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The Luminescence of Nanoscale Y₂Si₂O₇:Eu³⁺ Materials

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The Y₂Si₂O₇:Eu³⁺ sample was prepared with the sol-gel method. The Y₂O₃:Eu³ was dispersed in SiO₂, and the complex Y₂Si₂O₇:Eu³⁺ particles were synthesized at high annealing temperature. The sample consisted of nearly spherical particles with an average size about 60 nm. The ultraviolet excitation spectra and emission spectra were measured. The sample excited by short ultraviolet light showed strongly red luminescence and fine monochromaticity. The luminescence was strongest from the ⁵D₀ → ⁷F₂ electric dipole transition located at 611 nm. The excitation spectra of Y₂Si₂O₇:Eu³⁺ excited with ultraviolet lights showed that the peak of the Eu³⁺—O²⁻ charge transition band located at about 240 nm. During monitoring of different emission peaks of ⁵D₀ → ⁷F₂, the charge transition band in the excitation spectra shifted, and the relative intensity of emission spectra changed obviously under the excitation of different ultraviolet wavelengths. These results confirmed that the Eu³⁺ could be excited with ultraviolet radiation of different wavelengths. At low temperature, using Eu³⁺ ions as fluorescence probes, we monitored the emission peaks of ⁵D₀ → ⁷F₁ and ⁵D₀ → ⁷F₂ transitions and measured the excitation spectra of ⁷F₀ → ⁵D₀, ⁵D₀ → ⁷F₁, and ⁵D₀ → ⁷F₂ site-selective excitation spectra. These results indicated that Eu³⁺ ions are located in different local environments in the Y₂Si₂O₇ host.

Keywords: Sol-Gel, Luminescence Intensity, Y₂Si₂O₇:Eu³⁺.

1. INTRODUCTION

The syntheses and properties of nanomaterials of rare-earth ions doped have attracted much due to their potential applications such as up-conversion, display materials, bio-labels and cancer therapies.^{1–3} Because the sol-gel method has many advantages, such as high purity, low synthesis temperature, homogeneous doping, and ease of synthesizing nanostructure materials, it has been accepted as a widely applicable means to synthesize some materials and a special technology to synthesize nanosized materials. Owing to the potential applications of silicates, nanosized luminescent materials doped with rare earth laser materials, and fluorescence materials,^{4,7} the sol-gel method has widely been researched to synthesize them. Oxy-silicates are fine hosts for cathodoluminescent materials, for example, Y₂SiO₅:Tb³⁺ is a fine green cathodoluminescent material,^{8–11} and Y₂SiO₅:Eu³⁺ has potential important application value in optical memory of high density time-domain and frequency-domain. The Y₂SiO₅:Eu³⁺ is

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also a fluorescent material showing promise for use in coherence-time optical memory as used in high resolution display.¹² The spectrum properties of Y₂SiO₅:Eu³⁺ have been researched in many aspects.^{13–15} Recently, RE₂Si₂O₇ nanosized materials have some been studied. The RE₂Si₂O₇ materials are also important stationary-phase pyrosilicates and have been used as laser materials, ferromagnetic materials, ferroelectric materials, etc. The Lu₂Si₂O₇:Ce³⁺ is a good inorganic scintillator material also.¹⁶ The Y₂Si₂O₇:Eu³⁺ is a fine red luminescent material, and much research has focused on its synthesis, but there are few reports about Y₂Si₂O₇:Eu³⁺ nanosized materials.^{17–18} In our work, Y₂O₃:Eu³⁺ was scattered in SiO₂. The Y₂Si₂O₇:Eu³⁺ sample was prepared by annealing at 1,300 °C for 2.5 h. The excitation spectra and emission spectra of the sample excited with ultraviolet radiation of different wavelengths at room temperature have been measured. At low temperature, using Eu³⁺ ions as fluorescence probes, we measured ⁵D₀ → ⁷F₁ and ⁵D₀ → ⁷F₂ sites selective excitation spectra, which indicate that in the Y₂Si₂O₇:Eu³⁺ sample that we prepared, Eu³⁺ ions could locate in different local environments.

