Crystal Structure and Photoluminescence Properties of Eu-Doped Y_2O_3 Nanoparticles Prepared by Mechanical Milling

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We have used a top-down approach of the mechanical milling to fabricate $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanoparticles (NPs), and then studied their crystal structure and photoluminescence (PL) properties based on X-ray diffraction (XRD), electron paramagnetic resonance (EPR) and PL spectroscopy. XRD results revealed that the change of the milling time (t_m) from 0 to 540 minutes (min) decreased the average crystallite size (d) of NPs from ~ 83 nm (for $t_m = 0$ min) to below 3.5 nm (for $t_m = 540$ min). This varied lattice strain and defects, and caused the structural changes, which influenced directly the PL properties of NPs. Among the fabricated NP samples, those with $t_m = 5$ –10 min (corresponding to $d \approx 25$ –40 nm) offer strongest PL intensity at ~ 611 nm (due to the electronic transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$). The increase of the longer milling time (i.e., lowering d) reduces quickly the intensity of this emission, but slightly increased the intensity of auxiliary emissions. The nature of the observed phenomena was discussed. [doi:10.2320/matertrans.MA201556]

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1. Introduction

Y_2O_3 is a white-solid and air-stable substance, commonly used as an oxide host due to its high melting point ($\sim 2450^\circ\text{C}$), high thermal stability, large band-gap energy (~ 5.8 eV), high refractive index, wide transmission region, and low phonon-vibration frequency.¹⁾ It is considered as an important material for the fabrication of the light emitters when doped with the rare-earth elements.^{2–6)} Doping a small percentage of Eu^{3+} ions into Y_2O_3 (known as $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor) gives the red emissions with long-term stability, which have been widely applied to the display panels (CRTs, flat televisions and field-emission display), lighting lamps (fluorescent and mercury-free lamps), medical imaging, and many other modern optoelectronic devices.^{1–3)} It can additionally be doped with other ions (such as Er^{3+} , Yb^{3+} , Ho^{3+} , and Tm^{3+}) into the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ host to improve the lighting efficiency based on the photon upconversion processes.^{1,4)} More recently, Zhang and co-workers³⁾ have found an effective route to control the emission intensity and wavelength of the electronic transitions $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (in the wavelength range 605–640 nm) upon the applying of high pressure. With many outstanding features, Y_2O_3 -based phosphors have attracted much interest of both pure research and application.

The recent works have focused on the fabrication and structure characterization of the nanostructured $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphors as the active materials in the next generation optical and electronic devices.^{1,2,7–10)} These materials are usually synthesized according to a bottom-up approach by using soft-chemical techniques (sol-gel, hydrothermal, chemical precipitation, emulsion, spray pyrolysis and so forth).⁹⁾

After that, the annealing is used to modify their particle size. Another effective approach, known as “top-down” (such as combustion method,^{7,11,12)} and mechanical milling) can also be employed to prepare the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanoparticles (NPs). The earlier studies revealed that the optical properties of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphors strongly depend on the Eu-doping concentration, excitation wavelength, and annealing temperature.^{2,7,10,11,13)} An increase in the annealing temperature usually enhances the emission intensity because of the effects related to the lattice strain, defects and grain boundaries. The latest works, however, almost previous works focused on the issues of sample fabrication and processing conditions in order to achieve the high red-emission intensity in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphors. There is still the lack of knowledge of the influence of lattice strain, defects, and crystal structures on optical properties when the average crystallite size of NPs is decreased. Dealing with these problems, we have prepared $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NPs from a ceramic/bulk sample by using mechanical milling. By changing the milling time (t_m), one would obtain the NPs with various different sizes.

2. Experimental Details

First, an initial sample of Y_2O_3 doped with 5 mol% Eu was prepared by conventional solid-state reaction; the selection of 5 mol% Eu is based on optimized conditions shown in the previous studies (Refs. 7, 10, 11, 13)). The high-purity powders (3N) Y_2O_3 and Eu_2O_3 combined in the nominal stoichiometry were mixed and pre-annealed at 1000°C for 12 h. After the pre-annealing process, the mixture was re-ground, pressed into a pellet, and annealed at 1350°C for 24 h in air. The obtained pellet was then ground into powder and divided into parts for mechanical ball milling (Mixer/Mill 8000D) with milling times $t_m = 5, 10, 20, 30, 60, 120$,

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Fig. 1 XRD patterns of Y₂O₃:Eu³⁺ NPs prepared by mechanical milling with different milling times $t_m = 0$ –540 min.

