

EFFECT OF SINTERING TEMPERATURE ON PHOTOLUMINESCENCE OF $Y_2O_3:Tb^{3+}$ PHOSPHORS PREPARED BY LIQUID-PHASE REACTION METHOD

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Introduction

The increased demand for activator(Eu^{3+}, Tb^{3+}) doped rare-earth oxides with particle diameters less than 100 nm in display such as high definition, projection televisions and flat panel displays, has fueled the synthesis, development and introduction of efficient and inexpensive phosphors with enhanced photoluminescence(PL) properties [1]. Among synthesis methods such as precipitation, sol-gel, gas-phase condensation and spray pyrolysis, a liquid-phase reaction method(LPRM) was employed to enhance the activator doping amount and to control the particle size because smaller phosphors less than 100 nm can be obtained even at sintering temperature of 1000°C [1,2]. The LPRM was applied by using yttrium(III) acetate hydrate($C_6H_9YO_6 \cdot xH_2O$) as a precursor for the host lattice and terbium(III) acetate hydrate ($C_6H_9TbO_6 \cdot xH_2O$) for the activator, by maintaining the activation temperature as low as 350~500°C for the synthesis of efficient and inexpensive activator-doped $Y_2O_3:Tb^{3+}$ nanoparticles. Then, the luminescence and delay time of the phosphors were investigated.

Experimental

The apparatus used was a rotary evaporator(N-1000, Eyela, Japan). A Y_2O_3 precursor and an activator from Aldrich, yttrium(III) acetate hydrate($C_6H_9YO_6 \cdot xH_2O$) and terbium(III) acetate hydrate($C_6H_9TbO_6 \cdot xH_2O$), were dissolved in methanol at room temperature. An organic solvent comprising of diethylene glycol monoethyl ether acetate(DGMA, 99%, Aldrich) and diethylene glycol monoethyl ether(DGME, 99%, Aldrich) in 1:1 volume ratio was prepared by stirring for 30 min at 60°C using a hot plate to control the amount of the activator and the phosphor particle size. The process is described in detail elsewhere [1]. The Y_2O_3 was doped with 8 wt.% Tb. Finally, the $Y_2O_3:Tb^{3+}$ phosphor was synthesized by a two-step sintering for 1 h at temperatures from 350°C to 500°C in air and sintering for 1 h at 400°C in CO atmosphere.

X-ray diffraction(XRD, DMAX-III A, Rigaku, Japan) was performed using a Cu $K\alpha$ target in the range of 20-80° to determine the existing phase and particle size. Microstructure and specific surface area of phosphor

particles were examined by a transmission electron microscopy(TEM) and a BET(ASAP 2010, Micromeritics, UK). Photoluminescence(PL) properties were examined by a spectrometer(FS900CDT, Edinbergh Analytical Inc., UK) using an Xe lamp excitation source

Results and Discussion

XRD results of $Y_2O_3:Tb^{3+}$ powders are presented as a function of sintering temperature in Fig. 1. The (222), (400), (440) and (622) peaks of cubic Y_2O_3 oxides were observed. The broad peak indicates that particle size is small. The specific surface area and particle size were analyzed by using a multipoint BET surface area analyzer and an XRD width, respectively, as listed in Table 1. Interestingly, the powders sintered at 500°C exhibit the average particle size of ~10 nm, which is similar to the TEM result in Fig. 2(b).

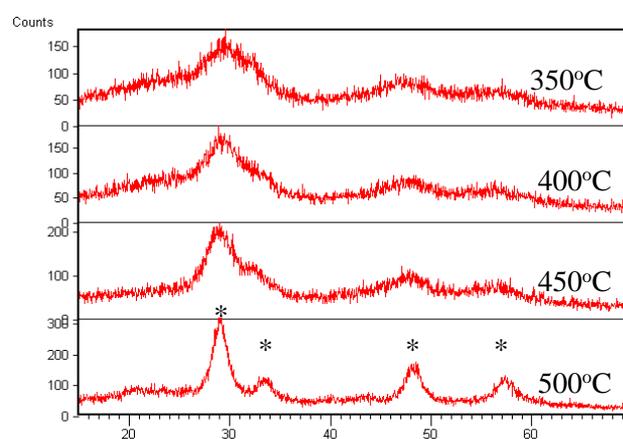


Fig. 1. XRD patterns of $Y_2O_3:Tb^{3+}$ nanocrystals sintered at various temperatures.

Table 1. Specific surface area and particle size of phosphor determined by BET and XRD

| Sintering temperature | Specific surface area (m^2/g) | Particle size (BET) | Particle size (XRD) |
|-----------------------|-----------------------------------|---------------------|---------------------|
| 350 | 70.52 | 8.5 | 5.6 |
| 400 | 48.31 | 12.4 | 4.6 |
| 450 | 76.26 | 7.9 | 3.5 |
| 500 | 64.35 | 9.3 | 5.9 |

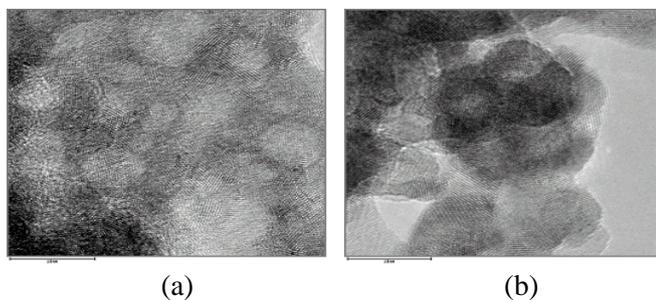


Fig. 2. TEM images of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ phosphors prepared at (a) 400°C and (b) 500°C.