2. EXPERIMENTAL DETAILS

A europium-doped yttrium silicate ($Y_{2-x}Si_xSi_2O_7:Eu^{3+}$; $X = 0.02$) sample was synthesized with the sol-gel method. Eu_2O_3 (99.99%), Y_2O_3 (99.99%), and tetraethoxysilane (TEOS) were used as the starting materials. Eu_2O_3 (0.1% mol) and qualified Y_2O_3 were dissolved in HNO_3 , and deionized water was added. TEOS was dissolved in alcohol. The above two solutions were mixed and vigorously stirred. The pH of the mixed solution was adjusted to 1–2 with HNO_3 . After precipitation, the obtained gel was dried at 80 °C for 8 h. The resultant dried gel was calcined at 1,300 °C for 2.5 h. The final sample was a powdery white complex $Y_2Si_2O_7:Eu^{3+}$ crystals. The morphology and structure were characterized by a Hitachi S-4800 field emission scanning electron microscope (FE-SEM) and a Cu-target radiator X-ray diffractometer (XRD). The excitation spectra ranging from 200 to 400 nm and emission spectra excited by different wavelength ultraviolet radiations were obtained with a Hitachi F-4500 fluorescence spectrophotometer. The high resolution emission spectra were measured at room temperature, with 266 nm light generated by a fourth-harmonic-generator pumped by the pulsed YAG:Nd laser. The excitation spectra of $F_0 \rightarrow {}^5D_0$ transition in Eu^{3+} ions and site-selective excitation spectra at low temperatures were measured by a Rhodamine 610 dye pumped by the YAG:Nd laser. All the spectra were recorded by a TRIAX-550 spectrometer, a R955 photomultiplier, and a 162 boxcar averager and processed by a computer.

3. RESULTS AND DISCUSSION

Figure 1 shows the SEM image of the complex $Y_2Si_2O_7:Eu^{3+}$ sample prepared by annealing at 1,300 °C. As seen, the particles are nearly spherical. The average size of the particles is about 60 nm. The smaller $Y_2Si_2O_7:Eu^{3+}$ granules with sizes about 10 nm are inside the SiO_2 particles. Figure 2 shows the XRD pattern of the sample. It could be seen that the sample consists of $Y_2Si_2O_7$ crystals and the major crystals belong to triclinic crystal of α -phase (JCPDS No. 38-0223).

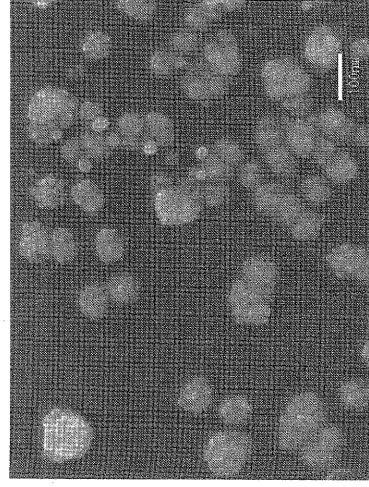


Fig. 1. SEM image of $Y_2Si_2O_7:Eu^{3+}$.

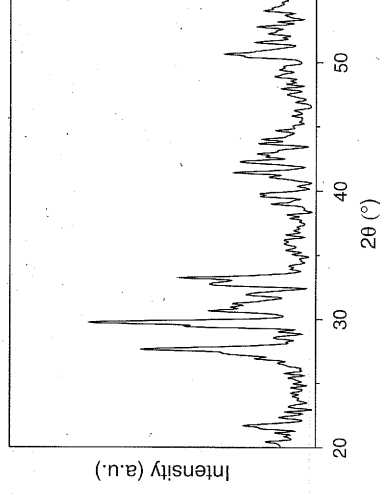


Fig. 2. XRD pattern of the $Y_2Si_2O_7:Eu^{3+}$.

