

Synthesis and characterization of $Y_{1x}VO_4 : Eu_x^{3+}$ nanoparticles by using starch as an impregnating matrix

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The nano-sized $Y_{1x}VO_4 : Eu_x^{3+}$ powders were synthesized by impregnation method using starch and metal salts ($YCl_3 \cdot 6H_2O$, $V_2OSO_4 \cdot 6H_2O$, $EuCl_3 \cdot 6H_2O$) as starting materials. The synthesized powders were characterized by XRD, FE-SEM and Photoluminescence. The particle size of the powders were controlled by preparation conditions, such as heat treatment temperature and concentration of Eu ion. As a result of the various synthesis conditions, 30 ~ 100 nm sized homogeneous $Y_{1x}VO_4 : Eu_x^{3+}$ particles were obtained at 600–800 °C for 3 hour. Crystallization and the growth of particles were accelerated with increasing sintering temperature and concentration of Eu ion. Crystallization of $Y_{1x}VO_4 : Eu_x^{3+}$ started around 500 °C, which the temperature is pyrolysis of starch, tetragonal phase generated at 600 °C. Moreover, above 600 °C, heat treatment time had influence on particle growth, and change of the concentration of Eu ion had also influence on growth of a crystal. Emission intensity of $Y_{1x}VO_4 : Eu_x^{3+}$ particles were enhanced with increasing heat treatment temperature and concentration of Eu ion.

Key words: $YVO_4 : Eu^{3+}$, Nanoparticle, Impregnation method.

Introduction

YVO_4 can easily form single crystals as well as demonstrates excellent mechanical properties; hence, it has been widely used as a host material for lasers, an optical polarizer, and a phosphor [1-3]. Thus far, various studies have been conducted on the synthesis of YVO_4 phosphors exhibiting high luminous efficiency. In these studies, Eu^{3+} has been extensively introduced into the host. During the substitution of Eu^{3+} in the YVO_4 host material, Eu^{3+} replaces Y^{3+} , and a $^5D_0 \rightarrow F_2$ transition occurs, resulting in the emission of red luminescence. Therefore Eu^{3+} has often been used as an activator for the synthesis of red phosphor [4-7]. Because $YVO_4:Eu^{3+}$ phosphor with the added Eu ions exhibits outstanding color purity and chemical stability, it has been used as a red phosphor in plasma display panels (PDP) and field-emission displays (FED). Moreover, because it exhibits chemical properties relatively more stable than those exhibited by sulfide phosphors, it is also used as a phosphor for white LED [8]. Phosphor using YVO_4 as the host is synthesized by liquid-phase methods, such as ion exchange, precipitation, sol-gel methods, and hydrothermal synthesis, as well as solid-phase methods and microwave heat treatment (HT) [9-13]. Wet synthesis methods, such as precipitation and sol-gel methods, are advantageous because they control

the size, shape, and surface conditions of the nanoparticles, which are well dispersed in liquids. However, these methods have been reported to exhibit disadvantages such as complicated synthetic pathways as well as the quenching of the luminescence of Eu^{3+} by OH⁻ present in the colloidal solution [14]. In addition to the synthetic methods, Y. Zuo et al. have synthesized a YVO_4 phosphor having a new composition by the simultaneous introduction of two activator ions into the host lattice and have reported improvement in luminous efficiency [9, 13]. A $YVO_4 : Eu^{3+}, Al^{3+}$ phosphor synthesized by the solid-phase method using Eu^{3+} , in addition to Al^{3+} and Bi^{3+} as co-activators, was reported to exhibit luminescence properties superior to those exhibited by $YVO_4 : Eu^{3+}$. In this study, $Y_{1x}VO_4 : Eu_x^{3+}$ phosphor nanoparticles were synthesized from their precursors, which were produced by the impregnation of natural organic polymers with metal salts, such as yttrium, vanadium, and europium dissolved in distilled water. The natural organic polymer (starch) was used as impregnating matrix, which is a type of polysaccharide. In addition, the effects of the HT temperature on the impregnated precursor and changes in the Eu ion concentration on the particle size and luminescence properties of the synthesized $Y_{1x}VO_4 : Eu_x^{3+}$ phosphor were investigated.

