Synthesis and luminescent properties of Eu^{3+}-doped YVO_4 by using a mild hydrothermal process

Young-Min Moon[1,2], **Sungho Choi**[1,*], **Sang Ho Lim**[2] **and Ha-Kyun Jung**[1]
[1]Advanced Materials Division, Korea Research Institute of Chemical Technology, P.O. Box 107,
Yuseong, Daejeon 305-600, Republic of Korea
TEL:82-42-860-7372, *e-mail: shchoi@krict.re.kr
[2]Division of Materials Science and Engineering, Korea University, Seoul 136-713,
Republic of Korea

Keywords : Yttrium vanadate, Nanostructures, Hydrothermal synthesis

Abstract

Nanoscale YVO_4:Eu^{3+} phosphor has been synthesized by a mild hydrothermal reaction at various experimental conditions. The particle and luminescent properties of nanophosphors were characterized with X-ray diffraction, electron microscopy and photoluminescence. It has been found that pH value play a key factor both controlling particle size and luminous efficiency.

1. Introduction

Up to date, various synthesis methods have been exploited to prepare nanoscale ceramic compounds, e.g., solid-state reaction, sol-gel and hydrothermal methods, etc [1,2]. The hydrothermal method, which uses autogenous pressure developed at temperatures above the boiling point of solution. The advantage of this process is obtaining phase pure compounds at a relatively lower annealing temperature without milling or calcinations [3]. Phosphors made up of small and controlled shape particles are of interest because they offer the possibility of high definition and much improved screen packing. YVO_4:Eu^{3+} phosphor has prominent characteristics under photo-excited radiation, such as good thermal and color gamut.

In this study, we have synthesized nanosized YVO_4:Eu^{3+} phosphors using the hydrothermal process. Particle size, morphology and luminescent properties under photo excitation were systematically investigated as a function of pH value and reaction time.

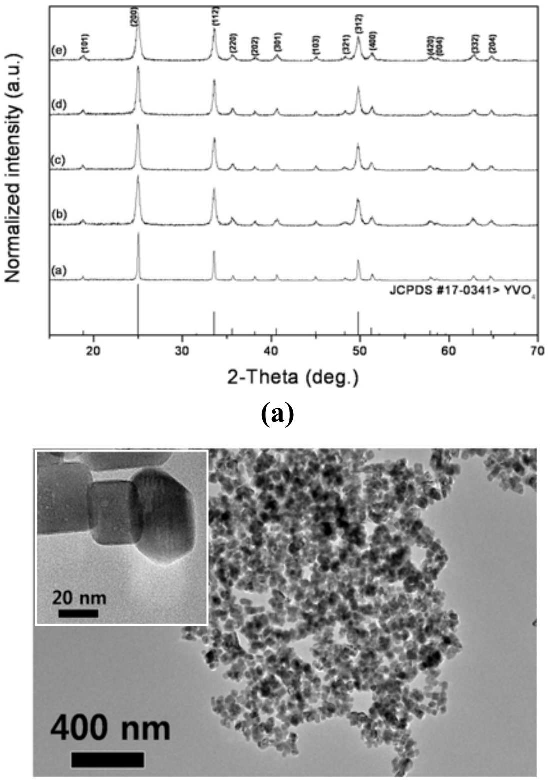
2. Experimental

High-purity of Y_2O_3 (99.99%), V_2O_5 (99.99%) and Eu_2O_3 (99.99%) were taken as the starting materials. Firstly, V_2O_5 was dissolved in diluted nitric acid and then stoichiometic amount of Y_2O_3 and Eu_2O_3 were added to this stock solution. Ammonia solution was added dropwise until the pH of the solution reached 4 – 10. After continuous stirring for 30 min, a given volume (100 mL) of mixture was transferred into a stainless steel autoclave (1 L) and sealed. The solution was heated up to 200℃ for various reaction times, and then cooled to room temperature. The resulting powders were separated by centrifugation, washing with distilled water several times and finally dried at 80 ℃ for 10 h in a vacuum oven.

