

Preparation and size effect on concentration quenching of nanocrystalline $\text{Y}_2\text{SiO}_5\text{:Eu}$

Weiping Zhang^{a,b,c,d}, Pingbo Xie^d, Changkui Duan^{d,1}, Kuo Yan^d, Min Yin^d,
Liren Lou^{b,d}, Shangda Xia^{a,d}, Jean-Claude Krupa^e

^a Structure Research Laboratory, University of Science and Technology of China, Academia Sinica, Hefei 230026, PR China

^b Laboratory of Excited State Processes, Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130021, PR China

^c State Key Laboratory of Rare Earth Materials Chemistry and Applications, Peking University, Beijing 100871, PR China

^d Department of Physics, University of Science and Technology of China, Hefei 230026, PR China

^e Radiochimie, Institut de Physique Nucleaire, B.P.N^o. 1, 91406 Orsay, France

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Abstract

Nanocrystalline $\text{Y}_2\text{SiO}_5\text{:Eu}$ was prepared by the sol-gel technique. The photoluminescence spectra and quenching concentration of nanocrystalline $\text{Y}_2\text{SiO}_5\text{:Eu}$ and normal $\text{Y}_2\text{SiO}_5\text{:Eu}$ synthesized by the high-sintering method were measured and compared. Higher quenching concentration and stronger luminescent intensity in nanocrystalline $\text{Y}_2\text{SiO}_5\text{:Eu}$ than in normal $\text{Y}_2\text{SiO}_5\text{:Eu}$ was observed. This is ascribed to the influence of a confinement effect on resonant energy transfer in nanosized particles. These properties show that nanocrystalline $\text{Y}_2\text{SiO}_5\text{:Eu}$ has important potential applications. © 1998 Elsevier Science B.V. All rights reserved.

During the past decades, the novel properties of nanosized materials have attracted considerable interest. New optical properties of nanosized materials [1], such as the blue shift of the luminescent peak of nanosized semiconductors, have been reported and explained. Some researches have found practical nanosized luminescent materials with novel properties. For example, Bhargava et al. reported the efficient nanocrystalline luminescent material ZnS:Mn with a decay time reduced by 5 orders of magnitude compared to the bulk materials [2]. We could also expect that a doped nanostructure may suppress resonant energy transfer and therefore produce high-concentration luminescent materials.

Oxysilicates are fine luminescent hosts [3]. Due to their high stability, they are widely used as cathodoluminescent phosphors [4]. $\text{Y}_2\text{SiO}_5\text{:Eu}$ was found to be a promising candidate for coherent time-domain optical memory applications [5]. Therefore, it is of practical importance to research on oxysilicates doped with rare-earth ions such as Eu.

In this Letter, we report luminescent properties of nanosized $\text{Y}_2\text{SiO}_5\text{:Eu}$ synthesized by the sol-gel technique and normal (μm scale) $\text{Y}_2\text{SiO}_5\text{:Eu}$ prepared by a high-sintering method. The emission spectra of these two kinds of materials were measured and the luminescent intensities varying with the concentration of Eu in these two kinds of materials were studied. As expected, suppression of concentration quenching was observed in nanosized $\text{Y}_2\text{SiO}_5\text{:Eu}$ compared to normal $\text{Y}_2\text{SiO}_5\text{:Eu}$. This

¹ Corresponding author. E-mail: rgxia@phys.ustc.edu.cn

phenomenon may result in a new class of high-quality luminescent materials.

To explain this phenomenon, we develop a new model based on the classical resonant energy transfer model counting a confinement effect and the influence of fluctuation in the distribution of traps in particles. The new model may be used to direct further experiments and better understand the physics of doped nanoscale materials and may be worthy of being quantified in further work.

The preparation process of nanocrystal is as follows: Yttrium oxide and europium oxide of 99.99% purity were dissolved in nitric acid separately. Ethyl silicate was dissolved in ethyl alcohol (absolute), and then mixed with yttrium nitrate and europium nitrate solutions according to the formulae $Y_{2-x}Eu_xSiO_5$ together with a surfactant. The mixture was stirred to achieve a uniform mixing, while the pH was regulated by ammonia or nitric acid. After warming by water-bath to 60°C for a period, the solution hydrolyzed to a sol and then to a gel. The gel was pre-heated to get rid of alcohol and water, was then ground to a powder, and finally heated to over 900°C to crystallize.

