JOURNALOF

Ceramic Processing Research

Synthesis of nano sized Eu³⁺ doped Y(P,V)O₄ phosphors by using cellulose assisted liquid phase precursor process

Ye Lim Song^{a,1}, Seung Hee Choi^{a,1}, Soo Jong Kim^b, Young Hyun Song^a, Takaki Masaki^a and Dae Ho Yoon^{a,*} ^aSchool of Advanced Materials Science and Engineering Sungkyunkwan University, Suwon 440-746, Korea

^bDepartment of Advanced Materials & Chemical Engineering, Halla University, Wonju 220-712, Korea

For the high luminescent efficiency, nano sized Eu^{3+} doped Y(P,V)O₄ phosphors are the promising red-emitting candidates for solar cell. In this study, $Y_{0.92}Eu_{0.08}(P_{0.508}V_{0.452})O_4$ of particle size of ~ 100 nm were obtained with high PL intensity by using the cellulose assisted liquid phase precursor process. Their excitation and emission spectra were analyzed. Crystal structure and particle morphologies of obtained phosphors were measured and analyzed with X-ray diffractometer (XRD), field emission scanning electron microscopy (FE-SEM), and photoluminescence (PL).

Key words: Red phosphor, LPP, High luminescence efficiency.

Introduction

Recently, the red phosphors have been studied and especially applied for PDP. The uniform thickness combined with smoother surface morphology and smaller grain size make it possible to define a smaller pixel spot size to achieve a higher resolution [1]. Among various lanthanide nanoparticles, rare earth phosphates have been extensively studied because of their high thermal, chemical, and mechanical stability [2].

Eu³⁺ doped yttrium orthovanadate (YVO:Eu³⁺) [3, 4] phosphors have been used as a red phosphors in color television and cathode ray tubes owing to its high luminescence efficiency upon electron beam excitation [5, 6]. A complete solid solution has been reported in $Y(P_{1-x}V_x)O_4$: Eu³⁺ thin films from x = 0 to x = 1 with xenotime structure [7], and the partial substitution of P for V exhibited the better luminescent properties [5, 8]. For the high luminescent efficiency, nano sized Eu³ doped $Y(P,V)O_4$ phosphors are the promising redemitting candidates for solar cell due to the Y(P,V)O₄ phosphors absorbed under 300 nm and emitted visible light. Oxide phosphors with aluminate, silicate, vanadate, phosphate, and borate groups generally exhibit the strong absorption in the VUV spectral region [6, 9]. Among the most widely used chemical methods, hydrothermal method using water or alcohol as solvent has been demonstrated to be a way to produce the nanostructure rare earth doped phosphates [2].

In this study, $Y_{0.92}Eu_{0.08}(P_{0.508}V_{0.452})O_4$ phosphors synthesized by using the cellulose assisted liquid phase

precursor (LPP) process [6]. This process can make homogeneous powder and nano sized phosphors compared with the solid state reaction (SSR) process. The excitation and emission spectra of the obtained nano sized phosphors were analyzed. Crystal structure and particle morphologies of obtained phosphors were measured and analyzed with X-ray diffractometer (XRD), field emission scanning electron microscopy (FE-SEM), and photoluminescence (PL).

Experimental

YCl₃nH₂O (Aldrich, 99.9%), H₃PO₄ (Aldrich, 99.9%), VOSO₄nH₂O (Aldrich, 99.99%), and EuCl₃ \cdot nH₂O (Aldrich, 99.9%) were used as a starting raw materials. The starting raw materials were mixed according to a molar ratio of Y_{0.92}Eu_{0.08} (P_{0.508}V_{0.452})O₄. The mixed solution was impregnated into a cellulose powders. The crystalline cellulose (Asahi KASEI, TG-101) was used as the template. The starting raw materials and crystalline cellulose were mixed with ratio 1 : 1 (solution: crystalline cellulose). For the comparison, the phosphors were synthesized using the starch as the template.