Crystal phase of these phosphors were investigated by XRD-Rikaku DMAX-33 X-ray diffractometer with Cu Ka (λ=1.5406 Å) radiation. The operation voltage and current were maintained at 40 kV and 40 mA, respectively. The emission spectra of the product were measured using a luminescence spectrometer at room temperature with a xenon lamp as an excitation source. All the measurements were recorded at room temperature. Finally, the temperature quenching was also measured both at room temperature and 5 K under excitation using He-Cd laser (325 nm).

3. Results and discussion

XRD patterns of hydrothermally grown YVO_4:Eu^{3+} samples under various pH conditions are presented in Fig. 1 (a). All diffraction patterns are well matched with the tetragonal YVO_4 phase (JCPDS 17-0341). Representative TEM image (pH=7) is also shown in Fig. 1 (b). One can see that the hydrothermally grown YVO_4:Eu^{3+} were polygonal shape and their mean diameter was ca. 25 nm which is similar to estimated values from XRD pattern using the Scherrer formula.



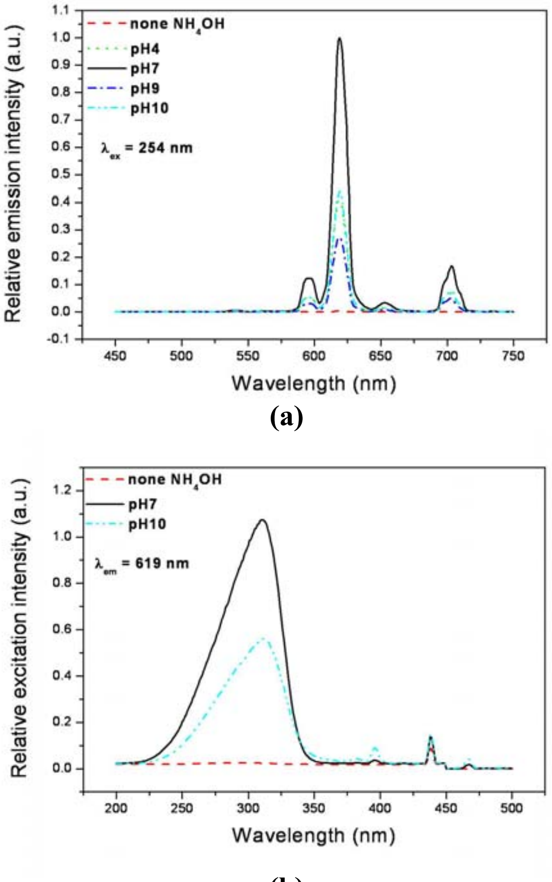
(a)

(b)

Fig. 1. (a) XRD patterns of hydrothermally prepared $YVO_4:Eu^{3+}$ with various pH values. (b) TEM image of $YVO_4:Eu^{3+}$ (with pH =7).

Fig. 2 represents the excitation and emission spectra of nanosized $YVO_4:Eu^{3+}$ phosphors. Like as a well-known behavior of Eu^{3+} ions located in a non-inversion symmetry site, the hypersensitive $^5D_0 \rightarrow {}^7F_2$ electronic dipole transition centered at 619 nm and other magnetic dipole transition peaks, $^5D_0 \rightarrow {}^7F_J$, are also illustrated. The emission intensity becomes stronger with the pH values increased up to 7 and then gradually decreased. This phenomenon might be related to the hydroxyl quenching effect, which induced by surface bound OH^- groups. The hydroxyl quenching effect on the luminescence of rare-earth ions has been investigated quite systematically at earlier works [4,5]. This is explained by a non-radiative energy transfer from the coupling of the $^5D_0$ states of the Eu^{3+} ions to the O-H vibration states [6].

