

Luminescence quenching of Ce³⁺ and energy transfer phenomenon in Ca₂Al₂SiO₇:Ce³⁺, Sm³⁺ phosphors

Dập tắt huỳnh quang của Ce³⁺ và truyền năng lượng trong vật liệu Ca₂Al₂SiO₇:Ce³⁺, Sm³⁺

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Abstract

In this work, Ce³⁺ and Sm³⁺ ions doped/co-doped Ca₂Al₂SiO₇ (CAS) phosphors were prepared by solid state reaction method at high temperature. X-ray diffraction results showed that the prepared samples had tetragonal single phases with selected synthesis conditions. Energy transfer process of Ce³⁺/Sm³⁺ pair in CAS phosphor was studied by photoluminescence (PL) and photoluminescence excitation (PLE) spectra. Emission intensity of Ce³⁺ in Ca₂Al₂SiO₇:xCe³⁺, (1mol%) Sm³⁺ phosphors clearly varied with Ce³⁺ concentration; and reached to maximum value at the concentration of 2 (mol%). Additionally, concentration quenching phenomenon was observed in Ca₂Al₂SiO₇: xCe³⁺, (1mol%) Sm³⁺ samples, which was arisen from dipole-dipole interaction.

Keywords: Energy transfer, luminescence quenching, calcium aluminosilicate.

Tóm tắt

Trong nghiên cứu này, ion Ce³⁺ và Sm³⁺ được pha/đồng pha tạp vào vật liệu Ca₂Al₂SiO₇ (CAS) chế tạo bằng phương pháp phản ứng pha rắn ở nhiệt độ cao. Kết quả nhiễu xạ tia X cho thấy các mẫu chế tạo với các điều kiện công nghệ đã chọn có cấu trúc đơn pha tetragonal. Quá trình truyền năng lượng giữa Ce³⁺/Sm³⁺ trong CAS được nghiên cứu thông qua phổ phát quang và kích thích phát quang. Cường độ phát quang của Ce³⁺ trong hệ vật liệu Ca₂Al₂SiO₇:xCe³⁺, (1mol%) Sm³⁺ thay đổi ứng với các nồng độ khác nhau và đạt cực đại tại 2 mol%. Ngoài ra, hiện tượng dập tắt huỳnh quang do nồng độ cũng được quan sát thấy trong hệ Ca₂Al₂SiO₇:xCe³⁺, (1mol%) Sm³⁺, là kết quả của quá trình tương tác lưỡng cực-lưỡng cực.

Từ khóa: Truyền năng lượng; dập tắt huỳnh quang; calcium aluminosilicate.

1. Introduction

Ca₂Al₂SiO₇ (CAS) phosphors doped with rare earth (RE) ions are fundamentally getting more attention of scientists due to their

potential applications in light-emitting diodes, mechanoluminescence dosimetry and laser [1-4]. The RE elements possessing unique 4f electrons have been investigated as potential

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candidates for luminescent centers in luminescent materials due to the $4f \rightarrow 4f$ or $5d \rightarrow 4f$ transitions, that can introduce novel fluorescence characteristics. In recent years, several popular RE^{3+} ions, such as Eu^{3+} , Er^{3+} , Ce^{3+} , Dy^{3+} , Tb^{3+} , have been doped/co-doped CAS phosphors to investigate luminescence and thermoluminescence characteristics [3-7]. In addition, several ions as Ce^{3+} , Eu^{2+} and Mn^{2+} were co-doped the CAS lattice in order to study the long persistent luminescence [8].

One of the interesting features energy transfer processes between RE^{3+} ions in the CAS materials was observed for pairs of Ce^{3+}/Tb^{3+} , Ce^{3+}/Mn^{2+} , and Tm^{3+}/Dy^{3+} [9-11], of which Ce^{3+} and Tm^{3+} ions are role as sensitizers and Tb^{3+} , Mn^{2+} and Dy^{3+} as activators. The energy transfer in this host has also been studied for $Bi^{3+}/Tb^{3+}/Sm^{3+}$ based on $Bi^{3+} \rightarrow Tb^{3+} \rightarrow Sm^{3+}$ energy transfer process [12]. However, there has been no report on the energy transfer in Ce^{3+}/Sm^{3+} pair in CAS material. It is known that Sm^{3+} ions doped phosphors with red luminescence due to $f \rightarrow f$ transitions are popular red phosphors. While Ce^{3+} emission is a broad band and strong intensity, which originated the $5d \rightarrow 4f$ transitions. These transitions depend strongly on the host lattices and, hence, a broad band emission of Ce^{3+} can covers the UV and blue light regions in various materials. In the case of the Ce^{3+} broad band emission around the blue light region, it can be used as a sensitizer for the Sm^{3+} activator when they were co-doped in materials and the Sm^{3+} emission intensity can be changed because of the energy transfer. In this work, the Ce^{3+} and Sm^{3+} ions co-doped $Ca_2Al_2SiO_7$ phosphors were prepared to evaluate the luminescent properties and the energy transfer process between Ce^{3+} and Sm^{3+} ions.

