

# Spectroscopic Characteristics of $\text{Ca}_2\text{Al}_2\text{SiO}_7: \text{RE}^{3+}$ Phosphors

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**Abstract--** Different rare-earth ion single doped  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  materials have been successfully synthesized by solid state reaction method. The emission of  $\text{Ce}^{3+}$  ion doped  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  phosphor is a broad band, while these of  $\text{Dy}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Sm}^{3+}$  or  $\text{Eu}^{3+}$  ion single doped materials are the narrow lines that characterised by transitions in the 4f electron configuration. The maximum emission intensity of each rare earth ion depends on the excitation radiation wavelength. Spectroscopic properties of  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  phosphors doped with rare earth ion ( $\text{Ce}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Sm}^{3+}$  or  $\text{Eu}^{3+}$ ) have been presented and discussed.

**Keywords--**  $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ,  $\text{RE}^{3+}$ , luminescence

## I. INTRODUCTION

Earth alkaline alumino silicate luminescent materials ( $\text{M}_2\text{Al}_2\text{SiO}_7$  with  $\text{M} = \text{Ca}, \text{Sr}$ ) doped with rare earth ions have been interested because their high luminescent efficiency and its spectral characteristic suitable for many applications, especially in lighting technology and display [1-4]. Researches on the luminescent characteristic of luminescent materials base on  $(\text{Ca}, \text{Sr})_2\text{Al}_2\text{SiO}_7$  lattice shows that the materials have many advantages such low cost, thermal stability and chemical stability, especially their high absorbance to near UV radiation which make it is suitable for a wide range of application. Therefore, researches on luminescent characteristic of materials base on  $\text{CaAl}_2\text{SiO}_7$  lattice attract lots of attention and have great significance in basic and applied research. A few recent years, there are

many investigations on the  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  single doped/codoped with rare earth ion that could use for fabricating laser, wLED as explaining mechanism of the photoluminescence and thermoluminescence [5- 8]. This paper presents systematic research results on the luminescent characteristics of  $\text{RE}^{3+}$  ion doped  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  (CAS) phosphors with  $\text{RE}^{3+}$ :  $\text{Ce}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  that were synthesized by solid state reaction method. Effects of the excitation radiation to the emission intensity of phosphors also were considered.

## II. EXPERIMENT

$\text{RE}^{3+}$  ( $\text{Ce}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ) ion single doped  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  materials have been synthesized by solid state reaction method. Initial materials used include  $\text{CaCO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{CeO}_2$ ,  $\text{Dy}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{Tb}_4\text{O}_7$  are weighted according to molar ratio, the concentration of  $\text{RE}^{3+}$  ion was constantly choose at 0.5 %mol. Then, the reagent mixture was grinded in an agate mortar for 2 hours, later was annealed at temperature 1280°C for 1 hour. The X-ray diffraction diagrams were taken by Bruker D8-Advance diffractometer. The Photoluminescent (PL) and Photoluminescent excitation (PLE) spectra were taken by FL3-22 fluorescence spectrometer, Horiba with a Xenon lamp 450 W.

### III. RESULTS AND DISCUSSION

#### A. Crystalline structure

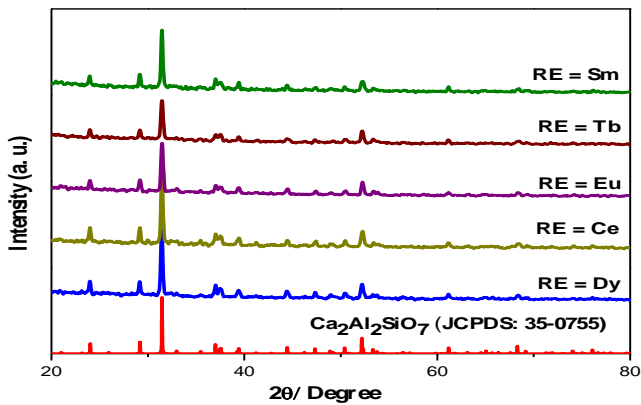


Fig. 1. XRD diagrams of samples CAS: RE<sup>3+</sup> (RE = Sm, Tb, Eu, Ce, Dy)

The crystalline structure of rare earth ions doped Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub> luminescent material was investigated by X-ray diffraction method. The XRD diagram of Samples CAS: RE<sup>3+</sup> (RE: Dy, Ce, Eu, Tb, Sm) are shown in Figure 1.

