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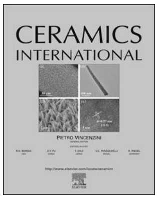

# Investigation on the preparation and luminescence property of $(Gd_{1-x}Dy_x)_2O_3$ ($x$=0.01–0.10) spherical phosphors

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## ABSTRACT

Uniform spheres of $(Gd_{1-x}Dy_x)_2O_3$ ($x$=0.01–0.10) have been converted from their colloidal precursor spheres synthesized via homogeneous precipitation. The synthesis, particle size control, luminescent properties and energy transfer of the $(Gd_{1-x}Dy_x)_2O_3$ were systematically studied by the combined techniques of fourier transform infrared (FT-IR) spectroscopy, x-ray diffractometry (XRD), field emission scanning electron microscopy (FE-SEM), photoluminescence excitation/ photoluminescence (PLE/PL) spectroscopy, and fluorescence decay analysis. The precursor exhibit mono-dispersed spherical morphology and its size can be efficiently controlled by adjusting the urea content. The phase pure $(Gd_{1-x}Dy_x)_2O_3$ oxides can be obtained by calcining precursor at 600 °C, and the spherical morphology remained at even high temperature of 1000 °C. The $(Gd_{1-x}Dy_x)_2O_3$ phosphors display strong yellow emission at 575 nm ($^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition of $Dy^{3+}$) and weak blue emission at 486 nm ($^4F_{9/2}\rightarrow{}^6H_{15/2}$ transition of $Dy^{3+}$) upon ultraviolet (UV) excitation of $Gd^{3+}$ at 275 nm ($^8S_{7/2}\rightarrow{}^6I_J$ transition of $Gd^{3+}$). The optimal content of $Dy^{3+}$ was found to be ~2 at% ($x$=0.02) due to the concentration quenching. Owing to the efficient $Gd^{3+}\rightarrow Dy^{3+}$energy transfer, the fluorescent property of the phosphor was significantly improved. The emission intensity of $(Gd_{1-x}Dy_x)_2O_3$ increased with calcination temperature and particle size increasing, while the lifetime for the 575 nm emission gradually decreased. The $(Gd_{1-x}Dy_x)_2O_3$ spheres developed in the present work is expected to be a promising yellow phosphor widely used in the lighting and display areas.

## 1. Introduction

Cubic-structured $Ln_2O_3$ (space group: $Ia\,\bar{3}$, Ln=La-Lu, and Y) oxides are very important inorganic materials. Among which, $Gd_2O_3$ as promising phosphor is one of the widely studied host matrix due to its good physical and chemical properties [1–3]. The $Gd^{3+}$ in $Gd_2O_3$ could be easily replaced by activator ions and exhibits colorful emission under UV excitation [3–5]. $Eu^{3+}$ and $Tb^{3+}$ activated $Gd_2O_3$ are famous red and green phosphors widely used in electroluminescent (EL), white light emitting diode (LED), plasma display panels (PDP), field emission displays (FED), cathode-ray tubes (CRT) and so forth [5–7]. In the recent years, many researchers have been focused on the $Dy^{3+}$ doped system owing to its unique luminescent properties. Commonly, $Dy^{3+}$ displays strong yellow and blue emission bands [8–10], and the relative intensity of the two main emission determined by the occupancy of $Dy^{3+}$ in the matrix environment. Thus, varied emissions can be achieved by tuning the coordination of $Dy^{3+}$ [11].

Monodisperse $(Gd_{1-x}Dy_x)_2O_3$ spheres as a promising type of phosphors were successfully synthesized and enhanced $Dy^{3+}$ emission were demonstrated in the present work. The $(Gd_{1-x}Dy_x)_2O_3$ system was chosen according to the following three main reasons: (1) the luminescent properties of phosphor depend strongly on its particle size and morphology [12,13]. Uniform spheres [14–16] are beneficial to improve the resolution of fluorescence components and easy to row into a compact fluorescent layer to reduce the scattering of excitation light to the maximum extent, and thus present excellent luminescent efficiency. Until so far, the $(Gd_{1-x}Dy_x)_2O_3$ spheres have been rarely reported; (2) $Gd^{3+}$ may sensitize the yellow and blue emission of $Dy^{3+}$ [17] through its intrinsic $^8S_{7/2}\rightarrow{}^6I_J$ transition centered at ~275 nm. Better luminescence of $Dy^{3+}$ in $Gd_2O_3$ than in $Y_2O_3$ lattices may thus be expected via an efficient energy transfer from $Gd^{3+}$ to $Dy^{3+}$, and is also experimentally demonstrated in this paper; (3) the smaller electronegativity of $Gd^{3+}$(1.20) than that of $Y^{3+}$(1.22) may result in an easier charge transfer (CT), and thus higher intensities of the PL bands [17,18].

