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Strong blue, green and red light emission at elevated temperatures from Y_2SiO_5 doped by the rare-earth ions

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The temperature dependence of the photoluminescence (PL) of the rare-earth ion activated Y_2SiO_5 was investigated from room temperature to 573 K. Ion activators such as Eu^{3+}, Ce^{3+}, Sm^{3+}, Tb^{3+} and some of their combinations were studied in this study. The most efficient blue, green and red phosphors at elevated temperature were found by doping the (Ce^{3+} + Tb^{3+}), Tb^{3+} and Eu^{3+} respectively, in this material system. Meanwhile, the relationship between the structure and the temperature dependence of the PL in $Re_xY_{2-x}SiO_5$ was also discussed. © *2001 Kluwer Academic Publishers*

1. Introduction

Thermal quenching is an important phenomenon, for most of phosphors, which leads to a rapid decrease in the luminescent intensity as the temperature rises and disappears at elevated temperature. From the point view of application, an attempt has been made to explore the excellent phosphors with less thermal quenching at elevated temperature.

Generally, the thermal quenching of light emission varies upon the nature of the activator and the host lattice. Blasse [1] had employed the configurational-coordiate diagram to describe and explain some of the phenomena related to luminescence, including the thermal quenching. With the aid of the configurational-coordiate diagram, the efficiency of luminescence in phosphors was described by the configurational-coordiate Δr, which reflects the difference between the equilibrium configuration of the excited state and that of the ground state. Accordingly, many researchers have studied luminescent materials with good temperature characteristics since the early 1960's, such as the silicates, borates, phosphates [2, 3] as well as some oxide hosts [4] with less thermal quenching. The Y_2SiO_5 is a promising structural material used at elevated temperatures, but the photoluminescent property of the rare-earth ion activated Y_2SiO_5 at elevated temperature has not being systematically studied. Therefore, as a purpose of this study, the high-temperature photoluminescent property of the Y_2SiO_5 based phosphors was systematically investigated.

2. Experimental

The Y_2SiO_5 precursor solutions activated with the ions of Eu^{3+}, Ce^{2+}, Sm^{3+}, Tb^{3+} (abbreviated, EYSO, CYSO, SYSO and TbYSO) and some of their combinations were synthesized by the metallorganic decomposition (MOD) technique [5] using yttrium nitrates [$Y(NO_3)_3 \cdot 3.4H_2O$], the nitrates of rare-earth ions such as the europium nitrates [$Eu(NO_3)_3 \cdot 2.9H_2O$] and tetraethyl orthosilicate [TEOS, $Si(OC_2H_5)_4$] as starting materials. Diethylene glycol monomethy1 ether [DGME, $CH_3OCH_2CH_2OCH_2CH_2OH$] and acetylacetone [$CH_3COCH_2COCH_3$] were selected as the solvent and diluent, respectively. The precursor in the Al_2O_3 crucible was thermally treated in an oven at 169°C for 12 h and then calcined in an air muffle-furnace at high temperature in order to fabricate the polycrystalline rare-earth ion activated YSO powders. These fine powders possessed the X_1-Y_2SiO_5 phase after calcining at 1050°C and the X_2-Y_2SiO_5 phase at 1400°C for 2 h.

The temperature dependence of the photoluminescence (PL) of YSO powders with various activators was investigated by a multichannel analyzer (Model PMA-11, Hamamatsu, Japan). The luminescence was excited by a UV light source with a long wavelength of 365 nm or a short wavelength of 254 nm, depending on the doped rare earth ion. In general, the change in the temperature dependence of the emission intensity was high enough. On the other hand, the temperature variation caused by the different excitation wavelength was too small to be considered in the UV wavelength range; therefore, it was reasonable not to regard as the temperature variation from the UV illumination in this study. The rate of temperature increase was about 2.5 K/min. The photoluminescence spectra were recorded after holding the temperature for 20 minutes in order to reach a thermal equilibrium to remove the influence of thermoluminescence. To evaluate the temperature dependence, the relative PL intensity was used,

