

Synthesis and Photo Luminescent Properties of Gd₂O₃ Based Rare Earth Nanophosphors*

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Abstract: In recent years, nanostructures, such as nanoplates, nanowires, nanotubes, and nanorods have attracted intensive attention due to their potential applications in a wide range of fields. Among these nanostructures, nanowires with small diameters and high aspect ratio are focused because of their novel physical properties and potential applications in catalysis and electronic, optical, optoelectronic, and magnetic devices. Therefore, much effort has been made toward the development of synthetic methodologies for fabricating inorganic nanowires, such as vapour-liquid-solid (VLS) growth processes, thermal evaporation, reverse micelles, hydrothermal routes and template confined methods. Among the various synthesis techniques, the hydrothermal method is a promising synthetic route, which can be better controlled through appropriate choice of reaction parameters, such as time, pH, and temperature. It has some advantages, such as lower reaction temperature, energy economy, easily controllable reaction conditions, size-selective growth, controllable morphology, smaller particle size, and better particle size distribution. It has been proven to be an effective and convenient process in preparing high-quality anisotropic nanowires due to its great chemical flexibility and synthetic tenability. Since the rapid advances in nanotechnologies, particularly, the development of new methods for materials synthesis, there has been consistently growing interest in studying the optical behaviour of rare-earth (RE) ions in nanomaterials. Rare-earth compounds are very important in many areas, such as high-quality phosphors, magnetic materials, and catalysts based on their novel electronic, optical, and chemical properties because of their unique properties originating from the electron transitions within the 4f shells. RE-doped inorganic nanophosphor is one of the most promising materials for a variety of applications in solid-state lasers, lighting and displays, and bio-labels. The Gd₂O₃ microcrystal doped with Eu³⁺ ions are well-known commercial red phosphors. Eu³⁺/Gd₂O₃ nanophosphors have also been used as fluorescent markers in a variety of immunosensing application. Since Gd³⁺ is a known contrast agent for magnetic resonance imaging (MRI), RE-doped Gd₂O₃ nanophosphors may function as both

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fluorescence and MRI labels. Despite the promising prospects of RE-doped Gd_2O_3 nanophosphors, their optical behaviours, particularly, the excited state dynamics of RE ions deserve much more attention. A clear understanding of these aspects, however, is essential for the development of novel bio-labels and nanosensors based on $\text{Er}^{3+}/\text{Gd}_2\text{O}_3$ nanophosphors with high luminescence efficiency. The luminescence decay in the nanocrystals shows non-exponential characteristics when excited directly with temperatures varying from 10 to 300 K. This effect is attributed to energy transfer to defects in the nanocrystals. The calculated quantum efficiencies at various temperatures suggest that the change of lifetime with the temperature is predominantly influenced by the multi-phonon transition process to the next low-lying multiplet. Unusually strong phonon side bands with rich structures in the excitation spectra of Er^{3+} have been observed in Gd_2O_3 nanocrystals for hypersensitive transitions.

Keyword: nanophosphors, Gd_2O_3 nanocrystals, rare earth nanomaterials.

1. Introduction

In this paper, spectroscopic properties, particularly, the excited-state dynamics of Er^{3+} in 40-50 nm Gd_2O_3 nanocrystals, are investigated based on laser- or xenon-excited spectroscopic experiments. The temperature-dependent lifetime of the green emission, which is thermally coupled to the upper state is experimentally determined by utilizing the efficient energy transfer between Gd^{3+} and Er^{3+} . Unusual phonon side bands with fine structures in the low temperature excitation spectra of Er^{3+} have been observed in Gd_2O_3 nanocrystals and analyzed.

Most of the previous work on $\text{Er}^{3+}/\text{Gd}_2\text{O}_3$ nanophosphors was focused on material synthesis, characterization, or an up conversion mechanism. To date, temperature dependence of the luminescence decay from the thermalized states and vibronic side bands in the excitation spectra of $\text{Er}^{3+}/\text{Gd}_2\text{O}_3$ crystals have not been thoroughly investigated. A clear understanding of these aspects, however, is essential for the development of novel bio labels and nanosensors based on $\text{Er}^{3+}/\text{Gd}_2\text{O}_3$ nanophosphors with high luminescence efficiency.

