CONCENTRATION QUENCHING MECHANISM OF TB^{3+} ION IN CALCIUM ALUMINOSILICATE PHOSPHORS

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Abstract: $Ca_2Al_2SiO_7$ phosphors doped with various Tb^{3+} ion concentration, $Ca_2Al_2SiO_7$: xTb^{3+} (x = 0.5, 1.0, 1.5, 2.0, 2.5 and 3.5 mol%) have been successfully synthesized by a solid-state reaction method at high-temperature 1280ºC. The X-ray diffraction diagram shows that the material has single-phased tetragonal structure. Photoluminescent study indicated that $Ca_2Al_2SiO_7$: xTb^{3+} phosphors reach to the highest emission intensity at x = 0.15 mol% and the luminescence quenching phenomenon occurs with higher concentration. The mechanism of concentration quenching process is determined due to the dipole-dipole interaction and the critical distance (R_c) was determined, R_c = 26.7 Å. The chromaticity coordinates of $Ca_2Al_2SiO_7$: xTb^{3+} phosphors were also presented.

Keywords: $Ca_2Al_2SiO_7$, Tb^{3+}, luminescent.

1. INTRODUCTION

Rare earth (RE) ions doped the calcium aluminosilicate phosphors have studied on the luminescent property as well as structural characteristic in the recent years [1]. Eu^{3+} ion doped $Ca_2Al_2SiO_7$ (CAS) material obtaining red emission had studied by Cai Jinjun [2]. Several studies had combined Ce^{3+} ion with other RE^{3+} ions as Dy^{3+}, Mn^{2+} co-doped into this lattice to investigate the luminescence, white light emission, thermoluminescence and mechanoluminescence properties [3-5]. The energy transfer between Ce^{3+} and Tb^{3+} ions using $Ca_2Al_2SiO_7$ as a host lattice for white emission color had investigated and reported [6]. The Thermoluminescence and Mechanoluminescence Properties of UV-Irradiated $Ca_2Al_2SiO_7$: Ce^{3+}, Tb^{3+} phosphor had also studied [7]. The fabrication method as sol-gel processes, combustion method and solid state reaction for $Ca_2Al_2SiO_7$ phosphor has reported in many papers [1, 2, 5, 8-11]. The preparation and spectroscopic properties Tb^{3+} doped $Ca_2Al_2SiO_7$ phosphor was presented in the previous our research [12], inside the luminescent characteristics of the Tb^{3+} ion doped $Ca_2Al_2SiO_7$ green luminescent material that synthesized by solid state reaction method. This paper presents studied results on the influence of Tb^{3+} ion doping

concentration and mechanism of concentration quenching of the $Ca_2Al_2SiO_7$ phosphors doped with Tb^{3+} ion that have been prepared by solid state reaction method.

2. MATERIALS AND METHODS

$Ca_2Al_2SiO_7$: $x$$Tb^{3+}$ (x = 0.5, 1.0, 1.5, 2.0, 2.5 and 3.5 mol%) materials were prepared by a solid-state reaction method at high temperature. Raw materials include of $CaCO_3$ (AR), Al_2O_3 (AR), SiO_2 (Sigma) and Tb_4O_7 (Merck). Firstly, the raw materials were weighed according to their nominal compositions, mixed homogeneously. A small amount of B_2O_3 that is role as fluxing agent was added during the mixing process. Next, this mixture was calcined at 1280ºC for 1 hour in air and then they were cooled down to room temperature to obtain the final samples [1, 10, 12]. The crystalline structure of the prepared samples was recorded by X-ray diffraction (XRD) using x-ray diffractometer (D8-Advance; Bruker, Germany). Luminescence characteristics were estimated via photoluminescence (PL) and photoluminescence excitation (PLE) spectra at room temperature using a fluorescence spectrophotometer (FL3-22; Horiba Jobin-Yvon) with Xenon-450W lamp.

