Research Article

Luminescent Properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ Nanocrystals Prepared by Molten Salt Synthesis

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A series of red phosphors $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ were prepared by the molten salt method with different surfactants. Their structures, morphologies, and the photoluminescent properties were investigated at room temperature. The particles size of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ can be controlled by adjusting the kinds of surfactants. The phosphor $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ prepared with NP-10 [polyoxyethylene (10) nonyl phenyl ether] shows regular morphology and higher crystallinity, and its average particle size is about 200 nm. Bright red light can be observed by naked eyes from the red phosphor under 254 nm excitation.

1. Introduction

In recent years, luminescent nanocrystals (NCs) doped with rare earth ions were paid more attentions because of their interesting luminescent properties. They can be as components in displays [1], light emitting diodes [2], biological assays [3], and optoelectronic devices [4]. Cubic $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ is one of the most important commercial red phosphors, which can be used in fluorescent lights, cathode ray tubes (CRTS), plasma display panel (PDP), and field emission display (FED) [5–9]. Many methods for synthesis of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor have been reported, including solution combustion method [10], sol-gel method [11], spray pyrolysis method [12], hydrothermal method [13], and precipitation method [14, 15].

Wet chemical methods have been widely developed to prepare the luminescent materials [16–18], since these processes have advantages of good homogeneity through mixing the starting materials at the molecular level in solution, a lower calcination temperature and a shorter heating time. However, sol-gel process often requires expensive (and environmentally unfriendly) organic precursors and solvents. Then a low-temperature technique, molten salt synthesis (MSS), is beginning to attract a great deal of interest. MSS is one of the simplest and most versatile approaches available to obtain single-phase powders at lower temperatures with

shorter reaction times and little residual impurities as compared with conventional solid-state reactions [19]. The ionic fluxes molten salts possess high reactivity toward different inorganic species and relatively low melting points, which is convenient for preparation of inorganic materials. As the reaction medium, the inorganic molten salts exhibit favorable physicochemical properties such as a greater oxidizing potential, and high mass transfer, high thermal conductivity, as well as relatively lower viscosities and densities, as compared to conventional solvents [20]. Furthermore, MSS is one of the most effective ways to prepare nanoscale shape-controlled materials [21–23].

In the present study, a series of red emission phosphors $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ were prepared by MSS with NaCl as the molten salt. Different surfactants such as polyoxyethylene (10) nonyl phenyl ether (NP-10), polyoxyethylene (5) nonyl phenyl ether (NP-5), octyl phenol together ethylene (10) ether oxygen (OP-10), and sodium dodecyl benzene sulfonate (LAS) were used to control the particles size of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$.

2. Experimental

2.1. Preparation of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were obtained from Aladdin Reagent limited company, China; NaOH, NaCl, and $\text{C}_2\text{H}_5\text{OH}$ were obtained from

SCHEME 1: The setup for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ prepared by MMS with different surfactants.

Guangzhou Chemical Reagent Factory; poly oxyethylene (10) nonyl phenyl ether (NP-10), polyoxyethylene (5) nonyl phenyl ether (NP-5), octyl phenol together ethylene (10) ether oxygen (OP-10), sodium dodecyl benzene sulfonate (LAS) were purchased from Guangzhou Chi Hung Trade LTD. Co. All chemical reagents are of analytical reagent grade. Distilled water was used throughout.

The process to prepare $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanocrystals with NP-10 (Y-NP10) is as follows: the raw materials $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (4.75 mmol), $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.25 mmol), and NaOH (15 mmol) were mixed for 30 min in agate mortar, and then NaCl (10 g) and NP-10 (1 g) were put in the mixture and were ground for 10 min. At last, the mixture was heated at 850°C for 4 h. The final product was the solidified melt, which was washed with distilled water and ethanol at room temperature, and then the product was dried overnight in air at 110°C . The process for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ prepared by MMS is shown in Scheme 1.

The methods for synthesis $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ with NP-5 (Y-NP5) and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ with OP10 (Y-OP10) and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ with LAS (Y-LAS) are similar with that of Y-NP10 mentioned above.

2.2. Measurements. The structure of the final product was examined by X-ray powder diffraction (XRD) using $\text{Cu K}\alpha$ radiation on Rigaku D/Max 2200 vpc X-ray diffractometer. The size and morphology of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ were observed by a scanning electron microscopy (SEM) on LEO-1530 electron microscope. The luminescent spectra of the sample were recorded on an FLS920 fluorescence spectrophotometer.