2. Experiments

Ce^{3+} and Sm^{3+} ions co-doped in $Ca_2Al_2SiO_7$ phosphors were prepared by a solid state reaction method at high temperature. The content of Ce^{3+} and Sm^{3+} (in mol%) in samples and the labels of samples are listed in Table 1. Raw materials used to synthesize phosphors include of $CaCO_3$ (AR), Al_2O_3 (AR), SiO_2 (Sigma), CeO_2 (Merck) and Sm_2O_3 (Merck). The raw materials were weighed according to their nominal compositions and a small amount of B_2O_3 used as a fluxing agent was added mixture. The mixture was mixed homogeneously for 2h. In next step, this mixture was calcined at $1280^\circ C$ for 1 h in air and then it was cooled down to room temperature to obtain final sample.

Table 1. Labels of $Ca_2Al_2SiO_7$ phosphors co-doped with Ce^{3+} and Sm^{3+} ions

Samples label	Ce^{3+} (mol%)	Sm^{3+} (mol%)
CASC00S10	0.0	1.0
CASC05S10	0.5	1.0
CASC10S10	1.0	1.0
CASC15S10	1.5	1.0
CASC20S10	2.0	1.0
CASC25S10	2.5	1.0
CASC30S10	3.0	1.0
CASC40S10	4.0	1.0
CASC10S00	1.0	0.0

Crystalline structures of the prepared samples were investigated by x-ray diffraction (XRD) using x-ray diffractometer (D8-Advance; Bruker, Germany). Luminescent properties were evaluated via photoluminescence (PL) and photoluminescence excitation (PLE) spectra at room temperature (300 K) using a spectrophotometer (FL3-22; Horiba Jobin-Yvon) with Xenon -450W lamp. The surface homology of the prepared samples was examined by a scanning electron microscope (SEM) (Jeol 6490, JED 2300; Japan).

3. Results and Discussion

3.1. X-ray diffraction and SEM images

The crystal structures of four samples CASC10S00, CASC00S10, CASC10S10 and CASC40S10 were pointed by X-ray diffraction using Cu K α (0.154 nm) radiation and their XRD patterns in the 20°-70° regions are presented in Fig. 1. As can be seen in Fig. 1, all diffraction peaks of the prepared samples coincide with the standard profile of Ca₂Al₂SiO₇ (JCPDS No. 35-0755) and no impurity phases are observed. This result indicates that the prepared samples get a tetragonal single phase with selected synthesis conditions and a small amount of dopants did not affect to the crystal structure of samples.

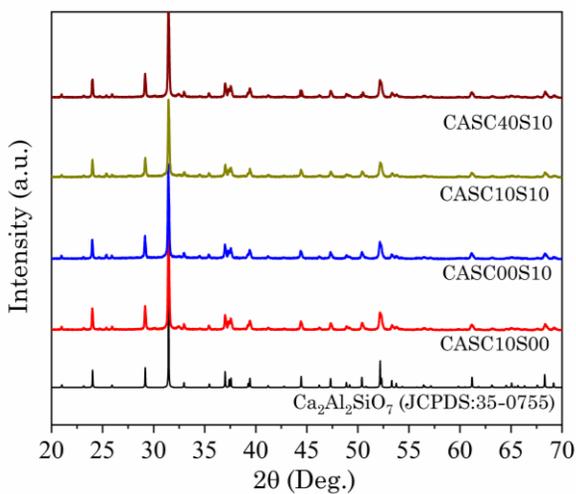


Fig. 1. XRD patterns of the CASC10S00, CASC00S10, CASC10S10 and CASC40S10 samples.

