J Electroceram (2007) 18:67–71
DOI 10.1007/s10832-007-9009-6

Effect of synthetic conditions on particle size and photoluminescence properties of Y_2O_3:Eu^{3+} nanophosphor

Sung-Jei Hong · Jeong-In Han

Received: 27 June 2005 / Accepted: 8 November 2006 / Published online: 28 February 2007

Abstract In this paper, effect of synthetic conditions on the particle size, crystal structure, and the photoluminescence properties of the Y_2O_3:Eu^{3+} nanophosphor was investigated. Solvent and dispersing agent were determined as the synthetic parameters. The nanophosphor synthesized from methanol solvent showed the smaller particle size of 4 nm. The XRD analysis indicates that the crystal structure of the Y_2O_3:Eu^{3+} nanophosphor is mainly cubic crystal with orientation of (222), (440), (400), and small peak of (511) indicating monoclinic crystal. The Y_2O_3:Eu^{3+} nanophosphor synthesized by using methanol solvent and 0.1 wt.% hydroxypropyl cellulose (HPC) as a dispersing agent showed higher degree of crystallization of 10.5 of $I_{(222)}/I_{(511)}$ ratio than that without HPC. Also, the photoluminescence properties of the nanophosphor showed red color that excitation and emission wavelengths of the nanophosphor were 250 and 611 nm, respectively. Using the 250 nm UV source, the highly intensive photoluminescence peak could be achieved at 611 nm under the synthetic condition of methanol solvent adding 0.1 wt.% HPC.

Keywords Nanophosphor · Synthetic condition · Y_2O_3:Eu^{3+} · Photoluminescence

1 Introduction

A nanophosphor has advantages to enhance the on/off rate by efficiently controlling the recombination behavior between electrons and holes. The phenomenon is due to discontinuous energy levels restricting electron transfer, and the restricted electron transfer affects the recombination rate of the activated ions. Two reasons for the change of electronic states in the ultrafine particles are reported in the literature [1, 2]. One reason is the particle size effect, which is a consequence of the strong reduction of allowed states in a small particle resulting in an increase of band gap [3]. The second reason is a much larger surface/volume ratio, which makes surface and interface effects dominant over volume effects. The literature reports that optical properties of cubic Y_2O_3:Eu^{3+} nanophosphor concentrate solely on the quantum size effect that occurs in particles having a nano-dimensional size. Therefore, from the nanophosphor, we can achieve advanced optical properties, owing to quantum size and surface effects originating from enlarging the band gap and widening the surface area with respect to volume of the bulk particles, respectively. However, particle size and crystal structure of the nanophosphor are strongly influenced by synthetic conditions [4, 5]. That is, solvent dissolving and mixing the raw materials of yttrium and europium organic compound affects the distribution of Y^{2+} and Eu^{3+} ion in the liquid state, and it determines the synthesized particle size. Also, the dispersing agent affects the distance between the Y-Eu cores by surrounding the cluster during synthesis. If the synthetic condition does not coincide with the uniform dispersion, it gives rise to an agglomeration of the primary particles. The agglomeration leads to a reduction of the surface area of the nanoparticles, and the optical properties of the nanophosphor come to be degraded. So, in this paper, we investigated the optimal condition to minimize the particle size, to optimize the crystal structure, and to enhance the photoluminescence properties by controlling the synthetic conditions of solvent and dispersing agent.

S.-J. Hong · J.-I. Han (✉)
Information Display Research Center, Korea Electronics Technology Institute,
#68, Yatap-dong, Bungdang-gu,
Seongnam-si, Gyeonggi-do 463-816, South Korea
e-mail: hanji@keti.re.kr

2 Experimental

As the solvent, distilled water and methanol were used. As a dispersing agent, 0.1 wt.% hydroxypropyl cellulose (HPC) was added into the methanol solvent. The nanophosphor was designed and synthesized as 10 wt.% Eu activator, which is optimal concentration [6], is doped into the yttrium oxide matrix. Yttrium acetate(99.9%) and europium acetate(99.9%) were dissolved into each of the two solvents, and the same solutions were mixed together, respectively. Then, the solvent was evaporated out of the mixed solution and the remained solute was dried in oven to make precursor. Finally, the precursor was heat-treated at 500 °C. The heat-treating temperature was determined after analyzing thermal behavior of yttrium acetate and europium acetate. Eu concentration in Y_2O_3 matrix was analyzed by energy-dispersion spectrometer (EDS). Particle size and crystal structure of the synthesized nanophosphor were analyzed with X-ray diffractometer (XRD, Rigaku Rotaflex D/MAX System) with monochromatic Cu Kα radiation (λ=0.1505 nm). 2θ range of the X-ray diffraction is from 20° to 80°, and the peak was detected in the order of 0.01°. In this paper, the degree of crystallization of the nanophosphor is defined as ratio of $I_{(222)}/I_{(511)}$. The $I_{(222)}$ and $I_{(511)}$ are the intensity of the X-ray peak at (222) and (511) direction, respectively. The well crystallized Y_2O_3:Eu^{3+} crystal has preferred orientation of (222) direction indicating the cubic structure, and the higher intensity ratio of (222) to that of (511) indicating monoclinic structure means the better crystallization to (222) direction. Also, photoluminescence (PL) properties were characterized at room temperature by exciting samples with a Xe lamp in combination with an interference filter. The wavelength range of the measurements was from 200 to 800 nm with the excitation wavelength of 254 nm.

3 Results and discussion

3.1 Effect of solvent on Y_2O_3:Eu^{3+} nanophosphor

The EDS analysis of Eu concentration in Y_2O_3 is shown in Table 1. The methanol solvent was used to this sample. The analysis certifies that 10 wt.% Eu is doped into Y_2O_3 matrix with a slight deviation. This is attributed to a uniform dispersion of Y^{2+} and Eu^{3+} ions in the liquid state solvent. So, the precursors were made using water and methanol solvent, respectively. In order to determine the heat-treating temperature, thermal behaviors of the two types of the precursors using water and methanol solvent were analyzed. The TG-DTA graphs of the two precursors are shown in Fig. 1. The similar behaviors are observed in the precursors using the two solvents. That is, weight loss and exo-thermic reactions are observed below 400 °C. It means that thermal decomposition occurs and organic component is burnt out at the temperature. However, as shown in Fig. 1a, the precursor using methanol solvent show somewhat more weight loss than that using water solvent. It is owing to the difference in organic amounts. That is, using the methanol solvent, the more amounts of the organic compounds generate the larger weight loss. The FT-IR analysis supports the phenomena as seen in Fig. 2. The two types of the precursors has similar organic structure, but the peak of the precursor using methane solvent is slightly more intensive than that using water solvent. This phenomenon is supposed to originate from the

Table 1 EDS analysis of Y_2O_3:Eu^{3+} nanophosphors.

	(Unit : wt.%)		
	Y	Eu	O
Position 1	53.8	9.7	36.5
Position 2	58.1	10.5	31.4
Position 3	57.3	10.2	32.5

