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Synthesis and Luminescence Properties of Eu^{3+}- doped Silicate Nanomaterial

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Abstract

In this paper, we introduce a sol-gel process for preparing $Y_2Si_2O_7$: Eu^{3+} nanocrystals. The rare earth compounds were dispersed in the SiO_2 colloids and the monodisperse nano-scale composite materials were prepared. The reactant mass fraction and heat treatment temperatures could affect the structures and emission spectrum properties of as-synthesized samples. The samples emit the strong red light upon excitation under the ultraviolet. The main peaks originate from $^5D_0$-$^7F_2$ electric dipole transition of Eu^{3+}. With regard to the samples treated at different temperatures, the emission spectra obtained under 266 nm excitation show different shapes of spectra lines and relative intensities, indicating that the Eu^{3+} ions have been located in different local environments.

Keywords: nanomaterials, $Y_2Si_2O_7$: Eu^{3+}, luminescence, emission spectra

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1. Introduction

Because of the potential application in high-resolution display and fluorescence labelling, the researches on rare-earth doped nanomaterials have been intensively concerned in the preparation methods and luminescence properties [1-2]. Compared to the traditional preparation methods, the sol - gel method is simple but has some advantages, such as good optics transparency and homogeneous doping and so on. Some researchers have used the sol-gel method to prepare the rare-earth doped silicate materials with excellent luminescence properties, for example, Tb-doped Y_2SiO_5 is a good green cathode ray luminescence material [3-4], Eu^{3+} doped Y_2SiO_5 has an important potential application in the high density time domain and frequency domain light memory[5]; W.P. Zhang et al observed a meaningful phenomenon that the quenching concentration and luminescence intensity are higher in the nanoscale Y_2SiO_5:Eu^{3+} sample than those in the corresponding bulk sample [6]. In recent years, some researchers have begun paying attention to $RE_2Si_2O_7$ nanomaterials but the research work mainly focused on the synthesis of materials rather than on luminescence properties [7]. In this article, $Y_2Si_2O_7$:Eu^{3+} samples were prepared through adjusting the reactant proportion and the annealing temperature. The samples have better luminescence properties and can produce strong red light excited by the ultraviolet light.

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2. Experiment

Eu_2O_3 (99.99%), Y_2O_3 (99.99%) and analysis pure ethyl tetrathoxysilanc (TEOS) were used as the starting materials. First Eu_2O_3 (0.1% mol) and Y_2O_3 (4.9% mol) were dissolved in HNO_3, then deionized water was added. The mixed nitrate solution was obtained. Excessive amount TEOS was dissolved in ethanol. The above two solutions were mixed and vigorously stirred to form a uniform solution. The pH of the mixed solution was adjusted to 1-2 by HNO_3. After aging process the mixed solution became the gel. The gel was heated to 80 ºC and the temperature was maintained for 8 hours to form a dry gel. The samples with various precursor fractions and heat treatment temperatures were prepared. The samples that contains 40 wt% Y_2O_3 and were annealed at 1000 ℃, 1200 ℃, and 1300 ℃, are labelled as **a, b, c** respectively. It is the same that samples that contained 5 wt% Y_2O_3 are labelled as **A, B, C**. For comparison, we have also prepared a sample (d) that contained 40 wt% Y_2O_3 and were annealed at 800 ℃. X-ray powder diffraction (XRD) data were collected on a Rigaku / Max 2550V/PC diffractometer with Cu-Kα radiation (λ=1.54178Å). The particle size morphology of the samples were observed by the Hitachl S-4800 field emission scanning electron microscope (FE-SEM). The samples were excited with 266 nm light generated by a fourth-harmonic-generator pumped by the pulsed YAG: Nd laser with 10ns pulse width and the emission spectra were measured with a TRIAX-550 spectrometer, a R955 photomultiplier, a 162 boxcar averager and processed by a computer.