2. Experimental Procedures

Synthesis: All the chemicals were of analytical grade and used without further purification. $\text{Gd}(\text{NO}_3)_3$ and $\text{Eu}(\text{NO}_3)_3$ aqueous solution were obtained by dissolving Gd_2O_3 (99.99%) and Eu_2O_3 (99.99%) in dilute HNO_3 solution under heating with ceaseless agitation. In a typical procedure, 1 mmol of $\text{Na}_2\text{H}_2\text{L}$ was first dissolved in 20 mL of deionized water. $\text{Gd}(\text{NO}_3)_3$ (0.95 mmol) and $\text{Eu}(\text{NO}_3)_3$ (0.05 mmol) in aqueous solution were then added into

the obtained solution to form a chelate gadolinium complex. Subsequently, 1 mmol of $\text{Na}_3\text{VO}_4 \cdot 12\text{H}_2\text{O}$ in 15 mL of deionized water was dripped into the solution under vigorous magnetic stirring. The pH value of the solution was adjusted to 10 with 1:1 (v/v) ammonia. The resultant solution was transferred to a 50 mL autoclave and maintained at 180°C for 24 h. Finally, the autoclave was cooled to room temperature naturally. The precipitates were separated by centrifugation, followed by washing with deionized water and ethanol several times. The final product was dried at 60°C in air for about 12 h.

Different reaction temperatures (140 , 160 , 200 , and 220°C), alkaline source (NaOH), of $\text{Na}_2\text{H}_2\text{L}$ to Gd^{3+} (0 , 0.25 , 3) were selected to investigate the effects of these factors on the morphological and structural properties of the samples, while other reaction parameters remained unchanged.

Characterization: The Gd_2O_3 nanowires were characterized by powder X-ray diffraction (XRD). Fourier transform infrared (FT-IR) spectra were measured with infrared spectrophotometer. The morphology and composition of the samples were inspected using a scanning electron microscope equipped with an energy dispersive X-ray spectrum shown in Fig. 1. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) images, and selected area electron diffraction (SAED) patterns were obtained using a transmission electron microscope operating at 200 kV shown in Fig. 2. Photoluminescence (PL) excitation and emission spectra were recorded with a spectrophotometer equipped with a 150 W xenon lamp as the excitation source. All the measurements were performed at room temperature.

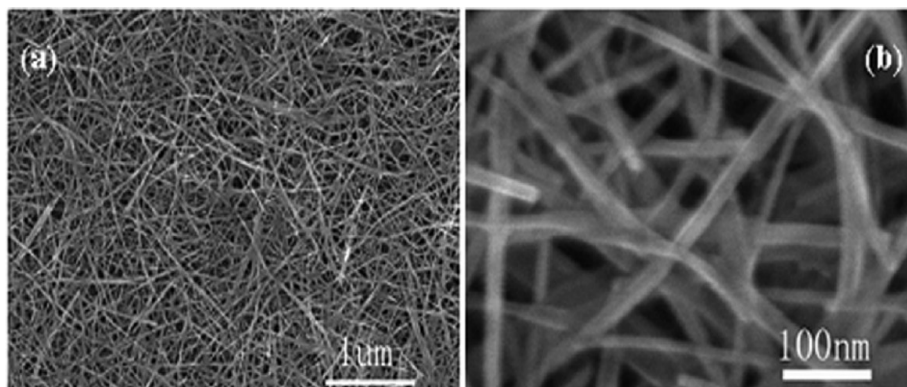


Fig.1. (a) Low- and (b) high-magnification SEM images of the Gd_2O_3 nanowires obtained at 180°C for 24 h ($\text{pH} = 10$)

