Photoluminescence properties of Eu^{2+}-activated Sr_3SiO_5 phosphors

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The fluorescence of Eu^{2+}-activated compounds is usually broadened and depends on the surrounding Eu^{2+} ions. Eu^{2+}-activated phosphors have been widely used in fluorescent and duplication lamps, as well as display devices, as the emission of Eu^{2+} can vary in a wide range from red to ultraviolet [1–3]. Eu^{2+} ions have complex energy levels and the first excited $4f^65d^1$ configuration lies close to the lowest excited $4f^7$ levels [4]. The transitions between the first excited $4f^65d^1$ configuration and the $4f^7$ ground state are dipole allowed [5]. Moreover, absorption and emission due to the transition between $4f^7$ and $4f^65d^1$ states of Eu^{2+} strongly depend on the crystal field acting on Eu^{2+} [6]. Therefore, the choice of host materials is a critical parameter for determining the optical properties of Eu^{2+} ions.

The silicate system is a useful luminescent host material with a stable crystal structure and high thermal stability as such, many studies on phosphors with silicate as a host have been conducted and numerous practical applications have been developed [7–9]. The Sr_3SiO_5 phosphor has recently been developed. This silicate phosphor is a yellow phosphor material that has applicability in white light-emitting diodes (LEDs) [10]. In this work, we report on the interesting photoluminescence properties of an Eu^{2+}-activated Sr_3SiO_5 compound.

All samples were prepared by a conventional solid-state reaction method. The starting materials used in the preparation of these phosphors were $SrCO_3$, SiO_2, and Eu_2O_3 powders of purity greater than 99.9%. Stoichiometric amounts of the starting materials were thoroughly mixed in acetone in an agate mortar and dried to 130 °C for about 24 hr to evaporate the solvent and successively heat-treated at several different temperature conditions, followed by an additional grinding and firing in a reduction atmosphere (5% H_2/95% N_2). The resulting powder samples were confirmed to be single phase by a RIGAKU D/MAX-2200V X-ray diffraction (XRD) system with CuKα radiation (Ni filter) and a diffracted beam graphite monochromator.

The excitation and emission spectra of the fired samples were measured using a Perkin-Elmer LS-50 luminescence spectrometer with a xenon flash lamp. The decay measurement was performed using a Nd:YAG laser at 570 nm emission for radiative recombination of Eu^{2+} ions in the Sr_3SiO_5 host matrix.

The excitation and emission spectra of Sr_3SiO_5:Eu sample are shown in Fig. 1. The strong absorption above 350 nm is consistent with the observed energy level scheme for absorption by Eu^{2+} having a $4f^7$ electronic configuration [11] and the tail of the excitation band is extended to longer wavelength, thus making possible efficient emission from the Sr_3SiO_5:Eu phosphor under the 450–470 nm excitation range.

The 570 nm emission band is ascribed to a radiation recombination of Eu^{2+} impurity ions in the Sr_3SiO_5 host matrix. The broadness of the emission band indicates an interaction between the host and the activator, which can be attributed to the presence of an excited electron in an outer shell of the Eu^{2+} ions. The transitions correspond to 4f–5d transitions.

In order to investigate the concentration quenching behavior of 570 nm emission, the fluorescence decay curves are examined in terms of Eu^{2+} concentration. As can be observed in Figs 2 and 3 Concentration quenching begins at 0.07 mol of Eu^{2+}. The decay curves are nonexponential, and their nonexponentiality increase in accordance with the increasing Eu^{2+} concentration. The nonexponentiality of the decay curves indicates that the probability of energy transfer among Eu^{2+} ions increases with increasing Eu^{2+} concentration. When there is no interaction between rare

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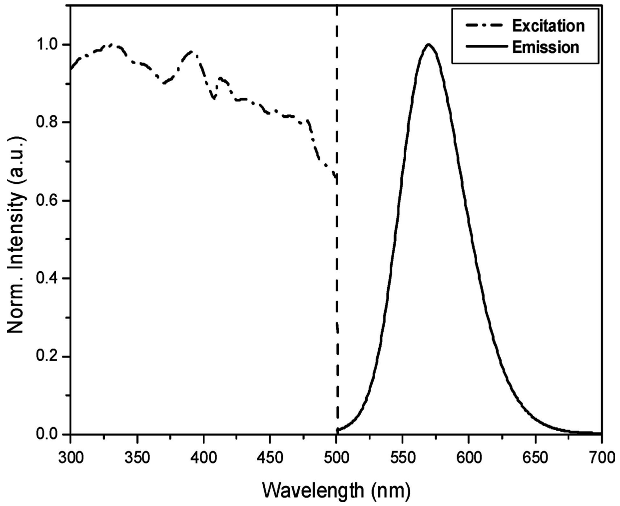