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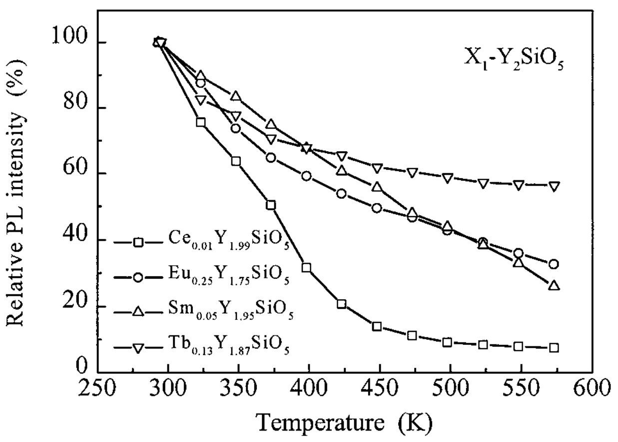

Figure 1 Temperature dependence of the PL in Y_2SiO_5 doped by Tb^{3+}, Eu^{3+}, Sm^{3+} and Ce^{3+} ions.

which was defined as Relative PL intensity (T) = PL intensity (T)/PL intensity (300 K).

3. Results and discussion

Fig. 1 shows the temperature dependence of the PL in the Eu^{3+}, Ce^{3+}, Sm^{3+} and Tb^{3+} activated X_1-Y_2SiO_5 from room temperature to 573 K. All samples had a decreased relative PL intensity with increasing temperature due to the thermal quenching phenomenon. The quenching rate strongly depended on the type of activators in Y_2SiO_5. In the examined YSO material system, the TbYSO had the lowest thermal quenching at elevated temperatures. In TbYSO, a very strong green emission at 543 nm was observed under the excitation at 254 nm as shown in Fig. 2. From 450 K to 573 K, the relative intensity of PL in TbYSO only changed 6%. Among them, the relative PL intensity of TbYSO basically remained unchanged at the level of about 57% from 548 K to 573 K. In order to develop excellent luminescent materials for application at elevated temperatures, the behavior of PL in TbYSO above 573 K will be further investigated. The intensity of the red emission (at about 600 nm) of the SYSO under the excitation at 254 nm linearly decreased as the temperature rose. The strong red emission at 612 nm was found in the EYSO under the excitation at 254 nm as shown in Fig. 3, in which, the relative PL intensity still remained above 30% at a temperature of 573 K. SYSO was similar to EYSO in the thermal quenching behavior, but the emission intensity of SYSO was weaker than that of EYSO. CYSO gave the strongest thermal quenching where the blue emission intensity rapidly decreased and dropped to 8% at 573 K. This is found, in X_1-YSO phosphors with a large rare-earth ion (From Ce to Tb ion) as an activator, the larger the radius of the rare-earth ion, the stronger the thermal quenching became.

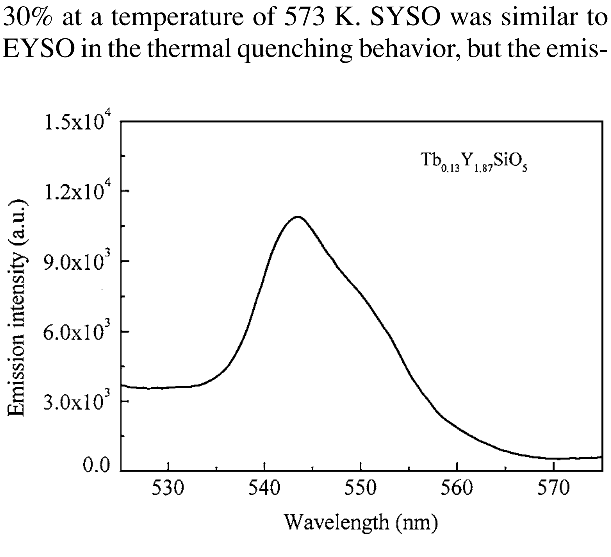

Figure 2 Emission spectrum of $Tb_{0.13}Y_{1.87}SiO_5$ at 573 K.

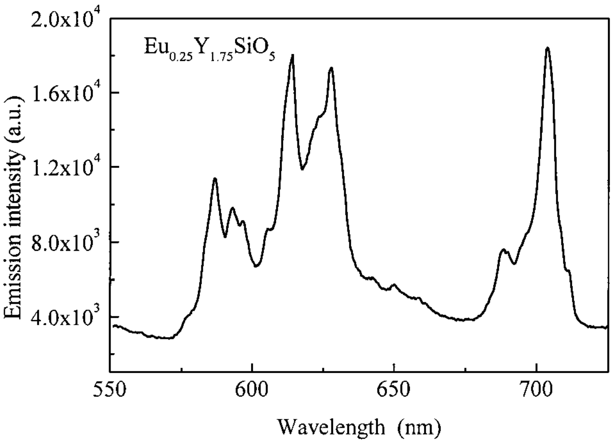

Figure 3 Emission spectrum of $Eu_{0.25}Y_{1.75}SiO_5$ at 573 K.

