Effect of Eu^{3+} ion Doping Concentration to Luminescent Properties of $Ca_2Al_2SiO_7$ Phosphor

Nguyen Manh Son
Department of Physics,
University of Sciences, Hue University, Vietnam

Le Van Thanh Son
University of Science and Education
University of Danang, Vietnam

Do Thanh Tien
Faculty of Basic Science, University of Agriculture and Forestry
Department of Physics, University of Sciences
Hue University, Vietnam

***Abstract*--Eu^{3+} ion doped $Ca_2Al_2SiO_7$ phosphors were synthesized by solid state reaction method that were sintered at 1280^{0}C for 1 hour. X-ray diffraction diagram showed the materials have single-phased tetragonal structure. The photoluminescent spectra of $Ca_2Al_2SiO_7$: Eu^{3+} have narrow lines, correspond to the transition of Eu^{3+} ions. Dipole-dipole (d-d) interaction plays a main role in concentration quenching of the material. The luminescent characteristics of the material will be presented and discussed.**

Keywords*--*$Ca_2Al_2SiO_7$: Eu^{3+}; photoluminescence; concentration quenching

I. INTRODUCTION

Many red fluorescence materials were synthesised from Eu^{3+} doped the different lattices as Y_2O_3, earth alkaline aluminate, earth alkaline silicate, borate,... which can use to produce the fluorescence lamp because these materials could absorb 254 nm radiation of mercury.

In recent years, white LED stimulated by near-UV radiation combined with red and green luminescent materials have attracted interest from many scientists. Materials could emit visible light with high efficiency under the stimulation of near UV radiation have been used to produce white LED. Earth alkaline alumino silicate materials have attracted a lot of attention from many scientists and became an interesting research orientation because its high chemical stability and better water-resistance than other materials synthesized on sulphide and aluminates lattice [1-3]. Earth alkaline alumino silicate phosphors doped with different rare earth ions (Eu^{3+}, Dy^{3+}, Tb^{3+}, Ce^{3+},...) could emit different emission in the visible. Inside, there are very many researches that introduced on the luminescence of this lattice doped Eu^{3+} ion [4-6] .

This paper presents results studied on the luminescent characteristics of the Eu^{3+} ion doped $Ca_2Al_2SiO_7$ red luminescent material that synthesized by solid state reaction method. Influence of Eu^{3+} doping concentration and mechanism of concentration quenching was discussed too.

II. EXPERIMENT

The Eu^{3+} ion doped $Ca_2Al_2SiO_7$ (CAS) phosphors are synthesized by the solid state reaction. The starting materials include $CaCO_3$, Al_2O_3, SiO_2 and Eu_2O_3 are weighted according to molar ratio and mixed with 4%wt of B_2O_3 as fluxing agent. The mixtures is grinded in an agate mortar for 1 hour, later is annealed at 1280^{o}C for 1 hour. CAS samples doped with Eu^{3+}ion that concentration can change from 0.25 to 3.0 %mol. The crystalline structure has been characterized by X-ray diffraction method by Brucker D8-Advandce diffractometer. Photoluminescence of the material has been taken by FL3-22 fluorescence spectrometer Horiba Jobin Yvon, USA with XFOR – 450W Xenon lamp.

III. RESULTS AND DISCUSSION

A. *Crystalline structure of Eu^{3+} doped $Ca_2Al_2SiO_7$ phosphors*

The X-ray diffraction diagram of samples CAS: Eu^{3+} (x %mol) with x = 0.25; 0.5; 1.0; 1.5; 2.0; 3.0 are shown in Fig. 1. All results of XRD diagrams show that the materials have $Ca_2Al_2SiO_7$ single-phased structure with pure tetragonal phase.