The crystal structure was analyzed by a Japanese D/max-rA X-ray diffraction apparatus. It is shown that the gel samples heated at 850°C are still amorphous, while those heated over 900°C are crystals whose diffraction data are consistent with those of JCPDS No. 21-1456. Dopant Eu ions substitute for Y in the lattice of nanocrystalline Y_2SiO_5 since the diffraction results have no significant change for different samples heated at the same temperature but with different Eu concentrations. It is shown that the Y_2O_3 phase and the Y_2SiO_5 phase coexist in sam-

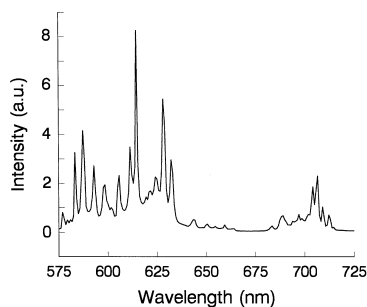


Fig. 1. Emission spectrum of nanocrystalline $Y_2SiO_5:Eu$ at room temperature.

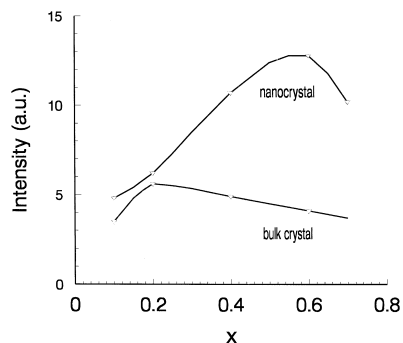


Fig. 2. Luminescent intensity of Eu varying with Eu concentration x , where x is also the mole fraction of Eu, for nanocrystalline and normal $Y_2SiO_5:Eu$ under UV excitation at 300 K.

ples synthesized by the high-sintering method to temperatures below 1500°C. The amount of the Y_2O_3 component decreases as the temperature rises, until to 1500°C the samples are pure Y_2SiO_5 phase. From the comparison of the synthesis temperature of the two methods, we see that the sol-gel technique is better than the high-sintering method in the preparation of crystalline particle materials.

The morphology and particle-size were studied by a Hitachi H-9000NAR high-resolution transmission electron microscope. Samples synthesized by the sol-gel technique and heated above 900°C are crystals with particle-size less than 50 nm. For samples synthesized by the same technique but heated to lower temperatures, chain-like and mesh-like particles, which were amorphous in scale of less than that of the former samples, were observed. Samples synthesized by the high-sintering method are composed of particles which are approximately 2 μm .

Emission spectra of nanocrystalline and normal $Y_2SiO_5:Eu$ excited by a UV lamp (excitation wavelength: 365 nm) were measured by a GDM-1000 double grating monochromator. The two spectra were found to have no obvious difference. The emission spectrum of nanocrystalline $Y_2SiO_5:Eu$ is shown in Fig. 1.

The luminescent intensities varying with the concentration of Eu (represented by x , which is also the mole fraction of Eu in the formulae $Y_{2-x}Eu_xSiO_5$) for nanocrystalline and normal $Y_2SiO_5:Eu$ under the same measuring conditions are shown in Fig. 2. The quenching concentration of normal $Y_2SiO_5:Eu$ is $x = 0.2$. As for nanocrystalline $Y_2SiO_5:Eu$, concen-

tration quenching emerges at about $x = 0.6$. The luminescent intensity of nanocrystalline $\text{Y}_2\text{SiO}_5\text{:Eu}$ at its quenching concentration ($x = 0.6$) is twice as large as that of normal $\text{Y}_2\text{SiO}_5\text{:Eu}$ at its quenching concentration ($x = 0.2$) and is larger than that of the commercial three-element color luminescent material $\text{YVO}_4\text{:Eu}$, suggesting potential applications of this kind of materials.

Now let us give some discussion of a possible mechanism of concentration quenching for nanocrystalline $\text{Y}_2\text{SiO}_5\text{:Eu}$. We consider the case where a number of luminescent centers are under continuous excitation. Due to the defects produced during the preparation process and trace impurities contained in the raw materials, the samples inevitably have quenching centers (traps) with very low concentrations. When an excited luminescent center is in the vicinity of a trap, the excited energy could be transferred easily to the trap from which it is lost nonradiatively. The energy on an excited luminescent center can also be transferred to other unexcited luminescent centers if these luminescent centers are close enough so that they could be coupled together by some interaction. It has been indicated [6] that for $\text{Y}_2\text{O}_3\text{:Eu}$, the interaction between the nearest Eu pairs is an exchange interaction. For our Eu-doped Y_2SiO_5 , the average interaction range is smaller than that of $\text{Y}_2\text{O}_3\text{:Eu}$ and the Eu concentration is much larger than that of $\text{Y}_2\text{O}_3\text{:Eu}$. The high quenching concentration of bulk material ($x = 0.2$) already indicates that significant energy transfer only occurs between Eu ions occupying two nearest Y sites. Thus we may also deal with an exchange or superexchange Coulomb interaction due to the difference in the spins of the ground and the excited multiplets of a luminescent center. If $P_n(t)$ denotes the probability of the n th luminescent center being in the excited state at time t , then $P_n(t)$ varies as