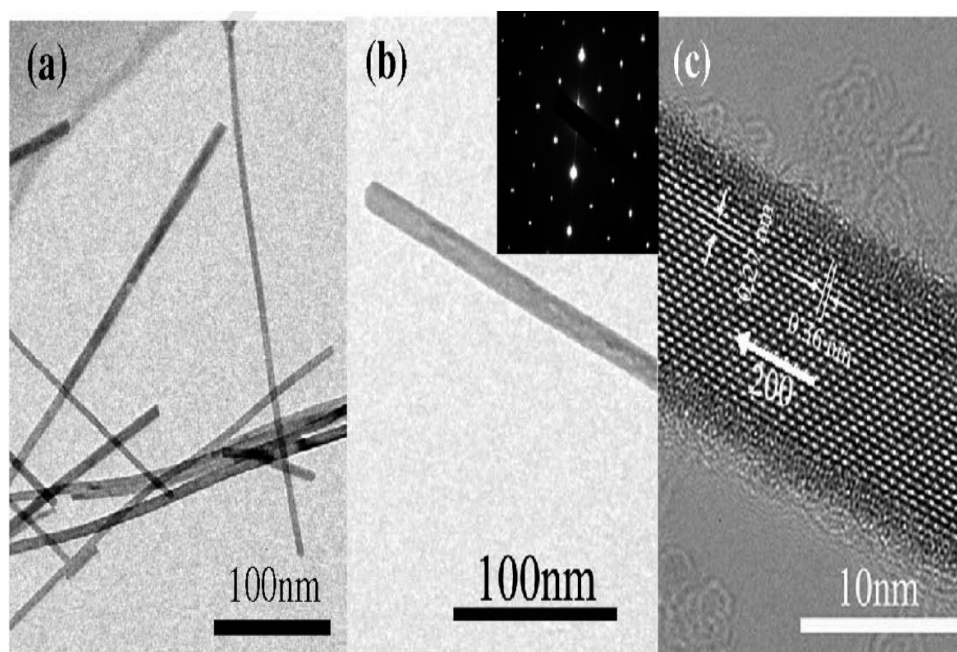


Fig.2. Typical TEM (a, b) and HRTEM (c) images of the Gd_2O_3 nanowires obtained at 180°C for 24 h. The inset in panel b is a corresponding SAED pattern of the nanowire

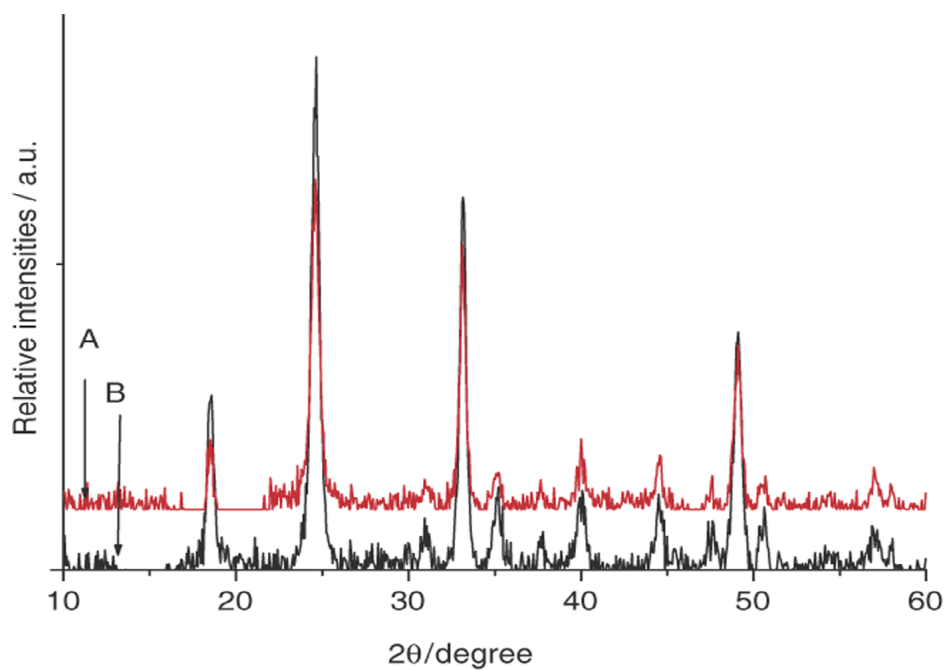


Fig.3. XRD pattern of the synthesized Gd_2O_3 nanowires. The standard data for the tetragonal Gd_2O_3 is also presented in the Fig. for comparison