Experimental

The $Y_{1x}VO_4 : Eu_x^{3+}$ nanopowder was synthesized by impregnation using $YCl_3 \cdot 6H_2O$ (Aldrich), $VOSO_4 \cdot 6H_2O$ (Wako Chemical Co.), and $EuCl_3 \cdot 6H_2O$ (Aldrich) as the

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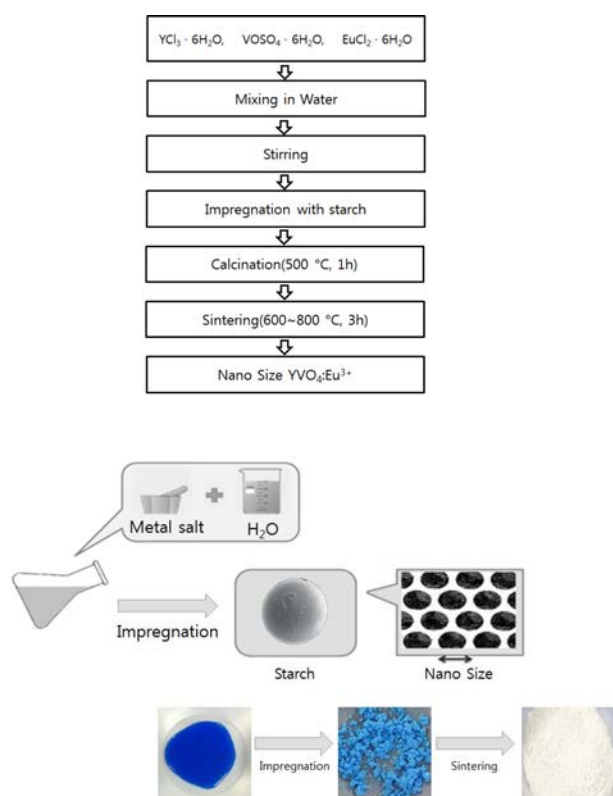


Fig. 1. Preparation procedures of $Y_{1-x}VO_4 : Eu_x^{3+}$ phosphors by impregnation method.

starting materials. Fig. 1 shows the flowchart of the preparing of $Y_{1-x}VO_4 : Eu_x^{3+}$. First, $YCl_3 \cdot 6H_2O$, $VOSO_4 \cdot 6H_2O$, and $EuCl_3 \cdot 6H_2O$ were dissolved in distilled water with the removal of ions to prepare a mixed solution. To investigate the effects of the Eu ion concentration on luminescence properties and particle size, mixtures were prepared with the Eu ion concentration ranging from 0.03 to 0.2 mol. After stirring the mixtures for 1 hr at room temperature, the mixtures were impregnated into the starch as the impregnating matrix. Starch, which is a natural polymer, exhibits density higher than that of an aqueous metal salt solution. The weight ratio of metal salt solution compared to starch was set to 1 : 1.2. The impregnated $Y_{1-x}VO_4 : Eu_x^{3+}$ precursor was dried at 80 °C for 24 hrs; then, calcination was performed for 3 h by varying the HT temperature from 600 to 800 °C at a heating rate of 5 °C/min. Granular $Y_{1-x}VO_4 : Eu_x^{3+}$ phosphor nanoparticles were obtained by the crushing of the calcined samples, and the properties of the synthesized samples were investigated by the following analysis methods. X-ray diffraction (XRD) analysis of the calcined powder samples was conducted at room temperature on a PAN analytical X-ray diffractometer (XPert PRO MPD) with monochromated Cu-K α radiation ($\lambda = 1.54\text{\AA}$). Diffractograms were recorded in the 2θ range from 10 ° to 80 ° at a resolution of 0.05 °. For examining the size, form, and distribution of powder particles, measurements were conducted using a scanning electron microscope (FE-SEM, model S-4300, HITACHI.). For a

more accurate comparative analysis of particle size and particle size distribution, the magnification of all samples was uniformly set to 10,000X, 30,000X, 50,000X, and 100,000X. Photoluminescence was observed with a SCINCO FluoroMate FS-2 fluorescence spectrophotometer equipped with a Xe lamp at room temperature.

Results and Discussion

In this study, starch was used as the matrix for the liquid-phase precursor method for producing $Y_{1-x}VO_4 : Eu_x^{3+}$ phosphor, which exhibited a uniform nanosized particle distribution. Fig. 2 shows the micro structure of starch used in the experiment. Starch is a natural polymer, which has a microfibrillar or micelle structure of less than 1 μ m, and this structure determines the form of the particles produced.

Figs. 2(a) and 2(b) show the state of the starch particles prior to impregnation by metal salts; circular particles were observed with a size of approximately 10 μ m. Figs. 2(c) and 2(d) show the state of starch particles after impregnation; the metal salts were impregnated uniformly by permeation into the fine structure of starch. As can also be observed in these figures, the size of the particles slightly increased after impregnation. By using fine-structure starch as the

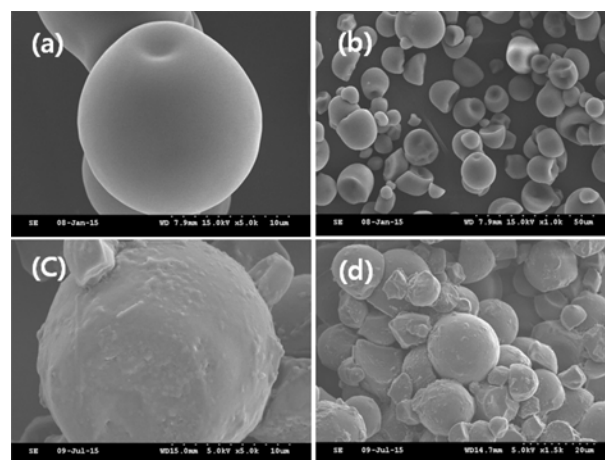


Fig. 2. FE-SEM images of (a), (b) starch, and (C), (d) impregnated starch.

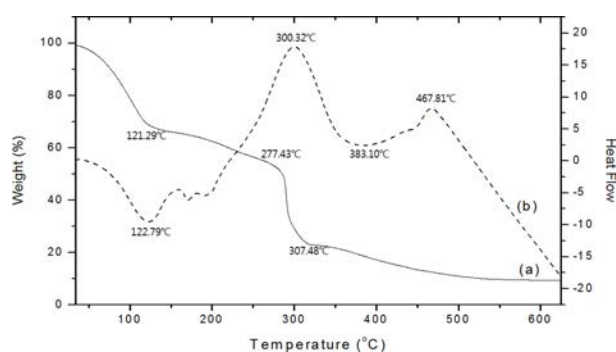


Fig. 3. Thermal analysis curves of impregnated precursor (a) TGA curve (b) DSC curve.

medium, an aqueous solution mixed with metal salts used as the starting material was uniformly impregnated into the fine structure of starch; consequently, a nanosized ceramic phosphor was produced, with a uniform particle size, by drying and HT processes.