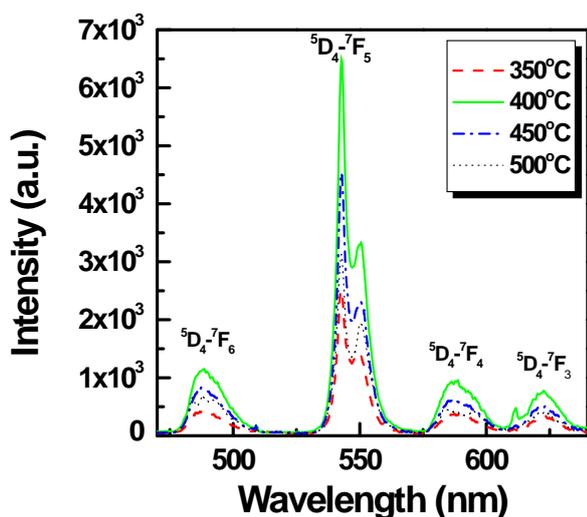


Fig. 3. Emission spectra of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ phosphors sintered at different temperatures, which are excited at 254 nm.

The effect of sintering temperature on the PL intensities of the $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ phosphors are shown in Fig. 3. It is clear that the PL intensity rose initially and then it was reduced gradually when the sintering temperature was above 400°C. The highest PL intensity was observed for the phosphors sintered at 400°C. The main emission peak of the phosphor was 543 nm, which corresponded to a typical $^5\text{D}_4 \rightarrow ^7\text{F}_5$ green emission transition [3]. The emission peaks at 487, 587, and 623 nm in Fig. 3 are characteristics of transitions from $^5\text{D}_4 \rightarrow ^7\text{F}_{j(j=6,4,3)}$, respectively. No $^5\text{D}_3 \rightarrow ^7\text{F}_j$ transition was observed due to higher Tb content [3].

The excitation spectra of phosphors are given in Fig. 4. The large bands at ~250 nm and ~304 nm represent the effects of Tb^{3+} ions (from $4f_7-5d$ bands to $4f_8$) and bulk $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ phosphor, respectively. The transfer mechanism of the excited carriers is found to be a function of sintering temperature. A typical PL property of bulk $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ phosphor is detected when the phosphors are sintered at 500°C.

The luminescence decay time of the phosphor was measured by using a time-resolved fluorometer. No relationship between decay time and sintering temperature was found. The decay time of the phosphors is 2.5 ms regardless of the phosphors prepared under different conditions.

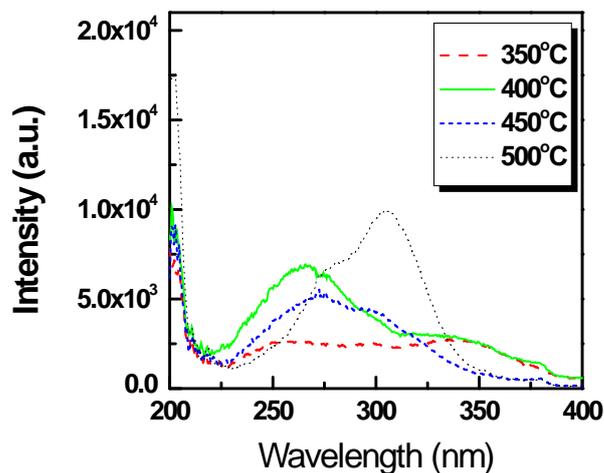


Fig. 4. Excitation spectra of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ phosphors sintered at various temperatures for 543 nm emission.

Conclusion

Terbium-doped $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ nanoparticles prepared at various temperatures from 350°C to 500°C were synthesized by LPRM to investigate the effect of sintering temperature on the optical properties of phosphors by using XRD, TEM, BET, spectrometer and fluorometer. The size of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ powders was in the range of 8-12 nm. The phosphors showed an initial increase in luminescence and then a subsequent decrease with increasing sintering temperature (above 400°C). The decay time (2.5 ms) showed no dependence of sintering temperature. The highest PL intensity was found for the phosphor sintered at 400°C due to $^5\text{D}_4 \rightarrow ^7\text{F}_5$ green emission transition.

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References

1. Park, C., Kwak, M., Choi, S., Song, Y., Hong, S., Han, J., and Lee, D.Y. Influence of Eu^{3+} doping content on photoluminescence of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ phosphors prepared by liquid-phase reaction method. *J. Lumin.*, **118**(2006) 199-204.
2. Goldburt, E.T., Kulkarni, B., Bhargava, R.N., Taylor, J., and Libera, M. Size dependent efficiency in Tb doped Y_2O_3 nanocrystalline phosphor. *J. Lumin.*, **72-74**(1997) 190-192.
3. Guo, P., Zhao, F., Li, G., Liao, F., Tian, S., and Jing, X. Novel phosphors of Eu^{3+} , Tb^{3+} or Bi^{3+} activated Gd_2GeO_5 . *J. Lumin.*, **105**(2003) 61-67.