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Phase transformation and spectroscopic adjustment of Gd_2O_3:Eu^{3+} synthesized by hydrothermal method

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ABSTRACT

The microcrystalline Gd_2O_3:Eu^{3+} phosphors were synthesized by the hydrothermal method with post annealing treatment. The powder X-ray diffraction (XRD) indicated the phase transformation from cubic to monoclinic occurred at about 1673 K. The morphologies and sizes were characterized by scanning electron microscopy (SEM). It was found that the morphology of Gd_2O_3:Eu^{3+} was altered from nanorod to microparticle as the phase changed from cubic to monoclinic. In order to evaluate the effects of sites and phases on luminescence behaviors, the photoluminescence (PL) properties of both phases were investigated. Dominant red emission was observed due to an efficient energy transfer among the sites as well as the strong excitation of O^{2-}–Eu^{3+} charge transfer band. It was calculated that the monoclinic structure has a higher degree of distortion. More importantly, the phase transformation resulted in the red shift of the strongest emission peak of Eu^{3+} from 610.5 to 622.5 nm, closer to the optical transmission window for bioimaging.

1. Introduction

Gadolinium oxide Gd_2O_3 is a well-known phosphor host material where the Gd^{3+} ions can be substituted by trivalent activators. Owing to the approximately equivalent ionic radii with Gd^{3+}, trivalent europium is suitable as the activator to detect the crystal field and the transfer process in case of more than one crystallographic site. Gd_2O_3 exhibits two stable structures at normal conditions: cubic C-form ($C_{2h}{}^3$) and monoclinic B-form ($T_h{}^7$). The crystallographic data and phase transformation of the rare earth sesquioxides were widely discussed and reviewed [1,2]. In term of luminescence property, it was first reported for cubic Gd_2O_3:Eu^{3+} by Wickersheim and Lefever [3] in 1964. Forest and Ban demonstrated the existence of two sites for Gd^{3+} [4]. The energy transfer between the two sites is induced by both the super exchange interactions among O^{2-} ligands and dipole–quadrupole interactions described by Buijs et al. [5]. In 1970 the monoclinic Gd_2O_3:Eu^{3+} was first investigated by Rice and Deshazer [6]. And the luminescence from higher states was studied by Daly and Schmidt [7] based on the spectra with selective site excitation by Dexpert-Ghys et al. [8].

Due to the unique luminescence properties and high chemical and physical stability, Gd_2O_3 phosphors doped with rare earth activators have been intensively investigated recently. Besides the applications in lighting and display fields [9,10], they have been used as contrast agent [11], drug carrier [12], multicolor reporter [13], upconversion material [14], etc. Among them, considerable attention has been paid to utilize the upconversion effect of nanosized phosphors for bioimaging [15–17]. It is known that the so called optical transmission window for bioimaging is in the region of 650–900 nm. The light with the wavelength in the region possesses combined virtues of a minimal autofluorescence and a relative deep light penetration through tissue [18]. Active ions characterized by infrared emission, such as Er^{3+}, Tm^{3+} and Ho^{3+}, are widely used with (near) infrared diode lasers as the excitation source. However, the luminescent efficiency of these ions is quite low and the heating effect becomes dominant, which hinder their applications. The Eu^{3+} ions exhibit much higher light-emitting efficiency. But the strongest emission is usually at the region of 611–616 nm [19–21] since the 4f orbital is shielded by the outer 5s5p orbital. One open question is how to adjust the light emission of Eu^{3+} and shift it into the optical transmission window for bioimaging.

Here, we report a hydrothermal synthesized microcrystalline Gd_2O_3:Eu^{3+} in the feature of phase transformation and spectroscopic adjustment to match the optical transmission window at a preliminary stage of investigation.

2. Experimental procedure

The phosphors Gd_2O_3 doped with 5.0 at% Eu^{3+} were prepared by hydrothermal method. Gd_2O_3, Eu_2O_3 (99.99%) and NaOH (A.R.)

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were used as the raw materials without further purification. Stoichiometric Gd_2O_3 (1.90 mmol) and Eu_2O_3 (0.10 mmol) were dissolved in 30 mL dilute nitric acid with agitation. Then NaOH solution (0.1 M) was added to obtain white precipitate with stirring for 30 min, which was transferred to a Teflon autoclave of 40 mL capacity and kept at 453 K for 24 h. After cooling to room temperature (RT), the white precursor $Gd(OH)_3:Eu^{3+}$ was separated by centrifugation and repeatedly washed with deionized water and ethanol for several times, then dried at 353 K for 12 h. The precursors were annealed at 1273–1673 K for 2 h to obtain the oxide phase Gd_2O_3: Eu^{3+}.

The structure of the samples was recorded by D8 ADVANCE X-ray powder diffraction (XRD Bruker Co., Germany) with Cu Kα radiation, operating at 40 kV and 40 mA. A step size of 0.02° was used with a scanning speed of 10°/min. The morphology and particle size were observed by thermal field emission scanning electron microscope (SEM FEI Quanta 400). The photoluminescence excitation and emission spectra and the decay curves were obtained on a FLS 920 spectrometer (Edinburgh Instruments) detected by red-sensitive PMT at RT. The excitation sources were a 450 W xenon lamp for steady state spectra and a 60 W μF flash lamp with an 1–2 μs pulse width for luminescence decay spectra.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of samples before and after annealing. The precursor is identified as $Gd(OH)_3:Eu^{3+}$ according to the standard card JCPDS 38-1042 (hexagonal, I41/a, $a=6.345$ Å and $c=3.63$ Å). When samples were annealed at the range of 1273–1573 K, all the patterns are indexed to the cubic $Gd_2O_3:Eu^{3+}$ crystal compared with the standard card JCPDS 65-3181 (Ia-3, $a=10.818$ Å). The diffraction peaks tend to be more intense and narrower upon increasing the annealing temperature due to better crystallinity and larger size of particles. Further increasing the annealing temperature to 1673 K leads to a phase transformation to monoclinic phase since the XRD pattern is in well agreement with the card JCPDS 42-1465 (C2/m, $a=14.095$ Å, $b=3.576$ Å and $c=8.769$ Å). Representative SEM images for both phases are shown in Fig. 1(b) and (c). The cubic sample appears as agglomerated nanorods with a 400–500 nm width and a 2–3 μm length. However, the phase transformation to monoclinic clearly induces the distinct change in morphology to irregular microparticles. Hence both the sintering temperature and crystalline phase have obvious effects on morphology and size of final sample.

