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Effect of doping concentration on particle growth and luminescence properties of monodispersed Dy^{3+}: Y_2O_3

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A B S T R A C T

Submicron-sized Dy^{3+}: Y_2O_3 particles were successfully prepared via an urea homogeneous precipitation method, followed by a calcination at 800 °C. TG-DSC, FT-IR, X-ray diffraction (XRD), Field emission scanning electron microscope (FE-SEM), scanning electron microscope (SEM), photoluminescence (PL), and photoluminescence excitation (PLE) spectra were used to characterize the prepared samples. The particles were spherical shape and monodispersed. More importantly, the spherical Y_2O_3 particles were found to have significant changes in size with varying dopant concentration of the Dy^{3+} ions, ranging approximately from 550 to 840 nm. The possible growth mechanism of the particles was proposed. Under 349 nm excitation, the crystalline powders exhibited blue and yellow emissions due to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions of Dy^{3+} ions, respectively. It was further found that with proper Dy^{3+} doping concentration, the luminescence color hue was tuned close to the ideal white light with color coordinates of (0.33, 0.33). The submicron-sized Dy^{3+}: Y_2O_3 phosphor is a promising candidate for the white light emitting diodes (WLEDs).

1. Introduction

Doping, which involves the intentional incorporation of suitable atoms/ions into the host lattice, is one of the effective routes to endow functional materials with optical, luminescence, electrical, and magnetic properties [1–5]. Rare earths (RE) are far more attractive doping elements for their abundant energy levels as well as luxuriant spectral properties [6–9]. To be mentioned, among the REs, Dy^{3+} was extensively studied due to the wide applications in the fields of thermal neutron dosimetry, white LEDs, photocatalysis, and dye-sensitized solar cells [10–13]. Especially, the luminescent properties of the Dy^{3+} doped materials are attracting increasing attentions. When excited by UV light, two intense bands are generated in the visible spectral range which correspond to the hypersensitive transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$ ($\Delta L = 2$, $\Delta J = 2$, yellow emission) and the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition (blue emission), respectively. By tuning the ratio of yellow to blue emission intensities (Y/B), white light can be realized [14]. At present, 19% of the global electric energy is consumed for illumination, therefore, more efficient, energy saving and environmentally friendly lighting technologies to reduce power consumption become pressing. In this aspect, Dy^{3+} doped luminescent materials for WLEDs devices are becoming attractive [15–17].

Luminescent properties of a material are strongly dependent on not only the phase structure, particle size, the morphology, and the shape [18–22], but also the intrinsic properties of host materials. Therefore, finding an appropriate host material is of vital importance. Among the metal oxides, Y_2O_3 crystals are considered to be one of the best candidates for RE doping, because of low cut-off phonon energy (380 cm^{-1}), high melting point (2400 °C), broad transparency, and wide band gap of 5.6 eV [23,24]. Additionally, the Y^{3+} ion has similarities in ionic radius and chemical properties compared to other REs, making Y_2O_3 an excellent host material for RE induced luminescent applications. To optimize the luminescent properties, many researchers are focusing on doping/co-doping in Y_2O_3 crystal lattice with different REs, tailoring pH of the solutions,

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or controlling the morphology and shape of the Y_2O_3 [25–30]. However, few attentions have been paid to the impact of doping concentration on particle growth of the phosphor and its luminescent property. The dopants are supposed to play important roles in crystal growth, since the ions locating at different lattice sites have their own reaction processes with corresponding surrounding environments. Hence, experiments should be carried out to seek the relationship between the dopants and the particle growth. In the present work, submicron-sized Dy^{3+}: Y_2O_3 spheres were prepared via a facial urea homogenous precipitation method, followed by a calcination at 800 °C. Different concentrations of Dy^{3+} ions were incorporated into the Y_2O_3 particles to investigate the possible mean that the dopants influence the final particle size and luminescence. The possible growth mechanism of Dy^{3+}: Y_2O_3 has also been proposed.

2. Experimental procedures

2.1. Preparation

The Dy^{3+}: Y_2O_3 submicron-sized spheres were synthesized via a homogeneous precipitation method. $Y(NO_3)_3 \cdot 9H_2O$ (99.99%), $Dy(NO_3)_3 \cdot 9H_2O$ (99.99%) and urea (analytic grade) were used as the starting materials. Firstly, the nitrates with a stoichiometric ratio were dissolved in deionized water to make a nitrate solution, according to the chemical formula $(Y_{1\text{-}x}Dy_x)_2O_3$, (Abbreviated as xDy^{3+}: Y_2O_3, herein after) ($0.5\% \le x \le 2\%$). The total concentration of Y^{3+} and Dy^{3+} ions was kept at 0.015 M. Then the precipitant urea was added with a molar concentration ratio of 35:1 to the total metal ions, and the mixed solution was stirred at room temperature for homogenization until a transparent solution was obtained. The solution was then heated in a water bath at 90 ± 2 °C for different time durations to help investigate the growth mechanism. A typical time duration was 5 h. After naturally cooled down to room temperature without any disturbance, the resultant suspension was filtered and washed repeatedly with deionized water and alcohol, respectively, to remove by-products during the reaction. The washed precipitate was then dried at 60 °C for 24 h. The resultant Y_2O_3: Dy^{3+} precursors were calcined at 800 °C for 2 h in a muffle furnace in air to obtain Y_2O_3: Dy^{3+} crystal powders.