Fig. 3(a) shows the thermal gravimetric analysis (TGA) results of starch impregnated by metal salts. From room temperature up to near 121 °C, a weight loss of approximately 35% was observed. This weight loss is attributed to the evaporation of crystalline moisture contained in the fine structure of starch, which is a vegetable polymer composed of polysaccharides. The weight gradually decreased between 121 °C and 277 °C; however, weight rapidly decreased between 277 °C and 307 °C. At temperatures ranging from 277 °C to 307 °C, rapid thermal decomposition occurred, which destroyed the organic polysaccharide structure; this decomposition resulted in a weight loss of 80%. Between 307 °C and near 600 °C, the weight of the thermal composition gradually decreased, and at 600 °C, starch used as the matrix exhibited complete thermal decomposition. Fig. 3 shows the differential scanning calorimetry curves; an endothermic peak was observed at 122 °C, attributed to the evaporation of crystalline moisture (Fig. 3(b)); an exothermic peak near 300 °C was observed, attributed to the thermal decomposition of organics; an exothermic peak was also observed near 470 °C, attributed to the generation of crystalline-phase $Y_{1-x}VO_4:Eu^{3+}$; these findings were consistent with TGA results. Fig. 4 shows the XRD patterns of $Y_{1-x}VO_4:Eu^{3+}$ powders calcined at 600 °C, 700 °C and 800 °C, respectively. As shown in the figure, the diffraction peaks of $Y_{1-x}VO_4:Eu^{3+}$ were distinctly observed. As the primary peaks exhibiting high diffraction intensity were in good agreement with the standard JCPDS card No. 01-072-0274, the crystalline phase of the synthesized $Y_{1-x}VO_4:Eu^{3+}$ phosphor is confirmed. The heating rate was set to start from room temperature to the final temperature over 6 hrs by electricity, while the calcination time for all experiments was fixed at 3 hrs. At 470 °C, the crystalline phase of $Y_{1-x}VO_4:Eu^{3+}$ started to form, and with increase in the calcination temperature from 600 °C to 800 °C, the intensity of the peaks also increased, indicating progress in crystallization. Fig. 5 shows the results obtained from field-emission scanning electron microscopy (FE-SEM), which measures the surface structure of the synthesized $Y_{1-x}VO_4:Eu^{3+}$ particles at a

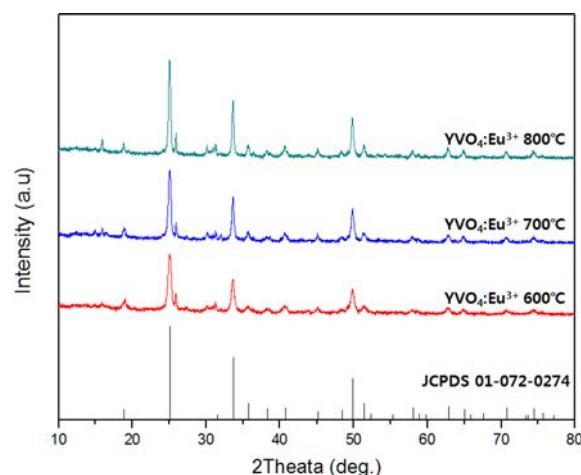


Fig. 4. XRD patterns of $Y_{1-x}VO_4:Eu^{3+}$ phosphors at various calcination temperatures.

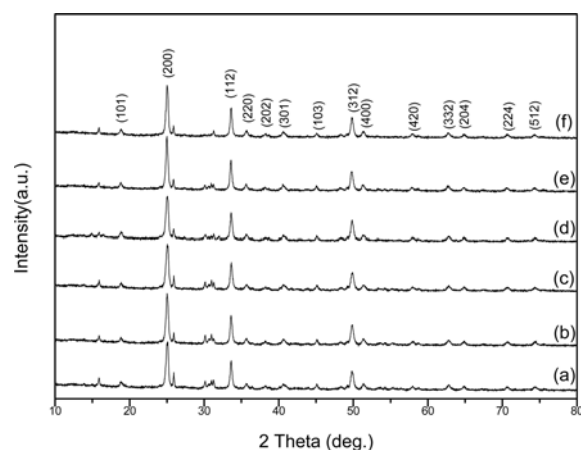


Fig. 6. XRD patterns of $Y_{1-x}VO_4:Eu^{3+}$ phosphors calcinated at 700 °C by 0.03, 0.05, 0.07, (d) 0.10, (e) 0.15, and (f) 0.20 mole of Eu concentrations.

fixed calcination time of 3 hrs and by the variation of HT from 600 to 800 °C. As can be observed in the XRD pattern in Fig. 4, at 600 °C, fine crystals had already formed, albeit the particles were small in size (30–50 nm) and irregular, thereby exhibiting poor crystallinity. Although it is not clearly visible, most of the particles were observed to be granular. With the increase in the calcination temperature to 700 °C, crystallinity increased, with growth in the particle size (100–200 nm), which again exhibited granular nature. Moreover, calcination at