3. Results and Discussion

The XRD patterns of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ prepared by MSS with different surfactants were shown in Figure 1. Curve (a) is very consistent with JCPDS43-1036 [Y_2O_3]. This reveals that the phosphor Y-NP5 shares the cubic structure with the single phase, and Eu^{3+} ions have been effectively built into the Y_2O_3 host lattices and occupied the Y^{3+} sites. Other three curves are similar with curve (a), the result shows that the single phase $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ can be prepared by MSS with different surfactants.

The SEM images of as-prepared samples Y-NP5, Y-NP10, Y-OP10, and Y-LAS are shown in Figure 2. $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NCs have been successfully prepared by MSS method with NP-5. The particles are about 100 nm (Figure 2(a)). The result shows that the introduction of the surfactant NP-5 can effectively prevent Y_2O_3 NCs growth. However their crystallinity is lower. Y-NP10 shows good crystallinity, and its size is about

FIGURE 1: The XRD patterns of Y-NP5, Y-NP10, Y-OP10, and Y-LAS.

200 nm. We also prepared $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ with other surfactants. Y-OP10 and Y-LAS particles sizes are about 500 nm and 1 μm , respectively.

The excitation spectra of Y-NP5, Y-NP10, Y-OP10, and Y-LAS are shown in Figure 3. The excitation spectra of these samples exhibit similar features; the broad excitation band from 230 nm to 290 nm is attributable to the charge transfer (CT) band from the $2p$ orbital of O^{2-} to the $4f$ orbital of Eu^{3+} . The sharp lines in 350–550 nm range are intraconfigurational $4f-4f$ transitions of Eu^{3+} ions in the host lattices.

Figure 4 is the emission spectra of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ prepared by MSS with different surfactants under 254 nm excitation. The strongest peak is at 611 nm, which is due to $^5D_0 \rightarrow ^7F_2$ transition in C_2 symmetry for Eu^{3+} . The other $f-f$ transitions of Eu^{3+} , such as $^5D_0 \rightarrow ^7F_1$ in 570–720 nm and $^5D_1 \rightarrow ^7F_1$ transitions in 520–570 nm are very weak. Y-NP10 shows intense red emission. Bright red light can be observed from this phosphor under 254 nm excitation (seeing Scheme 1). Its CIE (Commission Internationale de l'Eclairage, International Commission on Illumination) chromaticity coordinates are calculated to be $x = 0.592$, $y = 0.359$.

4. Conclusion

In summary, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NCs were prepared by MSS with different surfactants. The structures, morphologies, and

FIGURE 2: SEM images of Y-NP5, Y-NP10, Y-OP10, and Y-LAS.

FIGURE 3: The excitation ($\lambda_{\text{em}} = 611 \text{ nm}$) of Y-NP5, Y-NP10, Y-OP10, and Y-LAS.

the photoluminescent properties of the phosphors were studied. The particles size of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ can be controlled by adjusting the kinds of surfactants. The sample Y-NP10 shows regular morphology and intense red emission under UV excitation. Bright red light can be observed by naked eyes from this phosphor under 254 nm excitation.

FIGURE 4: The emission spectra ($\lambda_{\text{ex}} = 350 \text{ nm}$) of Y-NP5, Y-NP10, Y-OP10, and Y-LAS.