3. RESULTS AND DISCUSSION

3.1. Crystal structure of Tb^{3+} doped $Ca_2Al_2SiO_7$ materials

The crystalline structure of CAS materials doped with Tb^{3+} (x mol%) were pointed by X-ray diffraction (XRD) diagram using Cu Kα radiation. XRD pattern in 20-80º shows in Figure 1. As can be seen in Figure 1, all diffraction peaks of the prepared samples coincide with the $Ca_2Al_2SiO_7$ standard PDF card of 35-0755 [1, 7, 13] and no impurity phases are observed. It indicate that the obtained samples get the expected tetragonal single-phased structure of $Ca_2Al_2SiO_7$ material with the selected technique conditions of synthesis approach.
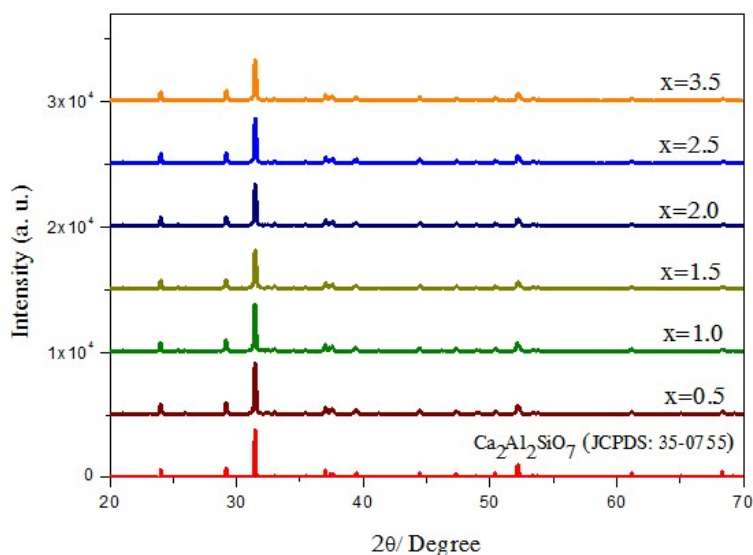

Fig. 1. The XRD diagram of CAS: Tb^{3+} (x mol%)

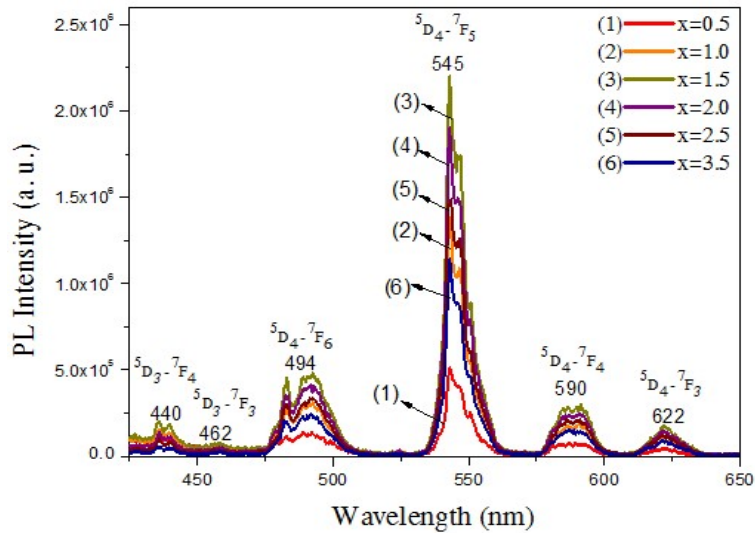## 3.2. Spectroscopic characteristics of $Ca_2Al_2SiO_7$ phosphors doped with diferent Tb^{3+} ion concentration

Fig. 2. PL spectra of CAS: Tb^{3+} (x mol%), λ_{ex}= 282 nm

Fig. 3. PLE spectra of CAS: Tb^{3+} (x mol%), λ_{em}=545 nm

Figure 2 shows the PL spectra of the CAS: Tb^{3+} (x mol%) phosphors with x = 0.5, 1.0, 1.5, 2.0, 2.5 and 3.5 mol% when being stimulated by a radiation of 282 nm. The spectra have narrow lines, corresponds to the transitions of Tb^{3+} ion. The peak at 545 nm, which has the highest luminescent intensity, corresponds to the $^5D_4 \rightarrow {^7F_5}$, other peaks at 440 nm, 462 nm, 494 nm, 590 nm, 622 nm have relatively weak intensity, correspond to the $^5D_3 \rightarrow {^7F_4}$, $^5D_3 \rightarrow {^7F_3}$ and $^5D_4 \rightarrow {^7F_6}$, $^5D_4 \rightarrow {^7F_4}$, $^5D_4 \rightarrow {^7F_3}$ electronic transitions of Tb^{3+} ion [1, 6, 7, 14].

The PLE spectra of CAS: xTb^{3+} (x mol%) corresponds to the emission at 545 nm is show in Figure 3. The spectra consist of a wide band in the UV region and a few narrow lines in the wavelength range from 310 nm to 550 nm. The PLE spectra have two main parts: (1) – A wide band in the region of λ < 300 nm – charge transfer band (CTB) due to Tb^{3+}- O^{2-} interaction. The CTB results from the transmission of one electron from 2p orbit of O^{2-} ion to $4f^8$ shell of Tb^{3+} ion, (2) – narrow lines in the range from 310 nm to 550 nm are assigned to the f-f