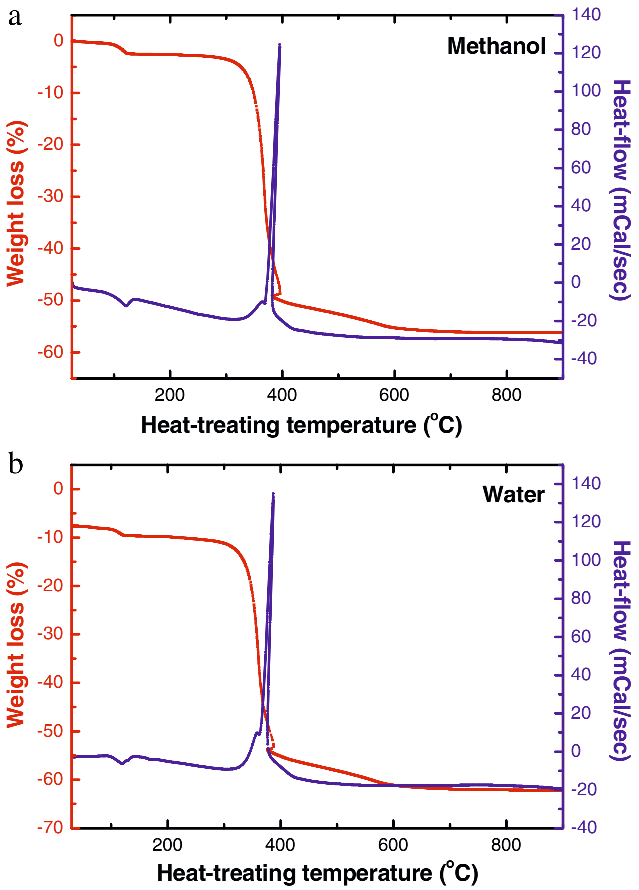

Fig. 1 Thermal behavior of Y_2O_3:Eu^{3+} nanophosphors according to solvents

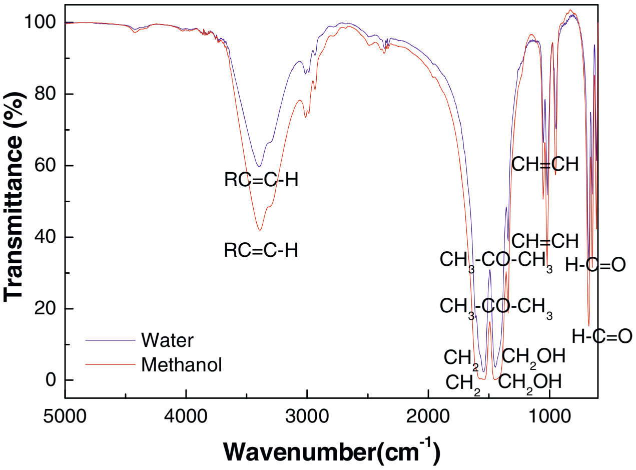

Fig. 2 FT-IR analysis of Y_2O_3:Eu^{3+} nanophosphors according to solvent

methanol solvent containing higher concentration of organic compounds. That is, water has only H^+ and OH^- ion, but methanol has complex of C, H, and O like C=C–H, CH_2–CO–CH_3, CH_2OH, CH=CH, etc. So, the distance between the Y-Eu core in the precursor using methanol solvent is more larger than that using water solvent. From the results, it is predicted that particle size using methanol is slightly small when the two precursors are heat-treated at the same temperature. So, the two precursors were heat-treated at 500 °C for 1 h. The heat-treating temperature was determined from the thermal analysis shown in Fig. 1. After that, XRD analysis was done to investigate the particle size and the crystal structure. From the X-ray peak, the particle size was calculated by using by Schrerrer's equation, $D = K \cdot \lambda / \beta \cdot \cos\theta$ where D, K, λ, β, and θ are mean particle size, constant, wavelength of the X-ray source, breath at half-maximum intensity, and Bragg angle of (222) plane in the diffraction pattern, respectively. Assuming that the morphology is round type particle, the K value is 0.9, and the calculated particle size of nanophosphors using methanol and water solvent are 4 and 6 nm, respectively. The particle size is slightly different, and it is coincident with the prediction. As well, the detected main peak is (222), (440), (400) with (222) preferred orientation indicating that the crystal is of cubic structure. The crystal structure according to

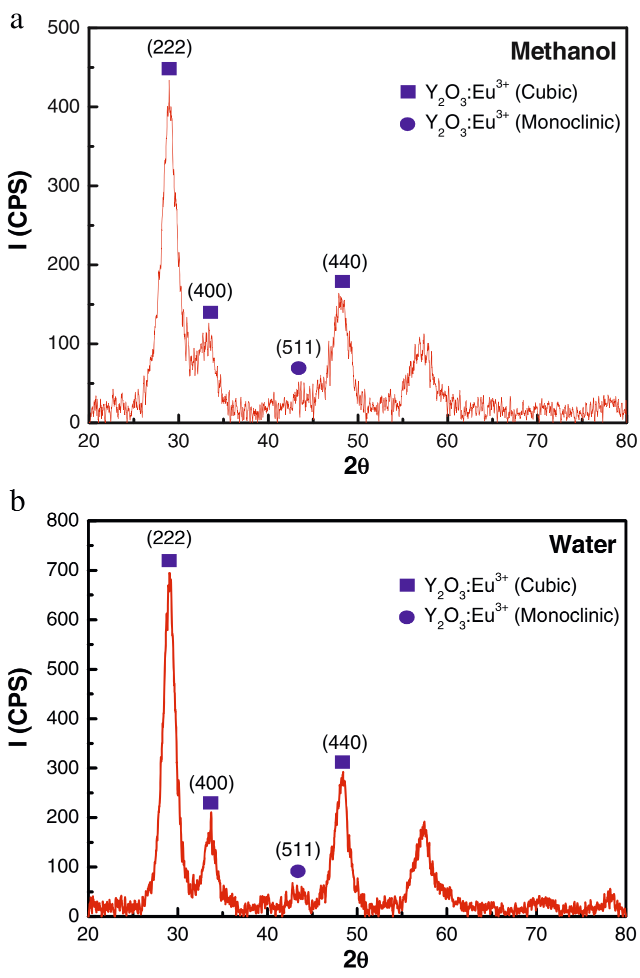

Fig. 3 X-ray diffraction pattern of Y_2O_3:Eu^{3+} nanophosphors according to solvents

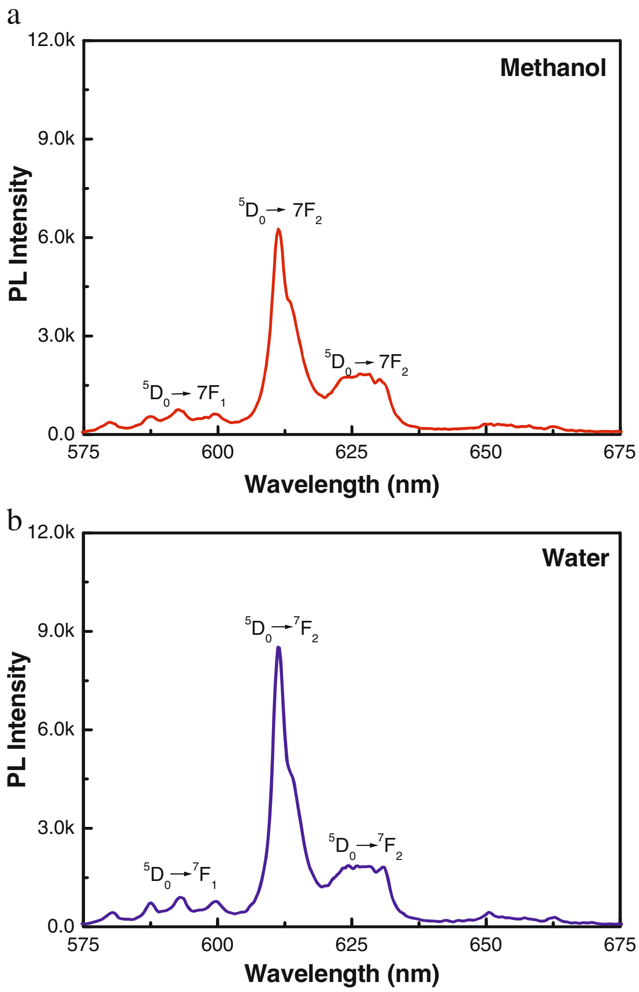

Fig. 4 Photoluminescence emission spectra of Y_2O_3:Eu^{3+} nanophosphors according to solvent (Excitation: 254 nm)

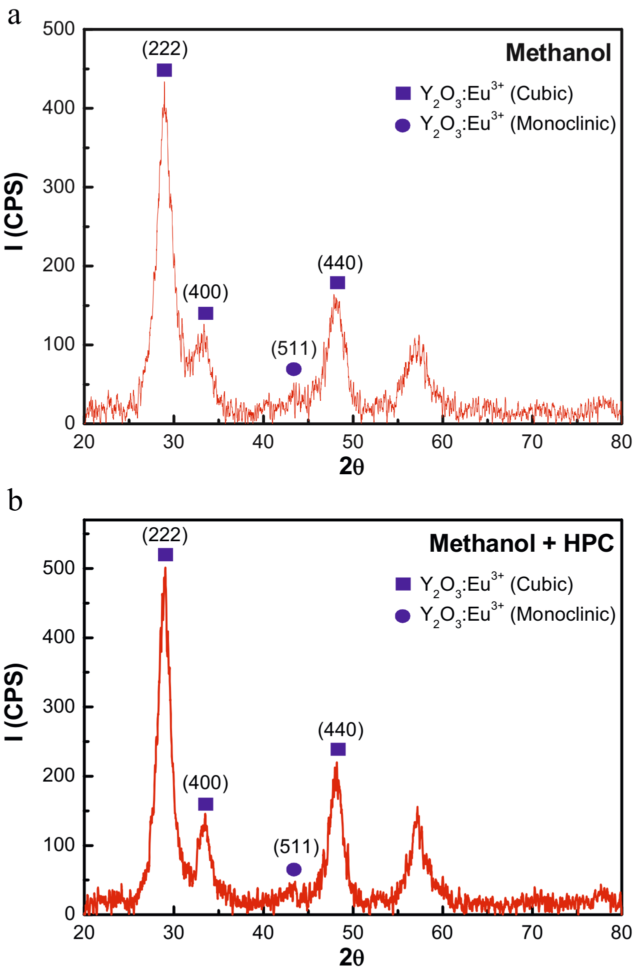

Fig. 5 X-ray diffraction pattern of Y_2O_3:Eu^{3+} nanophosphors according to dispersing agent