Figure 1 Excitation spectrum (*dotted line*) of the 0.07 mol Eu^{2+} in the Sr_3SiO_5 system ($\lambda_{em} = 570$ nm) and emission spectrum (*solid line*) of 0.07 mol Eu^{2+} in the Sr_3SiO_5 system ($\lambda_{ex} = 470$ nm).

earth ions, the emission decay curve is a single exponential [12]. Energy transfer is generally associated with multipolar interactions, radiation reabsorption, or exchange interaction. In the Eu^{2+} ion, the $4f^7 \rightarrow 4f^6 5d^1$ transition is allowed, while the exchange interaction is responsible for the energy transfer of forbidden transitions and the typical critical distance, which is about 5 Å [13]. It is thought that the exchange interaction plays no role in the energy transfer in the present case and will occur only as a result of an electric multipolar interaction.

In order to investigate the multipolar interaction scheme between Eu^{2+} ions, the decay behavior is analyzed using a direct quenching scheme [14]. Assuming that the interaction scheme is multipolar type, Inokuti-Hirayama's formula [15] could be applied to the emission of Eu^{2+}.

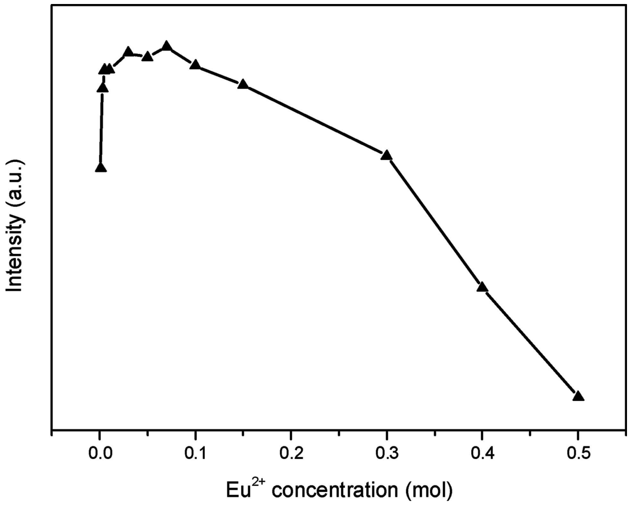

Figure 2 Emission intensities of Eu^{2+} fluorescence as a function of Eu^{2+} concentration of several sets of Sr_3SiO_5:Eu phosphor. The emission intensities were measured under UV excitation at 470 nm.

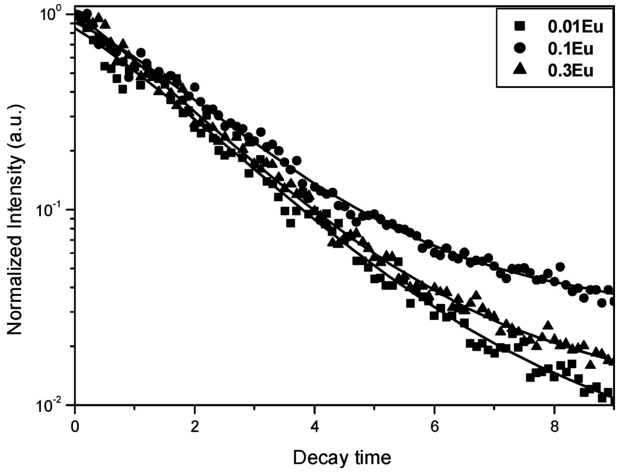

Figure 3 Normalized decay curves of yellow emission for several Eu^{2+} concentrations. The unit of decay time is microseconds.

$$\frac{I(t)}{I_0} = \exp\left[-\left(\frac{t}{\tau}\right) - \left(\frac{C}{C_0}\right)\Gamma\left(1-\frac{3}{S}\right)\left(\frac{t}{\tau}\right)^{3/S}\right] \tag{1}$$

where τ is the intrinsic lifetime of a single ion, C is the number of acceptors (quenching sites) per unit volume, $C_0 = 3/(4\pi R_c^3)$; where R_c is the critical interaction distance between Eu^{2+} and Eu^{2+} ions, and $\Gamma(1-3/S)$ is the gamma function. S is an indication of electric multipolar character; $S = 6$, 8, and 10 for dipoledipole (*d*–*d*), dipole–quadrupole (*d*–*q*), and quadrupole–quadrupole (*q*–*q*) interactions, respectively. In order to obtain a correct S value, the decay curves were plotted using Equation 2.