A surface homology and a particle size of the prepared phosphor powders were evaluated by SEM images and the result of SEM micrographs of the CASC10S00 and CASC10S10 samples are showed in Fig. 2. SEM images of two samples indicate that the particles are not uniform and tend to agglomerate, forming cluster and a large size.

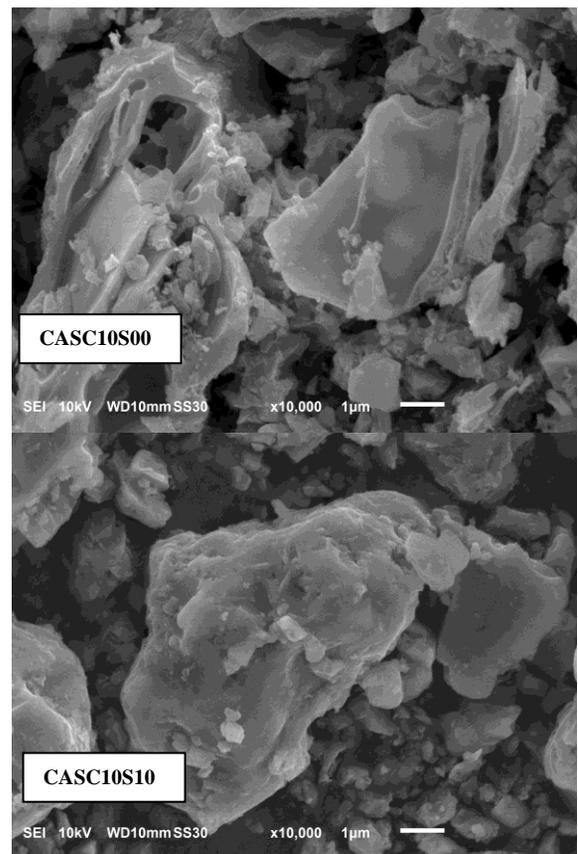


Fig. 2. SEM images of CASC10S00 and CASC10S10 samples.

3.2. Luminescent characteristics and energy transfer in CASCs phosphors

Fig. 3(A) presents photoluminescence and photoluminescence excitation spectra of the CASC00S10 sample at room temperature. PLE spectrum was monitored at emission wavelength of 602 nm (${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition) and showed characteristic multiple sharp peaks in the 300-500 nm region, which attributed to direct excitations from the ${}^6H_{5/2}$ ground state to the excited states of Sm³⁺ ions. The most intense excitation peak located at 402 nm derive from the ${}^6H_{5/2} \rightarrow {}^4F_{7/2}$ transition and other weaker peaks located at 360, 375, and 468 nm correspond to transitions from the ${}^6H_{5/2}$ level to ${}^4D_{3/2}$, ${}^6P_{7/2}$, and ${}^4I_{13/2}$ levels, respectively. It can be seen that the most intense excitation peak is the ${}^6H_{5/2} \rightarrow {}^4F_{7/2}$ transition (402 nm), which

gives a prominent emission of the Sm^{3+} ions. PL spectrum measured at room temperature under the excited radiation of 402 nm (${}^6\text{H}_{5/2} \rightarrow {}^4\text{F}_{7/2}$ transition) includes of three strong emission bands at 565 nm, 602 nm and 648 nm, which are due to the ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$, ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$, ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$ transitions of Sm^{3+} ions, respectively [13, 14].

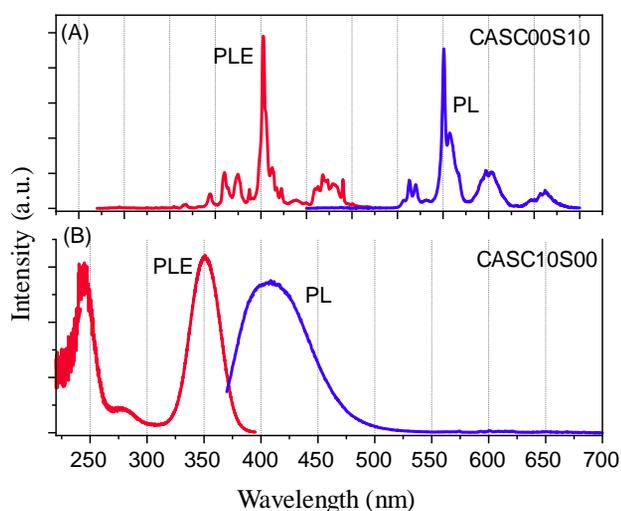


Fig. 3. PL and PLE spectra of (A) CASC00S10 and (B) CASC10S00.