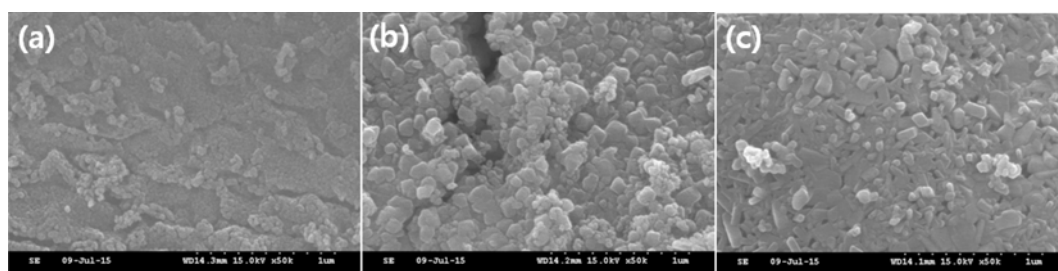


Fig. 5. FE-SEM images of $Y_{1-x}VO_4:Eu^{3+}$ phosphors at various calcination temperatures.

800 °C resulted in distinct changes in the form and size of the particles, with crystallization occurring at a wider range; a uniform particle size distribution was observed. Finally, at temperatures greater than 800 °C, crystallization accelerated, resulting in rapid crystal growth: the agglomeration of particles (100 nm) was observed over a broad range. Accordingly, to obtain single-phase $Y_{1-x}VO_4 : Eu_x^{3+}$ nanoparticles with a uniform particle size distribution, concentrations of Eu ions, used as the activator, were varied at temperatures less than 800 °C, before the start of agglomeration. Fig. 6 shows the XRD patterns of $Y_{1-x}VO_4 : Eu_x^{3+}$ powder heat-treated at 700 °C while varying the concentration of Eu ions from 0.03 to 0.2 mol. As the concentration of Eu ions was increased from 0.03 to 0.2 mol, the diffraction intensity increased. Fig. 7 shows the corresponding SEM images of the aforementioned $Y_{1-x}VO_4 : Eu_x^{3+}$ powder. Similar to that observed in the XRD results from Fig. 6, with increasing concentration, the particles underwent transition from the granular phase to a more complete crystalline phase. PL properties of these $Y_{1-x}VO_4 : Eu_x^{3+}$ phosphors have been studied. The excitation spectra of $Y_{1-x}VO_4 : Eu_x^{3+}$ when monitored at 617 nm is shown in Fig. 8. This Figure shows the excitation spectra of the $Y_{1-x}VO_4 : Eu_x^{3+}$ samples obtained under different Eu ion contents from 0.03 to mole at calcined condition of 700 °C, 3 hrs. The activator Eu is a lanthanide element emitting fluorescence in the Eu^{2+} and Eu^{3+} states. In the Eu^{3+} state, the electron configuration of Eu atom is $[Xe]6s^24f_7$ and $[Xe]4f_6$. Eu^{3+} exhibits luminescence properties by the transfer of electrons present in the incompletely filled 4f orbital [8, 15]. When Eu ions are added to YVO_4 , $Y_{1-x}VO_4 : Eu_x^{3+}$ exhibits a charge-transfer state between 250 and 320 nm, attributed to the transfer of electrons from the 2p orbital of oxygen to the empty 4f orbital of Eu [16]. As shown in Fig. 8, with the molar ratio of Eu^{3+} ranging from 0.03 to 0.2 mol, the $Y_{1-x}VO_4 : Eu_x^{3+}$ phosphor exhibited two excitation spectra: one spectrum exhibited a maximum excitation intensity at 309 nm, while the other spectrum exhibited very weak excitation intensities near 381 nm, 395 nm, and 467 nm. The former, which was a broad spectrum ranging from 220 nm to 360 nm, is attributed to an excitation signal generated by the charge-transfer transition between Eu^{3+} and O^{2-} . The latter is attributed to an excitation signal generated by the charge transfer of ${}^7F_0 \rightarrow {}^5L_7$, ${}^7F_0 \rightarrow {}^5L_6$, and ${}^7F_0 \rightarrow {}^5D_2$ or the transition from the ground state of 7F_0 to the charge-transfer state. As shown above, with the variation in the molar ratio of Eu^{3+} from 0.03 to 0.2 mol, the maximum excitation signal from the charge-transfer transition appeared at 309 nm, and the intensity of the excitation signal gradually increased with the molar ratio of Eu^{3+} . Fig. 9 shows the emission spectrum of $Y_{1-x}VO_4 : Eu_x^{3+}$ phosphor excited at 309 nm with the molar ratio of Eu^{3+} (0.03–0.2 mol). With the increase in the molar ratio of Eu ions, the emission intensity increased, with the maximum emission intensity

