Article

ENERGY TRANSFER BETWEEN Ce^{3+}-Dy^{3+} IN $Ca_2Al_2SiO_7$: Ce^{3+}, Dy^{3+} PHOSPHOR

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Abstract: Ce^{3+} and Dy^{3+} ions doped $Ca_2Al_2SiO_7$ (CAS) phosphors were prepared by the solid-state reaction at 1280^{0}C for 1h. X-ray diffraction patterns confirmed a tetragonal crystalline structure. The luminescent spectra of CAS: Ce^{3+}, Dy^{3+} phosphors consist a board band with peaking at 420 nm corresponding to the luminescence of Ce^{3+} ions and narrow lines of Dy^{3+} ions. The energy transfer from Ce^{3+} ion to Dy^{3+} ion is presented and discussed.

Keywords: $Ca_2Al_2SiO_7$, Ce^{3+}, Dy^{3+}, energy transfer

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1. Introduction

In lighting and display technology, luminescent material has an important role in manufacturing fluorescent lamp and LED which are highly efficient and energy saving. Rare earth doped luminescent materials are widely used in various applications because they are non-toxic, environmental friendly, and have high luminosity and life expectancy [1]. In recent years, white LED was excited by near ultra violet radiation that is combined with red, green and blue luminescent materials have attracted attention from many scientists. Materials that emit visible light with high luminescent efficiency under stimulation by near UV radiation or blue light have been applied in white LED manufacturing. Alkaline earth *alumino silicate* materials have attracted a lots of attention from scientist, and become an interesting research topic in the luminescent material field because their high chemical stability and better water resistance compared to the materials on sulfite and aluminate lattice [2-4]. This paper presents research results on luminescence and energy transfer from Ce^{3+} ion to Dy^{3+} ion in $Ca_2Al_2SiO_7$ lattice.

2. Experiments

Ce^{3+}, Dy^{3+} ion doped $Ca_2Al_2SiO_7$ (CAS) phosphor were prepared by the solid-state reaction. Chemical reagents include: $CaCO_3$ (99.9%, China), Al_2O_3 (99%, China), SiO_2 (99.9%, Korea) and CeO_2 (99.9%, Merck), Dy_2O_3 (99.9%, Merck). These precursors are weighted by molar ratio and mixed with 4 *weight* percent B_2O_3 (used as fluxing agents). The mixtures are well grinded for two hours by using an agate mortar. Then the mixtures were annealed at 1280^{o}C for 1 h. The X-ray diffraction (XRD) diagram was measured by using the diffractometer Bruker D8-Advance. Photoluminescence (PL) and Photoluminescence excitation (PLE) spectra were measured by Fluorescence spectrometer FL3-22 Horiba with 450W Xenon lamp.

3. Results and discussions

3.1. Crystal structure of single doped and co-doped CAS

The analysis results show that the samples have tetragonal phase structure, particularly $Ca_2Al_2SiO_7$ with lattice parameters: a = b = 7.69000 $\overset{0}{A}$, c = 5.06750 $\overset{0}{A}$, $\alpha = \beta = \gamma = 90^o$, and space group P-421m. The crystalline structure of the single-doped sample (CAS: Ce^{3+} (0.5 mol%), CAS: Dy^{3+} (1 mol%)) were compared to that of co-doped samples (CAS: Ce^{3+} (0.5 mol%), Dy^{3+} (1 mol%)) as shown in Fig. 1. The diffraction diagrams do not show any characteristic peaks of rare earth ions as well as of initial reagent components.