Figure 3 shows the excitation spectra of the complex $Y_2Si_2O_7:Eu^{3+}$ sample in the region of 200–300 nm. The excitation broadband that main peak located at 240 nm is the charge transfer band (CTB) of $Eu^{3+}-O^{2-}$. It is clear that CTB emission peaks produced red shift obviously when monitoring emission at 623 nm relative to 611 nm. The red shift may be caused by proportion changes that Eu^{3+} ions occupy different sites, and different CTB energies of different sites, which implies existing different local environments surrounding the Eu^{3+} ions in $Y_2Si_2O_7$ host.

Figure 4 shows the emission spectra of the sample excited by different wavelength ultraviolet light. The spectra were normalized to their maximum. When the excitation wavelength became longer, the emission peak splits became more obvious, and the relative emission intensity changed violently. At 580 nm and 622 nm, emission intensities became stronger more obviously than others. The emission peak from the ${}^5D_0 \rightarrow {}^7F_2$ transition from 619 nm shifted to 622 nm as excitation wavelength became longer. The above results suggest that Eu^{3+} ions in the $Y_2Si_2O_7$ host could be excited by different wavelengths of ultraviolet light. Because Eu^{3+} ions in the $Y_2Si_2O_7$ host occupied different sites, the effects of different local environments to these Eu^{3+} ions made that the position and shape of

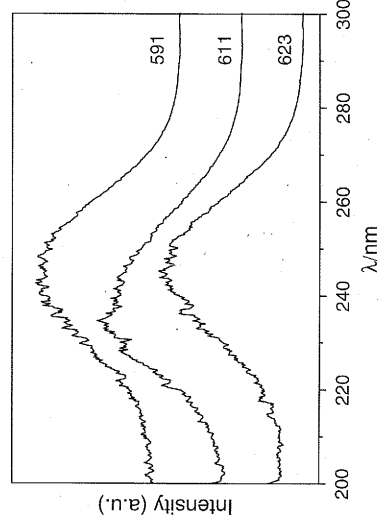


Fig. 3. The excitation spectra of the $Y_2Si_2O_7:Eu^{3+}$ monitoring the emissions of ${}^5D_0 \rightarrow {}^7F_1$ at 591 nm, and ${}^5D_0 \rightarrow {}^7F_2$ at 611 and 623 nm.

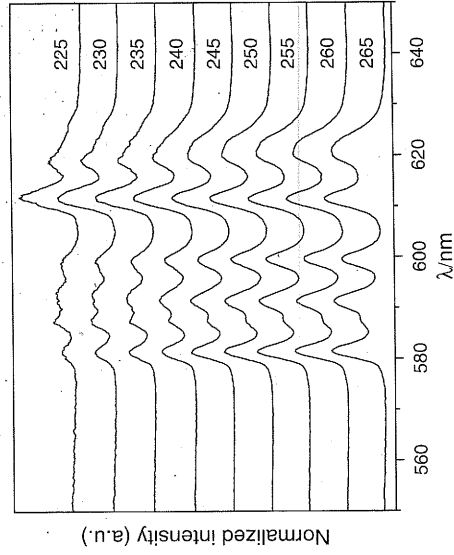


Fig. 4. The normalized emission spectra of $Y_2Si_2O_7:Eu^{3+}$ under different ultraviolet excitation wavelengths.

absorption and emission spectra of each other Eu^{3+} ion were different more or less. Owing to the limit of the instrument resolution factor, the emission spectra are not perfect. To penetrate their details we measured high resolution emission spectra excited with a 266 nm laser at room temperature.