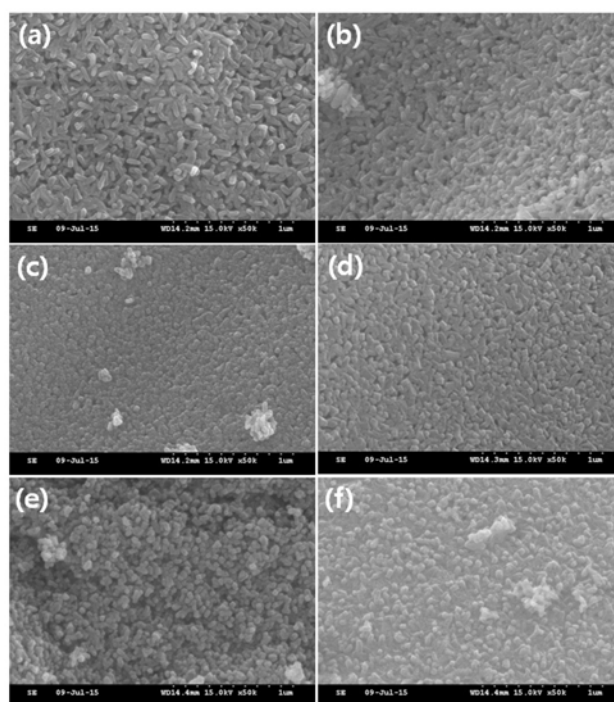


Fig. 7. FE-SEM images of $Y_{1-x}VO_4 : Eu_x^{3+}$ phosphors calcinated at 700 °C for by 0.03, 0.05, 0.07, (d) 0.10, (e) 0.15, and (f) 0.20 mole of Eu concentrations.

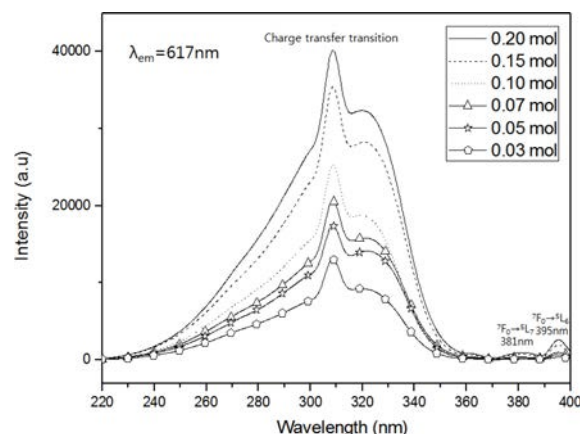


Fig. 8. The excitation spectra of $Y_{1-x}VO_4 : Eu_x^{3+}$ doped with various concentration of Eu_x^{3+} ion calcined at 700 °C in air for 3 hrs ($\lambda_{em} = 617$ nm).

