Electronic Materials Letters, Vol. 6, No. 1 (2010), pp. 13-15
DOI: 10.3365/eml.2010.03.013 Published 31 March 2010

Sol-Gel Synthesis of $CaAl_{12}O_{19}$:Mn Phosphor and Red Luminescence by Near-Ultraviolet/Blue Excitation

Jung Hyun Park and Myoung Seok Kwon*

Department of Materials Science and Engineering, University of Seoul,
90 Jeonnong-dong, Dongdaemun-gu, Seoul 130-743, Korea

$CaAl_{12}O_{19}$:Mn red-emitting phosphor has been synthesized by a novel sol-gel route for the possible applications for white LEDs or white OLEDs. The sol-gel derived $CaAl_{12}O_{19}$:Mn phosphor was crystallized into a single crystalline phase and showed red luminescence excited by NUV and blue wavelength. The main red emission peak was at 653 nm with satellite peaks while the excitation bands consisted of three peaks around 334 nm, 397 nm, and 468 nm. The sol-gel derived $CaAl_{12}O_{19}$:Mn red-emitting phosphor would be compatible for the possible application of white LEDs or white OLEDs through NUV- or blue- excitation.

Keywords: phosphor, sol-gel, $CaAl_{12}O_{19}$:Mn, red, luminescence, NUV, blue

1. INTRODUCTION

White LEDs require new phosphors excited by near-ultraviolet (NUV) light-emitting diodes (LEDs) or blue LEDs because many conventional phosphors for fluorescent lamps cannot be excited by NUV or blue LEDs.[1-3] White LEDs using NUV LEDs require blue-, green-, and red-emitting phosphors under a NUV excitation at approximately 400 nm, which is much longer than the 254 nm wavelength in mercury-based fluorescent lamps. Another type of white LED uses a blue LED chip, and therefore requires efficient phosphors emitting longer spectra under blue excitation at around 450 nm. Also, new phosphors can be integrated into possible white organic LED (OLED) structures using phosphor layers which can be excited under blue OLED device operation rather than through conventional color conversion layers. For integration of new phosphors with white LEDs, oxide phosphors are preferred over sulfide phosphors due to better stability during long-term device operation.

The authors previously reported simple ethanol-based sol-gel routes for nanocrystalline oxide phosphors[4-6] for PDP applications instead of the traditional high temperature solid state reaction with a micron-sized phosphor. The sol-gel process is considered to be very flexible for synthesizing nano-sized materials.[7-9] The process allows the desired composition, a high degree of uniformity, and a lower firing temperature to induce the final crystalline phases which are obtained easily compared to the conventional high temperature solid state reaction.[4-6]

*Corresponding author: mskwon@uos.ac.kr

According to our knowledge, $CaAl_{12}O_{19}$:Mn phosphor obtained by sol-gel route has not been reported. In this letter, the first time, we report a novel sol-gel route to synthesize $CaAl_{12}O_{19}$:Mn phosphor and red emission properties by NUV and blue excitation for possible application with white LEDs and white OLEDs operating through NUV/blue excitation from electronic devices. We used ethanol and deionized water as the solvent. For the metal precursors, Ca nitrate, Al nitrate, and Mn nitrate were used instead of other more expensive organic precursors used with conventional sol-gel routes.

2. EXPERIMENTAL PROCEDURE

Figure 1 shows the procedure to synthesize the $CaAl_{12}O_{19}$:Mn phosphor using an ethanol-based sol-gel route. A fixed molar amount of calcium nitrate and aluminum nitrate was dissolved in the ethanol and stirred for 1 h at room temperature. Manganese nitrate and deionized water were added to the solution, and the solution was stirred for an additional hour. The amount of deionized water was equal to the amount of ethanol. Finally, acetone was added to the solution, and the solution was stirred for 1 h to make a uniform solution. The final clear solution was dried in air at 60°C for 20 h, and transformed into dried amorphous gel powders. The gel powder was fired at 1400°C in air for 2 h to induce the crystallization of the dried gel powder.

X-ray diffraction (XRD, D8 Advanced X-ray, Bruker Axs.) was used to identify the crystalline phases of the sol-gel-synthesized $CaAl_{12}O_{19}$:Mn phosphor. Field emission scanning electron microscopy (FE-SEM, Hitachi S-4300) was used to observe the phosphor powder. The photoluminescence spec-