Figure 5 shows the emission spectrum excited by a 266 nm laser at room temperature. The emission spectrum originating mostly from the 5D_0 transition of Eu^{3+} ions consists of strongly sharp peaks at $^5D_0 \rightarrow ^7F_j$ ($j = 0, 1, 2, 3, 4$) of Eu^{3+} ions, and emission from 5D_1 is not seen. There are generally higher phonon frequencies in silicate or borate hosts than others, so it is difficult to detect emission from the 5D_1 transition of Eu^{3+} ions.¹⁸⁻¹⁹ In high-resolution emission spectra excited with 266 nm laser at room temperature, the fact that the strongest peak is located at 611 nm from the electric dipole transition suggests that Eu^{3+} ions in $Y_2Si_2O_7$ mostly occupy non-inversion symmetry centers.

We know that the intensities and split forms of emission peaks of the excitation broadband from the Eu^{3+} ions

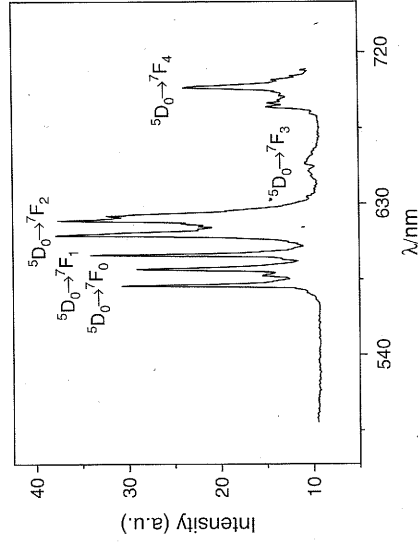


Fig. 5. The emission spectrum of $Y_2Si_2O_7:Eu^{3+}$ excited by a 266 nm laser.

$^7F_0 \rightarrow ^5D_0$ transition could be affected by site symmetry, co-ordination structure, and different site distribution. To better understand local environments and possible sites occupied by Eu^{3+} ions in $Y_2Si_2O_7$, we measured excitation spectra of the sample at 12 K. Figure 6 shows the excitation spectra of the $^7F_0 \rightarrow ^5D_0$ transition as monitoring $^5D_0 \rightarrow ^7F_2$ different emission peaks. When the emission peak of 611 nm was monitored, only a strong peak at 579.63 nm was seen. When the emission peak of 616 nm was monitored, a peak at 579.63 nm, a peak at 579.47 nm, and a broad peak centered at 578.4 were seen. When the emission peak of 622 nm was monitored, a peak at 579.10 nm and a peak at 579.63 nm were seen. The result of monitoring at 626 nm is the same as that at 611 nm. Generally, the number of sites that RE^{3+} can occupy relates to the crystal structure and number of O^{2-} surrounding the RE^{3+} . Now, a few results of researching $Y_2Si_2O_7$ were published. For example, Ching indicated that in $Y_2Si_2O_7$, monoclinical crystal belonging to the $P2_1/c$ space Y^{3+} could occupy one kind of site only, Si^{4+} could also occupy one kind of sites, O^{2-} could occupy four kinds of sites, and the lengths of their bonds range from 250 Å to 2.328 Å.²⁰ Felsche mentioned that the triclinic α - $Y_2Si_2O_7$ and α - $Ho_2Si_2O_7$ crystals are isostructural as $P1$ space symmetry and they are built up of $[Si_3O_{10}]^{8-}$ groups plus additional $[SiO_4]^{4-}$ tetrahedral groups, and Y^{3+} ions could locate in four different local environments.^{18,21} Our sample was verified by XRD. It could be seen that the sample consists of $Y_2Si_2O_7$ crystals and the major crystals belong to the α -phase triclinic crystal, so it is possible that the Eu^{3+} ions can locate in four different local environments in $Y_2Si_2O_7$. Therefore, we measured site-selective excitation spectra of the sample at 12 K.

