Optica Applicata, Vol. XL, No. 4, 2010

Chemical solution-derived $SrMg_2(PO_4)_2:Eu^{2+}$ blue phosphor for ultraviolet emitting diodes

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Eu^{2+}-doped $SrMg_2(PO_4)_2$ phosphor with blue emission was prepared by the low temperature chemical solution process using inorganic salts as a starting material. Transparent sol was preheated at 300 °C for 120 min and then precursor was finally annealed at 900 °C for 240 min in a reducing CO atmosphere. Crystallinity, surface morphology and luminescent properties have been investigated. The phosphor emits bright blue luminescence with a peak wavelength at 423 nm under near-ultraviolet excitation at 363 nm.

Keywords: $SrMg_2(PO_4)_2$, phosphor, blue, sol–gel.

1. Introduction

White light-emitting diodes (LEDs) offer benefits such as a high luminous efficiency, energy saving, maintenance and environmental protection and, therefore, they are tipped to be the next generation of solid-state lighting (SSL), replacing conventional incandescent and fluorescent lamps. However, white LED by the blue GaN-pumped yellow $Y_3Al_5O_{12}$ (YAG):Ce^{3+} phosphor has the following drawbacks; white emitting color changes with input power, low color rendering index due to two color mixing and low reproducibility due to the strong dependence of white color quality on the amount of phosphor [1, 2]. To overcome these problems, near-UV (350–410 nm) LED plus red-green-blue (RGB) white LEDs have been suggested. This type of white LED has a high tolerance to UV chip color variation and excellent color rendering index. However, the luminescent efficiency is low in this system due to the strong reabsorption of the blue light by the red or green phosphors [3]. The commercially

available phosphors for near-UV InGaN-based LEDs are mainly red $Y_2O_2S:Eu^{3+}$, green $ZnS:Cu^{+}$, Al^{3+} and blue $BaMgAl_{10}O_7:Eu^{2+}$, and these phosphors are unstable under UV irradiation [4].

Optical transitions of divalent europium ($4f-5d$) have been investigated in many phosphors. Spectra of Eu^{2+}-doped compounds are due to electric dipole transitions with parity allowed so that they occur with high transition probabilities. The emission colors vary from ultraviolet to red depending on the host lattice. Covalence, the size of the cation, and the crystal-field strength influence the emission color of Eu^{2+} [5, 6].

The compound $SrMg_2(PO_4)_2$ was confirmed to exist as a single phase in the $Sr_3(PO_4)_2-Mg_3(PO_4)_2$ system in 1961 by SARVER *et al*. [7], but only unindexed X-ray powder data were reported. Recently, the luminescent properties by near-UV excitation of solid-state reaction derived-$SrMg_2(PO_4)_2:Eu^{2+}$ have been reported [8, 9]. As an important family of luminescent materials, phosphate compounds have absorbed more and more attention because of their excellent thermal and chemical stability [10]. As far as we know, however, there is little information on the solution--based fabrication of $SrMg_2(PO_4)_2:Eu^{2+}$ phosphor.

In this work, the blue-emitting $SrMg_2(PO_4)_2:Eu^{2+}$ phosphor was prepared by sol–gel process. The excitation spectra, emission spectra and crystalline properties were investigated. The morphology of the phosphor was also characterized.

2. Experiment

The blue phosphor of $Sr_{1-x}Mg_2(PO_4)_2:Eu_x^{2+}$ ($x = 0.03$) was prepared using strontium nitrate [$Sr(NO_3)_2$], magnesium nitrate hexahydrate [$Mg(NO_3)_3{\cdot}6H_2O$], ammonium dihydrogen phosphate [$(NH_4)H_2PO_4$], and europium nitrate pentahydrate [$Eu(NO_3)_3{\cdot}5H_2O$]. The starting materials with stoichiometric molar ratio were dissolved with distilled water. Then, diluted HNO_3 solution was added dropwise with vigorous stirring at 70 °C for 12 hrs. The homogeneous solution was preheated at 300 °C for 120 min, and then precursor was finally annealed at 900 °C for 240 min in a reducing CO atmosphere.

X-ray diffraction (XRD) of the sample was examined on a D-Max-1200 (Rigaku, Japan) with CuKα radiation ($\lambda = 1.54056$ Å). The morphology of the sample was measured on field emission–scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). Photoluminescence and thermal luminescence stability from room temperature to 177 °C were measured using a spectrofluorometer (FP-6500, Jasco).