3. Results and Discussion

TEM and SEM images show that the size distribution of Er³⁺/Gd₂O₃ nanocrystals is broad, with an average size of 40-50 nm, and the nanoparticles tend to aggregate. For comparison, the particle size of the submicron counterparts is approximately 110-130 nm. The XRD patterns of both nanocrystals and bulk counterparts can be exclusively indexed as the cubic Gd₂O₃ phase, and no trace of characteristic peaks were observed for other impurity phases such as monoclinic Gd₂O₃ or erbium oxides. By means of the Debye-Scherrer equation, the average size of the nanocrystals is estimated to be approximately 41 nm,^{1, 2} in accordance with the observations of TEM and SEM. The phonon side bands in a spectrum of Er³⁺ in Gd₂O₃ crystals are expected to be much (at least 1 order of magnitude) weaker than the zero-phonon lines (ZPLs) since it is, in general, regarded as a weak electron-phonon coupling system. However, the stronger-than-expected phonon side bands appear in the laser excitation spectra transition of Er³⁺ in Gd₂O₃ nanocrystals at 5 K³. It should be noted that the above phonon side bands are also observed in the excitation spectra by a Xe lamp. However, the intensity ratio *R* (0.105) is only about one-third of that by laser excitation, which indicates that the intensity of phonon side bands is closely related to the excitation power. Currently, we could not conclude why and how the phonon side bands are related to the excitation power.

Photoluminescent Properties of Gd₂O₃ Nanowires

Fig. 4a gives the excitation and emission spectra (4b) of the Gd₂O₃ nanowires. The peak positions and the shape of the spectra are similar to those of the materials in other literature except that the intensity of our sample is relatively lower. The excitation spectrum consists of a strong broad band with maximum at 312 nm and a number of weak lines in the longer wavelength extending from 350 to 550 nm. The strong broad band is attributed to the charge transfer absorption from the oxygen ligands to the central oxygen atoms⁴.

It is important to note that the emission intensity of the nanowires increases with the temperature from 120 to 200°C (Fig. 4b). In general, radiative mechanisms compete with nonradiative mechanisms, and the defects in materials can form quenching centres, which lead to non-radiative recombination and luminescence quenching. Therefore, the change in emission intensity should be mainly associated with the defects that come from the surface states of nanoparticles after the recombination of electron-hole pairs⁵. The crystallization of the product improved with the increase of

the temperature, and the defects decreased accordingly. So the emission intensity increased for the samples prepared at higher temperature.