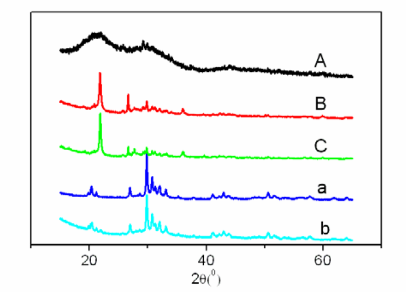

Fig.1 XRD patterns of sample A, B, C and sample a, b

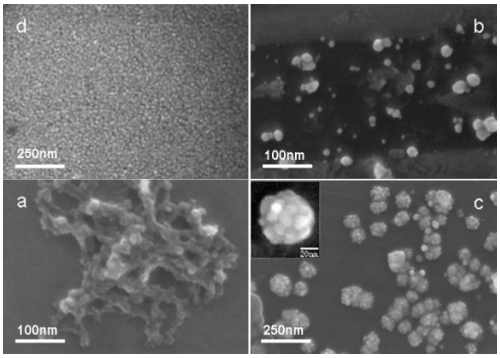

Fig.2 SEM images of $Y_2Si_2O_7$: Eu^{3+} sample a, b, c and d（800°C）
Inset in part c: enlarged image of a single composite particle

3. Results and discussion

Figure 1 shows the XRD patterns of the samples. A wide diffraction peak was observed for sample A. This represents that the sample **A** is mainly amorphous. The samples **B** and **C** are mixed phase structures that consists of $Y_2Si_2O_7$ crystals belonging to α- phase （No.21-1457）and δ- phase (No.42-0168) and also several unidentified peaks. The samples **a** and **b** consist of α-$Y_2Si_2O_7$ crystals (No.38-0223), and no impurities were observed. As a matter of fact, α-$Y_2Si_2O_7$ crystals could be formed starting at 1000 ℃. The pattern of sample **c** was given in literature [8]. It showed that α-$Y_2Si_2O_7$ crystal structure was dominating and a few β-$Y_2Si_2O_7$ diffraction peaks appeared. The result indicates that α-$Y_2Si_2O_7$ crystals is dominating in the sample **c** annealed at 1300℃. Some reports related to silicate materials indicated that the heat treatment temperature was a primary factor to determine the crystal structure. Because the crystal phase changes easily with the heat treatment temperature [9-10], it is very difficult to prepare a pure phase $Y_2Si_2O_7$ sample. But Figure 1 reveals more abundant information that even the crystal structures of products might be different even though the heat treatment temperature is the same but the Y2O3 mass is different. The sample **A** shows an amorphous structure, but the sample **a** is a pure phase $Y_2Si_2O_7$:Eu^{3+} crystal structure; the sample **B** is a multiphase structure but the sample **b** is a pure phase material. The XRD results show that the mass fraction of reactants is also a key factor in preparing $Y_2Si_2O_7$:Eu^{3+} materials. As SiO_2, Eu_2O_3, and Y_2O_3 are high melting point substances, the reaction can not achieve a balanced state or obtain a pure phase $Y_2Si_2O_7$:Eu^{3+} product if the heat treatment temperature is inappropriate. The increased proportion of Y_2O_3 in samples **a** and **b** can contribute to the contacting of the reactants with each other, provide a larger reaction area for the reactants, and speed the reaction. This might be the reason that the crystalline or even pure phase $Y_2Si_2O_7$:Eu^{3+} samples could be prepared at a lower temperature.

Figure 2 shows the scanning electronic microscope (SEM) photographs of the samples **d**, **a**， **b**, and **c**, in which their mass fractions are the same. It could be observed in Figure 2-d that the amorphous particles were evenly dispersed in the SiO_2 colloid and the particle size was smaller than 10nm. A significant change could be seen in Figure 2-a, in which the increasing temperature makes the chemical reaction speed up and the moisture reduces in the colloid, and the crystal structure $Y_2Si_2O_7$:Eu^{3+} begins to appear. In Figure 2-b, it could be clearly observed that the particles have an average size of about 15 nm and shows a trend of gathering. Figure 2-c shows that the particles have gathered into the monodisperse composite balls that have a uniform size distribution of about 60 nm. The inset demonstrates clearly that the nanoscale composite ball is composed of some smaller nanoparticles ($Y_{2-x}Si_2O_7$:$Eu^{3+}{}_x$, x=0.02) embedded in the SiO_2 framework. The SEM photographs could directly reflect the morphology and particle size distribution, and indirectly reflect the sample crystallization states. Figures 3 and 4 show the emission spectra of the samples excited with 266 nm at room temperature, in which all spectrum peaks have been normalized to their maximum value. The spectral changes of the samples with annealing temperature could clearly be seen in Figure 3.