The analysis results show that all of the samples have the desiring tetragonal phase structure of Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>. On the other hand, the XRDs show no characteristic peaks of rare earth ion as well as of initial reagents. The observation indicates that the small amount of rare earth dopant did not change the phase structure of the material.

#### B. Spectral characteristics of Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>: RE<sup>3+</sup> phosphors

Figure 2(b) is the PL spectrum of CAS: Ce<sup>3+</sup> excited by UV radiation at λ = 350 nm. The result shows that emission of sample CAS: Ce<sup>3+</sup> has a broad band ranging from 360 nm to 500 nm with maximum at 420 nm, correspond to the transition from 5d to 4f (<sup>5</sup>F<sub>5/2</sub> and <sup>2</sup>F<sub>7/2</sub>) electronic states of Ce<sup>3+</sup> ion in the host lattice. Figure 2(a) shows the PLE spectrum of CAS: Ce<sup>3+</sup> at emission wavelength of 420 nm, correspond to the excitation transition of Ce<sup>3+</sup> in CAS lattice. The PLE spectrum has two broad bands peaking at 280 nm and 350 nm, correspond to the absorption due to the transition from the ground state of 4f to the excited state 4f<sup>0</sup>5d<sup>1</sup> of Ce<sup>3+</sup> ion [2, 4]. The broad band emission locates in wavelength 360 – 500 nm shows that Ce<sup>3+</sup> ion not only is suitable for using as an activator but also a sensitizer in codoped materials that can emit visible light.

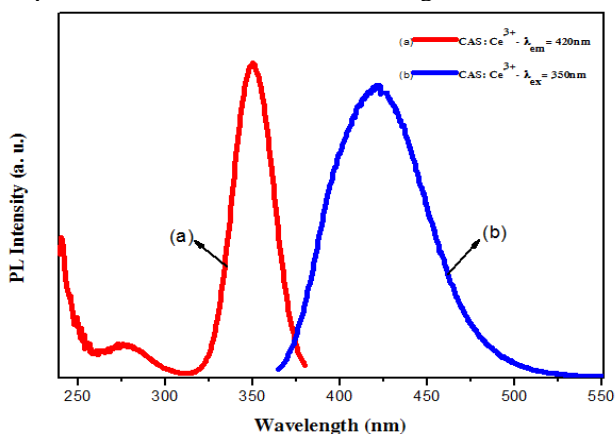


Fig. 2. PLE spectra (a) and PL spectra (b) of CAS: Ce<sup>3+</sup>

Figure 3(b) shows PL spectrum of CAS: Sm<sup>3+</sup> excited by the radiation at wavelength 350 nm. The spectrum has narrow lines ranging from 550 – 715 nm with maximum at 563 nm, 602 nm, 645 nm and 710 nm that correspond to the transitions in the 4f<sup>5</sup> electronic configuration of Sm<sup>3+</sup> ion from <sup>4</sup>G<sub>5/2</sub> excitation state to <sup>6</sup>H<sub>J/2</sub> ground states (J = 5, 7, 9, 11 respectively) [9]. Figure 2(a) shows PLE spectrum of Sm<sup>3+</sup> in the wavelength range of 325 – 500 nm. The spectrum shows the transitions from the ground state <sup>6</sup>H<sub>5/2</sub> to the <sup>4</sup>I<sub>9/2</sub> (478 nm), <sup>4</sup>I<sub>11/2</sub> (470 nm), <sup>4</sup>I<sub>13/2</sub> (459 nm), <sup>4</sup>M<sub>17/2</sub>, <sup>4</sup>G<sub>9/2</sub>, <sup>4</sup>I<sub>15/2</sub> (438 nm), <sup>6</sup>P<sub>5/2</sub>, <sup>4</sup>L<sub>13/2</sub> (421 nm), <sup>4</sup>F<sub>7/2</sub> (412 nm), <sup>6</sup>P<sub>3/2</sub> (405 nm), <sup>4</sup>G<sub>11/2</sub> (390 nm), <sup>4</sup>L<sub>17/2</sub> (374 nm), <sup>4</sup>D<sub>5/2</sub> (359 nm), <sup>4</sup>H<sub>9/2</sub> (344 nm) and <sup>4</sup>G<sub>9/2</sub> (331 nm) excited states of Sm<sup>3+</sup> ion. The highest emission intensity with peak at λ<sub>EX</sub> = 405 nm, corresponds to the <sup>6</sup>H<sub>5/2</sub>→<sup>6</sup>P<sub>3/2</sub> transition which is usually used in the fluorescent stimulation of Sm<sup>3+</sup> ions. The results show that CAS: Sm<sup>3+</sup> samples emit strong reddish orange light when being stimulated by blue LED. Therefore, this material has potential application in LED manufacture or reddish orange fluorescent lamp if stimulated with blue light.