transitions of Tb^{3+} ion. The peak has the high intensity at 368 nm, which corresponds to the $^7F_6$ $\rightarrow ^5G_5$ transition. Other weak peaks at 315 nm, 338 nm, 347 nm and 376 nm, correspond to the $4f - 4f$ inner-configuration transitions that could be assigned to the $^7F_6 \rightarrow ^5D_0$, $^7F_6 \rightarrow ^5L_8$, $^7F_6 \rightarrow ^5G_4$, $^7F_6 \rightarrow ^5D_3$, respectively [1,6,7,14]. The PL and PLE Spectra of CAS: xTb^{3+} (x mol%) have characteristic narrow lines of Tb^{3+} ions. The shape and position of the peaks in the both PL and PLE spectra remain unchanged as the concentration of Tb^{3+} ion dopant changes. The emission intensity increases as the concentration of Tb^{3+} ion in the lattice increases and reaches the highest value with the concentration of Tb^{3+} to 1.5 mol%. Beyond this value, the maximum emission intensity decreases due to concentration quenching effect. The relation between the maximum emission intensity and the Tb^{3+} ion concentration is showed in Figure 4. Besides, the excitation and emission transitions of Tb^{3+} ion in CAS phosphor shown in Figure 5.
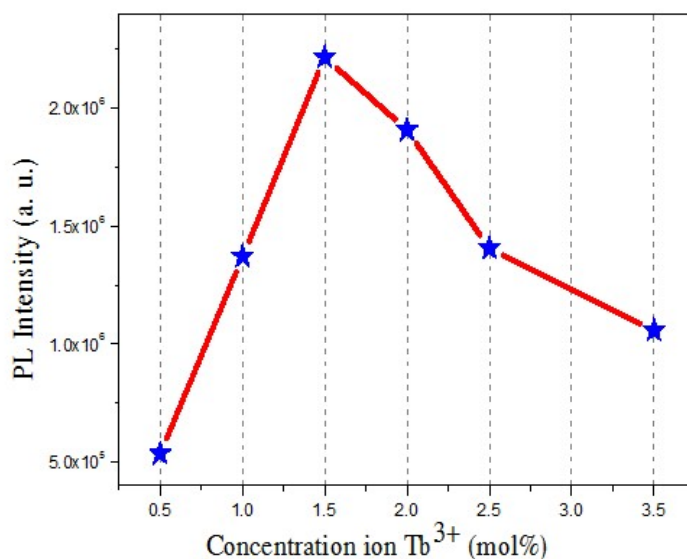

*Fig. 4. **The relation between maximum emission intensity and the concentration of Tb^{3+} ion***

The color coordinate of the emission was determined from the PL spectrum of CAS: Tb^{3+} phosphor. The result in Figure 6 indicates that the material emits green light when being stimulated by a wavelength of 282 nm with coordinate of x = 0.314, y = 0.503. It is suitable for green LED manufacturing when stimuleated by near ultraviolet radiation.
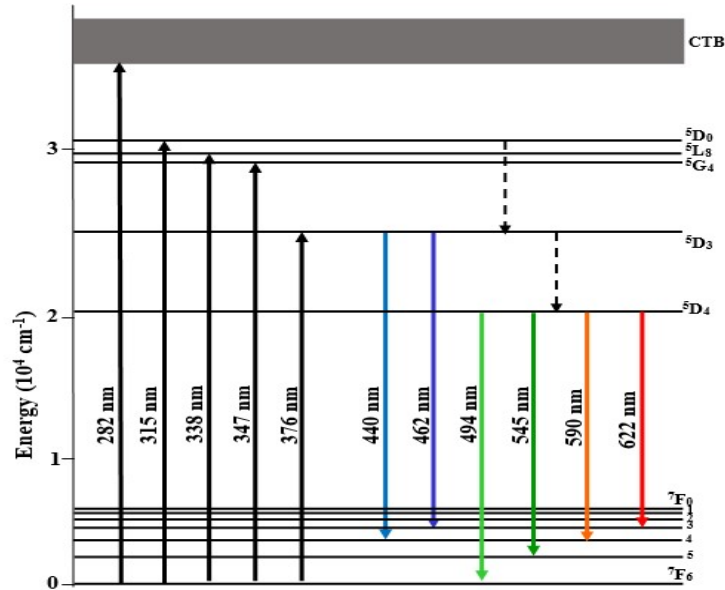
Fig. 5. The excitation and emission transitions of Tb^{3+} ion in CAS phosphor
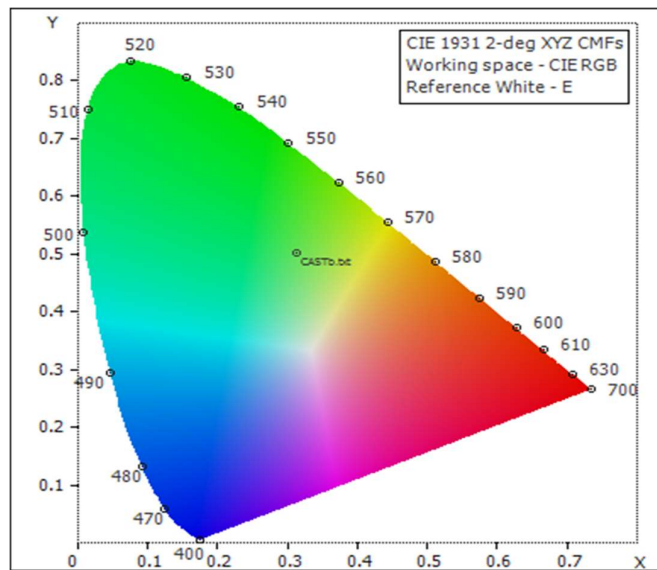