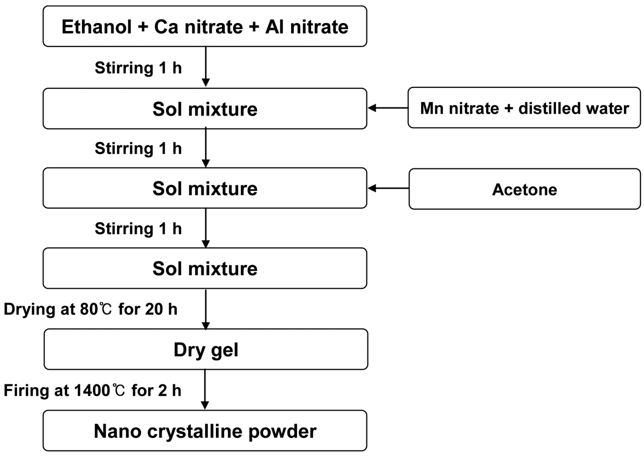

Fig. 1. Flowchart showing the sol-gel route for sol-gel-derived $CaAl_{12}O_{19}$:Mn phosphor.

tra and excitation spectra were measured using a fluorescence spectrometer (Hitachi F-4500) with a 150 W monochromatized Xe lamp. The luminescence spectra were measured using excitation wavelengths of 254 nm, 380 nm, 400 nm, 420 nm, and 450 nm.

3. RESULTS AND DISCUSSION

Figure 2 shows XRD patterns of the sol-gel-synthesized $CaAl_{12}O_{19}$:Mn phosphor. Formation of a single crystalline phase can be seen in the figure. The diffraction peaks came from the JCDPS Card. (No. 84-1613). The firing temperature (1400°C) was lower than a previous result by solid-state reaction. Murata *et al.* reported a solid-state reaction at 1923 K, 3 h in air, and red emission spectra without XRD patterns of the derived crystalline phases.[2] In our study, a lower temperature was sufficient to form a single phase crystalline $CaAl_{12}O_{19}$:Mn phosphor.

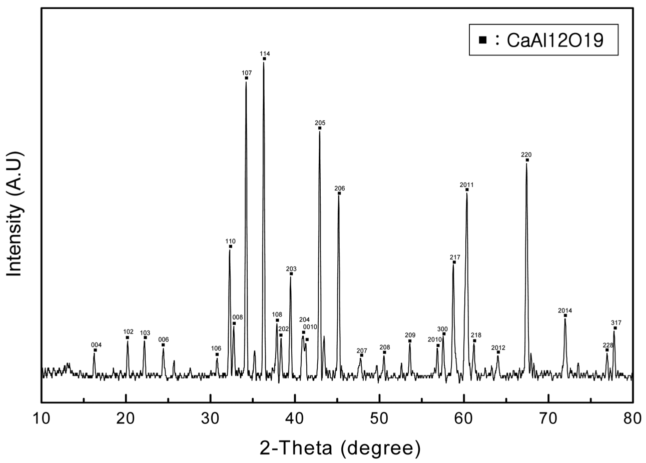

Fig. 2. XRD pattern of the sol-gel-derived $CaAl_{12}O_{19}$:Mn phosphor.

Figure 3 shows FE-SEM images of the sol-gel-derived $CaAl_{12}O_{19}$:Mn phosphor fired at 1400°C. The particles are agglomerated with each rod-like shape, as shown in Fig. 3.

Figure 4 shows the red emission spectra of the sol-gel-derived $CaAl_{12}O_{19}$:Mn phosphors with each different excitation wavelength. For the excitation at 254 nm, the red emission was not as efficient as that of a conventional lamp phosphor. However, the red emissions were efficient for NUV wavelengths of 380 nm, 400 nm, and 420 nm. The red emission was also efficient for blue excitation at 450 nm. The highest emission intensity was obtained by 400 nm excitation. The emission spectra show a narrow band between 600 nm and 700 nm with sharp peaks at 640 nm, 656 nm, and 664 nm. The main peak was at 656 nm, which is known to be due to the $^2E \rightarrow {}^4A_2$ transition of Mn^{4+} ion. The Mn ions are known to substitute the six oxygen-coordinated Al^{3+} sites.[2]

Figure 5 shows the excitation spectrum of the same

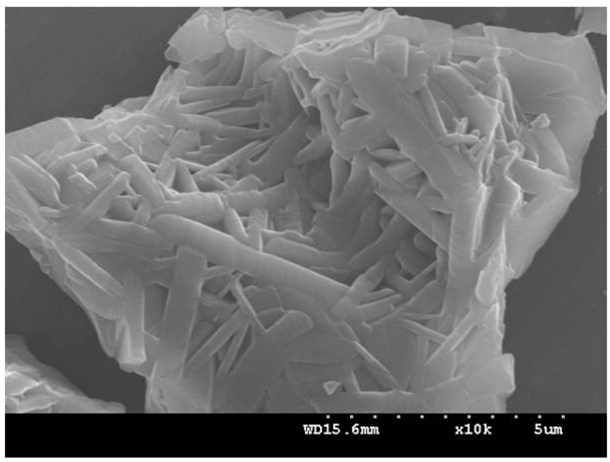

Fig. 3. FE-SEM image of the sol-gel-derived $CaAl_{12}O_{19}$:Mn.