And then the obtained phosphors were fired to 500 °C rapidly, and keep temperature for 1 hr to remove the cellulose. The fired phosphors were sintered the temperature 600 °C and keep for 3 hrs in air. Additionally the temperature was increased 600, 700, 800, and 1000 °C for 2 hrs. The phosphors used starch were fired temperature at 800 °C. To remove the impurity, the obtained powders were washed in potassium hydroxide solution (KOH) for 24 hrs at room temperature [10].

The photoluminescence properties of the obtained nano-phosphors were analyzed by Photoluminescence

¹These authors contributed equally.

^{*}Corresponding author:

Tel : +82-31-290-7388

Fax: +82-31-290-7410

E-mail: dhyoon@skku.edu

spectrometer (PL) (SINCO, FS-2, Republic of Korea) with a 150 W xenon lamp as the excitation source at room temperature. The crystal structure, particle size and morphologies were investigated X-ray diffractometer (XRD) (Rigaku, Japan, Cu K α , λ = 1.5406), and field emission scanning electron microscopy (SEM) (JEOL, JSM 7500F, Japan).

Results and Discussion

The X-ray diffraction indicate that the single phase $Y_{0.92}Eu_{0.08}P_{0.508}V_{0.452}O_4$ phosphors were obtained. Fig. 1 showed the XRD patterns of $Y_{0.92}Eu_{0.08}P_{0.508}V_{0.452}O_4$ phosphors using crystalline cellulose as template. The intensity of the diffraction peaks was increased with higher temperature up to 800 °C correspond with PL intensity shown in Fig. 4. The phosphors with high luminescence efficiency were appeared at well crystallized phosphors. Additionally, $Y_{0.92}Eu_{0.08}P_{0.508}V_{0.452}O_4$ phosphors using starch as template were compared with the phosphors



Fig. 1. The XRD pattern of $Y_{0.92}Eu_{0.08}P_{0.508}V_{0.452}O_4$ phosphors fired temperature 600, 700, 800, 1000 °C, and commercial YPV.



Fig. 2. The XRD pattern of $Y_{0.92}Eu_{0.08}P_{0.508}V_{0.452}O_4$ phosphors used starch and crystalline cellulose as template fired temperature 800 °C.



Fig. 3. The SEM images of $Y_{0.92}Eu_{0.08}P_{0.508}V_{0.452}O_4$ phosphors used crystalline cellulose, fired at (a) 600, (b) 700, (c) 800, (d) 1000 °C, (e) commercial YPV, and (f) phosphors used starch fired at 800 °C.

using crystalline cellulose as template. The XRD patterns of two phosphors were showed in Fig. 2. In the crystalline cellulose phosphors, it was appeared higher crystalline than the starch phosphors.

Fig. 3 shows the SEM images of each phosphors in firing temperature at 600, 700, 800, and 1000 °C. Fig. 3(a-d) shows particle size and morphology of the obtained phosphors using the crystalline cellulose as a template in fired at 600, 700, 800, and 1000 °C. Fig. 3(e) shows the SEM images of commercial YPV phosphors for the comparison. In the Fig. 3(a), the average particle size values of the fired at 600 °C phosphors were ~ 100 nm. The smallest particle size is the phosphors fired at 600 °C. The particle coarsening occurred increasing with temperature. Compared with the commercial YPV size was in the range of 1-2 μ m, the obtained Y_{0.92}Eu_{0.08}P_{0.508}V_{0.452}O₄ phosphors were



Fig. 4. The emission spectra of $Y_{0.92}Eu_{0.08}P_{0.508}V_{0.452}O_4$ phosphors used crystalline cellulose fired at 600, 700, 800, 1000 °C, and commercial YPV. The wavelength was appeared at 594, 618, and 700 nm under 254 nm excitation.