180, 360 and 540 minutes (denoted hereafter as min); the as-prepared sample is denoted as $t_m = 0$ min. To limit the unexpected impurities, we carried out the milling process in an Ar ambient, and used the grinding medium of zirconia vial and balls supplied by SPEX-SamplePrep. The crystal structure of the obtained products was checked by an X-ray diffractometer (Philips X'Pert) equipped with a Cu- $K_{\alpha 1}$ radiation source ($\lambda = 1.5406 \text{ \AA}$). Electron paramagnetic resonance (EPR) measurements were performed on a JEOL-TE300 spectrometer working at frequency $\nu = 9.45 \text{ GHz}$ (belonging to the X band). PL measurements were performed on a spectrophotometer (V-570 UV/VIS/NIR, Jasco), used an excitation wavelength of 265 nm. All investigations were performed on the samples in powder at room temperature.

3. Results and Discussion

Figure 1 shows the XRD patterns of Y₂O₃:Eu³⁺ NPs prepared by the mechanical milling with $t_m = 0$ –540 min. It appears that the increase of t_m decreases the intensity of XRD peaks. Concurrently, some peaks with low intensity disappear, and are blurred into the background signals. The detailed analyses reveal that the samples with $t_m = 0$ –30 min exhibit the single phase in a cubic structure (space group: $Ia\bar{3}$). With the longer milling times of $t_m > 30$ min, there is a secondary phase with a monoclinic structure (space group: $C2/m$). This tendency is similar to the case of the Y₂O₃:Eu³⁺ phosphor under high pressures.³⁾ Based on XRD data, we calculated the lattice constant (a) and the volume of unit cell (V) for the cubic phase, as shown on Table 1. These parameters increased with increasing t_m from 0 to 180 min. Particularly, an increase of t_m also widened the linewidth of XRD peaks due to the reduction of d , and the enhancement of lattice strain (ε) and defects. Using the Williamson-Hall (W-H) method,¹⁴⁾ we calculated the average values of d and ε from the relation

$$\beta \cos \theta = (K\lambda/d) + 2\varepsilon \sin \theta, \quad (1)$$

Table 1 Experimental parameters obtained from XRD analyses for Y₂O₃:Eu³⁺ NPs prepared by the mechanical milling with $t_m = 0$ –540 min. We could not calculate the parameters of some samples with $t_m \geq 180$ min due to the overlap of many XRD peaks.

t_m (min)	a ($\text{\AA}$)	V ($\text{\AA}^3$)	d (nm)	ε	Crystal phase
0	10.611	1196.4(2)	273.8	0.107	Cubic
5	10.618	1197.0(9)	38.5	0.138	Cubic
10	10.618	1197.0(9)	24.8	0.233	Cubic
20	10.620	1197.7(7)	17.5	0.313	Cubic
30	10.620	1197.7(7)	15.3	0.331	Cubic
60	10.623	1198.7(9)	5.0	0.449	Cubic and monoclinic
120	10.625	1199.4(6)	3.5	0.732	Cubic and monoclinic
180	10.631	1201.5(1)	—	—	Cubic and monoclinic

where the shape factor (K) is about 0.9. The results shown in Table 1 indicate that the increase of t_m from 0 to 540 min reduces d from 82.6 to below 3.5 nm, respectively, while ε increases several times. Notably, we could not calculate the parameters (a , V , d and ε) of the samples $t_m > 180$ min with the cubic structure because of the overlap of XRD peaks and of the mixture of the monoclinic phase.

The reduction of d also increases lattice defects due to a large surface-area-to-volume ratio. To study this problem, EPR spectroscopy was applied. The EPR technique is based on the microwave absorption of unpaired electron spins under the application of magnetic field H . It is a sensitive and useful tool in detecting paramagnetic centers (such as lattice defects and impurities) present in a material.¹⁵⁾ Figure 2 shows the EPR spectra of Y₂O₃:Eu³⁺ NPs with $t_m = 0$ –540 min. One can see that the resonant signals are single lines in the Lorentzian shape. The resonant intensity (Int) increases with increasing t_m , which can be described by a power function $Int \propto t_m^n$, with a non-universal exponent $n = 0.47$. This is ascribed to the enhancement of lattice defects because the Eu-doping concentration in the NPs is unchanged at 5 mol%. For the resonant field (H_r), its position at about 339.3 mT is independent of t_m . If using the equation of resonant condition

$$h\nu = g\mu_B H_r, \quad (2)$$

where g is the Landé splitting factor, and h and μ_B are the Plank constant and Bohr magneton, respectively), we obtained $g = 1.977$ for the samples.¹⁶⁾ In our case, the obtained g value is a little bit smaller than a theoretical value $g_e = 2.0023$ for free electrons. This proves that the resonant signals in Y₂O₃:Eu³⁺ NPs are generated from defects related to holes,¹⁶⁾ which are ascribed to oxygen vacancies (V_O).¹⁷⁾ More V_O defects created by increasing t_m enhance the EPR intensity.

The V_O defects influence directly the PL properties of Y₂O₃:Eu³⁺ NPs. In Fig. 3, PL spectra of the samples with $t_m = 0$ –540 min excited by wavelength 265 nm are shown. In the wavelength range from 560 to 720 nm, the luminescent emissions are generated from the electronic transitions 5D_0 – 7F_J ($J = 0, 1, 2, 3$, and 4) of Eu³⁺ ions, where 5D_0 – 7F_2 , 5D_0 – 7F_4 and 5D_0 – 7F_6 transitions are electric-dipole allowed while 5D_0 – 7F_1 transitions are magnetic-dipole allowed.^{3,9)}

Fig. 2 EPR spectra of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NPs with various milling times of $t_m = 0$ –540 min.

Fig. 3 PL spectra of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NPs with $t_m = 0$ –540 min excited by wavelength 265 nm. Electronic transitions $^5\text{D}_0-^7\text{F}_J$ (with $J = 0, 1, 2, 3$ and 4) of Eu^{3+} ions are also attached, after Refs. 3, 9). The inset shows an enlarged view of the PL-emission region of 603–640 nm for some typical samples.

Among these, the emission peaked at ~ 611 nm due to the $^5\text{D}_0-^7\text{F}_2$ transitions is dominant. Its peak position is stable while the emission intensity varies as a function of t_m . For the emissions in the range 603–640 nm (associated with the $^5\text{D}_0-^7\text{F}_J$ transitions) as changing t_m , one can observe clearly four lines peaked out at about 611, 614, 623 and 630 nm (denoted as P_1 , P_2 , P_3 and P_4 , respectively, as shown representatively in the inset of Fig. 3) because of the splitting $2J + 1$; the other line peaked at ~ 615 nm (Ref. 3)) is invisible, probably since its weak signal is blurred to the background. The spectral features of the emissions P_1 – P_4 are strongly changed when t_m (or d) varies. Here, the emissions P_2 and P_3 could be an indication of the formation of the secondary phase,¹¹⁾ which become more visible when $t_m > 60$ min. In Fig. 4, it shows the dependence of the integration intensity of these PL emissions on d , where d values of NPs with $t_m > 120$ min can be assigned to be smaller than 3.5 nm. It appears that the optimal d values in order to achieve the highest PL emission

Fig. 4 Dependences of the integration intensity of the emissions P_1 – P_4 on the crystalline size d . The d values of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NPs with $t_m > 120$ min can be considered to be smaller than 3.5 nm.

are about 25–40 nm, corresponding to $t_m = 5$ –10 min (notably, milling times shorter than 5 min leads to the inhomogeneity of NPs). Apart from these crystallite sizes, the emission intensity would be reduced. We believe that a strong reduction of the emission intensity as lowering d below 20 nm is related to the appearance of a secondary monoclinic phase. This circumstance is due to the fact that $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor has structural transformations from cubic $\rightarrow$ monoclinic $\rightarrow$ hexagonal. In the cubic structure, its emission intensity is strongest, which rapidly decreases when the monoclinic and hexagonal phases are constituted.³⁾ Additionally, the massive lattice defects present in the NPs could act as the electron traps that re-absorb PL emission generating from the electron transitions of Eu^{3+} ions. Meanwhile, the decrease of PL emission in the as-prepared sample with $d = 82.6$ nm could be due to the agglomeration of NPs that is related to the bulk effect.⁹⁾ These results reflect that if using $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NPs for lighting technology, then a careful study in order to find NPs with suitable sizes is necessary, particularly for NPs prepared from bulk samples upon the mechanical milling, and for NPs prepared by chemical methods accompanied with the heat treatment.

4. Conclusions

We fabricated $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NPs from the bulk sample by using the mechanical milling. By changing t_m , we obtained NPs with d ranging from 273.8 nm (for $t_m = 0$ min) to below 3.5 nm (for $t_m = 540$ min). The samples with the milling times $t_m = 0$ –30 min are single phase in the cubic structure while those with $t_m > 30$ min have the presence of the secondary monoclinic phase. The formation of the secondary phase could lead to the enhancement of lattice strain and defects. Using the EPR technique, we thought the defects present in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NPs to be the oxygen vacancy. Its concentration increases with increasing the milling time t_m (i.e., decreasing d). The changes of crystal structure and defect concentration influenced strongly the features of PL spectra. Detailed analyses of the PL emissions associated with the electronic transitions $^5\text{D}_0 \rightarrow ^7\text{F}_2$ indicated that the samples with $d \approx 25$ –40 nm give the strongest PL intensity.

Apart from these values, the emission intensity is decreased rapidly because of the constitution of the secondary monoclinic phase, lattice defects and/or bulk-related effects.

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REFERENCES

- 1) V. K. Rai, A. Pandey and R. Dey: *J. Appl. Phys.* **113** (2013) 083104.
- 2) Q. Dai, M. E. Foley, C. J. Breshike, A. Lita and G. F. Strouse: *J. Am. Chem. Soc.* **133** (2011) 15475–15486.
- 3) J. Zhang, H. Cui, P. Zhu, C. Ma, X. Wu, H. Zhu, Y. Ma and Q. Cui: *J. Appl. Phys.* **115** (2014) 023502.
- 4) Y. Zhang, D. Geng, X. Li, J. Fan, K. Li, H. Lian, M. Shang and J. Lin: *J. Phys. Chem. C* **118** (2014) 17983–17991.
- 5) S. Tezuka, Y. Sato, T. Komukai, Y. Takatsuka, H. Kato and M. Kakihana: *Appl. Phys. Express* **6** (2013) 072101.
- 6) S. Chandra, F. L. Deepak, J. B. Gruber and D. K. Sardar: *J. Phys. Chem. C* **114** (2010) 874–880.
- 7) Y. P. Fu: *J. Mater. Sci.* **42** (2007) 5165–5169.
- 8) C. H. Lee, K. Y. Jung, J. G. Choi and Y. C. Kang: *Mater. Sci. Eng. B* **116** (2005) 59–63.
- 9) A. V. Murugan, A. K. Viswanath, V. Ravi, B. A. Kakade and V. Saaminathan: *Appl. Phys. Lett.* **89** (2006) 123120.
- 10) L. R. Singh, R. S. Ningthoujam, V. Sudarsan, I. Srivastava, S. D. Singh, G. K. Dey and S. K. Kulshreshtha: *Nanotechnol.* **19** (2008) 055201.
- 11) T. L. Phan, M. H. Phan, N. Vu, T. K. Anh and S. C. Yu: *Phys. Stat. Sol. A* **201** (2004) 2170–2174.
- 12) P. K. Sharma, R. K. Dutta and A. C. Pandey: *Adv. Mat. Lett.* **2** (2011) 285–289.
- 13) V. B. Taxak, S. P. Khatkar, S. D. Han, R. Kumar and M. Kumar: *J. Alloy. Compd.* **469** (2009) 224–228.
- 14) G. K. Williamson and W. H. Hall: *Acta Metall.* **1** (1953) 22.
- 15) C. Kittel: *Introduction to Solid State Physics*, 8th ed., (John Willey & Sons, NJ, 2005).
- 16) M. Ikeya: *New Applications of Electron Spin Resonance*, (World Scientific Publishing, Singapore, 1993).
- 17) T. L. Phan, Y. D. Zhang, D. S. Yang, N. X. Nghia, T. D. Thanh and S. C. Yu: *Appl. Phys. Lett.* **102** (2013) 072408.