the detected X-ray peak is coincident with that of Y_2O_3:Eu^{3+} [7] (Fig. 3). A small peak (511) indicates that the crystal is of monoclinic structure. The monoclinic Y_2O_3 crystal is reported to have a lower solubility limit, compared to the cubic one [8]. In the case of doping Eu^{3+} into the monoclinic Y_2O_3 at more than 0.7%, a new crystal structure of Eu_2O_3 is precipitated and, as a result, two crystal structures co-exist together. The cubic structure is expected to show photoluminescence emission properties at 611 nm, and a nanophosphor including monoclinic structure is different, showing photoluminescence emission properties at 628 nm as well as at 611 nm [8]. In the XRD pattern, the Eu^{3+} ion was not detected. We suppose that this is due to the low concentration and uniform distribution as a nanocrystal. Also, in order to compare the difference of crystallization by the solvent, ratio of $I_{(222)}/I_{(511)}$ were analyzed. The ratio of nanophosphor using methanol and water shows 8.2 and 10.5, respectively. That is, the nanophosphor using methanol is slightly less crystallized. It is supposed that the heat energy delivered to the precursor using methanol solvent is lower than that using water solvent because the concentration of the organic compound of the methanol is higher. From those results, the photoluminescence emission properties of the nanophosphor using methanol solvent is expected to be inferior to that using water solvent. In fact, as shown in Fig. 4a and b, the nanophosphor using methanol solvent shows the less intensive photoluminescence emission spectra compared to that using water solvent. The both main peak is found at 611 nm, indicating the typical photoluminescence properties of Y_2O_3:Eu^{3+} phosphor. The photoluminescence properties found at 611 nm are due to the cubic structure of the synthesized nanophosphors. That is, the externally forced energy transfers the electron of the 2P oxide electronic state in the Y_2O_3 lattice to the $^5D_0$ state in Eu^{3+}, and red light is emitted by the photon generated from the $^5D_0 \rightarrow {}^7F_2$ transfer in the Eu^{3+} [8–10]. The secondary photoluminescence emission properties are seen at 628 nm. As expected, this originates from the monoclinic structure of the nanophosphors [11]. So, the expectation is

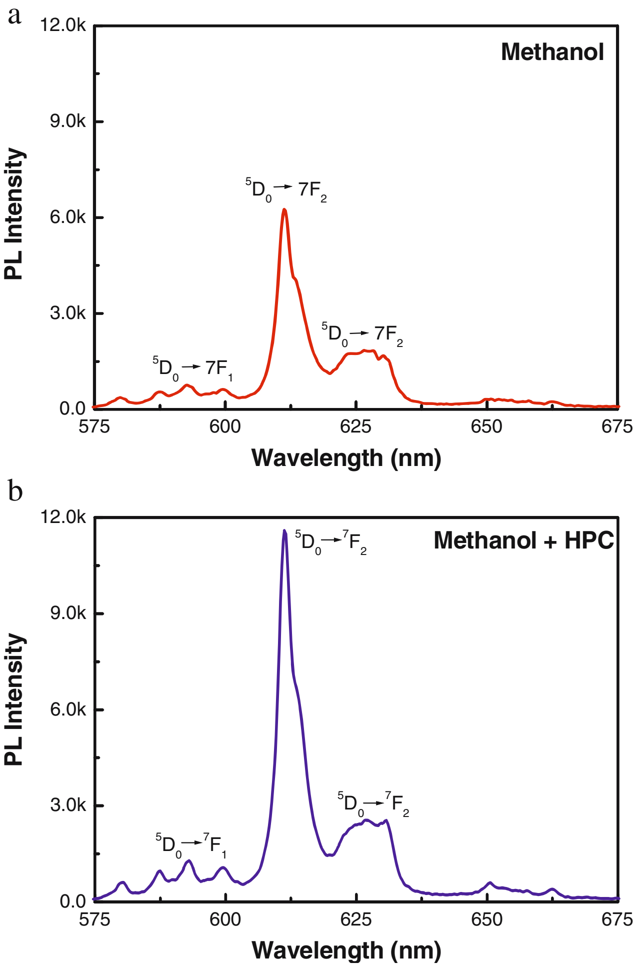

Fig. 6 Photoluminescence emission spectra of Y_2O_3:Eu^{3+} nanophosphors according to dispersing agent (Excitation: 254 nm)

coincident with the result, and the crystallization of the nanophosphor using methanol solvent should be improved.

