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In-situ sol–gel synthesis of luminescent Y_2SiO_5:Tb^{3+} nanophosphors derived from an assembly of hybrid precursors

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The fact that optical and electronic properties of nanocrystals and nanocrystalline materials of rare-earth oxides differ from those of conventional materials and can be influenced by the particle size has generated interest in this class of materials during the last few years [1–4]. Much research was focused on Y_2O_3 doped with Eu^{3+} ions because it is the unsurpassed red-emitting phosphor with high luminescence quantum efficiency for fluorescence lamps and projection television tubes [5–8]. But relatively little study has been made on nanometer complex rare-earth oxides except for special phosphors such as YAG [9, 10]. Rare-earth (RE) silicates belong to the class of important phosphors that have extensive applications [11–14]. Yttrium silicate doped with Tb^{3+} is an important green-emitting component of the three color centers, which also includes a Mn-activated phosphor [15] or YAG:Tb^{3+} [10]. Sohn *et al.* investigated the luminescence and the decay behavior of Tb-doped yttrium silicate in detail [16]. But the synthesis methods for these luminescent materials were mainly focused on the traditional solid state reaction or on soft chemical technologies such as chemical coprecipitation, sol–gel and colloidal reactions, etc. [17–19]. Jagannathan *et al.* [20] employed some organic polymers to serve both as fuel and as dispersing medium for nanocrystal formation, which can effectively limit the agglomeration of particles.

In this letter, we select an organic polymer, polyacrylamide (PAM), as the dispersing medium template, and the hybrid polymeric precursors were assembled with other functional components such as tetraethyl orthosilicate (TEOS) for the precursor of the silicate network, urea for the fuel, and rare-earth nitrate for the rare-earth oxide. The nanometer-sized Y_2SiO_5:Tb^{3+} was synthesized by thermolysis of the hybrid precursors at 1100 °C. The scheme for the synthesis process was shown in the following:

$$\begin{aligned}&1.98Y(NO_3)_3 + 0.02Tb(NO_3)_3 + Si(OC_2H_5)_4\\&\quad + 5.0\,PAM + 5.0\,NH_2{-}CO{-}NH_2\\&\quad \rightarrow Y_{1.98}\,Tb_{0.02}\,SiO_5 + CO_2\uparrow + H_2O\uparrow\\&\quad + NH_3\uparrow + NO_2\uparrow\end{aligned}$$

The XRD patterns for Y_2SiO_5:Tb^{3+} (Fig. 1) show that the resultant product was also indexed to crystallize in the monoclinic system (X_1 type) with space group $P2_{1/c}$ for lower thermolysis temperature. There exist two different RE^{3+} sites of low local symmetry C_1, which differ in coordination to oxygen: the first site is nine-coordinated, with eight silicon-bonded oxygen atoms and one non-silicon-bonded oxygen atom (free oxygen atom); the second site is seven-coordinated, with four silicon-bonded oxygen atoms and three free oxygen atoms. The average crystallite size was estimated from the full width at half maximum of the diffraction peak by the Sherrer equation [10, 11]:

$$D_{\mathrm{hkl}} = k\lambda/[\beta(2\theta)\cos\theta)] \qquad (1)$$

where $\beta(2\theta)$ is the width of the pure diffraction profile in radians, k is 0.89, λ is the wavelength of the X-rays (0.154056 nm), θ is the diffraction angle, and D_{hkl} is the average diameter of the crystallite. From the estimated data, the nanometer Y_2SiO_5:Tb^{3+} materials are found in the range of 70–100-nm size. The nanometer sizes were relatively large for thermolysis temperatures higher than 1000 °C.

We further used a scanning electron microscope (SEM) to measure the nanometer Y_2SiO_5:Tb^{3+} samples (as shown in Fig. 2). There exist some conglomeration phenomena in the SEM micrographs for the thermal decomposition at higher temperature. It can be predicted approximately that the Y_2SiO_5:Tb^{3+} crystal particle size is less than 100 nm, which agrees with the data from the XRD estimation. The organic polymer, polyacrylamide (PAM), was combined as a dispersing medium to form the polybasic hybrid precursor template of nanometer size. So the nanometer size of Y_2SiO_5:Tb^{3+} can be controlled and determined by the hybrid precursors. Therefore, this preparation technology connects the assembly of hybrid material with the synthesis of nanometer material, which can be expected to be a candidate for the synthesis of other luminescent materials based on rare-earth oxides.

The excitation spectrum of the green fluorescence corresponded to the $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+} in Tb^{3+}-doped nanometer Y_2SiO_5 ($\lambda_{em} = 542$ nm), which shows an asymmetric band with several excitation splits in the ultraviolet–visible region (as shown in Fig. 3). The excitation bands consist of the $4f^8$–$4f^75d^1$ absorption bands of Tb^{3+} in the short ultraviolet region within the range between 230–270 nm and *f–f*

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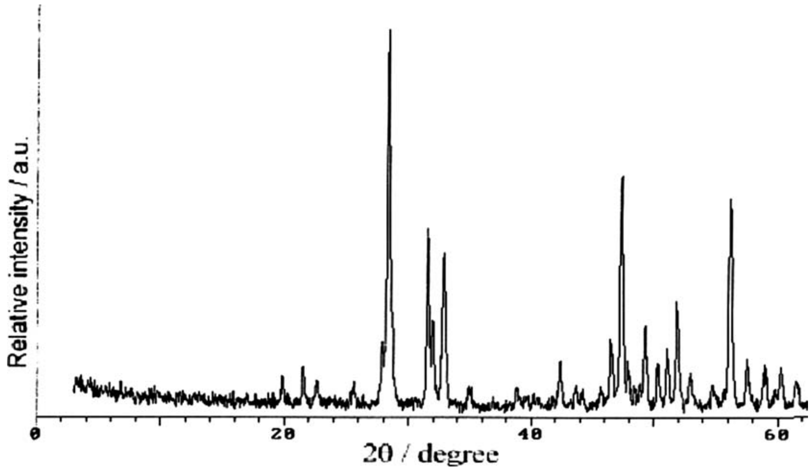

Figure 1 XRD pattern of nanometer Y_2SiO_5:Tb^{3+}.

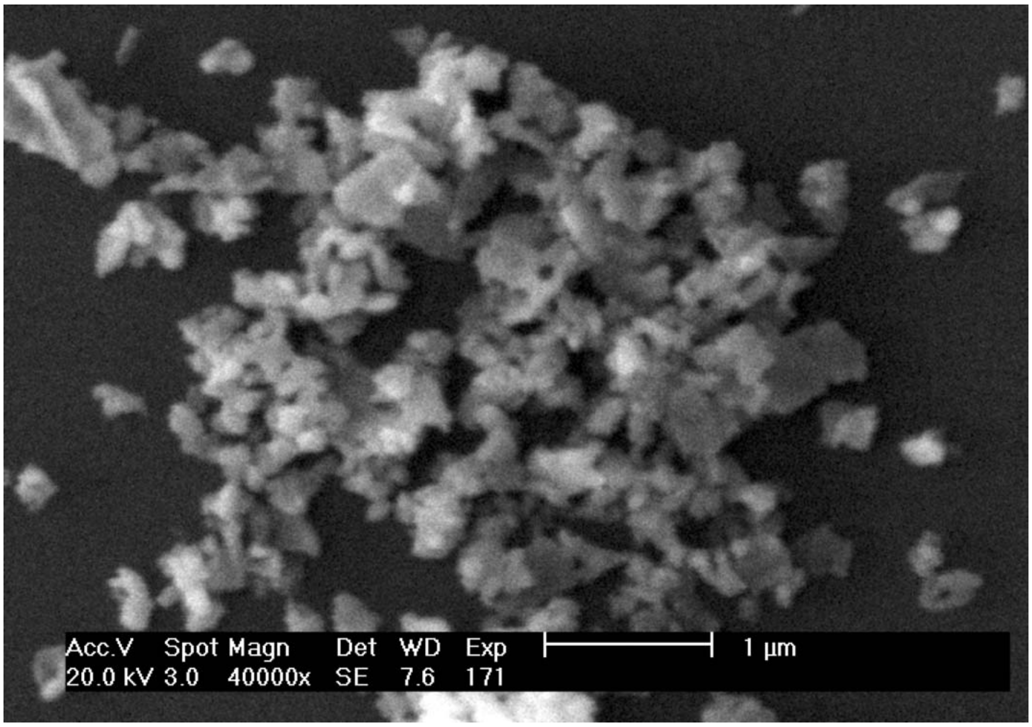

Figure 2 SEM microscope of nanometer Y_2SiO_5:Tb^{3+}.