Fig. 2 (b) shows the excitation spectra with the various pH values. The broad band centered at 312 nm could be induced by two different luminescence processes; (1) attributed to the charge transfer from the oxygen ligands to the central vanadium atom inside the VO_4^{3-} groups and (2) assigned to the charge transfer transition between Eu^{3+} and O^{2-}, that is an electron transfers from O^{2-} ($2p^6$) orbital to the empty orbital of $4f^6$ for Eu^{3+} [7,8]. Like as the emission behavior under different pH values, the optimized medium condition is essential to form a highly luminescent nanophosphors. When the solution was in strong acidity (none NH_4OH), broad band not observed at the around 312 nm due to vanadium ions existed as VO^{2+} [9].

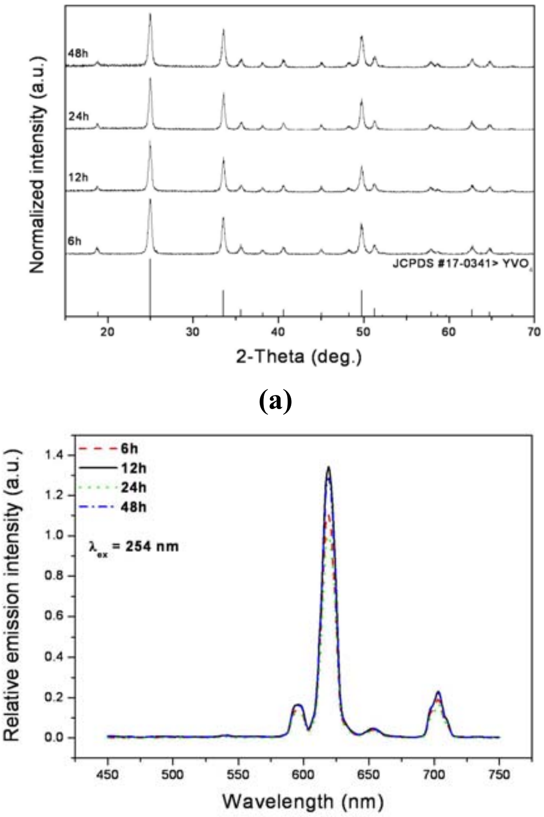


(a)

(b)

Fig. 2. (a) Emission and (b) excitation spectra of hydrothermally prepared $YVO_4:Eu^{3+}$ with various pH values.

Fig. 3 shows the XRD patterns and PL spectra of $YVO_4:Eu^{3+}$ phosphors with various reaction time. All samples were prepared at a fixed pH value (= 7), in which the highest emission intensity under photoexcitation like as Fig. 2. Based on these results, all prepared samples are tetragonal phase with similar luminous efficiency irrespective of reaction time.



(a)

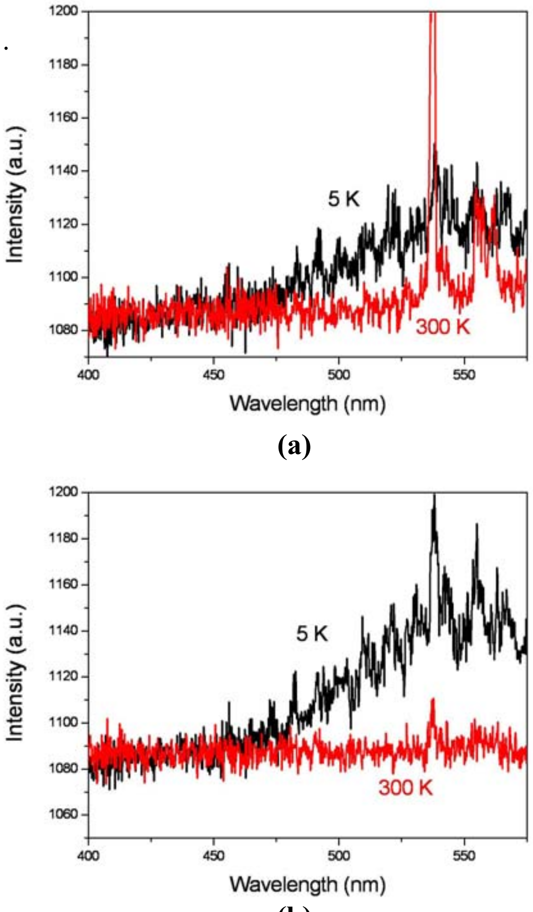
(b)

Fig. 3. (a) XRD patterns and (b) emission spectra of hydrothermally prepared $YVO_4:Eu^{3+}$ with various reaction time.