Figure 3 (B) gives PL and PLE spectra of the CASC10S00 sample at room temperature. The PLE spectrum monitored at emission wavelength of 420 nm consists of three broad bands at 244, 278 and 350 nm, which assigned to the electronic transitions from the ground state to the different crystal field splitting bands of excited 5d state of Ce^{3+} . One observes that the absorption (350 nm) extends into the near UV part of the photoluminescence excitation spectrum; this makes this material also suitable for application with near UV LED. The PL spectrum, excited by $\lambda_{\text{ex}}=350$ nm, has a broad band emission with center around 420 nm, which is due to the 5d \rightarrow 4f transition of Ce^{3+} and this band well overlaps the strong excitation peak of Sm^{3+} (402 nm) indicating a possibility of the energy transfer from Ce^{3+} to Sm^{3+} if they are co-doped in this material.

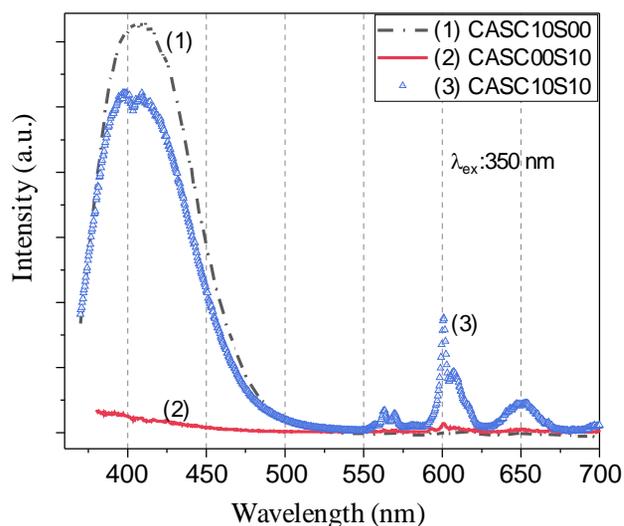


Fig. 4. PL spectra of CASC10S00, CASC00S10 and CASC10S10 samples under the excitation radiation of 350 nm.

To investigate the energy transfer in this material, the PL spectra of three samples CASC10S00, CASC00S10 and CASC10S10 under the same excited radiation of 350 nm were measured and shown in Fig. 4. It is noted that $\lambda_{\text{ex}}=350$ nm is not suitable to excite Sm^{3+} but it is a good excitation wavelength for Ce^{3+} (see more Fig. 3). Emission intensity of Sm^{3+} in CASC00S10 (only Sm^{3+}) is very weak while that in CASC10S10 (co-doped Ce^{3+} and Sm^{3+}) is strong, that means there is the energy transfer from Ce^{3+} to Sm^{3+} in CASC10S10 material. In addition, the emission intensity of Ce^{3+} at 420 nm in CASC10S10 is lower than that in CASC10S00 sample although they are the same concentration of Ce^{3+} (1 mol%). It shows a part of the emission energy of Ce^{3+} transferred to Sm^{3+} ion that makes the emission intensity of Ce^{3+} decrease and the emission intensity of Sm^{3+} increase (presented above). These observations confirm the energy transfer from Ce^{3+} to Sm^{3+} ions in CASC10S10 material.

Besides that, result of PLE spectra of CASC00S10 and CASC10S10 monitored at 602 nm (Sm^{3+} emission) in Fig. 5 also show an evidence of the energy transfer phenomenon. Clearly, by monitoring 602 nm emission of Sm^{3+} the excitation spectrum of CASC10S10

not only contains the f→f absorption transitions of Sm³⁺ (peaks in 380-500 nm) but also the f→d broad band absorption of Ce³⁺ (260-380 nm), which indicated the existence of energy transfer from Ce³⁺ to Sm³⁺ ions in CASC10S10 sample. The simple model for the energy transfer from Ce³⁺ to Sm³⁺ ions in CASC10S10 material is presented in Fig. 6.