$$\ln\left[-\ln\left(\frac{I(t)}{I_0}\right) - \left(\frac{t}{\tau}\right)\right] \quad \text{vs} \quad \ln\left[\frac{t}{\tau}\right]^3 \tag{2}$$

This plot should yield a straight line with a slope equal to 1 /S. The fitting results of 570 nm emission of Sr_3SiO_5:Eu with respect to the Eu^{2+} concentration are shown in Fig. 4. As can be seen from Fig. 4, most of the S values are determined at about 6. This indicates that the dominant interaction character of Eu^{2+} is *d*–*d* coupling in the present case.

According to Blasse [16], the critical concentration of activator should be determined where the measured decay time becomes half of the radiative lifetime by revoking the definition of the critical energy transfer distance (R_c). Therefore, it is necessary to know the critical distance value for energy transfer by the electric *d*–*d* interaction. The concentration quenching can be attributed, in many cases, to energy transfer from one activator to another ion until an energy sink in the lattice is reached [17]. It is thought that the concentration quenching is related to an interaction between an activator and another ion. This kind

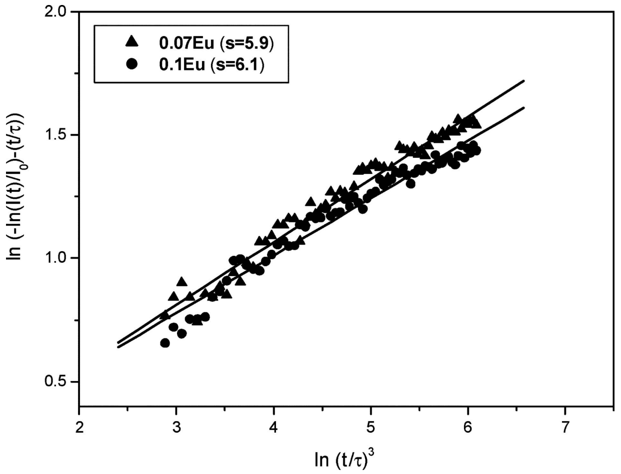

Figure 4 A plot of the experimental data in terms of Eu^{2+} concentrations according to Equation 2.

of interaction allows the absorbed excitation energy to reach a particular quenching center, and as such the critical concentration depends on the probability of transfer. For that reason, the critical concentration of concentration quenching can be used as a measure of the critical distance of energy transfer. It is thus possible to obtain the value of the critical distance from the fitting results of the following relationship.

$$\frac{C}{C_0} \quad \text{vs} \quad \frac{4\pi C}{3} \tag{3}$$

The definition of C and C_0 has already been given in Equation 1. The C/C_0 value was obtained from the decay curve fitting using Equation 1. The slope of the straight line in Fig. 5, represents the critical distance R_c (in this case, $R_c = 7.1$ Å).

In summary, we have synthesized a Eu^{2+}-doped Sr_3SiO_5 yellow phosphor, and investigated its photoluminescence properties. The emission band of the Sr_3SiO_5:Eu phosphor is observed and this phosphor emits efficiently under the 450–470 nm excitation range. The critical distance value of energy transfer between Eu^{2+} ions and the electric multipolar character were obtained experimentally from the decay fitting results.

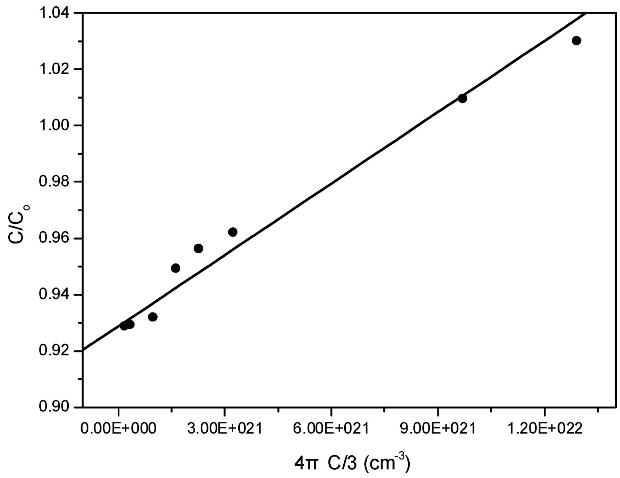

Figure 5 A plot of (C/C_0) vs. ($4\pi C/3$) analyzed using linear curve fit.

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