3. Results and discussion

Measurement of XRD of powder sample was performed to verify the phase purity and to check the crystal structure. The crystal structure of $SrMg_2(PO_4)_2$ was reported by Lucas (JCPDS-File 52-1590). It has the monoclinic crystal system with the cell parameters $a = 8.733$ Å, $b = 5.022$ Å, $c = 23.724$ Å; $\alpha = 90°$, $\beta = 90.35°$, $\gamma = 90°$. Figure 1 shows the XRD pattern of $SrMg_2(PO_4)_2:Eu^{2+}$ phosphor. The peaks of

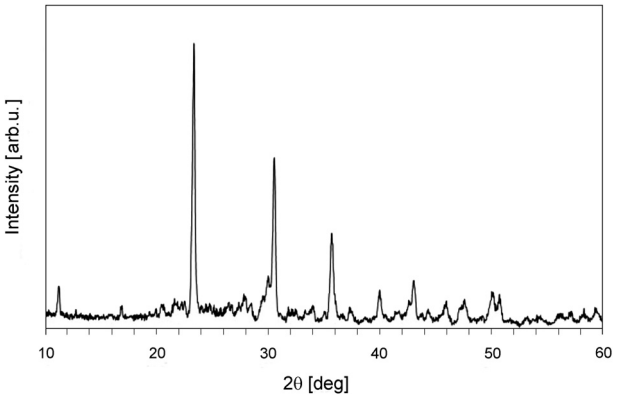

Fig. 1. XRD pattern of $SrMg_2(PO_4)_2:Eu^{2+}$ powder after annealing at 900 °C.

(003), (113), (116), (310), (119), and (223) reflections at 11.12°, 23.3°, 30.47°, 35.63°, 39.92°, and 42.95° show that $SrMg_2(PO_4)_2$ crystallites are grown. The XRD pattern shows that the sample is single-phased and consistent with PCPDS-File 52-1590, and the doped Eu ion has little influence on the host structure. Considering the effect of ionic sizes of cations, we propose that Eu^{2+} is expected to preferably occupy the Sr^{2+} and Mg^{2+} sites, since the ionic radius of Eu^{2+} (1.09 Å) is close to that of Sr^{2+} (1.12 Å) and Mg^{2+} (0.66 Å). However, the P^{5+} sites with ionic radius of 0.35 Å are too small for Eu^{2+} to occupy [11]. The result of Fig. 1 indicates that well-crystalline phosphor could be obtained at 900 °C in this work. Compared with solid-state method, the temperature of the preparation is reduced to at least 200–300 °C [9, 10].

During the application of phosphors, the size distribution and shape of the particles are very important. Figure 2**a** shows the FE-SEM image of $SrMg_2(PO_4)_2:Eu^{2+}$ particles which were thermally treated at 900 °C for 240 min under a reduction atmosphere. The particles were agglomerated and have an elliptical shape. The phosphor particles grew to achieve diameters of 0.5–1 μm, which is suitable for fabrication of the SSL devices. Also, the $SrMg_2(PO_4)_2:Eu^{2+}$ phosphor particles exhibited regular

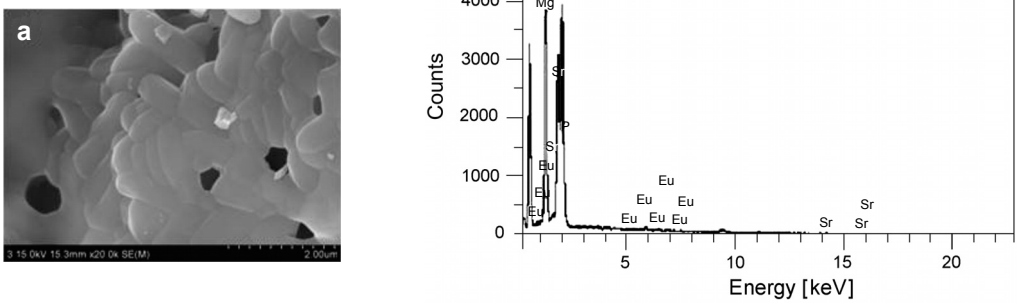

Fig. 2. FE-SEM image (**a**) and EDX analysis (**b**) of $SrMg_2(PO_4)_2:Eu^{2+}$ powder after annealing at 900 °C.