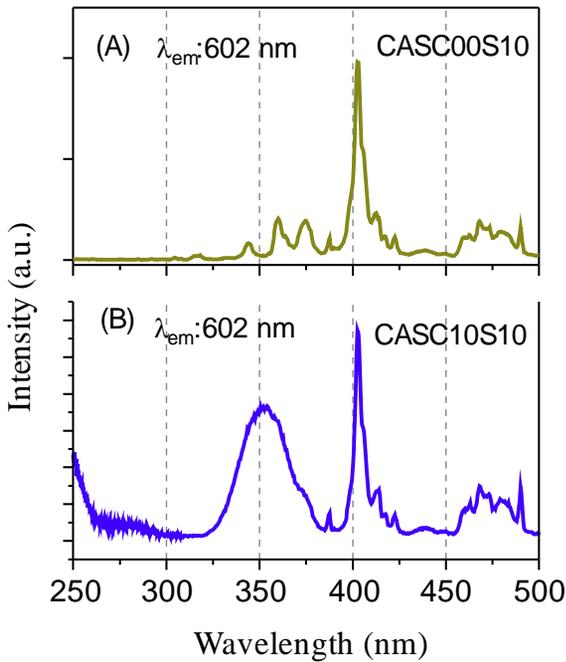


Fig. 5. PLE spectra of the CASC00S10 (A) and CASC10S10 (B) samples monitored at 602 nm wavelength.

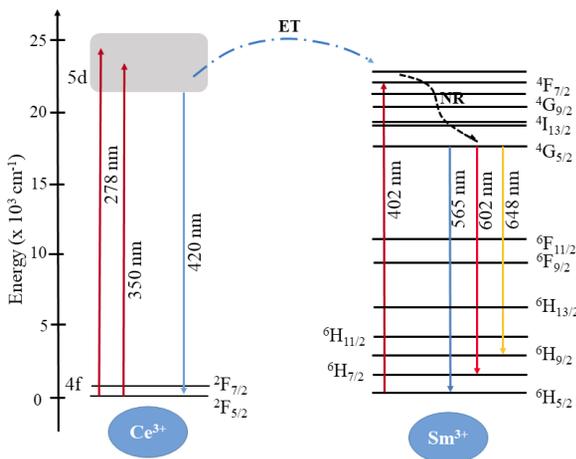


Fig. 6. Energy transfer model from Ce³⁺ to Sm³⁺ in CASC10S10 material.

3.3. Luminescent characteristics of CAS phosphors with different Ce concentration

Figure 7 shows the PL spectra of the CASCxS10 (x=05, ..., 40 as labeled in Table 1) phosphors with various Ce³⁺ concentrations under the excitation wavelength of 350 nm. Insets in Fig. 7 present the emission intensities of Ce³⁺ (420 nm) and Sm³⁺ (602 nm) as a function of Ce³⁺ concentrations. As can be seen that, both Ce³⁺ and Sm³⁺ emission increases with the increasing of Ce³⁺ concentration from 0.5 to 2.0 mol%, then it decreases for higher doping concentration. However, reason of the Ce³⁺ emission intensity change is different to Sm³⁺: In the case of the Sm³⁺ emission, because the Sm³⁺ concentration is fixed at 1 mol%, therefore, the change of Sm³⁺ emission intensity due to the energy transfer from Ce³⁺ ions. This process is affected by the change of Ce³⁺ emission intensity; For the Ce³⁺ emission, when the Ce³⁺ concentrations increase, a lot of luminescent centers are formatted which make the increasing of emission intensity of Ce³⁺. If continue doping higher, emission intensity decreases due to a concentration quenching phenomenon. It is shown in Fig. 7, the concentration quenching phenomenon occurred from 2.0 mol%, which relates to the critical transfer distance (R_c) based on the report of Blasse [15] as below:

$$R_c = 2 \left(\frac{3V}{4\pi \cdot x_c \cdot N} \right)^{1/3} \quad (1)$$

Where, V is the unit cell volume of matrix, x_c is the critical concentration, and N is the number of cations in a unit cell. For CASCxS10 materials, $V = 299.672 \text{ \AA}^3$, $x_c = 0.03$ (Ce³⁺ + Sm³⁺), and $N = 2$ [16], so the value of R_c can be determined to be around 11 Å by using Eq. 1. The concentration quenching mechanisms are due to non-radiative energy transfer between ions, which include exchange interaction and electric multipole interaction. Because the critical distance of this material (11 Å) is larger