Here, $Re_xY_{2-x}SiO_5$ (Re—the rare-earth ion) might be written in the from of $Re_xSi_{x/2}O_{5x/2} \cdot Y_{2-x}Si_{1-x/2}O_{5-5x/2}$ when the yttrium ion in Y_2SiO_5 was partially substituted by the trivalent rare-earth activator. All of the host parts, $Y_{2-x}Si_{1-x/2}O_{5-5x/2}$ should have the same temperature characteristics; therefore, the effect of temperature on the PL of $Re_xY_{2-x}SiO_5$ should be mainly ascribed to the $Re_xSi_{x/2}O_{5x/2}$, that is, Re_2SiO_5. Felsche [6] presented two structural configurations in the rare-earth Re_2SiO_5 oxyorthosilicates: a stable X_1-type (or A type) with a space group of $P2_1/C$ for the large rare-earth ions La to Tb, and the X_2-type (or B type) with a space group of B2/b for the smaller rare-earth ions Tb to Lu. On the other hand, the host, $Y_{2-x}Si_{1-x/2}\,O_{5-5x/2}$ (Y_2SiO_5), also possesses the two structures of X_1- and X_2-types, which corresponded to the low temperature phase and high temperature phase, respectively [7]. Table I lists the unit cell dimensions of Y_2SiO_5 and Re_2SiO_5 related to our work. From Table I, it can be seen that for larger rare-earth activators, such as Ce^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+}, the lattice parameters and the unit cell volume of Re_2SiO_5 have the same level with the X_1-Y_2SiO_5 host. The unit cell volume of Re_2SiO_5 also decreased with the decreasing ionic radius of Re^{3+}. Correspondingly, introducing this

TABLE I Lattice parameters, ion radii and unit cell volumes of Y_2SiO_5 and some Re_2SiO_5 materials

	a (Å)	b (Å)	c (Å)	V (Å^3)	r_{Re} (Å^3)
*X_1-Y_2SiO_5	6.630	6.972	9.012	399.4	0.90
*Ce_2SiO_5	6.974	7.359	9.285	452.4	1.034
Sm_2SiO_5	6.821	7.112	9.161	424.4	0.964
Eu_2SiO_5	6.790	7.054	9.142	417.9	0.950
$Tb_2SiO_5(X_1)$	6.714	6.990	9.083	406.1	0.923
*$Tb_2SiO_5(X_2)$	6.778	8.008	9.679	876.8	0.923
Tm_2SiO_5	6.662	10.313	14.302	828.5	0.869
*X_2-Y_2SiO_5	6.730	10.410	12.460	852.25	0.90

*Data from the XRD database.

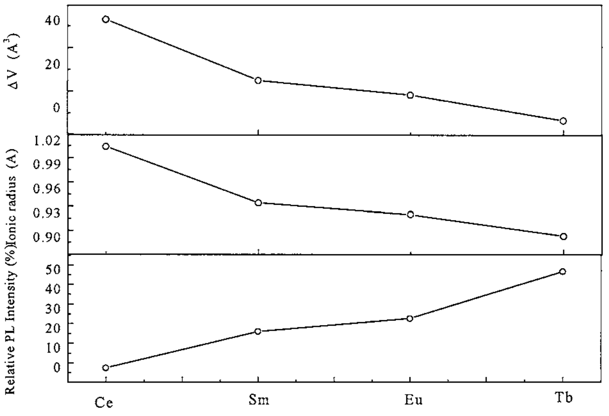

Figure 4 The unit cell volumes, ionic radii, and the PL intensity of the rare earth in the X_1-$Re_xY_{2-x}SiO_5$.