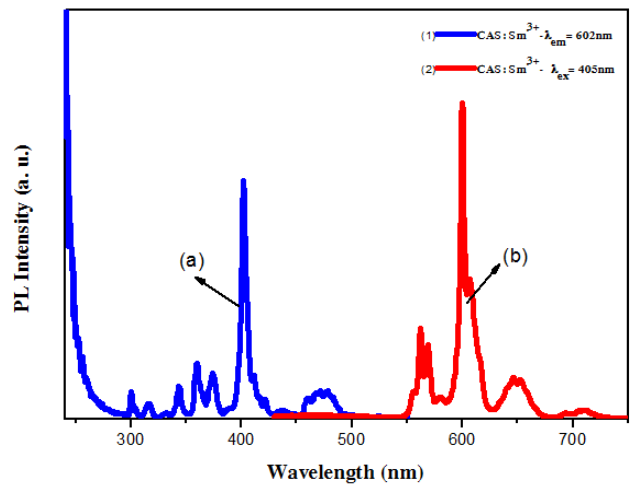


Fig. 3. PLE spectra (a) and PL spectra (b) of CAS: Sm<sup>3+</sup>

The PL spectrum of CAS: Dy<sup>3+</sup> Figure 4(b) consists of the narrow lines at λ = 478 nm, 575 nm and 664 nm. Peaks at λ = 478 nm, 575 nm have high intensity correspond to the <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>15/2</sub> and <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>13/2</sub> transitions of Dy<sup>3+</sup> ion. Meanwhile, peak at 664 nm has lower intensity which corresponds to the <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>11/2</sub> transition. The PLE spectrum of CAS: Dy<sup>3+</sup> with a radiation wavelength of 575 nm is shown in Figure 4(a). The PLE spectrum has narrow lines peak at 322 nm (<sup>6</sup>H<sub>15/2</sub>→<sup>6</sup>P<sub>3/2</sub>), 350 nm (<sup>6</sup>H<sub>15/2</sub>→<sup>4</sup>M<sub>15/2</sub>, <sup>6</sup>P<sub>7/2</sub>), 363 nm (<sup>6</sup>H<sub>15/2</sub>→<sup>4</sup>I<sub>11/2</sub>), 383 nm (<sup>6</sup>H<sub>15/2</sub>→<sup>4</sup>I<sub>13/2</sub>, <sup>4</sup>F<sub>7/2</sub>), 425 nm (<sup>6</sup>H<sub>15/2</sub>→<sup>4</sup>G<sub>11/2</sub>), 451 nm (<sup>6</sup>H<sub>15/2</sub>→<sup>4</sup>I<sub>15/2</sub>), 472 nm (<sup>6</sup>H<sub>15/2</sub>→<sup>4</sup>F<sub>9/2</sub>), correspond to the transitions from the ground state <sup>6</sup>H<sub>15/2</sub> to different excited states of Dy<sup>3+</sup> ion in the 4f<sup>9</sup> electronic configuration [3].