than the distance of the exchange interaction ($<5 \text{ \AA}$), hence, the exchange interaction could not be attributed to the concentration quenching mechanism in CASCxS10 phosphors. Therefore, the electric multipole interaction between the Sm^{3+} ions has been accounted for the concentration quenching mechanism in the CASCxS10 phosphors. According to Dexter, when the doping concentration is high enough, the interaction mechanism between ions can be determined by the relationship between emission intensity and doping concentration as below [17-19]:

$$\lg\left(\frac{I}{x}\right) = c - \frac{\theta}{3} \lg x \quad (2)$$

Where I is Ce^{3+} emission intensity, x is the doping concentration, c is constant and $\theta=6, 8, 10$ stands for the dipole-dipole, dipole-quadrupole and quadrupole-quadrupole, respectively. Using Eq. 2 with Ce^{3+} concentrations from 2.0 to 4.0 mol%, the curve of the $\lg(I/x)$ vs the $\lg(x)$ of the CASCxS10 samples is presented in Fig. 8. It clearly shows that the relation between $\lg(I/x)$ and $\lg(x)$ is approximately linear with slope of -2.028 , and therefore the θ value equals $6.056 (\approx 6)$. This result indicates that the dipole-dipole interaction is the major mechanism of the concentration quenching phenomenon in the CASCxS10 phosphors.

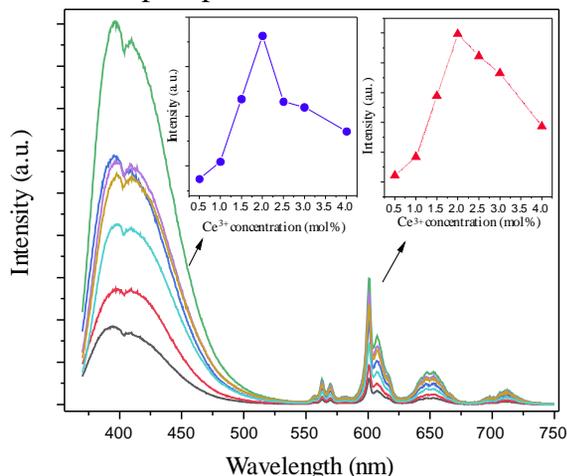


Fig. 7. PL spectra of CASCxS10 samples along with the change of Ce^{3+} concentration (insets presenting PL intensity at 420 nm (Ce^{3+}) and at 602 nm (Sm^{3+}) at various Ce^{3+} concentration).

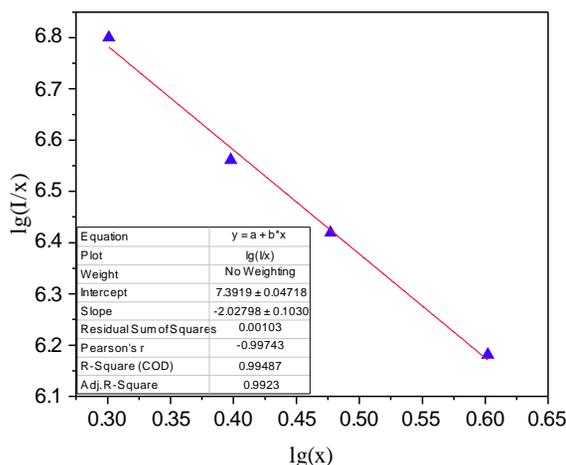


Fig. 8. Relationship between $\log(I/x)$ and $\log(x)$ of CASCxS10 phosphors.

4. Conclusion

Ce^{3+} and Sm^{3+} doped/co-doped $\text{Ca}_2\text{Al}_2\text{SiO}_7$ phosphors were successfully synthesized, showing tetragonal single phases through X-ray diffraction, and a particle aggregation with large particle size via SEM images. The photoluminescence and photoluminescence excitation spectra confirmed the existence of energy transfer from Ce^{3+} to Sm^{3+} . Interestingly, the fluorescence intensity of CAS varied as a function of Ce^{3+} concentrations, and reached to maximum at the content of 2.0 mol%. The major mechanism of intensity quenching since Ce^{3+} content greater than 2.0 mol% can be interpreted by the dipole-dipole interaction.

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