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Luminescence properties of Eu^{2+} doped Sr_2SiO_4-$Mg_2(Si_2O_6)$ mixed phases for white-light emitting diodes

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Alkaline-earth silicate phosphors doped with divalent europium ion (Eu^{2+}) were synthesized by traditional solid-state reaction. The structure of the phosphors was confirmed by XRD profiles. These phosphors exhibited an intense blue emission band in the visible region originated from the 4f-5d transitions of Eu^{2+} ion. The effect of SiO_2 concentration in this phosphor with emission intensity and band positions has been discussed. With a combination of different emission bands, the phosphors emit white color indicating as promising candidates for white light emitting diodes.

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1. Introduction

The white light emitting diode has been received tremendous progress in recent years for its wide applications in solid-state lighting because it has great potential to significantly surpass the energy efficiencies of traditional incandescent and fluorescent lighting. There are basically two approaches for generating white light using LEDs. First approach is to produce white light utilizes combination of blue LED with yellow luminescence. Another approach is by using blue-green-red combinations of phosphors and excitation sources. In these approaches the combination of near-UV (NUV) LED and blue, green and red emitting (BGR) phosphors may be the most convenient way to obtain high quality for white light based light emitting diodes. The alkaline earth silicate phosphors are useful luminescent hosts with stable crystal structures, high physical and chemical stability [1,2]. Recently, rare earth activated Si-based phosphors have emerged as an important family of luminescent materials due to their multi-color phosphorescence and resistance to acid and oxygen [3]. Alkaline earth silicate phosphors with rare earth and/or transition metals suitable for near-UV excitation, which possess high color stability than blue chip excitation in commercial white light emitting diode (YAG:Ce^{3+}) [4,5]. Europium is a special element in lanthanides, which exhibits the property of valence fluctuation either divalent or trivalent with different luminescence characteristics due to different vacancies. Optical transitions of divalent europium have been investigated in many compositions [6-9]. These phosphors show broad emission through 4f-5d transition of Eu^{2+} activator and the peak position of this emission spectra depend on the nature of the Eu^{2+} surroundings in host lattices. Few studies have been carried out on the luminescence properties of europium doped $Sr_3MgSi_2O_8/Sr_2SiO_4$ [4,10,11]. However, so far the luminescence properties of Eu^{2+} in Sr_2SiO_4-$Mg_2(Si_2O_6)$ mixed phases phosphors have not been reported.

In this paper, we synthesized Sr_2SiO_4-$Mg_2(Si_2O_6)$:Eu^{2+} (SMS) powders by solid state reaction in the reduced atmosphere. The luminescence properties of SMS phosphors were characterized and discussed. The effect of SiO_2 concentration on the luminescence properties of present phosphors was analyzed and their utility for white light emitting diodes was discussed in detail by calculating the color coordinates.

2. Experimental

The phosphors of Sr_2SiO_4-$Mg_2(Si_2O_6)$ with 0.1 mol% doped Eu_2O_3 were synthesized by the solid state reaction method. The starting materials $SrCO_3$, MgO, SiO_2, Eu_2O_3 were taken to prepare the following phosphors according to the molar ratio:

SMS08 : 2 $SrCO_3$. 1 MgO . 0.8 SiO_2
SMS10 : 2 $SrCO_3$. 1 MgO . 1.0 SiO_2
SMS12 : 2 $SrCO_3$. 1 MgO . 1.2 SiO_2

The weighed raw materials were mixed homogeneously in an agate mortar for 1 h. The mixtures were sintered in a reduced atmosphere (95% N_2 + 5% H_2) by using tube furnace at 1150 °C for 4 h.

The crystalline phases of the prepared phosphors were investigated by X-ray powder diffraction using Cu Kα radiation (X′ pert MPD, Philips) by collecting the XRD patterns in the range $20^o \leq 2\theta \leq 70^o$. UV-excited luminescence spectra and excitation spectra were recorded on a Perkin-Elmer LS-50B luminescence spectrometer with Monk–Gillieson type monochromators by using xenon discharge lamp used as an excitation source. The luminescence from the samples was collected with photomultiplier tube (PMT, Hamatsu, R928) mounted on a spectrometer (Dongwoo, DM 701). All measurements were performed at room temperature. The morphology of the powder phosphors was observed by a JEOL-5600 scanning electron microscope (SEM).

3. Results and discussion

The XRD patterns of europium doped SMS phosphors sintered at 1150 ^{0}C for 4 h in the reductive atmosphere are depicted in Fig. 1. The XRD peaks were closely matched with the standard monoclinic β-Sr_2SiO_4 and orthorhombic $Mg_2(Si_2O_6)$ crystal structures (JCPDS: 76-1630 and 86-0431) in the present work for all phosphors indicating that SMS phosphors formed with two mixed crystal phases Sr_2SiO_4 and $Mg_2(Si_2O_6)$.

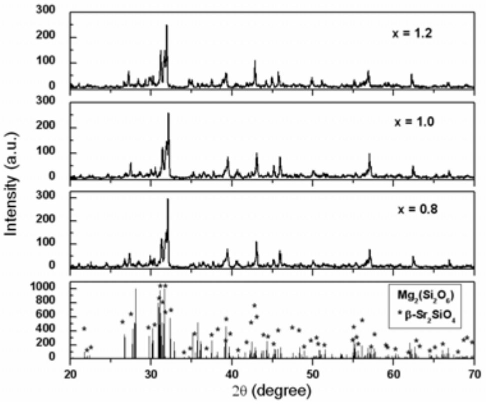

Fig. 1. XRD profiles of europium doped SMS phosphors.

The scanning electron microscope (SEM) photograph of the europium doped SMS10 phosphor is shown in Fig. 2. The phosphor consists of irregular spherical shape and inhomogeneous particle distribution in the range of 170 nm to micro meter size. Crystallization granules and agglomeration of particles were observed in SMS phosphors.

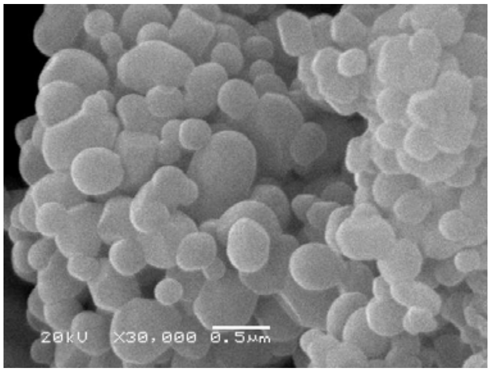

Fig. 2. SEM photograph of europium doped SMS10 phosphor.

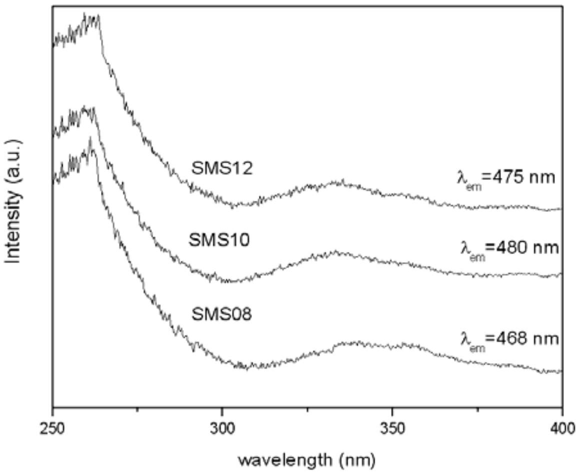

Fig. 3. The excitation spectra of europium doped SMS phosphors.

The excitation spectra of the SMS phosphors by monitoring the emissions at 468 nm, 480 nm and 475 nm for SMS08, SMS10 and SMS12, respectively, are shown in Fig. 3. The narrow peak is located around 261 nm and a broad band in the range 310 to 375 nm with a peak maximum at 335 nm. The excitation peak at 261 nm corresponding to the charge transfer band of Eu^{3+}-O^{2-}, may be due to electron transfer from 2p orbital of O^{2-} ions to 4f shells of Eu^{3+} ions [12].

Emission spectra of three SMS phosphors exciting at 254 and 330 nm are shown in Fig. 4 with solid line and dotted line, respectively.

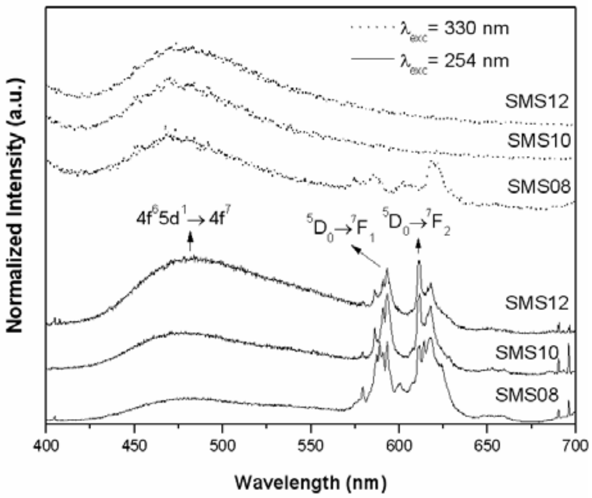

Fig. 4. The emission spectra of europium doped SMS phosphors.