Different luminescence behaviors can be adjusted by different crystalline phases. Fig. 2 exhibits the emission spectra of Gd_2O_3: Eu^{3+} in both phases excited by charge transfer band at 266 nm as a non-selective excitation. Different spectra can be observed and the peaks are narrower for cubic structure (Fig. 2(a)). The coordination geometry of Eu^{3+} as Fig. 2(a) inset shows that Eu^{3+} ions locate at two nonequivalent sites coordinating with six oxygen atoms. One is noncentrosymmetric C_2 site and the other is centrosymmetric S_6 site in a 3:1 population ratio. Only magnetic transition is allowed for S_6 site and there is an efficient energy transfer from S_6 to C_2 as the $^5D_0$ state of Eu^{3+} (S_6) lies 87 cm^{-1} higher than the $^5D_0$ state of Eu^{3+} (C_2) [5,22]. Despite being electric dipole forbidden, the intraconfigurational f–f transitions of Eu^{3+} are allowed by the forced electric dipole principle [23,24]. In this case, the peaks centered at 610.5 nm are due to the forced electric dipole $^5D_0 \rightarrow {}^7F_2$ transition (C_2). The weaker peaks are derived from the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition as 581 (S_6), 587 (C_2), 592 (C_2), 595 (S_6) and 598 nm (C_2) in correct with the number of Stark states for both symmetries. Besides, the $^5D_0 \rightarrow {}^7F_0$ transition is only allowed for the C_2 site corresponding to the single peak at 580 nm. As for monoclinic structure (Fig. 2b), the spectrum presents better

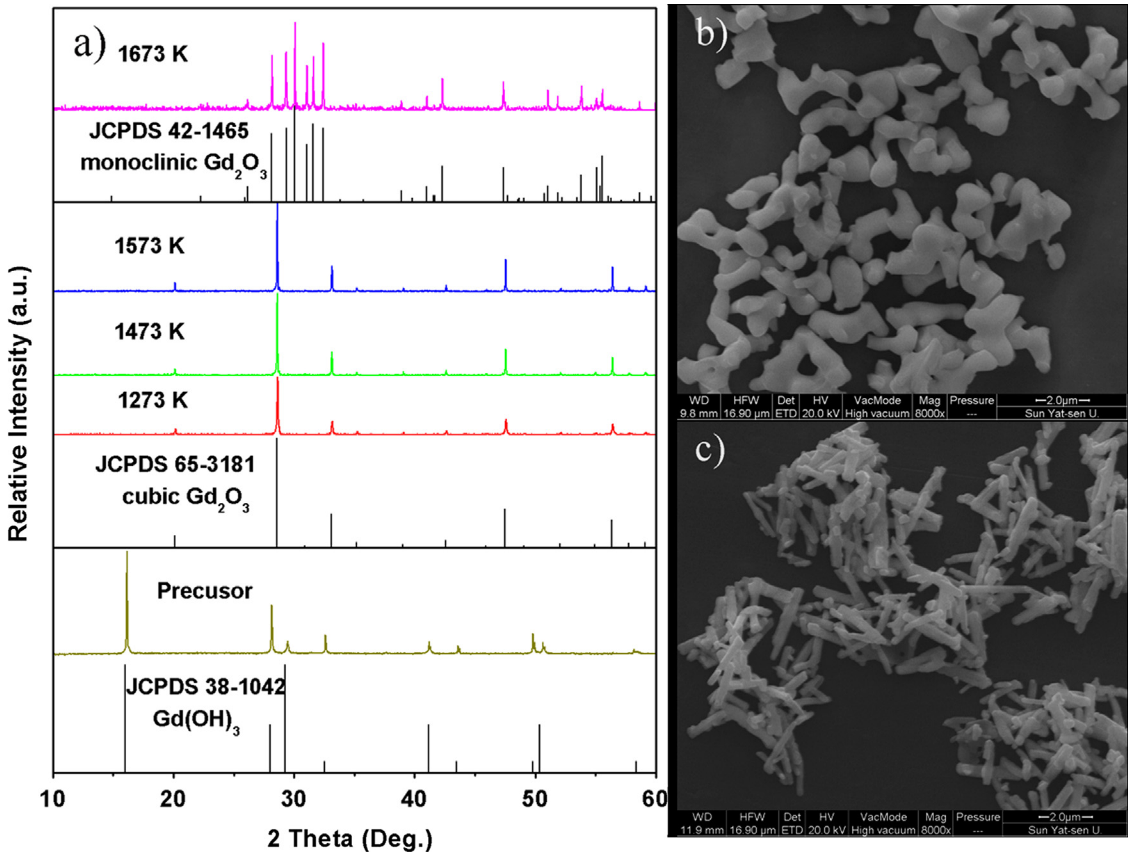

Fig. 1. (a) XRD patterns of the precursor and the phase transformation from cubic to monoclinic and SEM images of $Gd_2O_3:Eu^{3+}$ annealed at (b) 1673 K and (c) 1473 K.