Based on crystalline size and emission intensity, the overall luminescent property is closely related to the pH value than process time. These results indicate that a justified pH range is a key parameter to acquire the “emissive stable” phosphor, which control the individual competing reaction steps; formation of VO_4^{3-} and surface bonded hydroxyl groups acting non-radiative emission sites.

Finally, we have investigated the thermal quenching effect on nanosized $YVO_4:Eu^{3+}$ phosphors. In general, the host sensitized energy transfer in rare-earth activated phosphors is known to be a thermally activated process and, with a rate sufficiently high, occurs between nearest neighbors only [10]. YVO_4 does not show luminescence at room temperature but illuminates a blue emission centered at 420 nm below 200 K.

Fig. 4 presents temperature dependent emission spectra of $YVO_4:Eu^{3+}$ phosphors. These results indicate that the proper pH value is essential to get thermodynamically and optically stable nanophosphors with both minimized surface hydroxyl groups and highly efficient luminescence process.



(a)

(b)

Fig. 4. Emission spectra of $YVO_4:Eu^{3+}$ at 5 and 300 K with different pH value, (a) pH=7 and (b) pH=10. (λ_{ex} = 325 nm)

4. Summary

Nanoscale Eu^{3+}-doped YVO_4 has been readily synthesized by a mild hydrothermal process and it has been found that pH value play a key factor both controlling particle size and luminous efficiency. That is, even if a phase pure YVO_4 can be obtained over a wide pH range, the highly luminescent nanophosphors are only achievable at pH = 7.

As a result, Eu^{3+}-doped YVO_4 nanophosphors prepared at optimized pH condition constrain both the hydroxyl quenching and the self-activated host emission, which leads to highly efficient red emission of luminescent center.

5. References

1. M. Yu, J. Lin, Z. Wang, J. Fu, S. Wang, H. J. Zhang, Y. C. Han, *Chem. Mater.,* **14**, 2224 (1988).
2. H. Zhang, X. Fu, S. Niu, G. Sun, Q. Xin, *J. Solid State Chem.,* **177**, 2649 (2004).
3. W. J. Dawson, *Am. Ceram. Soc. Bull.,* **67**, 1673 (1988).
4. N. E. Alekseev, V. P. Gapontsev, Yu. G. Anikiev, M. E. Zhabotinskii, V. B. Kravchenko, Yu. P. Rudnitskii, in Progress in Science and Technology (Radio Engineering Series), VINITI, Moscow, Vol. **18**, (1978).
5. T. Moon, S. T. Hwang, D. R. Jung, D. Son, C. Kim, J. Kim, M. Kang, B. Park, *J. Phys. Chem.,* **111**, 4164 (2007).
6. R. Schmechel, M. Kennedy, H. von Seggern, H. Winkler, M. Kolbe, R. Fischer, L. Xaomao, A. Benker, M. Winterer, H. Hahn, *J. Appl. Phys.*, **89**, 1679 (2001).
7. A. Huignard, T. Gacoin, J. P. Boilot. *Chem. Mater.,* **12**, 1090 (2000).
8. Y. H. Wang, U. Kyota, H. Takizawa, *J. Electrochem. Soc.,* **148**, 430 (2001).
9. R. C. Ropp, B. Carroll, *J. Inorg. Nucl. Chem.,* **39**, 1303 (1977).
10. C. Hsu, R. C. Powell, *J. lumin.,* **10**, 273 (1975).