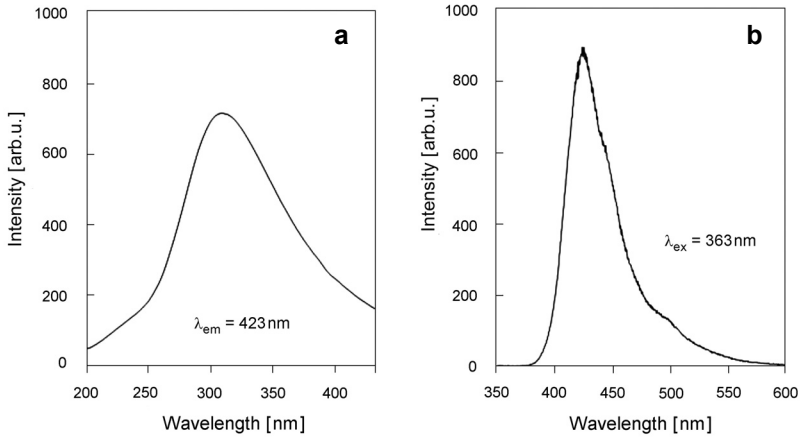

Fig. 3. Excitation (**a**) and emission (**b**) spectra of $SrMg_2(PO_4)_2:Eu^{2+}$ powder.

morphology characteristics without any visible admixture of any impurity phases. The composition of the particles is identified by energy-dispersive X-ray (EDX) spectroscopy. The EDX pattern is displayed in Fig. 2**b**. It indicated that the product obtained is composed of Sr, Mg, P and a small quantity of Eu. The Sr : Mg : P ratio is 1 : 2 : 2 that is in accord with the chemical formula of $SrMg_2(PO_4)_2$.

The excitation and emission spectra of $SrMg_2(PO_4)_2:Eu^{2+}$ particles excited with a 363 nm near-UV light at room temperature are illustrated in Figs. 3**a** and 3**b**, respectively. The excitation spectra show a broad absorption band within the 200–400 nm UV range and this is due to transition from the $4f^7$ ground state of Eu^{2+} to the $4f^6 5d^1$ excited state.

Figure 3**b** shows the emission spectra of $SrMg_2(PO_4)_2:Eu^{2+}$ phosphor under 363 nm near-UV excitation. Under 363 nm radiation, the $SrMg_2(PO_4)_2:Eu^{2+}$ phosphor shows intense and broad blue emission at 423 nm. No emission peaks of the Eu^{3+} ($^5D_0 - {}^7F_1$ at about 590 nm and $^5D_0 - {}^7F_2$ at about 615 nm) were observed in the spectra, indicating that Eu^{3+} ions in the matrix had been reduced to Eu^{2+} completely under the reducing atmosphere. In a previous work [10], the emission peak wavelengths of the $SrMg_2(PO_4)_2:Eu^{2+}$ phosphors vary with Eu^{2+} concentration, and there was red shift in the emission wavelength from 413 nm to 424 nm with the increase of Eu^{2+} concentration from $x = 0.005$ to $x = 0.10$. From Fig. 3**b**, it can be seen that the maximum emission peak of the $SrMg_2(PO_4)_2:Eu^{2+}$ phosphor, about 423 nm in this work, slightly shifts to red. This red shift may be due to some changes in the crystal field around Eu^{2+}, because the crystal field strength of Eu^{2+} ion in the Sr^{2+} ion site in $SrMg_2(PO_4)_2:Eu^{2+}$ is proportional to the inverse of the cation to anion distance or the cell parameters of the hosts. With an increase in Eu^{2+} ion in the $SrMg_2(PO_4)_2$ host, the cell parameters of the phosphor decreased leading to the crystal field strength increasing because of the difference of ionic radii between Eu^{2+} (1.09 Å) and Sr^{2+} (1.12 Å), resulting in the emission shifts to longer wavelength [12].

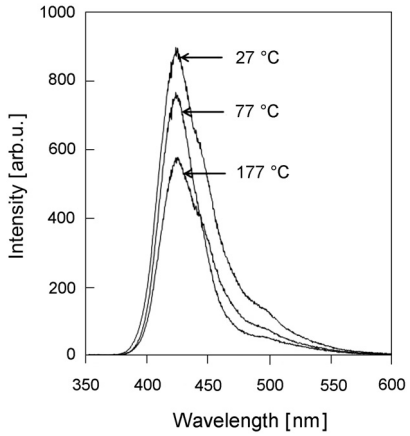

Fig. 4. Variation of emission spectra of $SrMg_2(PO_4)_2$:Eu^{2+} powder for different temperatures.

Generally, making use of the temperature-dependence of the phosphor in high power LED is very important since it has great influence on the light output and color rendering index. Figure 4 indicates the temperature-dependence of luminescence intensity for $SrMg_2(PO_4)_2$:Eu^{2+} phosphor under excitation at 363 nm. It shows the changing relative emission intensity of the samples from room temperature (27 °C) to 177 °C. With increasing temperature up to 77 °C and 177 °C, the emission intensities of $SrMg_2(PO_4)_2$:Eu^{2+} are decreased to 86% and 65% of the initial value, and 63% for the previous $SrMg_2(PO_4)_2$:Eu^{2+} phosphor prepared by solid-state reaction [9]. This implies that $SrMg_2(PO_4)_2$:Eu^{2+} phosphor prepared by sol–gel method exhibits comparable thermal stability and can be used as a blue phosphor for a white LED under near-UV light excitation.