The emission spectra consist of one strong broad emission in the blue and two emission bands in the region 550-700 nm based on the excitation source and SiO_2 concentration. The main broad emission peak in the range

410-550 nm ascribed to the $4f^65d^1 \rightarrow 4f^7$ transition, reveals that Eu^{2+} ion existed and the reduction of $Eu^{3+} \rightarrow Eu^{2+}$ occurred in the SMS phosphors. These results indicate that (i) there are no oxidizing ions, (ii) the Eu^{2+}ion non-equivalently replaces the Sr^{2+} ion and (iii) the substituted Sr^{2+} ion has similar radius to that of Eu^{2+} ions [13]. A red shift has been observed in energy positions of the 4f-5d transition with increasing SiO_2 concentration (Figure 4). Moreover, the emission lines in the range from 550-700 nm clearly belongs to the f-f transitions of Eu^{3+} ion, which are prominent under excitation of 254 nm and designated to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions at 593 and 611 nm, respectively. Luminescence due to Eu^{3+} is not clearly visible in the SMS10 and SMS12 samples under the excitation of 330 nm. The intensity ratio of the bluish green, yellow and red bands varies with the change of SiO_2 concentration as well as excitation wavelengths.

The calculated colour coordinates (x = 0.309, y = 0.316) of SMS08 phosphor under the excitation of 330 nm are close to the standard of NTSC (x = 0.3101, y = 0.3162) white light and the coordinates (x = 0.330, y = 0.336) of SMS10 phosphor at excitation of 254 nm, which are close to the standard of CIE (x = 0.3333, y = 0.3333) white light. From these values, it is evident that the chromaticity coordinates of these phosphors doped with europium ion are located in the white-light region.

4. Conclusions

In summary, the europium doped SMS phosphors were prepared by varying SiO_2 concentration and the luminescence characteristics were studied. XRD patterns revealed that the samples were crystalline and formed with two phases. From the emission spectra, it is stated that europium ions are present both in divalent as well as trivalent oxidation states in the sample. The main excitation peaks around 335 and 260 nm and the main broad emission peak at 480 nm are ascribed to the $4f^7 \rightarrow 4f^65d^1$ transition of Eu^{2+} in this matrix. The calculated CIE chromaticity coordinates of SMS08 and SMS10 phosphors are close to the standards of NTSC and CIE of white light coordinates. These above results suggested that SMS08 and SMS10 phosphors would be promising materials to develop white LED by NUV chip.

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References

[1] K. Yamazaki, H. Nakabayashi, Y. Kotera, A. Ueno, Electrochem. Soc. **133**, 657 (1986).
[2] A. A. Sabbagh Alvani, F. Moztarzadeh, A. A. Sarabi, J. Lumin. **115**, 147 (2005).
[3] L. Lin, M. Yin, C. Shi, W. Zhang, J. Allos Compd. **455**, 327 (2008).
[4] J. K. Park, M. A. Lim, C. H. Kim, H. D. Park, J. T. Park, S. Y. Choi, Appl. Phys. Lett. **82**, 683 (2003).
[5] X. Sun, J, Zhang, X. Zhang, S. Lu, X. Wang, J. Lumin. **122**, 955 (2007).
[6] Z. Zhang, Y. Wang, J. Lumin. **128**, 383 (2008)
[7] A. A. Setlur, A. M. Srivastava, H. L. Pham, M. E. Hannah, U. Happek J. Appl. Phys. **103**, 053513 (2008).
[8] F. Clabau, A. Garcia, P. Bonville, D. Gonbeau, T. L. Mercier, P. Deniard, S. Jobic J. Solid State Chem. **181**, 1456 (2008).
[9] Q. Zhang, J. Wang, M. Zhang and Q. Su Appl. Phys. B. **92**, 195 (2008).
[10] J. S. Kim, P. E. Jeon, Y. H. Park, J. C. Choi, H. L. Park, G. C. Kim, T. W. Kim, Appl. Phys. Lett. **85**, 3696 (2004).
[11] J. H. Lee, Y. J. Kim, Mater. Sci. Eng. B **146**, 99 (2008).
[12] J. Yang, L. Yang, W. Liu, Y. Zhang, H. Fan, Y. Wang, H. Lu, J. Lang, D. Wang, J. Alloys Compounds **454**, 506 (2008).
[13] M. Peng, Z. Pei, G. Hong and Q. Su, Chem. Phys. Lett. **371**, 1 (2003).

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