAN-analytical diffractometer with Cu Kα radiation (λ = 1.5405 Å) operating at 45kV, 40mA. The morphology and the composition of the products were examined by scanning electron microscopy (SEM, JED-2300) equipped with an energy-dispersive spectrometry (EDS). Energy dispersive spectrometry (EDS) attached to the JEOL 2300 was used to determine the composition of the products. The photoluminescence properties of the phosphor (excitation and emission) were measured using a Shimadzu RF5301PC Spectrofurophotometer at room temperature.

Results and discussion

Structural property

The overall structure and phase purity of as synthesized products were characterized by XRD. Fig. 1 shows a typical XRD pattern of the M₁₋ₓAlₓO₉:Euₓ (M = Ca, Ba, Sr). All the phosphors are hexagonal structure with the space group P63/mmc. The diffraction peaks of BaAl₂O₄, SrAl₂O₃ and CaAl₂O₄ can be easily indexed with the JCPDS card no 00-026-0135, card no. 00-026-0976 and card no. 00-25-0122 respectively. No other crystalline phases were detected within the detection limit. The XRD results indicated that the as synthesized products are highly pure, single-phase.

The small amount of doped rare earth ions has virtually no effect on the phase structures. The average sizes calculated from XRD reflections for BaAl₂O₄, CaAl₂O₄ and SrAl₂O₃ by application of Scherrer’s equation are 40, 51 and 51 nm, respectively. It is known that the full-width at half-maximum (FWHM) can be expressed as a linear combination of the contribution from the lattice strain and crystalline size. The effects of the strain and particle size on the FWHM can be expressed by the following equation:

\[ D_{hl} = 0.9 \frac{\lambda}{\beta \cos \theta} \]

where \( \beta \) is the measured FWHM (in radians), \( \theta \) is the Bragg angle of the peak, \( \lambda \) is the X-ray diffraction wavelength.
Investigations. The photoluminescence emission spectra for the M\textsubscript{1−x}Al\textsubscript{x}O\textsubscript{19}: Eu\textsuperscript{3+} (M = Sr, Ba, Ca) phosphors by 320 nm excitation shown in Fig. 2 a-c. The spectra consist of broad, single peaked emission band in the blue region of the spectrum in M\textsubscript{1−x}Al\textsubscript{x}O\textsubscript{19}: Eu\textsuperscript{3+} (M = Ba, Sr) phosphors. These bands were assigned to the Eu\textsuperscript{2+} ions (4f\textsuperscript{7} → 4f\textsuperscript{6}5d\textsuperscript{1} transition), judging from the range of wavelength. The peak position slightly shifted higher wavelength with the increase of Eu\textsuperscript{2+} ions. Two emission peaks were recognized at 389 and 420 nm for Sr\textsubscript{1−x}Eu\textsubscript{x}Al\textsubscript{2}O\textsubscript{19} and at 460 nm for Ba\textsubscript{1−x}Eu\textsubscript{x}Al\textsubscript{2}O\textsubscript{19}. The ratio of two peaks almost fixed, although the intensity of two peaks varied with x. The intensity with different concentration of Eu\textsuperscript{3+} ions shows a specific pattern. The intensity reached a maximum at x = 0.05 for Sr\textsubscript{1−x}Eu\textsubscript{x}Al\textsubscript{2}O\textsubscript{19} and x = 0.03 for Ba\textsubscript{1−x}Eu\textsubscript{x}Al\textsubscript{2}O\textsubscript{19}. The PL emission in Ca\textsubscript{1−x}Eu\textsubscript{x}Al\textsubscript{2}O\textsubscript{19} phosphor observed at 592 and 615 nm sharp peaks in the red region of the spectrum due to \textsuperscript{5}D\textsubscript{0} → \textsuperscript{7}F\textsubscript{0} and \textsuperscript{5}D\textsubscript{0} → \textsuperscript{7}F\textsubscript{1} transition of Eu\textsuperscript{3+} ion, in this phosphor Eu\textsuperscript{3+} ion may be enter in side symmetry of lattice of the host material during preparation of phosphor as well changing matrix crystal structure and formation of aggregation of nanoparticles, therefore Eu ion observed in the Eu\textsuperscript{3+} valence state. The intensity with different concentration of Eu\textsuperscript{3+} ions shows a specific pattern. The intensity reached a maximum at x = 0.03 for Ca\textsubscript{1−x}Eu\textsubscript{x}Al\textsubscript{2}O\textsubscript{19}.

Fig. 2a, b and c show the emission spectrum of BaAl\textsubscript{2}O\textsubscript{19}: Eu\textsuperscript{2+}, SrAl\textsubscript{2}O\textsubscript{19}: Eu\textsuperscript{2+} and CaAl\textsubscript{2}O\textsubscript{19}: Eu\textsuperscript{3+} at the 320 nm excitation. At this excitation it is observed that the Eu ions are incorporated in divalent form in BaAl\textsubscript{2}O\textsubscript{19}, Eu\textsuperscript{2+} and SrAl\textsubscript{2}O\textsubscript{19}: Eu\textsuperscript{2+} phosphors. Arakawa [11] reported the emission of SrAl\textsubscript{2}O\textsubscript{19}: Eu for 325 nm excitation prepared by solid state reaction at 390, 480 and 530 nm for BaAl\textsubscript{2}O\textsubscript{19}: Eu phosphor. In present study, the combustion method is applied to prepare the phosphor. Due to rapid and high temperature, the nano crystalline size particles are formed. In our case the main peaks of emission spectra of the luminescent nanoparticles shift to shorter wavelength (from 590 to 460 nm and then to 420 nm) in BaAl\textsubscript{2}O\textsubscript{19}: Eu\textsuperscript{2+} and SrAl\textsubscript{2}O\textsubscript{19}: Eu\textsuperscript{2+} correspondingly, the luminescence changes from yellow-red to blue-green and then to blue-purple. This phenomenon is derived from the changing matrix crystal structure. The Sr\textsuperscript{2+/3+} Ba\textsuperscript{2+} and Eu\textsuperscript{2+} ions are very similar in their ionic size (i.e. 1.12 Å/1.35 Å\textsuperscript{−} and 1.20 Å, respectively). Consequently, when occupied by Eu\textsuperscript{2+} ions, the Sr\textsuperscript{2+/3+}/Ba\textsuperscript{2+} sites will have quite similar local distortions and the influence on the SrAl\textsubscript{2}O\textsubscript{19}/BaAl\textsubscript{2}O\textsubscript{19} crystal structure is small. But the radii of Ca\textsuperscript{2+} (i.e. 0.99 Å) is different from Eu\textsuperscript{3+}. So, the structure of CaAl\textsubscript{2}O\textsubscript{19} will be greatly distorted when the Ca\textsuperscript{2+} sites are occupied by Eu\textsuperscript{3+} ions. Anamorphic crystal lattices result when the surroundings of Eu\textsuperscript{3+} are changed and so the emission wavelengths change correspondingly. When Eu\textsuperscript{3+} substitutes for Ca\textsuperscript{2+} in CaAl\textsubscript{2}O\textsubscript{19}: Eu\textsuperscript{3+} experiences lesser repulsion owing to the expansion of the crystal lattice. In contrast, when Eu\textsuperscript{3+} substitutes for Sr\textsuperscript{2+/3+} Ba\textsuperscript{2+} in SrAl\textsubscript{2}O\textsubscript{19}/BaAl\textsubscript{2}O\textsubscript{19}, Eu\textsuperscript{2+} endures lesser attraction owing to shrinkage of the crystal lattice. This is why the wavelength

Fig. 3. SEM-EDS and X-ray mapping of (a) SrAl\textsubscript{2}O\textsubscript{19}, (b) CaAl\textsubscript{2}O\textsubscript{19} and (c) BaAl\textsubscript{2}O\textsubscript{19}.

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of CaAl$_2$O$_{19}$: Eu$^{3+}$, shifts to a longer wavelength compared with BaAl$_2$O$_{19}$: Eu$^{3+}$. $M_{1-x}$Eu$_x$Al$_2$O$_{19}$ ( $M$ = Sr, Ba) has a magnetoplumbite structure and is $\beta$-alumina type material. It is well known that there are four possible occupying positions for optically active ions in $\beta$-alumina. That is, these positions are Beever-Ross (BR) and mid-oxygen (MO) sites in the conduction plane, and four-fold Al(2), (3) and six-fold Al(1) and (4) within the spinel block. The position of these alkaline earth ions in the conduction plane of $\beta$-alumina is generally determined by short-range Coulomb interaction according to ionic radius. Accordingly, Ba$^{2+}$ ions are only located at the BR site by Coulomb interaction due to large ionic radius, whereas Sr ions can be located at both BR and MO sites due to intermediate ionic radius. Therefore the emission spectra with two peaks for Sr$_{1-x}$Eu$_x$Al$_2$O$_{19}$ can be easily understood. It is also seen form the SEM images and X-ray mapping that the Eu$^{3+}$ ions are not entering into the lattice but replace the Ba and Sr ions in, BaAl$_2$O$_{19}$: Eu$^{2+}$ and SrAl$_2$O$_{19}$: Eu$^{3+}$ lattice easily and side symmetry in CaAl$_2$O$_{19}$: Eu$^{3+}$ phosphor due to Eu$^{3+}$ ion.

Morphology and X-ray mapping

The typical morphology and X-ray mapping of powders is shown in Fig. 3, which displays an SEM micrograph of a powder synthesized by combustion method. Fig. 3a shows the SrAl$_2$O$_{19}$: Eu powder, which is formed by large porous aggregates, with typical sizes of 1–10 $\mu$m (Fig. 3a). In Fig. 3b, micrographs of CaAl$_{19}$O$_{12}$: Eu shows the pores produced by the fast expulsion of gases during the combustion process can be observed. SEM observations with higher magnification showed that these aggregates were constituted by nanoparticles. It is worth remarking that the shape of nanoparticles is typical of powders synthesized by the combustion process, and it has been found for other materials [12, 13]. This is an important result, since it confirms that the calcination temperature can be reduced in order to get a higher specific surface area and a smaller crystallite size. Moreover, in some faces the holes are observed which formed during the gas evolution such as N$_2$, H$_2$ and nascent oxygen. Fig. 3a show the SrAl$_2$O$_{19}$: Eu phosphor consists of a flower like structure, while more porous and dense nano rod like structure is observed at higher magnification for CaAl$_2$O$_{19}$: Eu (Fig. 3b). In contrast, the BaAl$_2$O$_{19}$: Eu (Fig. 3c) show phosphor which comprises of nano size spherical particles.

Conclusion

In present work $M_{1-x}$Al$_2$O$_{19}$: Eu, ($M$ = Ca, Ba, Sr) phosphor were synthesized by combustion method and their optical properties investigated. The main peaks of emission spectra of the luminescent nanoparticles shift to shorter wavelength (from 590 to 460 nm and then to 420 nm) in BaAl$_2$O$_{19}$: Eu$^{2+}$ and SrAl$_2$O$_{19}$: Eu$^{2+}$ phosphors correspondingly, the luminescence changes from yellow-red to blue-green and then to blue-purple and Eu$^{3+}$ emission in red region observed in CaAl$_2$O$_{19}$. Eu$^{3+}$ phosphor due to aggregation of nanoparticles. By combining MAI$_{12}$O$_{19}$: Eu ($M$ = Ca, Ba, Sr) phosphor with near UV chips, intense blue green (Ba), blue purple (Sr) and yellow-red (Ca) LEDs, white LED can be produced. The emission spectra for 320 nm excitation (Solid state excitation) are 3 times superior to 254 nm excitation (Mercury excitation). These results shows that the MAI$_{12}$O$_{19}$: Eu ($M$ = Ca, Ba, Sr) phosphor exhibit potential application in the field of white LEDs.

References

1. Shionoya, S.; Yen, W.M., in Phosphor Hand Book, CRC Press, Washington DC, 1999, 391–432. DOI: 10.1016/S0009-2614(00)01362-2.
2. Poort, S.H.; Blokpoel, W.P.; Blasse, G. Chem. Mater. 1995, 7, 1547 DOI: 10.1021/cm00056a022.
3. Blass, G.; Brill, A. Philips Res. Rep. 1968, 22, 201.
4. Murayama, Y.; Takeuchi, N.; Aoki, Y.; Matsuzawa, T. US Patent 5,424,006, 1995.
5. Nakamura, T.; Kaiya, K.; Takahashi, N.; Matsuzawa, T.; Rowlands, C.C.; Beltran, P.; Smith, G.M.; Riedi, P.C. J. Mater. Chem. 2000, 10, 2566. DOI: 10.1039/B004061O.
6. Qiu, J.; Gueta, A.L.; Hira, K. Chem. Phys. Lett. 2001, 333, 236. DOI: 10.1016/S0009-2614(00)01362-2.
7. Douth, A.; Capron, M. J. Eur. Ceram. Soc. 2003, 23, 2075. DOI: 10.1016/S0955-2219(03)00015-3.
8. Chen, I.C.; Chen, T.M. J. Mater. Res. 2001, 16, 1293. DOI: 10.1557/JMR.2001.0181.
9. Lee, I.Y.; Kang, Y.C.; Park, H.D.; Ryu, S.K. J. Alloys Compounds 2003, 353, 252. DOI: 10.1016/S0925-8388(02)01197-0.
10. Merkle, L.D.; Zandi, B.; Momcorge, R.; Guyot, Y.; Verdun, H.R.; McIntosh, B. J. Appl. Phys. 1996, 79, 1849. DOI: 10.1063/1.361085.
11. Arakawa, T.; Nagata, N. J. Alloys and Compounds 2006, 408, 864. DOI: 10.1016/j.jallcom.2005.01.074.
12. Frai, L.B.; Lamas, D.G.; Walso´e de Reca, N.E. Mater. Lett. 2001, 47, 262. DOI: 10.1016/S0167-577X(00)00246-9.
13. Blanchetti, M.F.; Jua´rez, R.E.; Lamas, D.G.; Walso´e de Reca, N.E.; Pe´rez, L.; Cabanillas, E. J. Mater. Res. 2002, 17, 2185. DOI: 10.1557/JMR.2002.0169.
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