Fig. 5. The emission spectra of $Y_{0.92}Eu_{0.08}P_{0.508}V_{0.452}O_4$ phosphors used crystalline cellulose fired at 800 °C (red line), used starch (blue line) and commercial YPV (black line).

more small and roundish shape. The phosphors used starch as the template were showed in the Fig. 3(f) which the rod like shape compared with the phosphors used crystalline cellulose as the template. Jung-Hoo Shin reported that the roundish shaped phosphors exhibited more improved luminescence properties than elongated or plate shaped phosphors. The roundish shaped phosphors were obtained by the liquid phase precursor process.

The emission spectra of $Y_{0.92}Eu_{0.08}P_{0.508}V_{0.452}O_4$ phosphors using crystalline cellulose as the template excited at 254 nm was shown in Fig. 4. The phosphors fired temperature at 600, 700, 800, and 1000 °C were observed emission band wavelength at 594, 618, and 700 nm. The intensity was enhanced with increasing the temperature up to 800 °C phosphors, and then decrease the intensity of the phosphors fired at 1000 °C. The

phosphors fired at 800 °C were comparable commercial YPV. The emission spectra at 618 nm was showed the higher intensity than commercial YPV.

Fig. 5 was showed the emission spectra of the phosphors used crystalline cellulose and starch. It was also appeared higher intensity at the phosphors used crystalline cellulose compared with the phosphors used starch.

Conclusions

 $Y_{0.92}Eu_{0.08}P_{0.508}V_{0.452}O_4$ phosphors were synthesized by using cellulose assisted liquid phase precursor (LPP) process. Crystalline cellulose and starch were used as a template for the experiment. We could obtained nano sized particles under ~ 100 nm. The phosphors absorbed at UV range, and gave a red color light at emission wavelength 594, 618, and 700 nm under 254 nm excitation. The photoluminescence intensity of the obtained phosphors fired 800 °C using the crystalline cellulose as the template was higher than commercial YPV phosphors. The synthesized $Y_{0.92}Eu_{0.08}P_{0.508}V_{0.452}O_4$ nano sized phosphors having these properties were promising candidate for the solar cell.

Acknowledgments

This work was supported by "Human Resources Program in Energy Technology" of the Korea Institute of Energy Technology Evaluation and Planning (KETEP), granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea. (No. 20154030200870).

References

- M. Yu, J. Lin and S.B. Wang, Appl. Phys. A 80 (2005) 353-360.
- G. Du, W. Guo, J. M. K. Al-zyadi, Y. Han, P. Liu and Z. Liu, J. Nanopart. Res. 15 (2013) 1-8.
- H. Zhang, M. Lu, Z. Xiu, G. Zhou, S. Wang, Y. Zhou, S. Wang, Mater. Sci. Eng. B 130 (2006) 151-157.
- J. Wang, Y. Xu, M. Hojamberdiev, J. Peng and G. Zhu, Mater. Sci. Eng. B 156 (2009) 42-47.
- J.H. Shin, S.W. Choi, S.H. Hong, S.J. Kwon, S.Y. Seo, H.S. Kim, Y.H. Song and D.H. Yoon, J. Alloys Compd. 509 (2011) 4331-4335.
- W.J. Park, M.K. Jung, J.W. Moon, T. Masaki, S.J. Im and D.H. Yoon, J. Nanosci. Nanotechnol. 9 (2009) 4371-4375.
- K.S. Sohn, I.W. Zeon, H. Chang, S.K. Lee and H.D. Park, Chem. Mater. 14 (2002) 2140-2148.
- 8. B. Yan and X. Q. Su, Mater. Sci. Eng. B 116 (2005) 196-201
- 9. C.C. Wu, K.B. Chen, C.S. Lee, T.M. Chen and B.M. Cheng, Chem. Mater. 19 (2007) 3278-3285.
- D.S. Jo, Y.Y. Luo, K. Senthil, T. Masaki and D.H. Yoon, Opt. Mater. 33 (2011) 1190-1194.