observed at a molar ratio of 0.2 mol. All phosphor samples exhibited emission spectra, exhibiting peaks with weak emission intensities at 594 nm, 651 nm, and 699 nm. The peak at 594 nm is attributed to the ${}^5D_0 \rightarrow {}^7F_j$ ($j = 1$) transition of Eu^{3+} , suggesting that a ${}^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition occurs when $j=1.17-18$). The peak at 651 nm is attributed to the ${}^5D_0 \rightarrow {}^7F_3$ transition, while the weak peak at 699 nm is attributed to the ${}^5D_0 \rightarrow {}^7F_4$ transition [19, 20]. Figs. 10 and 11 show the emission and excitation spectra of $Y_{1-x}VO_4 : Eu_x^{3+}$ phosphor, respectively, synthesized by fixing the concentration of Eu ions to 0.1 mol and changing the HT temperature for synthesis from 600 to

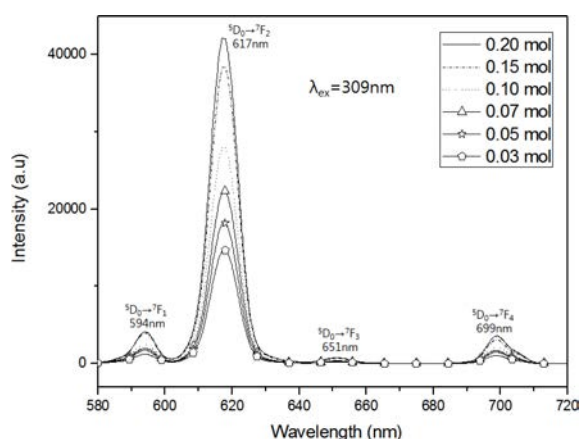


Fig. 9. The emission spectra of $Y_{1-x}VO_4:Eu^{3+}$ doped with various concentration of Eu^{3+} ion calcined at 700 °C in air for 3 hrs ($\lambda_{ex}=309$ nm).

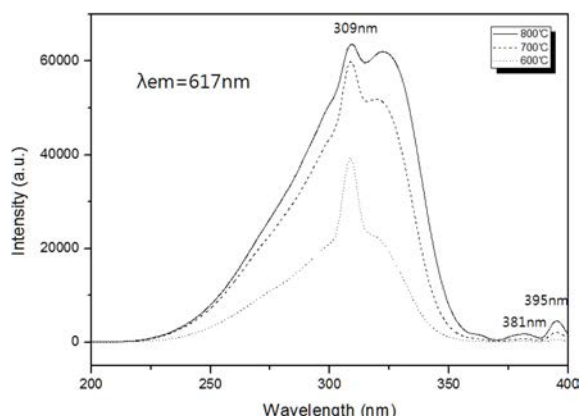
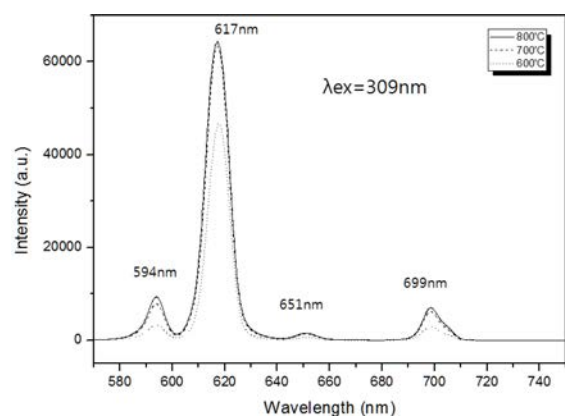


Fig. 10. The emission (a) and excitation (b) spectra of $Y_{1-x}VO_4:Eu^{3+}$ phosphors at various temperatures with the fixed 0.1 mole of Eu ion concentration.

800 °C. As can be observed in the emission curve excited at $\lambda_{ex} = 309$ nm (Fig. 10), with increasing synthesis temperature, the emission intensity increased. An excitation spectrum was measured by the control of the emission wavelength at 617 nm (Fig. 11); it also showed that with the increase in the synthesis temperature, the emission intensity also increased, which was consistent with the results shown in Fig. 10.