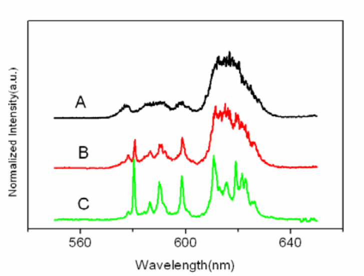

Fig.3 Emission spectra of sample A, B and C

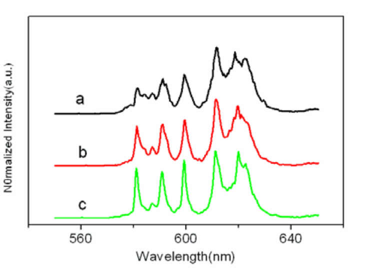

Fig.4 Emission spectra of sample a, b and c

Even if the reactant mass fractions are the same, the spectrum structures might not be the same. the sample **A** emission spectrum shows a broadband that is the amorphous material performance, which is consistent with the XRD results; in the sample **B** spectrum**,** the Eu^{3+} transition originated from $^5D_0 \rightarrow {}^7F_2$ is stronger than from $^5D_0 \rightarrow {}^7F_1$; the sample C spectral lines are obviously narrowed and split, which is caused by better crystallization as the heat treatment temperature increase. In addition, we also observed the changes of the relative intensity of the spectral lines, in which $^5D_0 \rightarrow {}^7F_1$ transition increase is faster than $^5D_0 \rightarrow {}^7F_2$ as temperature increase.

Figure 4 shows that the emission spectra of samples **a**, **b** and **c**. When the samples were prepared at lower temperature the transition intensity of $^5D_0 \rightarrow {}^7F_2$ could be increased and the colour purity could be improved. These might be attributed to that the smaller particle size could make the local environment of Eu3 + ion change, the symmetry reduce, and the Eu3 + ion occupy the non-inversion center of symmetry. When the samples were prepared at higher temperature, their particle size, the crystallization, and inversion symmetry centres were all increased. L D Sun group [11] reported that the colour purity of the YBO_3: Eu^{3+} nanocrystals were better than the corresponding bulk material. The emission spectra of all samples were compared. The results indicate that the spectra structures in Figure 3 are affected less by the annealing temperature and the luminescence properties are better than Figure 4. We consider that $Y_2Si_2O_7$:Eu^{3+} product with high phase purity could be obtained at the same heat treatment temperature if the reactant proportion is appropriate. Because $Y_2Si_2O_7$: Eu^{3+} nanoparticles were embedded in SiO2 host framework balls, the doped Eu^{3+} ions might be stable and less affected by external factors. The one of main factors affecting the sample luminescence intensity is the $Eu3^+$ ions local environment. The suitable reactant mass fraction could reduce environment defects that might affect the luminescence properties. For example, the Eu^{3+} ions in the sample **b** are less affected by the external environment than in the sample **B**.

Conclusion

In this article, we reported that the Y2Si2O7: Eu3 + nanocrystal samples were prepared with the sol-gel method at different annealing temperatures and in different reactant mass fractions. When Y2O3 mass fractionIn are too small the pure phase structure Y2Si2O7:Eu3 + could not be formed. Only when the reactant mass fraction is appropriate in chemical synthesis, the Y2Si2O7 Eu3 + structure with high phase purity might be obtained. When the samples were prepared at lower temperatures the color purity was improved and the particle size decreases, which is related to the local environment of Eu3 + ions. We thought that heat treatment temperature is one of the most important factors. The appropriate reactant proportion is the essential condition to prepare the higher phase purity and better luminescence property $Y_2Si_2O_7$:Eu^{3+} nanoscale samples.

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