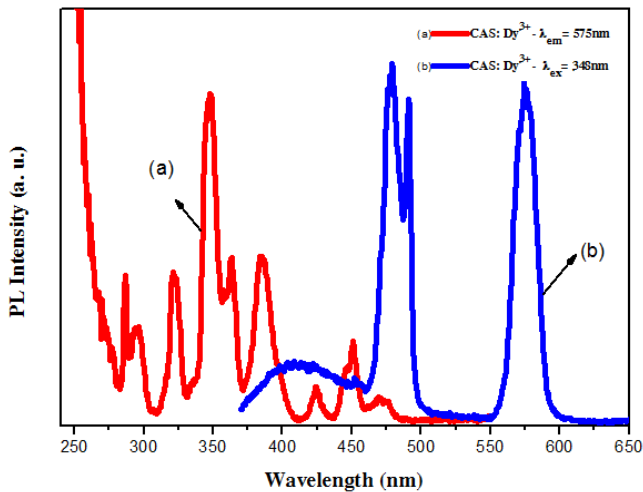


Fig. 4. PL spectra (a) and PLE spectra (b) of CAS: Dy<sup>3+</sup>

In the figure 5(b), the PL spectrum of CAS: Eu<sup>3+</sup> excited by a radiation at 393 nm that consists of narrow lines correspond to the transitions of Eu<sup>3+</sup> ion from the excited state <sup>5</sup>D<sub>0</sub> to the ground states <sup>7</sup>F<sub>J</sub> (J = 0, 1, 2, 3, 4). The peak at 586 nm corresponds to the <sup>5</sup>D<sub>0</sub> – <sup>7</sup>F<sub>1</sub> electric dipolar transition of Eu<sup>3+</sup> ion. The peak at 617 nm corresponds to the <sup>5</sup>D<sub>0</sub> – <sup>7</sup>F<sub>2</sub> magnetic dipolar transition of Eu<sup>3+</sup> ion which depends of the symmetry of the crystal field. Other peaks at 578 nm, 656 nm and 702 nm are relatively weak, corresponds to the <sup>5</sup>D<sub>0</sub> – <sup>7</sup>F<sub>0</sub>, <sup>5</sup>D<sub>0</sub> – <sup>7</sup>F<sub>3</sub> and <sup>5</sup>D<sub>0</sub> – <sup>7</sup>F<sub>4</sub> transitions [1, 5]. The characteristic broad band of Eu<sup>2+</sup> ion was not observed in the PL spectrum. Figures 5(a) shows the PLE spectrum of CAS: Eu<sup>3+</sup> monitored at wavelength of 617 nm. The spectrum has a strong broad band at about 260 nm (not depicted in the figure) and a few narrow lines in the range of 310 nm – 550 nm. The peak that has the strongest intensity at 393 nm corresponds to the <sup>7</sup>F<sub>0</sub> → <sup>5</sup>L<sub>6</sub> transition of Eu<sup>3+</sup> ion. Other weak peaks at 360 nm, 374 nm, 380 nm, 412 nm, 463 nm, 523 nm and 530 nm were ascribed to be the 4f - 4f interconfiguration transitions of Eu<sup>3+</sup> ion in the lattice that consist of the <sup>7</sup>F<sub>0</sub> → <sup>5</sup>D<sub>4</sub>, <sup>7</sup>F<sub>0</sub> → <sup>5</sup>G<sub>2</sub>, <sup>7</sup>F<sub>1</sub> → <sup>5</sup>L<sub>7</sub>, <sup>7</sup>F<sub>0</sub> → <sup>5</sup>D<sub>3</sub>, <sup>7</sup>F<sub>0</sub> → <sup>5</sup>D<sub>2</sub>, <sup>7</sup>F<sub>0</sub> → <sup>5</sup>D<sub>1</sub>, <sup>7</sup>F<sub>1</sub> → <sup>5</sup>D<sub>1</sub> transitions, respectively.