$$\begin{aligned} \frac{dP_n(t)}{dt} = & -\left(\gamma_r + X_n + \sum_{n'} W_{nn'}\right)P_n(t) \\ & + \sum_{n'} W_{n'n}P_{n'}(t) + g \end{aligned}$$

where γ_r is the radiative decay rate of excited luminescent centers, $W_{nn'}$ is the energy transfer rate from the n th to the n' th luminescent center, X_n is the energy transfer rate to traps near the n th luminescent center and g is the continuous pump rate resulting

from the UV lamp excitation. Usually, X_n for Eu ions with traps nearby will be much larger than γ_r . As for normal $\text{Y}_2\text{SiO}_5\text{:Eu}$, when the concentration of luminescent centers is small, the luminescent centers can be thought of as 'isolated' and only a few luminescent centers having traps nearby will give their energy to the traps. Consequently, the luminescence quenching is not significant. As the concentration of luminescent centers increases (for normal $\text{Y}_2\text{SiO}_5\text{:Eu}$, at about $x = 0.2$), the luminescent centers may be near enough to form a 'resonant energy transfer net' in the crystal, so that energy can be easily transferred from one luminescent center to another. Generally, the energy transfer rate is comparable with the radiative decay rate of an isolated luminescent center when the distance between the luminescent centers is about 5–10 Å. While in our case, due to the small average interaction range (< 5 Å) and the high concentration of Eu, exchange/superexchange interaction result in a much faster energy transfer rate than the radiative decay rate in $\text{Y}_2\text{SiO}_5\text{:Eu}$. Therefore, the energy on most of the excited luminescent centers will be transferred to traps before it is emitted via a radiative transition. Thus concentration quenching occurs.

In nanosized materials, due to the limited number of primitive cells per particle, on average there are only a few traps in one particle, so the traps distribute randomly with a considerably large fluctuation between particles. Some particles may contain many traps while others may contain no trap at all. The energy of a luminescent center can only be transferred resonantly within one particle since the energy transfer is hindered by the particle boundary. As the concentration of luminescent centers increases, quenching occurs first in particles containing many traps. Those particles containing few or no traps quench at only high concentration or do not quench at all. Therefore, quenching occurs at higher Eu concentration in nanosized material than in normal materials. This phenomenon will be seen more clearly in samples with smaller particles. In the limiting case, quenching probably will not appear at all since few particles contain traps. Further work concerning the relation between the quenching effect and particle-size are under development.

In the above analysis, we have not taken the influence of the high proportion of the surface in

nanosized samples into account. The experimental results show that the particle surface of our samples contributes little to the nonradiative relaxation: at the same Eu concentration below quenching concentration of normal samples, the luminescent intensity of a nanosized sample is no weaker than that of the normal sample.

In conclusion, nanocrystalline $\text{Y}_2\text{SiO}_5\text{:Eu}$ with particle-sizes less than 50 nm was synthesized by the sol-gel technique. The photoluminescence spectra and luminescent quenching concentration of nanocrystalline $\text{Y}_2\text{SiO}_5\text{:Eu}$ were measured and compared to those of normal $\text{Y}_2\text{SiO}_5\text{:Eu}$ prepared by a high-sintering method. As expected, a much higher quenching concentration ($x = 0.6$ in the nanocrystal compared to $x = 0.2$ in a normal crystal) and a stronger luminescent intensity than in normal $\text{Y}_2\text{SiO}_5\text{:Eu}$ and the commercial product $\text{YVO}_4\text{:Eu}$ were observed. A simple model has been established to explain these phenomena. The preparation technique is easy to realize, suggesting attractive applica-

tions. The high quenching concentration may occur with the high luminescent efficiency and the high luminescent probability as suggested by other work [1] and provide new possibilities for improving luminescent materials.

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