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References

- [1] T. Jüstel, H. Nikol, and C. Ronda, "New developments in the field of luminescent materials for lighting and displays," *Angewandte Chemie*, vol. 110, pp. 3250–3271, 1998.
- [2] A. L. Rogach, N. Gaponik, J. M. Lupton et al., "Light-emitting diodes with semiconductor nanocrystals," *Angewandte Chemie*, vol. 47, no. 35, pp. 6538–6549, 2008.
- [3] M. Dahan, T. Laurence, F. Pinaud et al., "Time-gated biological imaging by use of colloidal quantum dots," *Optics Letters*, vol. 26, no. 11, pp. 825–827, 2001.
- [4] K. E. Gonsalves, G. Carlson, S. P. Rangarajan, M. Benaissa, and M. José-Yacamán, "Synthesis and characterization of a nanostructured gallium nitride-PMMA composite," *Journal of Materials Chemistry*, vol. 6, no. 8, pp. 1451–1453, 1996.
- [5] R. G. Pappalardo and R. B. Hunt, "Dye-laser spectroscopy of commercial $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ phosphors," *Journal of the Electrochemical Society*, vol. 132, pp. 721–730, 1985.
- [6] C. R. Ronda, "Phosphors for lamps and displays: an application view," *Journal of Alloys and Compounds*, vol. 225, no. 1-2, pp. 534–538, 1995.
- [7] T. Justel, H. Nikol, and C. Ronda, "New development in the field of luminescent materials for lighting and displays," *Angewandte Chemie*, vol. 37, pp. 3084–3103, 1998.
- [8] X. Jing, T. Ireland, C. Gibbons et al., "Control of $\text{Y}_2\text{O}_3\text{:Eu}$ spherical particle phosphor size, assembly properties, and performance for FED and HDTV," *Journal of the Electrochemical Society*, vol. 146, no. 12, pp. 4654–4658, 1999.
- [9] C.-H. Kim, I.-E. Kwon, C.-H. Park et al., "Phosphors for plasma display panels," *Journal of Alloys and Compounds*, vol. 311, no. 1, pp. 33–39, 2000.
- [10] W. W. Zhang, M. Xu, W. P. Zhang et al., "Site-selective spectra and time-resolved spectra of nanocrystalline $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$," *Chemical Physics Letters*, vol. 376, no. 3-4, pp. 318–323, 2003.
- [11] G. S. Wu, Y. Lin, X. Y. Yuan, T. Xie, B. C. Cheng, and L. D. Zhang, "A novel synthesis route to $\text{Y}_2\text{O}_3\text{:Eu}$ nanotubes," *Nanotechnology*, vol. 15, no. 5, pp. 568–571, 2004.
- [12] K. Y. Jung and K. H. Han, "Densification and photoluminescence improvement of Y_2O_3 phosphor particles prepared by spray pyrolysis," *Electrochemical and Solid-State Letters*, vol. 8, no. 2, pp. H17–H20, 2005.
- [13] X. Wang and Y. Li, "Synthesis and characterization of lanthanide hydroxide single-crystal nanowires," *Angewandte Chemie*, vol. 41, no. 24, pp. 4790–4793, 2002.
- [14] G. Wakefield, E. Holland, P. J. Dobson, and J. L. Hutchison, "Luminescence properties of nanocrystalline $\text{Y}_2\text{O}_3\text{:Eu}$," *Advanced Materials*, vol. 13, pp. 1557–1560, 2001.
- [15] A. P. Jadhav, C. W. Kim, H. G. Cha et al., "Effect of different surfactants on the size control and optical properties of $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ nanoparticles prepared by coprecipitation method," *Journal of Physical Chemistry C*, vol. 113, no. 31, pp. 13600–13604, 2009.
- [16] G. S. Wu, Y. Lin, X. Y. Yuan, T. Xie, B. C. Cheng, and L. D. Zhang, "A novel synthesis route to $\text{Y}_2\text{O}_3\text{:Eu}$ nanotubes," *Nanotechnology*, vol. 15, no. 5, pp. 568–571, 2004.
- [17] A. Kumar and J. Kumar, "Perspective on europium activated fine-grained metal molybdate phosphors for solid state illumination," *Journal of Materials Chemistry*, vol. 21, no. 11, pp. 3788–3795, 2011.
- [18] J. Yang and J. Lin, "Sol-gel synthesis of nanocrystalline $\text{Yb}^{3+}/\text{Ho}^{3+}$ -doped Lu_2O_3 as an efficient green phosphor," *Journal of the Electrochemical Society*, vol. 157, pp. K273–K278, 2010.
- [19] B. Yan and F. Lei, "Molten salt synthesis, characterization and luminescence of $\text{ZnWO}_4\text{:Eu}^{3+}$ nanophosphors," *Journal of Alloys and Compounds*, vol. 507, no. 2, pp. 460–464, 2010.
- [20] S. V. Volkov, "Chemical reactions in molten salts and their classification," *Chemical Society Reviews*, vol. 19, no. 1, pp. 21–28, 1990.
- [21] J.-H. Park, D.-H. Lee, H.-S. Shin, and B.-K. Lee, "Transition of the particle-growth mechanism with temperature variation in the molten-salt method," *Journal of the American Ceramic Society*, vol. 79, no. 4, pp. 1130–1132, 1996.
- [22] C.-Y. Xu, Q. Zhang, H. Zhang, L. Zhen, J. Tang, and L.-C. Qin, "Synthesis and characterization of single-crystalline alkali titanate nanowires," *Journal of the American Chemical Society*, vol. 127, no. 33, pp. 11584–11585, 2005.
- [23] Y. Mao, T.-J. Park, F. Zhang, H. Zhou, and S. S. Wong, "Environmentally friendly methodologies of nanostructure synthesis," *Small*, vol. 3, no. 7, pp. 1122–1139, 2007.