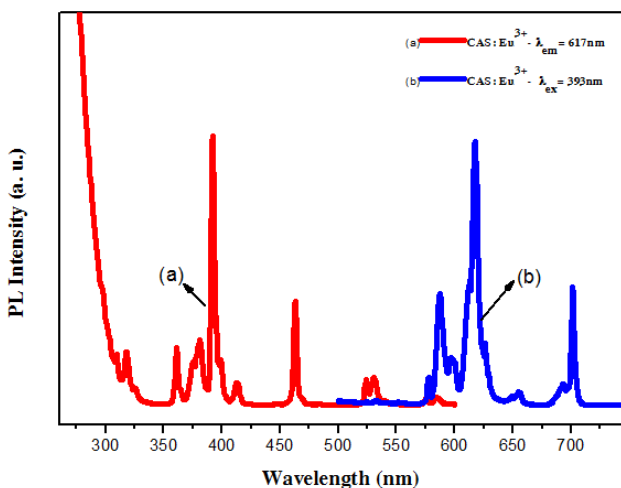


Fig. 5. PLE spectra (a) and PL spectra (b) of CAS: Eu<sup>3+</sup>

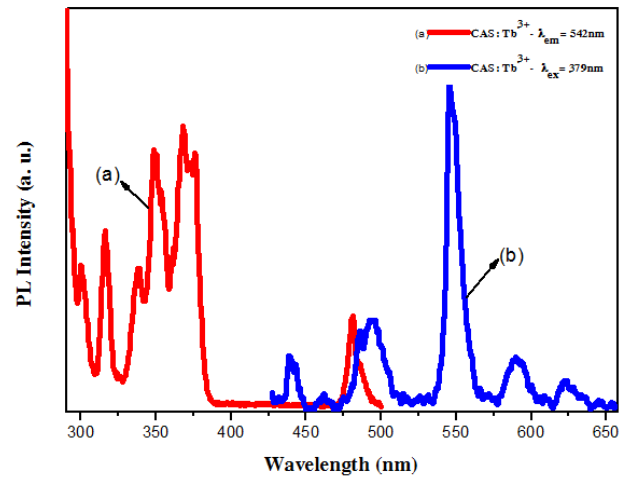


Fig. 6. PLE spectra (a) and PLE spectra (b) of CAS: Tb<sup>3+</sup>

Figure 6(b) shows the PL spectrum of CAS: Tb<sup>3+</sup> excited by the radiation at 379 nm. The spectrum has narrow lines correspond to the transitions of Tb<sup>3+</sup> ion. The peak at 545 nm has the highest intensity that corresponds to the <sup>5</sup>D<sub>4</sub> – <sup>7</sup>F<sub>5</sub> transition. The other peaks at 440 nm, 462 nm, 494 nm, 590 nm and 622 nm are relatively weak, correspond to the <sup>5</sup>D<sub>3</sub> – <sup>7</sup>F<sub>4</sub>, <sup>5</sup>D<sub>3</sub> – <sup>7</sup>F<sub>3</sub>, <sup>5</sup>D<sub>4</sub> – <sup>7</sup>F<sub>6</sub>, <sup>5</sup>D<sub>4</sub> – <sup>7</sup>F<sub>4</sub> and <sup>5</sup>D<sub>4</sub> – <sup>7</sup>F<sub>3</sub> transitions, respectively [4, 7]. The PLE spectrum of CAS: Tb<sup>3+</sup> monitored at wavelength 545 nm is shown in the figure 6(a). The spectrum has a board band in UV region and narrow lines in the range of 310 nm – 500 nm. The peak has the strongest intensity at 368 nm correspond to the <sup>7</sup>F<sub>6</sub> → <sup>5</sup>G<sub>5</sub> transition of Tb<sup>3+</sup> ion. Other weak peaks at 315 nm, 338 nm, 347 nm and 376 nm, 481 nm that were assumed to be the 4f - 4f interconfiguration transition of Tb<sup>3+</sup> ion in the host lattice, could be assigned to <sup>7</sup>F<sub>0</sub> → <sup>5</sup>D<sub>0</sub>, <sup>7</sup>F<sub>6</sub> → <sup>5</sup>L<sub>8</sub>, <sup>7</sup>F<sub>6</sub> → <sup>5</sup>L<sub>8</sub>, <sup>7</sup>F<sub>6</sub> → <sup>5</sup>D<sub>3</sub>, <sup>7</sup>F<sub>6</sub> → <sup>5</sup>D<sub>4</sub> transitions, respectively.