3.2 Effect of dispersing agent on Y_2O_3:Eu^{3+} nanophosphor

So, hydroxypropyl cellulose (HPC) was added to the methanol solvent as a dispersing agent. The role of the HPC is to weaken the organic bond in the methanol and to enhance the crystallization at the same heat-treating temperature. The concentration of HPC was set to 0.1 wt.% known as optimal point. After adding, the nanophosphor was synthesized following the same process. As a result, shown in Fig. 5, the crystallization was enhanced. That is, the ratio of $I_{(222)}/I_{(511)}$ of the nanophosphor using methanol solvent was increased to from 8.2 to 10.5 by adding the dispersing agent. The particle size calculated from the Schrerrer's equation is 4 nm, and ultrafine size is kept well. So, the HPC is effective to enhance the crystallization of the nanophosphor maintaining the particle size. From those results, the photoluminescence emission properties of the nanophosphor using HPC added methanol solvent is expected to be superior to that using pure methanol solvent. In fact, as shown in Fig. 6(a) and (b), the nanophosphor using HPC added methanol solvent shows two times intense photoluminescence emission spectra compared to that using pure methanol solvent. The photoluminescence peak is more intensive than that using the water solvent as seen in Fig. 4b. It is owing to the particle size. That is, the photoluminescence emission properties of the smaller sized nanophosphor with the same degree of the crystallization are enhanced. The decay time of the nanophosphor was measured as 2.4 ms, and the research to shorten the decay time is being continued. So, the highly crystallized nanophosphor with ultrafine particle size could be achieved and the photoluminescence properties could be enhanced by optimizing the synthetic conditions in this paper.

4 Conclusion

In this paper, to enhance the photoluminescence properties of the Y_2O_3:Eu^{3+} nanophosphor, effect of synthetic conditions on the physical properties such as particle size and crystal structure, and the photoluminescence properties of the Y_2O_3:Eu^{3+} nanophosphor was investigated. As a result, the Y_2O_3:Eu^{3+} nanophosphor synthesized using 0.1 wt.% HPC added methanol solvent showed ultrafine size of 4 nm and high degree of crystallization of 10.5 of $I_{(222)}/I_{(511)}$ ratio. Also, using the 250 nm UV source, the highest intensive photoluminescence peak could be achieved at 611 nm under the synthetic condition of methanol solvent adding 0.1 wt.% HPC in this paper.

References

1. R. Schmechel, H. Winkler, L. Xaomao, M. Kennedy, M. Kolbe, A. Benker, M. Winterer, R.A. Fischer, H. Hahn, H. von Seggern, Scr. Mater. **44**, 1213 (2001)
2. D. Dosev, B. Guo, I.M. Kennedy, J. Aerosol Sci. **37**, 402 (2006)
3. K. Oshima, J. Korean Phys. Soc. **43**(5), 661 (2003)
4. Y. Sun, L. Qi, M. Lee, B.I. Lee, W.D. Samuels, G.J. Exarhos, J. Lumin. **109**, 85 (2004)
5. S.J. Hong, M.G. Kwak, J.I. Han, J. Korean Phys. Soc. **45**, 721 (2004)
6. H.J. Shin, M.K. Lee, C.C. Hwang, K.J. Kim, T.H. Kang, B. Kimy, G.B. Kim, C.K. Hong, K.W. Lee, Y.Y. Kim, J. Korean Phys. Soc. **42**, 808 (2003)
7. S.J. Hong, J.I. Han, H.J. Kim, H.K. Chang, C. Kim, Proc. Pac. Rim **2002**, 187 (2002)
8. J. McKittrick, C.F. Bacalski, G.A. Hirata, K.M. Hubbard, S.G. Pattillo, K.V. Salaza, M. Trkula, J. Am. Ceram. Soc. **83**(5), 1241 (2000)
9. R.N. Bhargava, J. Cryst. Growth **214~215**, 926 (2000)
10. M. Abdullah, C. Panatarani, T.-O. Kim, K. Okuyama, J. All. Comp. **377**, 298 (2004)
11. R. Bazzi, M.A. Flores, C. Louis, K. Lebbou, W. Zhang, C. Dujardin, S. Roux, B. Mercier, G. Ledoux, E. Bernstein, P. Perriat, O. Tillement, J. Col. Int. Sci. **273**, 191 (2004)