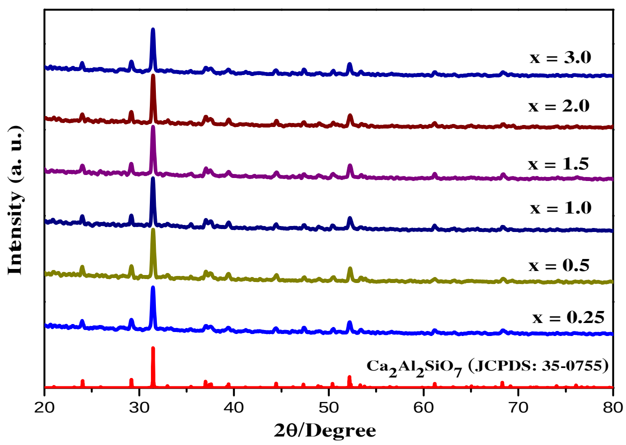

Fig 1. The XRD diagram of CAS: Eu^{3+} (x %mol) phosphors

B. *Spectroscopic properties of CAS phosphors doped with different Eu^{3+} ion concentration*

Figure 2 show PL spectra of CAS: Eu^{3+} (x %mol) materials with x = 0.25; 0.5; 1.0; 1.5; 2.0; 3.0 excited by UV radiation at λ = 393 nm. The Spectra have narrow lines of Eu^{3+} ions. The spectra consist narrow lines, correspond to the transitions of Eu^{3+} ion, from $^5D_0$ excited state to ^7F_J (J = 0, 1, 2, 3, 4) ground states. The emission at λ = 586 nm

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corresponds to magnetic dipole transition $^5D_0$ – $^7F_1$. The emission at λ = 617 nm correspond to electric dipole transition $^5D_0$ – $^7F_2$ which depends on the symmetry of the

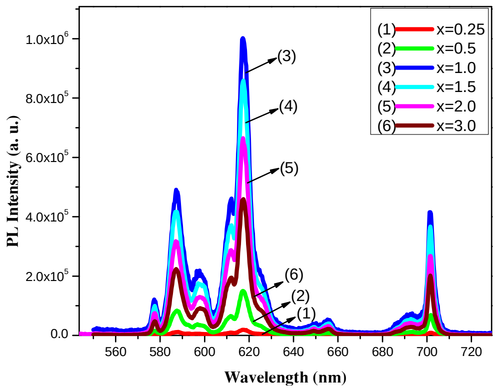

Fig 2. PL spectra of CAS: Eu^{3+} (x %mol), λ_{ex}=393 nm

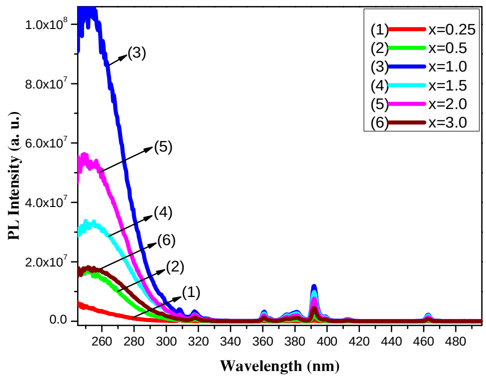

Fig 3. PLE spectra of CAS: Eu^{3+} (x %mol), λ_{em} = 617 nm

crystalline field. Other peaks at λ = 578 nm, 656 nm and 702 nm are relatively weak, corresponding to the transitions $^5D_0$ – $^7F_0$, $^5D_0$ – $^7F_3$ and $^5D_0$ – $^7F_4$ [2], [4], [6-7]. Broad band emission of Eu^{2+} ion was not observed in the PL spectra of CAS: Eu^{3+}.

Figure 3 show PLE spectra of CAS: Eu^{3+}(x %mol) at emission wavelength λ = 617 nm. The spectra have a wide band in the UV region and narrow lines in the range from 310 nm to 550 nm. The PLE spectrum consists of 2 main parts: (1) - A wide band with strongest intensity at **λ** = 260 nm characteristics for charge transfer (CTB) due to Eu^{3+}- O^{2-} interaction, (2) - narrow lines in the range from 310 nm to 550 nm, which are assigned to the f-f transition of Eu^{3+} ions. The line at **λ** = 393 nm which has the high intensity is assigned to the $^7F_0 \rightarrow {}^5L_6$ transition of Eu^{3+}. Other weaker peaks at **λ** = 360 nm, 374 nm, 380 nm, 412 nm and 463 nm, 523 nm, 530 nm are assumed to be the 4f - 4f interconfigurational transitions of Eu^{3+} ion in the lattice that could be assign to $^7F_0 \rightarrow {}^5D_4$, $^7F_0 \rightarrow {}^5G_2$, $^7F_1 \rightarrow {}^5L_7$, $^7F_0 \rightarrow {}^5D_3$, $^7F_0 \rightarrow {}^5D_2$, $^7F_0 \rightarrow {}^5D_1$, $^7F_1 \rightarrow {}^5D_1$ transitions, respectively [4, 6].