Fig. 6. CIE Color coordinates of CAS: Tb^{3+} when being stimulated by radiation of 282 nm

3.3. Mechanism of concentration quenching in CAS: Tb³⁺ phosphor

The mechanism of concentration quenching in CAS: Tb^{3+} material occurs when the concentration of Tb^{3+} ion is over 1.5 mol% as shown in Figure 4. According to the theory of concentration quenching by Dexter and Blasse, the critical radius (R_C) of the energy transmission is given by [10, 15]:

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

Where, x_c is the critical concentration, i.e the dopant concentration beyond which the

luminescent intensity begins to decrease. N is the number of cation in the unit cell and V is the unit cell volume [10]. For CAS material, $V = 299.39 Å^3$, $N = 2$ [9, 10], $x_c = 0.015$ (based on the PL spectra in Figure 4). Substituting these values to (1), R_C is about 26.7 Å. The luminescent concentration quenching mechanism is non-emission energy transmission processes. These processes include charge exchange, reabsorption or multipolar interaction. Charge exchange occurs in the range of less than 5Å. Therefore, it cannot be accounted for the concentration quenching process because the R_c is much greater than 5Å. Therefore, multipolar interaction is accounted for the concentration quenching of the CAS material. According to Dexter, the relation between luminescent intensity and concentration of activation center is given by the follow formula [10, 15]:

$$\frac{I}{x} = \frac{K}{1 + \beta(x)^{Q/3}} \tag{2}$$

Where I is the luminescent intensity of CAS: Tb^{3+}, K and β are the constants in the same stimulation condition, while x is the concentration of activation center. The parameter $Q = 6$, 8, 10 corresponds to dipole - dipole (d - d), dipole - quadrupole (d - q), quadrupole - quadrupole (q - q) interactions respectively. The Q value can be determined from the graph [10, 16]:

$$\log\left(\frac{I}{x}\right) = c - \frac{Q}{3}\log x \tag{3}$$

Based on the equation (3), the Q value could be determined from the graph of log (I/x) and logx. The log (I/x) vs logx graph of CAS: Tb^{3+} at different Tb^{3+} concentration is shown in Figure 7. The graph's slope is -1.9080. From this result, $Q = 5.7240$ can be determined, approximately 6. It indicates that dipole - dipole (d - d) interraction plays a main role in the concentration quenching of CAS: Tb^{3+}.
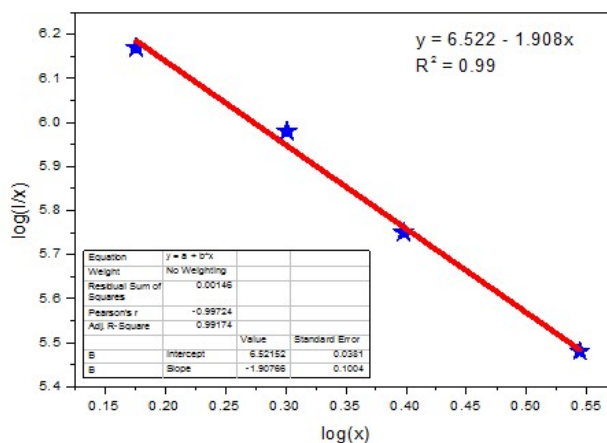

Fig. 7. The relation between log (I/x) and log(x) of CAS: Tb^{3+} (x mol%)

4. CONCLUSIONS

The Tb^{3+} ion doped $Ca_2Al_2SiO_7$ phosphors have been successful synthesized by solid state reaction method. The XRD diagram shows that the material has $Ca_2Al_2SiO_7$ single phase structure. The PL spectra of $Ca_2Al_2SiO_7$: Tb^{3+} phosphors have the narrow lines which

correspond to the emission of Tb^{3+} ion. The phosphors emit the green emission when absorb near near ultraviolet radiation. radiation with high luminance. The luminescent intensity varies according to Tb^{3+} ion concentration and reaches the highest value of the concentration of Tb^{3+} ion equal to 1.5 mol%. The concentration quenching of the phosphor mainly results from dipole - dipole interaction.

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