Figure 7 shows emission spectra from $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ exciting different $^5D_0 \rightarrow ^7F_0$ sites at 12 K. In all emission spectra, some excited by 579.04 nm, 579.44 nm, and 579.72 nm laser wavelengths showed several different characteristics compared with others—such as clear structure, stronger spectrum peaks, and more splits. The

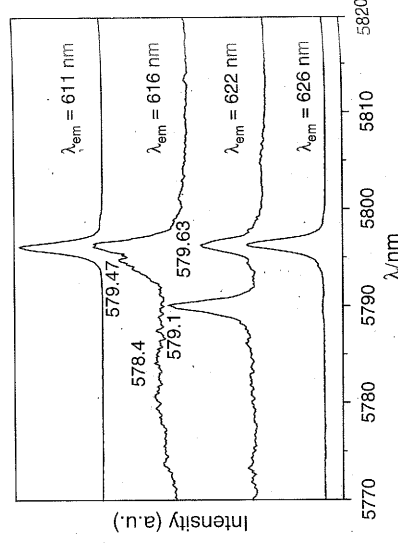


Fig. 6. Excitation spectra of $Y_2Si_2O_7:Eu^{3+}$ monitored at 611, 616, 622, and 626 nm at 12 K.

mmetry, ion. To ble sites d excita- tions the monitor- he emis- g peak at 616 nm, 9.47 nm. When peak at 616 nm. The s that at Eu^{3+} can or of O^{2-} searching indicated the $P_{21/c}$ I^{4+} could our kinds 250 Å to $\text{Y}_2\text{Si}_2\text{O}_7$ spacer cups plus ons could Our sam- le sample is belong that the nments in excitation $\rightarrow {}^7\text{F}_1$ and K. In all 79.44 nm, al differ- as clear plits. The

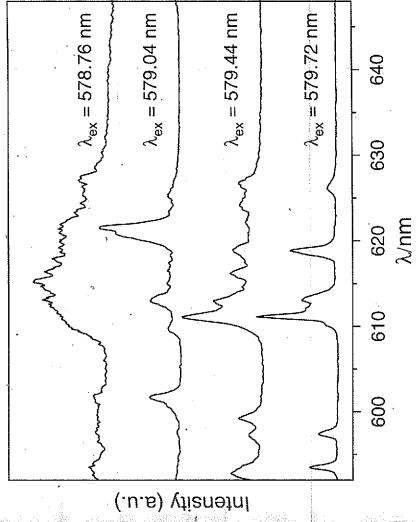


Fig. 7. Emission spectra of $\text{Y}_2\text{Si}_2\text{O}_7:\text{Eu}^{3+}$ excited by different excitation wavelengths at 12 K.

emission peak excited by 578.6 nm is relatively broad and contains no fine structures. Because the sample is nanosized, these characters might originate from excitation of different sites in $\text{Y}_2\text{Si}_2\text{O}_7:\text{Eu}^{3+}$ or others, such as the great surface actions and amorphous residuals, which need to be researched assiduously.

4. CONCLUSION

We prepared a nanosized $\text{Y}_2\text{Si}_2\text{O}_7:\text{Eu}^{3+}$ sample with the sol-gel method and analyzed the sample. The emission spectra excited by ultraviolet light signified that Eu^{3+} ions in $\text{Y}_2\text{Si}_2\text{O}_7$ mainly occupy non-inversion symmetry centers. It is possible that the Eu^{3+} ions could be located in different local environments. The site selective excitation spectra at low temperature suggest that Eu^{3+} ions could occupy several different local environments in the $\text{Y}_2\text{Si}_2\text{O}_7:\text{Eu}^{3+}$ sample that we prepared. We analyzed the luminescence characteristics of the $\text{Y}_2\text{Si}_2\text{O}_7:\text{Eu}^{3+}$ sample. We shall continuously experiment in different doping concentrations and annealing temperatures to better understand the local environments of Eu^{3+} ions located in $\text{Y}_2\text{Si}_2\text{O}_7$ nanocrystals.

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