The shape and the peak position of both PL and PLE spectra remain unchanged as the concentration of Eu^{3+} dopant ion change. The emission intensity increases as the concentration of Eu^{3+} in the host lattice increase and reaches

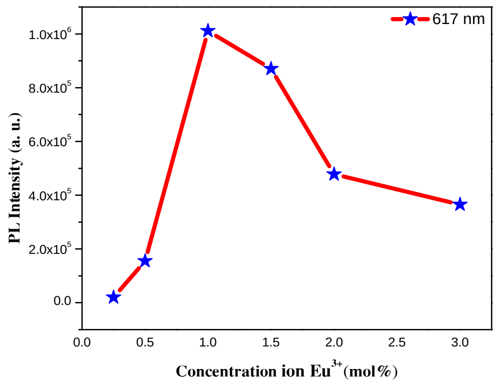

Fig 4. The dependence of maximum emission intensity vs the concentration of Eu^{3+} ions

the maximum value with concentration of Eu^{3+} ion at 1.0 %mol. Later, the maximum emission intensity decreases due to concentration quenching effect. The relation between the maximum emission intensity and the Eu^{3+} concentration is shown in Figure 4.

C. Mechanism of concentration quenching

The mechanism of concentration quenching in CAS: Eu^{3+} material occurs when the concentration of Eu^{3+} ions over 1.0 %mol (as show in Figure 4). According to the theory of concentration quenching by Dexter and Blasse, the critical radius (R_C) of the energy transfer is given by [3, 7]:

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

Where, x_c is the critical concentration i.e. the dopant concentration beyond which the luminescent intensity begins to decrease. For CAS material, V is the unit cell volume is determined from XRD pattern, V = 299.4Å^3, N is the number of cation ion in the unit cell, N = 2 [3] and x_c = 0.01. Substituting these values to the formula (1), R_C is determined about 30.6Å. Therefore, multipolar interaction is accounted for the concentration quenching of the CAS: Eu^{3+} material. At that time, the relation between luminescent intensity and concentration of activation center is given by the formula [8]:

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

Where, I is the luminescent intensity of CAS: Eu^{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. The Q value can be determined from the graph:

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

The log(I/x) vs logx graph of CAS: $Eu^{3+}$with different concentration of Eu^{3+} ion is shown in Figure 5. The graph's slope is -2.0015. From this result, we found that Q = 6.0045,

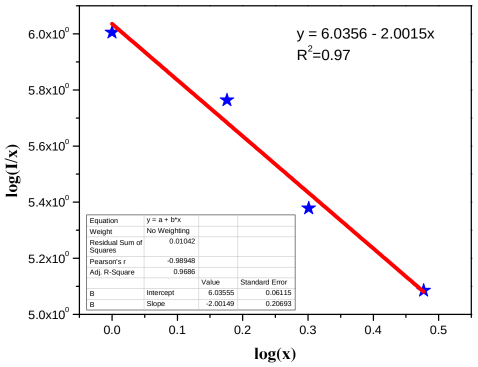

Fig. 5. The relation between log(I/x) and log(x) of CAS: Eu^{3+} (x% mol)

approximately 6. It indicates that dipole-dipole (d-d) interaction plays a main role in the concentration quenching of CAS: Eu^{3+} phosphor.

IV. CONCLUSION

The CAS: Eu^{3+} phosphors with the tetragonal phase structure have been successfully synthesized by the solid-state reaction. The PL spectra of CAS: Eu^{3+} have narrow lines correspond to the electronic transition of Eu^{3+} ions. The emission of phosphor locates at the red region of visible spectrum with high luminance. The photoluminescent intensity varies according to concentration of Eu^{3+} ion and reaches maximum emission intensity with the concentration of Eu^{3+} ion at 1.0 %mol. The concentration quenching of the phosphor results by dipole-dipole interaction.

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