2.2. Characterization

Phase identification of the prepared Y_2O_3: Dy^{3+} crystal powders was carried out using X-ray diffraction (XRD) on a Japan Rigaku D/MAX 2200PC diffractometer with Cu Kα radiation ($\lambda = 1.54056$ Å). Thermal analysis of the precursors was measured by thermogravimetric/differential scanning calorimetry (TG/DSC, STA449C, NETZSCH, Germany) at a heating rate of 10 °C/min in air. Both the precursors and the powders were mixed with KBr for FT-IR measurement at room temperature using the Fourier transform infrared spectroscopy (Nexus 670, Nicolet). The morphologies of the precursors and the powders were observed using a scanning electron microscope (SEM, JSM-6390, JEOL, Tokyo, Japan), and a field emission scanning electron microscope (FE-SEM, HITACHI SU8010, Japan). Photoluminescence excitation and emission spectra were measured on a JobinYvon FL3-221 fluorescence spectrophotometer with the resolution of 1 nm using a 450 W Xenon lamp as the excitation source. All emission spectra are corrected for the spectral response of the measuring system.

3. Results and discussion

Fig. 1 shows TG/DSC curves of the Y_2O_3 precursors kept for 5 h in a water bath. The total weight loss is about 40.4%, which can be mainly divided into three periods. Below 180 °C, the first period experiences a weight loss of about 10 wt%, and the endothermic peak at around 159.2 °C is due to the evaporation of absorbed water and the release of bound water. The second period of weight loss occurs in the temperature range between 180 and 625 °C, with a total weight loss of 14.06%, which corresponds to the decomposition and oxidation of NO_3^- ions. A weight loss of 16.34% happens during the third reaction stage. As depicted in the DSC curve, there is an endothermic peak centered at 636.2 °C and an exothermic peak centered at 784.2 °C, respectively. They are attributed to the decomposition of hydroxides and carbonates, and the crystallization of the Y_2O_3 crystals, respectively. The TG-DSC results indicate that the Y_2O_3 crystals are supposed to be obtained below 800 °C.

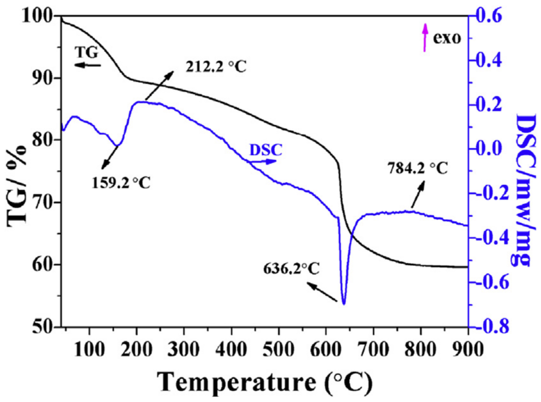

Fig. 1. TG-DSC curves of the Y_2O_3 precursor aging for 5 h.

FT-IR analysis is crucial for the understanding the composition of the products and reaction mechanism. The FT-IR spectra of both the Y_2O_3 precursors and the powders calcined at 800 °C are presented in Fig. 2. It can be seen from the curve of the precursors, the broad-band centered at 3434 cm^{-1} can be attributed to the couple effects of water molecules. The strong absorption peaks at 1530 cm^{-1} and 1412 cm^{-1} can be assigned to the split asymmetrical stretching vibration of carbonate and nitrate groups, respectively, indicating that abound of CO_3^{2-} and NO_3^- groups are adsorbed on the precursor particles. After calcined at 800 °C for 2 h, the curve shows some new bands locating at 562, 465, and 431 cm^{-1}, which are characteristic of Y—O vibrations, indicating the forming of Y_2O_3 crystals. This result is consistent with that of the TG-DSC analysis. According to the TG-DSC and FT-IR results, as well as an early study

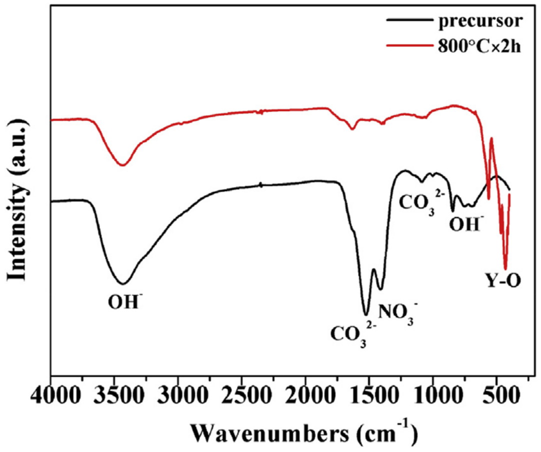

Fig. 2. FT-IR spectra of the precursor and the powder calcined at 800 °C for 2 h.