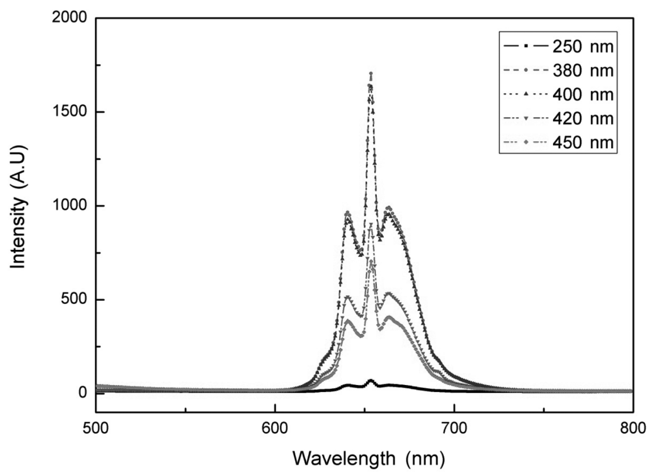

Fig. 4. Emission spectra of the sol-gel-derived $CaAl_{12}O_{19}$:Mn phosphor with different excitation wavelengths.

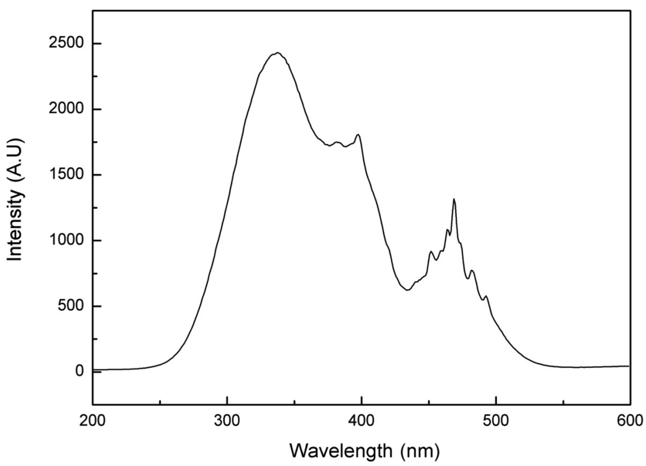

Fig. 5. Excitation spectrum of the sol-gel-derived $CaAl_{12}O_{19}$:Mn phosphor.

$CaAl_{12}O_{19}$:Mn phosphors with a fixed emission wavelength with maximum intensity, as shown in Fig. 4. The excitation spectrum exhibits a broad band between 250 nm and 550 nm with three main peaks occurring at about 334 nm, 397 nm, and 468 nm.

4. CONCLUSION

$CaAl_{12}O_{19}$:Mn red-emitting phosphor was synthesized by a novel sol-gel route for possible applications with white LEDs or white OLEDs using NUV excitation or blue excitation. Our simple ethanol-based sol-gel procedures were carried out in an air environment without additional reducing processes. The sol-gel-derived $CaAl_{12}O_{19}$:Mn phosphor was crystallized into a single crystalline phase and showed red luminescence excited by NUV and blue wavelengths. The main emission peak was at 653 nm with satellite peaks, while the excitation bands showed three main peaks at around 334 nm, 397 nm, and 468 nm.

REFERENCES

1. H. Tamaki and Y. Murazaki, *Phosphor Handbook, 2nd ed*. (eds., W. M. Yen, S. Shionoya, and H. Yamamoto), p. 533, CRC Press, Boston (2007).
2. T. Murata, T. Tanoue, M. Iwasaki, K. Morinaga, and T. Hase, *J. Luminescence* **114**, 207 (2005).
3. Z. Hao, J. Zhang, X. Zhang, X. Sun, Y. Luo, S. Lu, and X. Wang, *Appl. Phys. Lett.* **90**, 261113 (2007).
4. C. J. Kim and M. S. Kwon, *J. Mat. Sci.* **41**, 6138 (2006).
5. M. S. Kwon, C. J. Kim, H. L. Park, T. W. Kim, and H. S. Lee, *J. Mat. Sci.* **40**, 4089 (2005).
6. M. S. Kwon, H. L. Park, T. W. Kim, Y. Huh, W. Choi, and J. Y. Lee, *Met. Mater. Int.* **12**, 263 (2006).
7. A. S. Edelstein and R. C. Cammarata, *Nanomaterials: Synthesis, Properties and Applications* , p. 145, Institute of Physics Publishing, Bristol and Philadelphia (1996).
8. K. Hwang, J. Kim, D.-R. Jung, C. Kim, T. Moon, D. Son, and B. Park, *Electron Mater. Lett.* **3**, 201 (2007).
9. H. J. Kim, Y. K. Jeong, H. G. Kim, and B. H. Choi, *Electron Mater. Lett.* **4**, 131 (2008).