Conclusions

In this study, $Y_{1-x}VO_4:Eu^{3+}$ nanoparticles were synthesized by a method that produces ceramic nanoparticles by the impregnation of aqueous metal salt solutions into a polymer matrix under varying conditions. Starch was used as the polymer matrix, and by controlling the HT temperatures and the concentrations of Eu ions being added, optimal conditions for synthesizing $Y_{1-x}VO_4:Eu^{3+}$ nanoparticles were identified. At a temperature ranging from 600 °C to 800 °C, with increasing calcination temperature, crystallization was accelerated, and particle growth (30–200 nm) was observed. As shown, when producing $Y_{1-x}VO_4:Eu^{3+}$ phosphor nanoparticles using the liquid-phase precursor method, HT temperature and time affected crystalline growth and particle size. Moreover, at a temperature ranging from 600 to 800 °C, higher calcination temperature resulted in a higher phosphor emission intensity; when the Eu ion concentration was fixed to 0.2 mol, remarkable emission properties were observed.

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References

1. C.H. Huang, G. Zhang, M. Mei, L.X. Huang, X.J. Huang, H.Y. Shen, Opt. Comm. 224 (2003) 1-4.
2. Q. Mingxin, D.J. Booth, G.W. Baxter, and G.C. Bowkett, Appl. Opt. Vol. 32[12] (1993) 2085-2086.
3. Y. Wang, Y. Zuo, H. GaO, Mat. Res. Bull. 41 (2006) 2147-2153.
4. Y. Liu, H. Xiong, N. Zhang, Z. Leng, R. Li, S. Gan, J. Allo. and Comp. 653 (2015) 126-134.
5. Y.-S. Chang, F.-M. Huang, Y.-Y. Tsai, L.-G. Teoh, J. Lumin. 129 (2009) 1181-1185.
6. A. Huignard, V. Buisette, A.-C. Franville, T. Gacoin, and J.-P. Boilot, J. Phys. Chem. 107[28] (2003) 6754-6759.
7. J.Y. Jang, S.Y. Ahn, J.H. Bang, K.D. Ma, C.S. Kim, S.H. Cho, J. KIEEME 25[4] (2012) 298-303.
8. M.N. Luwang, R.S. Ningthoujam, S.K. Srivastava, R.K. Vasta, J. Mater. Chem. 21 (2011) 5326-5337.
9. V.B. Bhatkar, IJESIT 2[1] (2013) 426-432.
10. Y.M. Moon, S.H. Choi, H.K. Jung and S.H. Lim, Kor. J. Mater. Res. 18 [10] (2008) 511-514.
11. B.A. Miura, N.H. Ferreira, P.F. Oliveria, E.H. de Faria, D.C. Tavares, L.A. Rocha, K.J. Ciuffi, E.J. Nassar, J. Lumin. 159 (2015) 93-99.
12. K. Uematsu, A. Ochiai, K. Toda, M. Sato, J. Allo. and Comp. 408-412 (2006) 860-863.
13. W.J. Park, Y.H. Song, D.H. Yoon., J. Kor. Crys. Gro. and Crys. Tech. 18[4] (2008) 169-173.
14. L. Yanhong, H. Guanyan, J. Solid. Sta. Chem. 178,

- (2005) 645-649.
15. W.M. Yen, S. Shionoya, H. Yamamoto, in "luminescence of rare earth ions", Phorphos handbook, CRC Press, 2007, pp. 192.
 16. M. Yun, W. Zhang, S. Xia, J.C. Krupa, J. Lumin. 68 (1996) 335-339.
 17. J.Y. Jang, S.H. Ahn, J.H. Bang, K.D. Ma, C.H. Kim, S.H. Cho, J. KIEEME. 25[4] (2012) 298-303.
 18. F.W. Kang, Y.H. Hu, H.Y. Wu, G.F. Ju, Chin. Phys. Lett. 28[10] (2011) 4.
 19. B.F. dos Santos Jr., R. Araujo, M.E.G. Valerio, M.V. dos S. Rezende, Solid State Science 42 (2015) 45-51.
 20. Y.Y. Zuo, W.J. Ling, Y.H. Wang, J. Lumin. 132 (2012) 61-63.