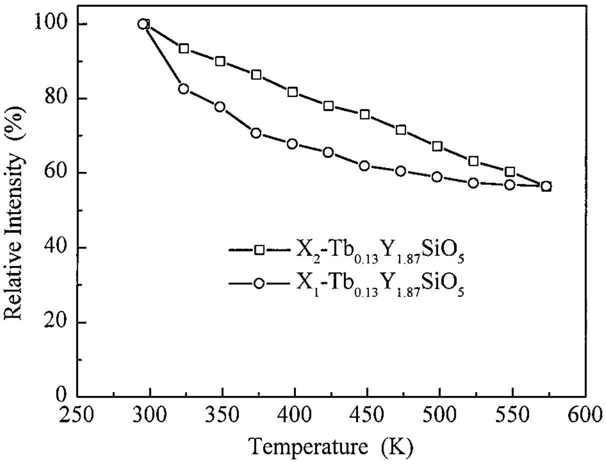

Figure 5 Temperature dependence of the PL in TbYSO.

result into the $Re_xSi_{x/2}O_{5x/2} \cdot Y_{2-x/2}Si_{1-x/2}\ O_{5-5x/2}$, we can understand the effects of the activators on the PL of $Re_xY_{2-x}SiO_5$ as shown in Fig. 4. The difference of the unit cell volume of the X_1-$Re_xSi_{x/2}O_{5x/2}$ with the X_1-Y_2SiO_5 host (ΔV) would influence the microstructure around the Re^{3+} center, which would produce a change in the local electric field, thus influencing the crystalline field, sequentially lead to the change in the PL. Besides, the increase of the unit cell volume in $Re_xSiO_{5x/2}$ would compel the activator environment to expand in order to make room for the activator, thus increasing the length of the Re-O bonding. This would alter the strength of the thermal vibration of phonons as the temperature rises, thus enhancing the thermal quenching of the PL. Therefore, the temperature dependence property in the PL became inferior with the increasing activated ion radius or the difference of the unit cell volume (ΔV) of Re_2SiO_5 from the X_1-Y_2SiO_5 host, as demonstrated in Fig. 4. This result is consistent with the discussion based on the configuration-coordinate diagram of the luminescence centers made by Blasse [1], but this model is simple and very easy to understand.

From Table I, it was also found that the difference in the unit cell volumes between Tb_2SiO_5 (1) and X_1-YSO was the smallest. Therefore, the Tb^{3+} ion activated X_1-YSO exhibited less thermal quenching on the PL in Fig. 1. It was worth noting that the Tb_2SiO_5 may have two types of structures according to the preparation process based on the discussion of Felsche [6]. This was reasonable that Tb_2SiO_5 should have the X_2-type structure in X_2-type host and correspondingly the X_1-type structure in X_1-type host. Therefore, the difference in the unit cell volumes between Tb_2SiO_5 and the host always were always small in magnitude (7 Å^3 for X_1-type host and 25 Å^3 for X_2-type host), thus leading to the excellent temperature characteristics of PL in TbYSO as shown in Fig. 5. The relative intensity of the PL from Tb^{3+} ions in both YSO hosts exhibited almost same values at 573 K. They were 56.8% for the X_1-type host and 56.4% for the X_2-type host. Between room temperature to 573 K, the relative intensity of the PL in X_2-type host was slightly higher than that in X_1-type host. This may be related to the coordination number of the Tb^{3+} to O^{2-} ions, which was 7 and 9 in the X_1-type, and greater than 6 and 7 in the X_2-type. In this case, the vibration of phonons in X_1-type host was enhanced to a certain extent for the same temperatures, which led to a higher thermal quenching in X_1-type host than that in X_2-type host. It implied that both coordination number of the Tb^{3+} and the difference in the unit cell volume, ΔV would influence the thermal quenching in TbYSO. This was easily conceived as the effect of the coordination number probably was predominant at the beginning, the effect of the ΔV became more and more important as the temperature rose. These two effects became equivalent and thus finally led to almost the same relative intensity at 573 K.

The efficient energy transfer from Ce^{3+} to Tb^{3+} in X_1-Y_2SiO_5 is well known. It has been found that the excitation into the Ce^{3+} band at 360 nm results in a 38% Ce^{3+} emission and a 62% Tb^{3+} emission, which is due to the energy transfer from the Ce^{3+} 4f-5d absorption to the Tb^{3+} $4f^8$-$4f^7$ 5d absorption [8]. As a result, the green Tb^{3+} $^5D_4$ emission $^5D_4$-^7F_j ($j = 6, 5, 4, 3$) was enhanced. However, the strong green emission was not observed in the composition of $Ce_{0.005}Tb_{0.017}Y_{1.978}SiO_5$ and the strong blue emission at 431 nm was found as shown in Fig. 6. It was related to a very low Tb^{3+} concentration, which had only 0.86% of Y^{3+} in this