A variety of approaches have been adopted to prepare the rare earth oxides such as solid state reaction [7], combustion [1], sol-gel [1,3], hydrothermal [19], spray pyrolysis [20], precipitation method [21], etc.

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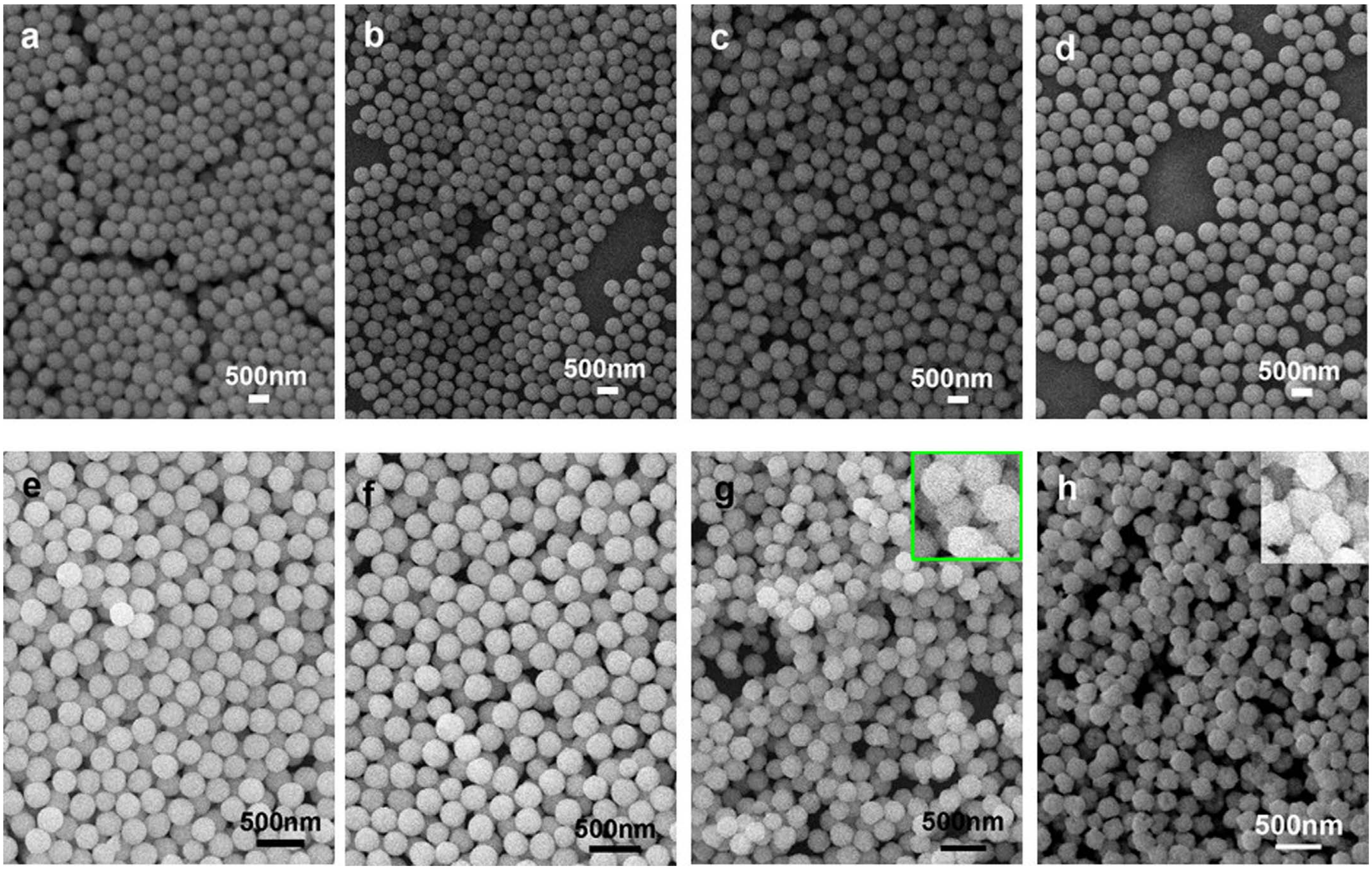

**Fig. 1.** FE-SEM morphologies of the $(Gd_{1-x}Dy_x)_2O_3$ precursors with (a) $x$=0, (b) $x$=0.02, (c) $x$=0.05, (d) $x$=0.10, and the $x$=0.02 resultant products calcined at (e) 600 °C, (f) 850 °C, (g) 1000 °C and (h) 1200 °C respectively.