C. Effect of excitation radiation to the luminescence of Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>: RE<sup>3+</sup>

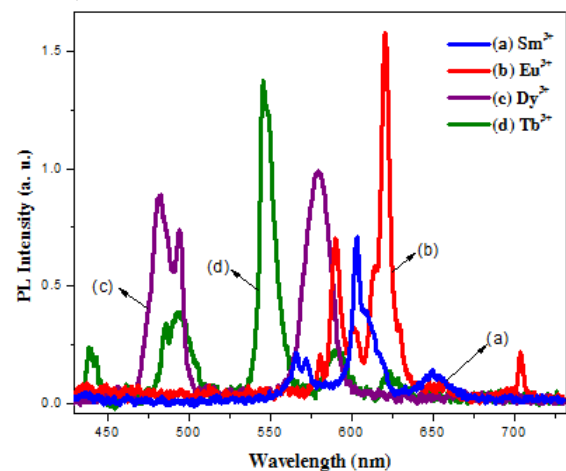


Fig. 7. PL spectra of CAS: RE<sup>3+</sup> excited by a radiation at 365 nm

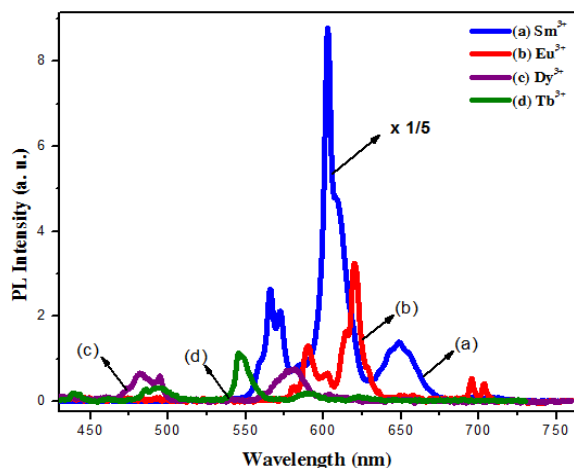


Fig. 8. PL spectra of CAS: RE<sup>3+</sup> excited by a radiation at 405 nm

Luminescent efficiency and intensity of all phosphors can be change by the excitation radiation. Therefore, the influence of 365 nm and 405 nm excitation radiation to the CAS: RE<sup>3+</sup> phosphors as show in the figure 7 and 8. The luminescent intensity of the phosphors are different when they are excited by the radiation of 365 nm and alternates CAS: Eu<sup>3+</sup> > CAS: Tb<sup>3+</sup> > CAS: Dy<sup>3+</sup> > CAS: Sm<sup>3+</sup>. On the other hand, when exciting by a radiation of 405 nm, the luminescent intensity of CAS: Sm<sup>3+</sup> is much higher than that of CAS: Eu<sup>3+</sup>, CAS: Tb<sup>3+</sup>, CAS: Dy<sup>3+</sup>. It means that CAS: Sm<sup>3+</sup> phosphor can use to produce wLED that is pumped blue LED.

#### IV. CONCLUSION

RE<sup>3+</sup> ion single doped Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub> phosphors have been successfully synthesized by solid state reaction method. The emission of CAS: RE<sup>3+</sup> phosphor locates the visible band, i.e. these of CAS: Ce<sup>3+</sup> phosphor is blue light, these of CAS: Dy<sup>3+</sup> is yellow light, these of CAS: Sm<sup>3+</sup> is yellow-red light, these of CAS: Eu<sup>3+</sup> is red light and these of CAS: Tb<sup>3+</sup> is green light. The emission of these phosphors is produced by the electronic transitions of RE<sup>3+</sup> ion in the lattice. The emission intensity of CAS: Sm<sup>3+</sup> phosphor is strongest when

excited by the radiation with wavelength 405 nm. This material can use to make wLED.

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