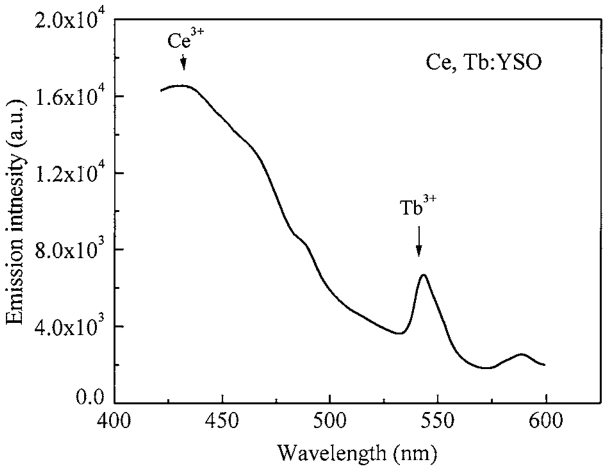

Figure 6 Emission spectrum of the Ce^{3+} and Tb^{3+} doubly doped YSO at 573 K.

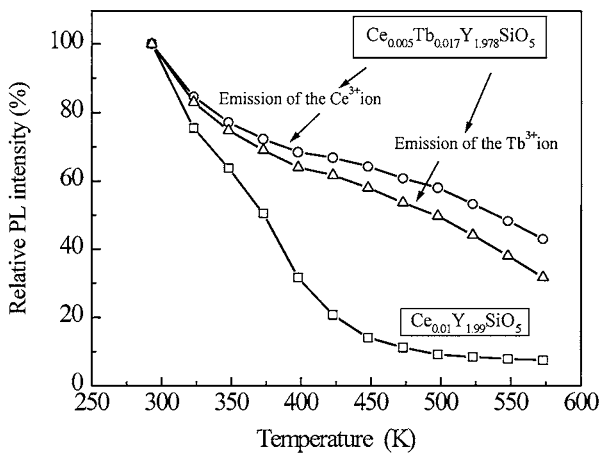

Figure 7 Temperature dependence of the PL in the Ce^{3+} and Tb^{3+} doubly doped YSO.

composition. In this case, the back-transfer Tb^{3+} ($^5D_3$)-Ce^{3+} was stronger than the Tb^{3+} ($^5D_4$)-Ce^{3+} transition [9, 10]; therefore, the strongly blue emission from the Ce^{3+} ion was observed. The blue-to-green intensity ratio was about 1.8 at room temperature. Fig. 7 described the thermal quenching behavior of the PL of the Ce^{3+} and Tb^{3+} co-activated Y_2SiO_5. Obviously, the doubly doping of Tb^{3+} and Ce^{3+} ions not only increased the emission intensity, but also remarkably improved the temperature characteristics above room temperatures. The relative emission intensity at 431 nm at temperature of 573 K increased more than six times in comparison with the single doped CYSO. Simultaneously, the blue-to-green intensity ratio reached 2.3. This means that the enhancement in intensity and the improvement in the temperature characteristics of the blue emission were at the expense of the temperature characteristics of the Tb^{3+} emission. The relative intensity of the Tb^{3+} emission in the doubly doped YSO was also clearly decreased with temperature, which dropped to 32% from the 57% of the Tb^{3+} emission in the singly doped TbYSO at 573 K. This illustrates that the temperature characteristics of the PL for the Y_2SiO_5 co-activated with Ce^{3+}, Tb^{3+} ions could be effectively improved.

4. Conclusion

The temperature dependence of the photoluminescence of the rare-earth ion activated Y_2SiO_5 was investigated from room temperature to 573 K. The Eu^{3+}, Ce^{3+}, Sm^{3+} and Tb^{3+} activators in X_1-Y_2SiO_5 strongly depended on the ion radius and lattice size of the activators, Re_2SiO_5. The strong green and red phosphors at elevated temperature were found by activation using the Tb^{3+} and Eu^{3+}, respectively. The most efficient blue emission could be achieved by doubly doping of the Ce^{3+} and Tb^{3+} ions, where the back-transfer from Tb^{3+} to Ce^{3+} played a very important role in enhancing the emission intensity and improving high temperature photoluminescent property.

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