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Ba^{2+}, Mg^{2+} Doped $Sr_3Al_2O_5Cl_2:Eu^{2+}$ Phosphor for Potential Application in Light-Emitting Diodes

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The Ba^{2+} and Mg^{2+} doped $Sr_3Al_2O_5Cl_2:Eu^{2+}$ synthesized *via* traditional solid reaction. Photoluminescence spectrum, powder x-ray diffraction and thermal quenching were used to detect these phosphors. The results showed that both of Ba^{2+} and Mg^{2+} doped sample showed an enhanced luminescent property. Additionally, due to the difference in the ion radius, the crystal field would alter with changed lattice parameters. The Ba^{2+} doped sample showed a blue shift from 620 to 610 nm while the Mg^{2+} doped showed a red-shift from 620 to 630 nm. The thermal quenching also investigated in detail. In general, these phosphors showed potential application in light emitting diodes to obtain warm white light.

Keywords: Light emitting diode, Red phosphor, Thermal stability.

INTRODUCTION

With the emerging global energy crisis, solid-state lighting has attracted much attention as a low-energy, robust, long-lifetime and compact alternative to traditional lighting sources[1,2]. Recently, phosphor-converted white light-emitting diodes are regarded as a new lighting source for the next generation and they have presented excellent performance in solid state lighting, such as solid-state multicolor three-dimensional displays, back lighting, flashlights, *etc.*[3]. In phosphor-converted-light-emitting diodes, phosphors are key materials to down-convert near-ultra-violet (nUV)/blue pump light from InGaN light-emitting diodes into visible light. It is the fact that most conventional phosphors for fluorescent lamps are not suitable for phosphor-converted white light-emitting diodes. Thus more demands and challenges are induced for white light phosphor-converted-light-emitting diodes. Moreover, for general indoor lighting application, "warmer" white light is more recommended, which creates a comfortable, cozy light atmosphere while "cooler" white light tends to get a bit harsh, unsuitable for indoor application. At present, the most widely used technique to obtain white light emission is the combination of a blue InGaN light-emitting diode chip and a yellow phosphor ($YAG:Ce^{3+}$)[4,5]. Although it has been well developed and commercially used for several years, the following problems arose people's attention: white emitting color changes with input power, poor color rendering index ($R_a \approx 70$-80) and high CCT (≈7750 K) for lacking red component, which is unsuitable to use in warm white light-emitting diodes. Thus, phosphor materials with a broad red emission spectrum must be developed with a high efficiency for use in near ultraviolet light-emitting diodes.

Halophosphate-based phosphors such as (Ca, Sr, Ba)$_5(PO_4)_3Cl$ doped Sb^{3+} and Mn^{2+} have been widely applied in fluorescent lamps[6]. Accordingly, Kang *et al.*[7] doped Eu^{2+} ions into $Sr_5(PO_4)_3Cl$ to produce blue emitting phosphor for plasma display panel and light-emitting diode applications because of their broad excitation band from vacuum ultraviolet to ultraviolet and high luminescence. Many researchers are working on halo-based phosphors that emit in the range of blue or green light[8,9]. The Eu^{2+}-doped $Sr_3Al_2O_5Cl_2$ produces a broadband emission peaked at 620 nm, which is a potential orange-yellow phosphor for white light emitting diodes[10]. This long wavelength emitting phosphor attracts our intense interest. However this phosphor has not been optimized. As well known, doping some ions would make the phosphor getting more stable or more lightness. Thus, in this paper, we report Ba and Mg doped $Sr_3Al_2O_5Cl_2:Eu^{2+}$ phosphor synthesized by two steps solid-state reaction and its optical properties were investigated. This improved phosphor exhibits a great potential to act as a blue phosphor for near ultraviolet chip excited white light-emitting diodes.

EXPERIMENTAL

The investigated phosphors in this work were synthesized through the solid-state reaction with $SrCO_3$ (A.R.), Al_2O_3 (A.R.), $SrCl_2{\cdot}6H_2O$ (A.R.), $BaCO_3$ (A.R.), MgO (A.R.) and Eu_2O_3 (99.99 %) as raw materials. Stoichiometric mixtures of

raw materials were homogeneously mixed and ground and subsequently the mixture were placed in alumina crucibles with covers and sintered at 1100 °C for 4 h under ambient atmosphere in an electric tube furnace and the sintered products were ground again in an agate mortar. Then the powder products were sintered at 900 °C for 2 h in a reducing atmosphere (N_2:H_2 = 95:5) to reduce the Eu from its trivalent state to its divalent state. After firing, the samples were cooled to room temperature in the furnace and ground again into powder for subsequent use.