Sol–gel derived Eu^{2+}-activated $SrMg_2(PO_4)_2$ phosphor showing a homogeneous surface and particle shape, which are favorable as regards the luminescent properties because of the lesser contamination or fewer dead layers on the phosphor surface, is exceptionally attractive as a near-UV convertible phosphor. Moreover, compared with the solid-state reaction, the temperature of preparation is reduced to at least about 200–300 °C.

4. Conclusions

Using a sol–gel method, Eu^{2+}-activated single-phase $SrMg_2(PO_4)_2$ blue phosphor was prepared. Well-crystalline particles with a regular elliptical shape could be obtained at 900 °C. The excitation spectra show a broad absorption band within the 200–400 nm UV range and this is due to transition from the $4f^7$ ground state of Eu^{2+} to the $4f^6 5d^1$ excited state. Under 363 nm radiation, the $SrMg_2(PO_4)_2$:Eu^{2+} phosphor shows intense and broad blue emission at 423 nm. $SrMg_2(PO_4)_2$:Eu^{2+} prepared by sol–gel exhibits comparable thermal stability and can be used as a blue phosphor for a white LED.

References

[1] XIA G., ZHOU S., ZHANG J., XU J., *Structural and optical properties of YAG:Ce^{3+} phosphors by sol–gel combustion method*, Journal of Crystal Growth **279**(3–4), 2005, pp. 357–362.

[2] JIA D., WANG Y., GUO X., LI K., ZOU Y.K., JIA W., *Synthesis and characterization of YAG:Ce^{3+} LED nanophosphors*, Journal of The Electrochemical Society **154**(1), 2007, pp. J1–J4.

[3] KANG C.K., CHEN T.M., *White light generation under violet–blue excitation from tunable green--to-red emitting $Ca_2MgSi_2O_7$:Eu, Mn through energy transfer*, Applied Physics Letters **90**(16), 2007, p. 161901.

[4] NEERAJ S., KIJIMA N., CHEETHAM A.K., *Novel red phosphors for solid-state lighting: The system $NaM(WO_4)_{2-x}(MoO_4)_x$:Eu^{3+} (M = Gd, Y, Bi)*, Chemical Physics Letters **387**(1–3), 2004, pp. 2–6.

[5] KIM J.S., KWON A.K., PARK Y.H., CHOI J.C., PARK H.L., KIM G.C., *Luminescent and thermal properties of full-color emitting $X_3MgSi_2O_8$:Eu^{2+}, Mn^{2+} (X = Ba, Sr, Ca) phosphors for white LED*, Journal of Luminescence **122–123**, 2007, pp. 583–586.

[6] LIN Y., TANG Z., ZHANG Z., NAN C.W., *Luminescence of Eu^{2+} and Dy^{3+} activated $R_3MgSi_2O_8$-based (R = Ca, Sr, Ba) phosphors*, Journal of Alloys and Compounds **348**(1–2), 2003, pp. 76–79.

[7] SARVER J.F., HOFFMAN M.V., HUMMEL F.A., *Phase equilibria and tin-activated luminescence in strontium orthophosphate systems*, Journal of The Electrochemical Society **108**(12), 1961, pp. 1103–1110.

[8] WU Z., LIU J., GONG M., *Thermally stable luminescence of $SrMg_2(PO_4)_2$:Eu^{2+} phosphor for white light NUV light-emitting diodes*, Chemical Physics Letters **466**(1–3), 2008, pp. 88–90.

[9] GUO C., LUAN L., DING X., HUANG D., *Luminescent properties of $SrMg_2(PO_4)_2$:Eu^{2+}, and Mn^{2+} as a potential phosphor for ultraviolet light-emitting diodes*, Applied Physics A **91**(2), 2008, pp. 327–331.

[10] TANG Y.S., HU S.F., LIN C.C., BAGKAR N.C., LIU R.S., *Thermally stable luminescence of $KSrPO_4$:Eu^{2+} phosphor for white light UV light-emitting diodes*, Applied Physics Letters **90**(15), 2007, p. 151108.

[11] LEE S.H., PARK J.H., SON S.M., KIM J.S., PARK H.L., *White-light-emitting phosphor: $CaMgSi_2O_6$: Eu^{2+}, Mn^{2+} and its related properties with blending*, Applied Physics Letters **89**(22), 2006, p. 221916.

[12] CHARTIER C., BARTHOU C., BENALLOUL P., FRIGERIO J.M., *Photoluminescence of Eu^{2+} in $SrGa_2S_4$*, Journal of Luminescence **111**(3), 2005, pp. 147–158.

Received December 2, 2009