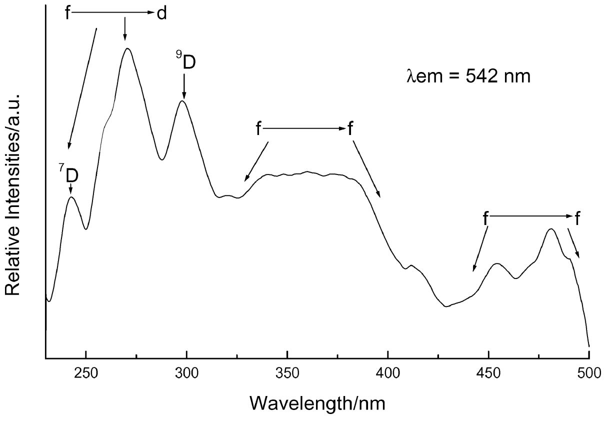

Figure 3 Excitation spectrum of nanometer Y_2SiO_5:Tb^{3+}.

absorption lines of Tb^{3+} in the longer wavelength region in the range of 300–500 nm. The former would be attributed to the mixing of a charge-transfer band due to Tb–O interaction (CTB) and the 4f–5d transition bands in the Tb^{3+} center lying in the band gap region of the host matrix. The first shoulder at 241.5 nm in this region would seem to be assigned to the ^{7}D level of the 4f–5d transition of Tb^{3+} ion, and the two peaks 260 and 272 nm belong to the 4f–5d of Tb^{3+}. Besides this, it can also be seen that the peak at 294 nm corresponded to the ^{9}D level of the $4f^7 5d^1$ configuration in the Tb^{3+} center, assuming that the Tb^{3+} ions have an octahedral environment [21]. In fact, there exist two different distorted octahedral sites for Y in the Y_2SiO_5 host, and some Tb^{3+} sites in the host lattice are nine- and seven-coordinated to oxygen atoms, showing a $P2_1/C$ symmetry, which can lead to a good understanding of the excitation behavior of Y_2SiO_5:Tb^{3+}. Besides this, there also exists the excitation band originated from the f-f transition.

Fig. 4 shows the corresponding emission spectra of nanometer Y_2SiO_5:Tb^{3+}, which exhibits the

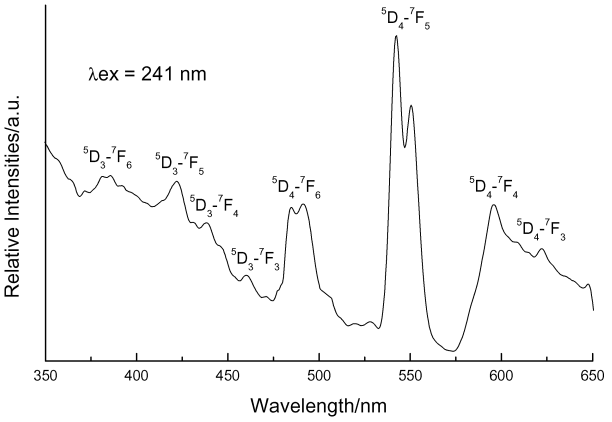

Figure 4 Luminescence spectrum of nanometer Y_2SiO_5:Tb^{3+}.

characteristic green luminescence originated from the transitions between the excited $^5D_4$ level and ^7F_J ($J = 6, 5, 4, 3$) level of the Tb^{3+} ion, i.e., four peaks at around 489, 543, 592, and 622 nm, respectively. Besides this, the emission can also be observed for the transition between the $^5D_3$ level and ^7F_J($J = 6, 5, 4, 3$) for the low doping concentration of Tb^{3+} (only 1.0 mol%) in Y_2SiO_5, showing at 385.5, 422, 438, and 460 nm, respectively. The strongest emission peak is located at 543 nm, corresponding to the typical hypersensitive transition $^5D_4 \rightarrow {}^7F_5$ for Tb^{3+} ion. When the host matrix Y_2SiO_5 absorbed the ultraviolet light energy, the Tb^{3+} ion was excited by the energy transfer from the absorption energy and then nonradiatively relaxed to the $^5D_4$ and $^5D_3$ levels of terbium ion. Finally, the transition takes place from the $^5D_4$ and $^5D_3$ to the ^7F_J level of Tb^{3+}. Because of the limited resolution of the apparatus in our limited measurements, it was not possible for us to observe clearly in order to obtain enough information on the possible multiple sites occupied by Tb^{3+}.

In summary, the synthesis of Y_2SiO_5:Tb^{3+} nanophosphors was achieved at 1100 °C by assembling hybrid precursor sol–gel technology. The particle size is in the range of 70–100 nm. The nanometer Y_2SiO_5:Tb^{3+} exhibits the characteristic green fluorescence of Tb^{3+} ion at 542 nm. This indicates it is a candidate technology for the synthesis of nanometer rare-earth oxides.

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