In this paper, the monodisperse spherical particles of $(Gd_{1-x}Dy_x)_2O_3$ were synthesized by homogeneous precipitation method using the urea as precipitant [14–16]. The phase evolution, structural characteristics, morphologies and luminescent properties of the resultant product were studied in detail by the combined techniques of XRD, FE-SEM, PLE/PL spectroscopy and fluorescence decay analysis. The observed optical properties were successfully correlated with the processing temperature, particle size and $Dy^{3+}$ contents. Comparative studies were also made with the $(Y_2O_3)$:$Dy^{3+}$ phosphor systems to reveal the superiority of $(Gd_2O_3)$:$Dy^{3+}$. In the following sections, we report the synthesis, phase evolution, and photoluminescent performances of the $(Gd_2O_3)$:$Dy^{3+}$ phosphors.

## 2. Experiment procedure

The reagents required for this experiment mainly include $Gd_2O_3$ (99.99%, Huizhou Ruier Rare Chemical Hi-Tech Co. Ltd., Huizhou, China), $Dy_2O_3$ (99.99%, Huizhou Ruier Rare Chemical Hi-Tech Co. Ltd., Huizhou, China), urea $(CO(NH_2)_2 \cdot 12H_2O$, > 99%, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) and nitric acid (AR, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China). $Y_2O_3$ (99.999%, Huizhou Ruier Rare Chemical Hi-Tech Co. Ltd., Huizhou, China) was used to prepare the $(Y_{0.98}Dy_{0.02})_2O_3$ oxide for comparison.

The rare earth nitrates $RE(NO_3)_3$ (RE=Gd and Dy) were prepared by dissolving $Gd_2O_3$ and $Dy_2O_3$ in hot nitric acid. The mother salt solution was obtained by mixing $Gd(NO_3)_3$ and $Dy(NO_3)_3$ according to the chemical formula of $(Gd_{1-x}Dy_x)_2O_3$. The precipitant urea was adding to the mother solution and then dissolved in distilled water to make a total volume of 500 mL. The mixed solution was first homogenized under magnetic stirring for 60 min, and then heated from room temperature to target temperature 90 ± 1 °C within 60 min. After reacting for 2 h at 90 ± 1 °C, the precipitate was collected via centrifugation, washed two times with distilled water, rinsed with ethanol, and dried at 80 °C for 12 h in air. The dried precursor was calcined in air at various predetermined temperatures (600–1200 °C) for 4 h to yield oxides [14–16]. In each case, the total concentration of $Dy^{3+}$ and $Gd^{3+}$ was fixed at 0.015 mol/L in order to insure the same reaction condition. The $Dy^{3+}$ content, expressed as $x$=Dy/(Gd+Dy) atomic ratio ($x$=0, 0.01, 0.02, 0.03, 0.05, 0.075 and 0.10), was varied to reveal its effects on the characteristics of the precursor and the resultant $RE_2O_3$ powders. The concentration ratio of urea to $RE^{3+}$ indicated as $R$ (R=40, 60, 80, no special explanation $R$=40) was changed to reflect the urea content effect on the phosphor particle size. The $(Y_{0.98}Dy_{0.02})_2O_3$ oxides for comparison were synthesized by the same method mentioned above.

The X-ray diffraction patterns were recorded at room temperature using nickel-filtered CuKα radiation in the 2θ range 10–50° at a scan rate of 4.0° 2θ/min (Model D8 ADVANCE, BRUKER Co., Germany). Particle morphologies were observed via FE-SEM with an acceleration voltage of 10 kV (Model QUANTA FEG 250, FEI Co., America). Fourier transform infrared (FTIR) spectra are performed by the standard KBr method (Model NICOLET-380, Thermo electron Co., USA). The photoluminescence excitation (PLE) and photoluminescence (PL) spectra in the UV region were collected by an FP-6500 fluorescence spectrophotometer equipped with a Φ60-mm intergating sphere (Model ISF-513, JASCO, Tokyo, Japan) and a 150-W Xe-lamp as the excitation source. The external quantum efficiency ($\varepsilon_{ex}$, the total number of emitted photons divided by the total number of excitation photons) and the internal quantum efficiency ($\varepsilon_{in}$, the total number of emitted photons divided by the number of photons absorbed by the sample) of the phosphors are derived from the following equations using the built-in analysis software: