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Multiband luminescence of Eu^{3+} based on $Y_2Zr_2O_7$ nanocrystals

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Abstract

Eu^{3+} doped yttrium zirconate ($(Y_{1-x}Eu_x)_2Zr_2O_7$) nanocrystals were synthesized by a simple sol–gel combustion method, and characterized by X-ray diffractometry (XRD), transmission electron microscopy (TEM), UV–vis absorption and photoluminescence (PL) spectroscopy. Photoluminescence spectra of $(Y_{1-x}Eu_x)_2Zr_2O_7$ ($x = 0.005$–0.15) show multi-peaks corresponding to the f–f transitions $^5D_0$–^7F_J ($J = 1, 2, 3, 4$ and 5) of Eu^{3+}. Both the $^5D_0$–$^7F_1$ magnetic dipole transition and the $^5D_0$–$^7F_2$ electric dipole transition are intense and the $^5D_0$–$^7F_2$ emissions split into several peaks depending on the doping concentration. The fine structure of the PL spectra is related to host lattice and the local situation around Eu^{3+}.

Keywords: Sol–gel growth; Nanostructures; Luminescence spectroscopy; Luminescence

1. Introduction

There is persistent interest in searching for a more inexpensive and effective red phosphor. The material research focuses on the development of host materials for the Eu^{3+} activator. Considering the intensity and spectra feature, the crystalline materials is more promising hosts compared with glass matrix [1]. Using crystalline hosts, we can control the site symmetries of Eu^{3+} through chemical modification of hosts, such as making solid solutions and introducing lattice defects. By doing so, we can realize multiband emissions of Eu^{3+}, which are useful in reproducing natural light in optical devices because of the better spectral overlap.

The luminescence of Eu^{3+} is due to intraconfigurational f–f transitions [2], usually from the excited $^5D_0$ state to ^7F_J ($J = 1, 2, 3, 4$ and 5) levels of $4f^6$. The 4f energy levels of Eu^{3+} are hardly affected by the crystal field because of the shielding effect of the $5s^25p^6$ electrons. However, the selection rules and transition probabilities between states strongly depend on the crystal field. When the Eu^{3+} ions embedded in a site with inversion symmetry, the $^5D_0$–$^7F_1$ magnetic dipole transition (MDT) is dominating with emission wavelength of about 590 nm, while in a site without inversion symmetry the $^5D_0$–$^7F_1$ electric dipole transition (EDT) around 610–620 nm is the strongest [2–4]. Furthermore, the ^7F_J ground state undergoes crystal-field splitting, which also influences the emission wavelength of all $^5D_0$–^7F_J transitions [5].

In the present paper, we introduce Eu^{3+} into a new host yttrium zirconate ($Y_2Zr_2O_7$). It is well known that rare-earth-metal zirconates $RE_2Zr_2O_7$ with larger RE^{3+} ion radius, crystallize with the pyrochlore structure, whereas $RE_2Zr_2O_7$ with smaller RE^{3+}, crystallize with the defected fluorite structure [6]. $Gd_2Zr_2O_7$ lies at the boundary and it has the pyrochlore crystal structure when prepared at 1500 °C and the fluorite structure when heated at 1600 °C [7]. The two structures are very similar and can be discriminated by the existence of (1 1 1), (3 3 1) and (5 1 1) XRD reflections, which are characteristic of the pyrochlore phase [8,9]. Because of the small size of the Y^{3+}, $Y_2Zr_2O_7$ adopts a defected fluorite structure. $Y_2Zr_2O_7$ has been researched for its electrical behavior [10], considering the probability of replacing YSZ (yttrium stabilized zirconia). Here, we choose $Y_2Zr_2O_7$ crystals as Eu-activated luminescence material, for its capability of accommodating Eu^{3+} in the Y site. The synthesis, characterization and photoluminescence of Eu^{3+} doped $Y_2Zr_2O_7$ nanocrystals are discussed below in detail.

2. Experimental

Zirconyl acetate ($ZrO(Ac)_2$), yttria(Y_2O_3), europia (Eu_2O_3), ammonium nitrate (NH_4NO_3) and urea were used as starting materials. All the chemicals we used were analytic reagent. $ZrO(Ac)_2$ was used as an aqueous acetic solution with 20.05 wt% ZrO_2, and the aqueous rare earth nitrate ($Y(NO_3)_3$, $Eu(NO_3)_3$) solutions were produced previously from the corresponding rare earth oxides. For pure $Y_2Zr_2O_7$, $Y(NO_3)_3$, $ZrO(Ac)_2$ and NH_4NO_3 were first mixed in the

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ratio of 1:1:3. After 30 min stirring, the requisite amount of urea was added to the mixed solution. The mixture was stirred for 1 h, and then the transparent sol was heated to give an opal gel. Ammonia solution was needed to adjust pH value of the solution to be 7–8. The as-prepared gel was dried at 100 °C for 12 h, and then heated in a muffle furnace at 600 °C for 10 min. The Eu^{3+}-doped samples $(Y_{1-x}Eu_x)_2Zr_2O_7$ were prepared slightly differently, just replacing 0.5–15 mol% amount of $Y(NO_3)_3$ by $Eu(NO_3)_3$.

The crystalline structure of the products was analyzed by X-ray diffraction (XRD) using a Japan RigaKu D/MAX 2200PC diffractometer with Cu Kα radiation (λ = 0.15418 nm) and graphite monochromator. Transmission electron micrograph (TEM) images were taken with a JEM-100CX transmission electron microscope. The UV–vis absorption measurement was proceeded in alcohol solution with a UV 757 CRT spectrophotometer, and the absorbency has been normalized to unity in order to remove the influence of the solution concentration. The photoluminescence (PL) spectra were measured with an Edinburgh FLS920 fluorescence spectrometer at room temperature. The spectral resolution is 1.0 nm.

3. Results and discussion

Fig. 1 shows the XRD patterns of the prepared yttrium zirconate. All the four main peaks (2 2 2), (4 0 0), (4 4 0) and (6 2 2) are in agreement with the formation of fluorite structure [11], though the JCPDS data corresponding to $Y_2Zr_2O_7$ phase are still not available for comparison. The reflections of (1 1 1), (3 3 1) and (5 1 1), which are always the characteristics of pyrochlore structure, are inexistent in Fig. 1 [9]. The average crystalline size calculated using Scherrer equation is about 40 nm. From Fig. 1, no different phase such as the Eu_2O_3 phase is detected even at high Eu concentrations (15%). $Y_2Zr_2O_7$ can accommodate a large amount of Eu^{3+} in the Y site, because of the similar structure between $Eu_2Zr_2O_7$ and $Y_2Zr_2O_7$.

A typical TEM image is shown in Fig. 2. It can be found that $Y_2Zr_2O_7$ grains of about 35–45 nm, which agrees within experimental error to the size determined by XRD, have developed with heavy agglomeration.

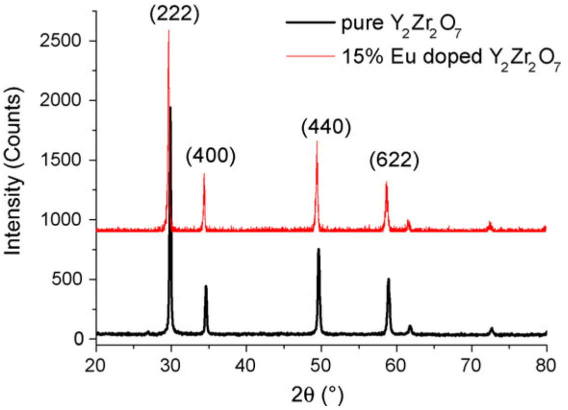

Fig. 1. XRD patterns of pure and 15% Eu-doped $Y_2Zr_2O_7$ nanocrystals.

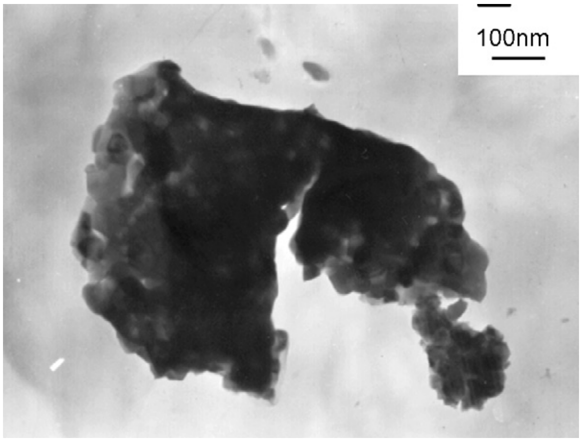

Fig. 2. TEM image of $Y_2Zr_2O_7$ nanocrystals.

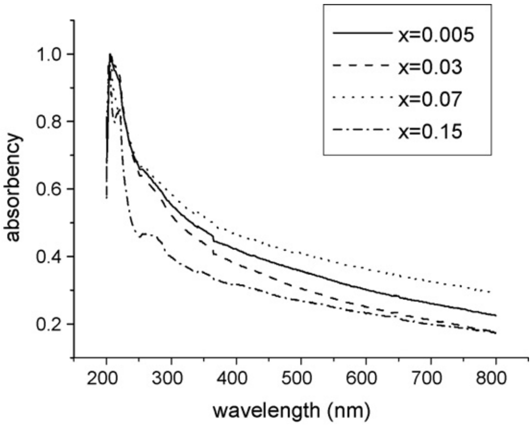

Fig. 3. Absorption spectra of $(Y_{1-x}Eu_x)_2Zr_2O_7$ samples (x = 0.005, 0.03, 0.07 and 0.15).

Fig. 3 shows the optical absorption spectra of $(Y_{1-x}Eu_x)_2Zr_2O_7$ samples in the UV–vis range. One can see that the absorption features are influenced by the Eu^{3+} concentration. The broad absorption band between 250 and 300 nm is attributed to the charge transfer state (CTS) of Eu^{3+}, which is caused by the electron transferred from the oxygen 2p orbital to the empty 4f orbital of europium. Another CTS centered at about 220 nm is overlapped by the host absorption between 200 and 250 nm. The Eu^{3+} related absorption becomes more distinct as the doping level rising, and when x = 0.15, a visible absorption peak appears at 221 nm. The CTS absorption shows more than one lines, and this may be due to the ununiform A site which Eu^{3+} is located.

Fig. 4(a) shows the emission spectrum of $(Y_{1-x}Eu_x)_2Zr_2O_7$ nanocrystals (x = 0.03) following excitation at 239 nm at room

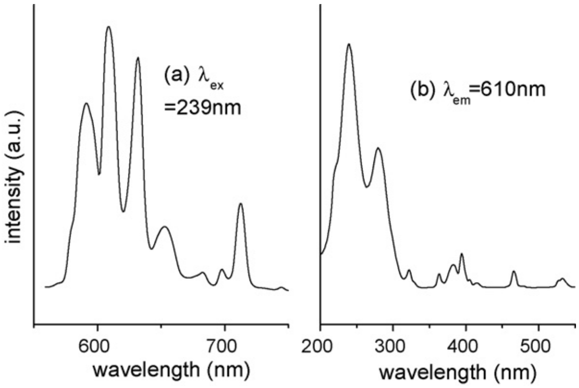

Fig. 4. PL (a) emission and (b) excitation spectra of $(Y_{1-x}Eu_x)_2Zr_2O_7$ nanocrystals (x = 0.03).