Detection method: The phase identification of samples was carried out by a Rigaku D/Max-2400 X-ray diffractometer with Ni-filter Cu Kα radiation. The excitation and emissison spectra were measured by a FLS-920T fluorescence spectrophotometer with Xe 900 (450 W xenon arc lamp) as the light source. All measurements were carried out at room temperature except the thermal quenching.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the pure $Sr_3Al_2O_5Cl_2$, $Sr_{2.81}Ba_{0.09}Al_2O_5Cl_2$:0.1$Eu^{2+}$ and $Sr_{2.85}Mg_{0.05}Al_2O_5Cl_2$:0.1 Eu^{2+}. All the observed peaks can be indexed to the pure phase of $Sr_3Al_2O_5Cl_2$ and match well with JCPDS card 80-0564, indicating the high purity and crystalline of the samples in this work. The doping of Eu^{2+}, Ba^{2+} and Mg^{2+} does not make any noticeable variation of the XRD patterns. As well known, $Sr_3Al_2O_5Cl_2$ crystallizes as an orthorhombic structure presented in the inset of Fig. 1 with a space group of $P2_12_12_1$ and lattice constants of a = b = c = 9.4039 Å. Consequently, the lattice constants changed to 9.4231 Å and 9.3721 Å, while doped with suitable Ba^{2+} and Mg^{2+}, respectively. This should due to the different ion radius between Ba^{2+}, Mg^{2+} and Sr^{2+} (1.34 Å, 0.66 Å and 1.12 Å for each).

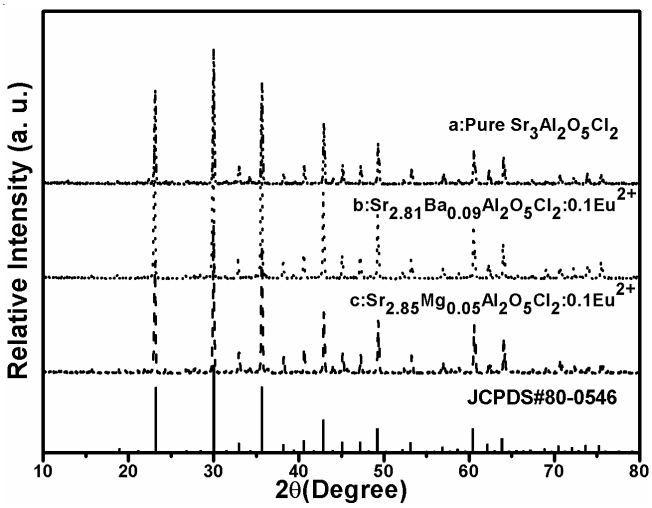

Fig. 1. XRD patterns of pure $Sr_3Al_2O_5Cl_2$, $Sr_{2.81}Ba_{0.09}Al_2O_5Cl_2$:0.1$Eu^{2+}$, $Sr_{2.85}Mg_{0.05}Al_2O_5Cl_2$:0.1$Eu^{2+}$ and JCPDS Card No. 80-0546

Fig. 2 presents the emission spectra of $Sr_{2.9-x}Ba_xAl_2O_5Cl_2$: 0.1 Eu^{2+} (x = 0, 0.01, 0.05, 0.09 and 0.13) with various Ba^{2+} contents. As clearly can be seen, the un-doped sample emits orange-yellow luminescence with a peak wavelength of 620 nm, which corresponds to the 4*f*-5*d* transition of Eu^{2+} ions[11]. The emission intensity was highest at a Ba^{2+} content of x = 0.09 and was then about 171 % higher than the un-doped sample. However, the intensity decreased gradually as the Ba^{2+} content increased. In addition, the emission peak showed a remarkable blue-shift from 620 to 610 nm. As well known, the blue-shift usually should ascribe to the weaker crystal field around Eu^{2+} ions. Accordingly, the larger Ba^{2+} ions replace the smaller Sr^{2+} ions would resulted in an increased lattice parameter and make the crystal field became weaker. Then, the blue-shift can well illustrate.

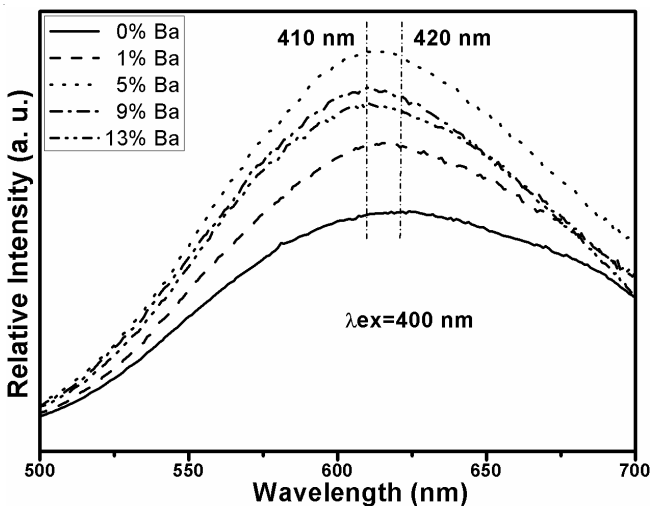

Fig. 2. Emission spectra of serious Ba^{2+} concentration of $Sr_{2.9-x}Ba_xAl_2O_5Cl_2$: 0.1$Eu^{2+}$

Further more, the emission spectra of $Sr_{2.9-x}Mg_xAl_2O_5Cl_2$: 0.1$Eu^{2+}$ (x = 0, 0.01, 0.05, 0.09 and 0.13) with various Mg^{2+} contents were shown in Fig. 3. The emission intensity was highest at an Mg^{2+} content of x = 0.05 and was then about 162 % higher than the un-doped sample. However, the intensity decreased gradually as the Mg^{2+} content increased too. Compared to the blue-shift of the Ba^{2+} doped samples, the Mg^{2+} doped samples show red-shift from 620 to 630 nm. Distinctly, this red-shift should ascribe to the stronger crystal field, which is due to the smaller Mg^{2+} ions occupied Sr^{2+} sites and make the lattice parameter smaller.

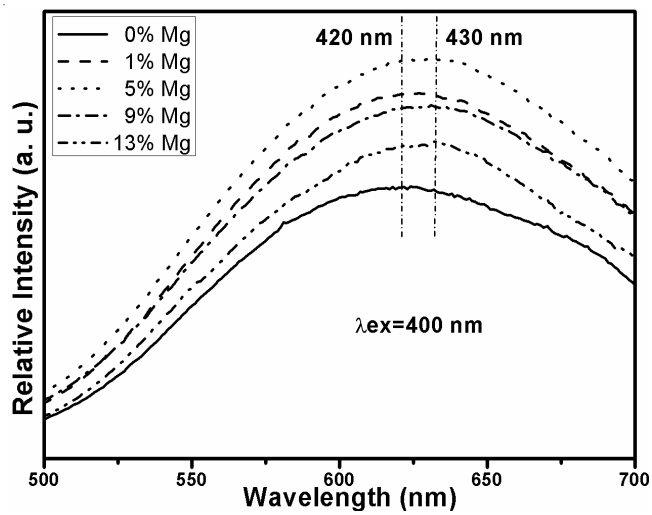

Fig. 3. Emission spectra of serious Mg^{2+} concentration of $Sr_{2.9-x}Mg_xAl_2O_5Cl_2$: 0.1 Eu^{2+}

Additionally, Ba doped samples showed a higher quenching concentration compared to Mg doped samples. As well known, the nonradiative energy transfer between Eu^{2+} ions would reduce the emission intensity. The transfer is caused by electric multipole-multipole interactions, which depend on distance according to Dexter's theory[12]. Since the fluorescence mechanism of Eu^{2+} in the $Sr_3Al_2O_5Cl_2$ host is an allowed 4*f*-5*d* electric-dipole transition, multipole-multipole interactions are the probable cause of nonradiative energy transfer and the possibility of energy transfer by an exchange interaction can be excluded. With the doping of Ba^{2+} and Mg^{2+} ions, the lattice parameter would changed and the distance between the Eu^{2+} ions would also change. The critical distance between Eu^{2+} ions for energy transfer was calculated using the relation that was proposed by Blasse and Grabmaier[13],

$$R_C \approx 2\left[\frac{3V}{4\pi x_c N}\right]^{1/3} \quad (1)$$

where V is the volume of the unit cell, x_c is the critical concentration of the activator ion and Z is the number of formula units per unit cell. For $Sr_3Al_2O_5Cl_2$ host, N = 12(Z*3), x_c = 0.15 and the volume of the unit cell V are 836.72 $Å^3$ and 823.21 $Å^3$, respectively. Thus, the obtained Rc values are 9.62 Å and 9.51 Å. Obviously, the Mg^{2+} doped sample showed a smaller Rc values, which means with the Mg^{2+} doping, the would make the critical distance between Eu^{2+} ions smaller, consequently, a lower quenching concentration would obtain.

As for practical light-emitting diodes application, the proposing phosphors should meet the requirements below: When measured at 150 °C, the change of efficiency should be lower than 10 % and CIE changes (both CIE x and CIE y) should be lower than 0.015 and the quantum efficiency of phosphors should higher than 70 %. Thus, we measured the temperature quenching characteristics and the quantum efficiency. For $Sr_{2.9}Al_2O_5Cl_2:0.1Eu^{2+}$, $Sr_{2.81}Ba_{0.09}Al_2O_5Cl_2:0.1Eu^{2+}$ and $Sr_{2.85}Mg_{0.05}Al_2O_5Cl_2:0.1Eu^{2+}$, when measured at 150 °C, the emission intensities are 69.2, 63.6 and 78.7 %, the CIE x are 0.014, 0.021 and 0.010, the CIE y are 0.007, 0.007 and 0.009 (Fig. 4), which are lower than 0.015 except the $Sr_{2.81}Ba_{0.09}Al_2O_5Cl_2:0.1Eu^{2+}$. And the quantum efficiencies are 89.9, 84.9 and 91.2 %, respectively. All this characteristics show that the Mg doped sample showed a more potential application in light-emitting diodes to obtain warm white light.

Conclusion

In this study, Ba^{2+} and Mg^{2+} doped $Sr_3Al_2O_5Cl_2:Eu^{2+}$ synthesized. The structure, photoluminescence and thermal properties were investigated. The results showed that both of Ba^{2+} and Mg^{2+} doped sample showed an enhanced luminescent property. The optimized concentration of Ba^{2+} and Mg^{2+} were 9 and 5 %, respectively. Additionally, due to the difference in the ion radius, the crystal field would alter with changed lattice parameters. The Ba^{2+} doped sample showed a blue shift from 620 to 610 nm while the Mg^{2+} doped showed a red-shift from 620 to 630 nm. Thermal quenching also investigated. The Mg^{2+} doped sample showed a slightly better thermal stability than Ba^{2+} doped sample. In conclusion, these phosphors showed potential application in light-emitting diodes to obtain warm white light.

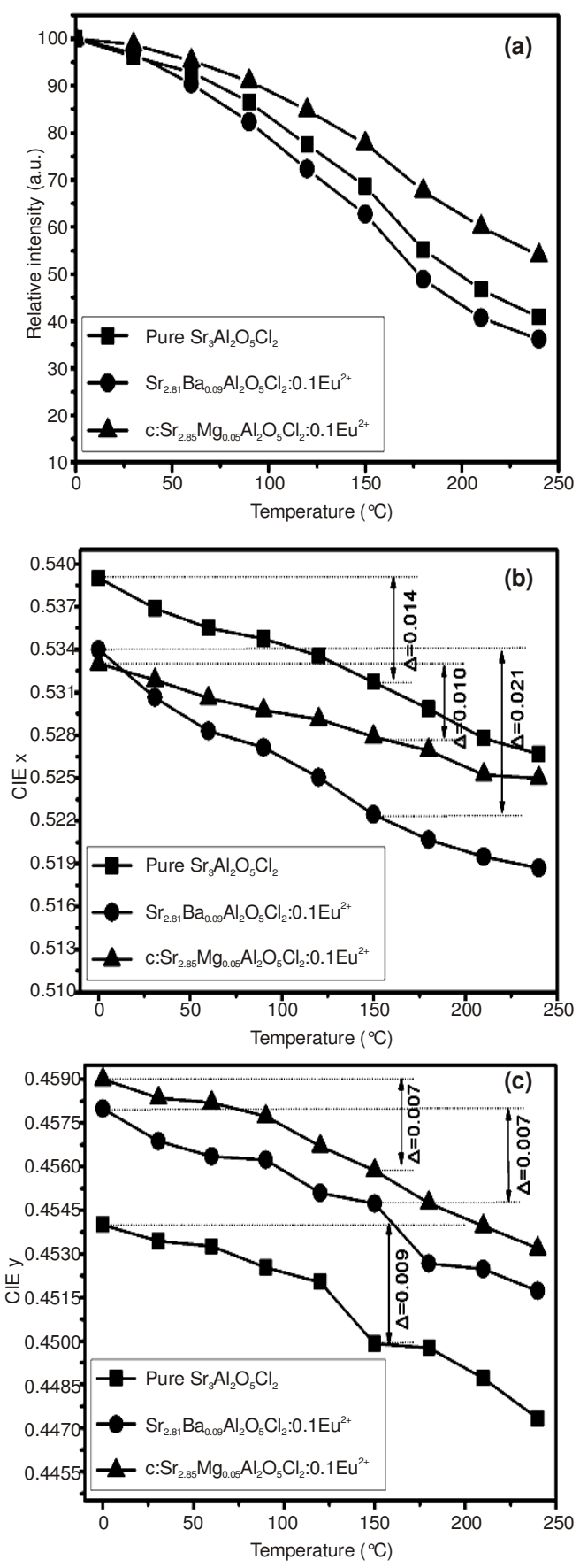

Fig. 4. Temperature-dependent emission intensities of $Sr_{2.9}Al_2O_5Cl_20.1Eu^{2+}$, $Sr_{2.81}Ba_{0.09}Al_2O_5Cl_2:0.1Eu^{2+}$ and $Sr_{2.85}Mg_{0.05}Al_2O_5Cl_2:0.1Eu^{2+}$ (a) CIE x (b) and CIE y (c)

REFERENCES

1. J.M. Phillips, M.E. Coltrin, M.H. Crawford, A.J. Fischer, M.R. Krames, R. Mueller-Mach, G.O. Mueller, Y. Ohno, L.E.S. Rohwer, J.A. Simmons and J.Y. Tsao, *Laser Photonics Rev*., **1**, 307 (2007).
2. E.F. Schubert and J.K. Kim, *Science*, **308**, 1274 (2005).
3. J.S. Kim, P.E. Jeon, J.C. Choi, H.L. Park, S.I. Mho and G.C. Kim, *Appl. Phys. Lett*., **84**, 2931 (2004).
4. W.B. Im, Y.-I. Kim, N.N. Fellows, H. Masui, G.A. Hirata, S.P. DenBaars and R. Seshadri, *Appl. Phys. Lett*., **93**, 091905 (2008).
5. S. Nakamura and G. Fasol, The Blue Laser Diode, Springer, Berlin (1996).
6. H.G. Jenkins, A.H. McKeag and P.W. Ranby, *J. Electrochem. Soc*., **96**, 1 (1949).
7. Y.C. Kang, J.R. Sohn, H.S. Yoon, K.Y. Jung and H.D. Park, *J. Electrochem. Soc*., **150**, 38 (2003).
8. X. Zhang and X.G. Liu, *J. Electrochem. Soc*., **139**, 622 (1992).
9. Z.G. Xia, Q. Li and J.Y. Sun, *Mater. Lett*., **61**, 1885 (2007).
10. Y.S. Tang, S.F. Hu, W.H. Ke, C.C. Lin, N. Bagkar and R.S. Liu, *Appl. Phys. Lett*., **93**, 131114 (2008).
11. Y.S. Tang, S.F. Hu, C.C. Lin, N.C. Bagkar and R.S. Liu, *Appl. Phys. Lett*., **90**, 151108 (2007).
12. D.L. Dexter, *J. Chem. Phys*., **21**, 836 (1953).
13. G. Blasse and B.C. Grabmaier, Luminescent Materials, Springer, Berlin Heidelberg (1994).