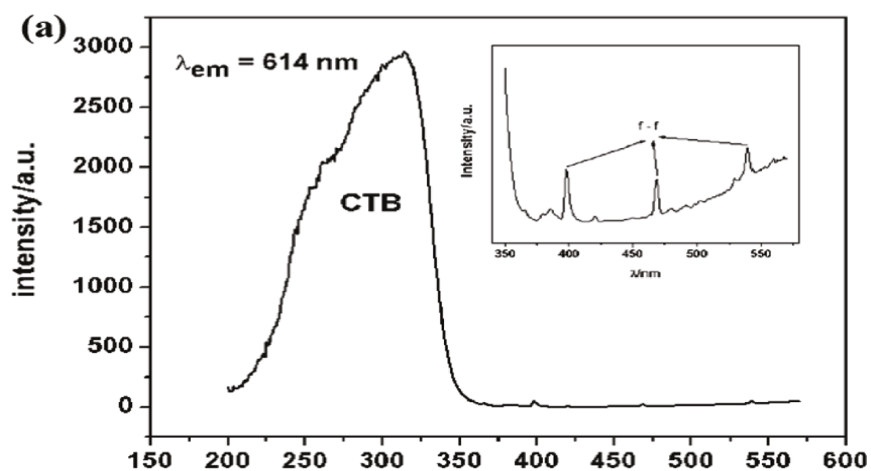


Fig.4. (a) Excitation spectrum of the Gd_2O_3 nanowires obtained at 180°C

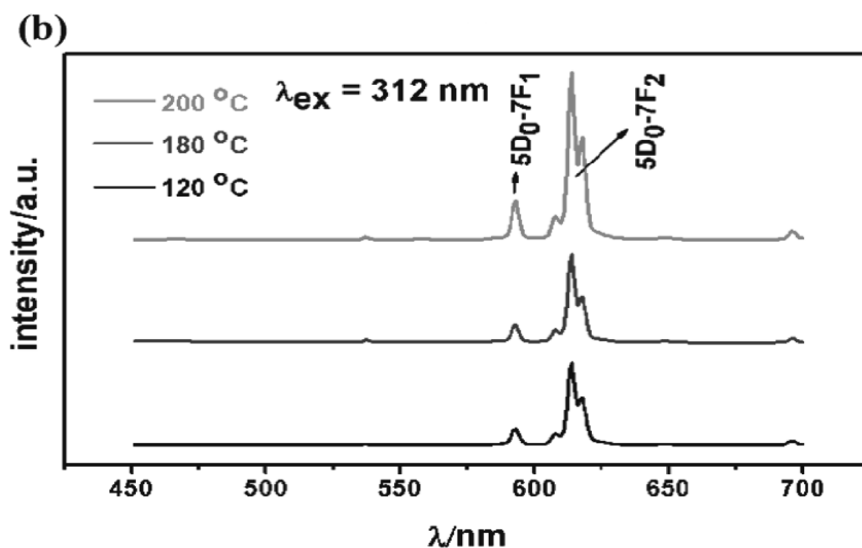


Fig.4. (b) emission spectra of the Gd_2O_3 nanowires obtained at different temperatures excited at 312 nm. Inset shows the expanded region of 340-580 nm

4. Conclusion

In summary, we have employed a simple soft-templating approach to synthesize Gd_2O_3 nanowires with diameters of about 15 nm and lengths of several micrometers. The synthetic method was based on the chelating and

capping ability of Na₂H₂L. Irregular aggregated nanoparticles formed in the absence of Na₂H₂L, revealing the importance of the template in the synthesis of the nanowires. The investigation of synthesis parameters reveals that the reaction conditions play an important role in determining the aspect ratios and final morphologies of the products. The possible formation mechanism for the nanowires was suggested in terms of the electron microscopy investigations and the crystal structure. The fluorescence decay dynamics for the Gd₂O₃ nanowires reveal that the average lifetime is 0.721 ms. The obtained nanowires with high aspect ratio exhibit a strong red emission under ultraviolet excitation, which may have potential applications in mini-optoelectronic devices. Moreover, our method provides a guidance that we can choose some organic additives properly to control the morphology of nanomaterials.

The excited-state dynamics of Er³⁺ (1 atom %) in 40-50 nm Gd₂O₃ nanocrystals has been investigated using laser and xenon excitation in spectroscopic experiments, along with theoretical analyses. The RT emission and excitation spectra obey an excellent reciprocity relationship. The luminescence decay of Er³⁺ in the nanocrystals shows non-exponential characteristics when excited directly to the thermally coupled multiplet with temperatures varying from 10 to 300 K. This effect is attributed to energy transfer to defects in the nanocrystals. The non-exponential decays can be well fitted in terms of electric dipole-dipole interaction between the donor and acceptor. It turns out that the population feeding from Gd³⁺ to Er³⁺ is efficient enough to overwhelm the ET of Er³⁺ in the emitting state to ions at defect sites. The temperature dependence of the observed lifetimes has been well interpreted by a simple model, which takes into account the contributions from both multiphonon transition and the thermally coupled levels. The calculated quantum efficiencies at various temperatures suggest that the change of lifetime with the temperature is predominantly influenced by the multiphonon transition process to the next low-lying multiplet. Unusually strong phonon side bands with rich structures in the excitation spectra of Er³⁺ have been observed in Gd₂O₃ nanocrystals for hypersensitive transitions.

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