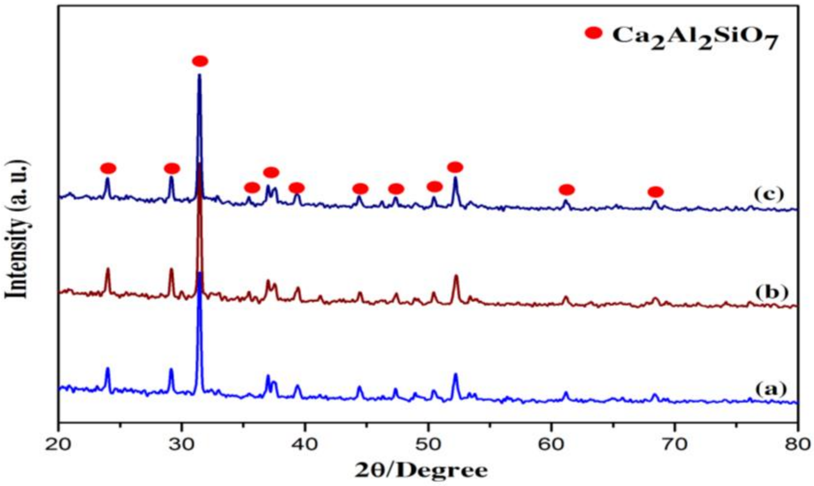

Fig. 1. The XRD diagrams of CAS: Dy^{3+} (1 mol%) (a), CAS: Ce^{3+} (0.5 mol%) (b) and CAS: Ce^{3+} (0.5 mol%), Dy^{3+} (1 mol%) (c).

3.2. Energy transfer between Ce^{3+}, Dy^{3+} in the $Ca_2Al_2SiO_7$ phosphor

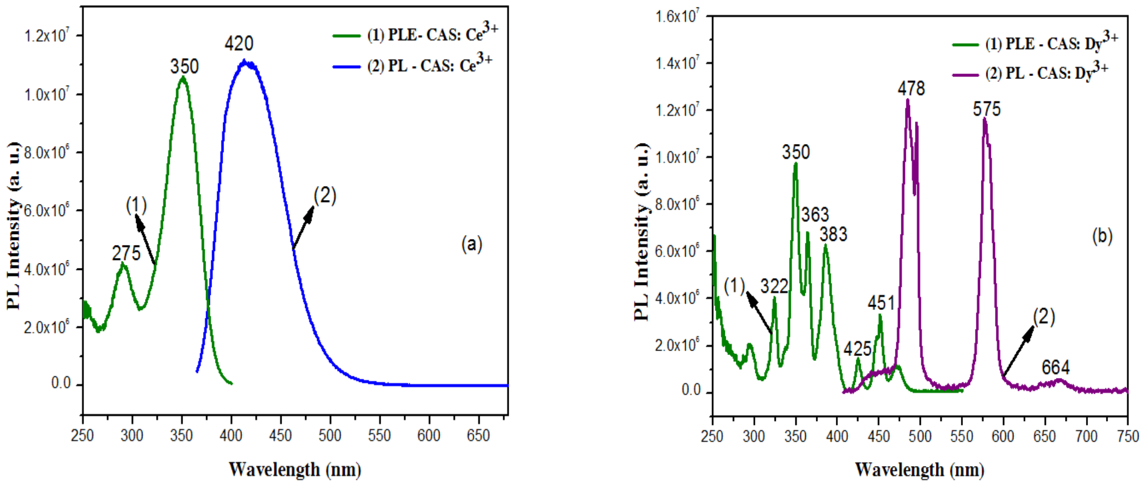

Fig. 2. (a) PLE spectra of CAS: Ce^{3+} (0.5 mol%) with λ_{em}=420 nm

and PL spectra of CAS: Ce^{3+} (0.5 mol%) with λ_{ex}=350 nm, (b) PLE spectra of CAS: Dy^{3+} (1.0 mol%) with λ_{em}=575 nm and PL spectra of CAS: Dy^{3+} (1.0 mol%) with λ_{ex}=350 nm

Fig. 2(a) shows the photoluminescence excitation (PLE) and emission (PL) spectra of Ce^{3+} doped CAS. The PLE spectra of CAS: Ce^{3+} (line 1) monitored at 420 nm exhibits two distinct excitation bands at 275 and 350 nm, which is assigned to the 4f–5d transitions of Ce^{3+}. Besides, the PL spectra of Ce^{3+} ions in CAS (line 2) has a broad band ranging from 365 nm – 525 nm with a maximum at 420 nm, which is attributed to the 5d-4f transition of Ce^{3+} [6-8], which has high intensity. Meanwhile, Fig. 2(b) the PLE spectra of CAS: Dy^{3+} (line 1) monitored at 575 nm, shows characteristic narrow lines corresponding to f-f absorption transition of Dy^{3+}, which are appeared at 322 nm ($^6H_{15}\rightarrow{}^6P_{3/2}$), 350 nm ($^6H_{15}\rightarrow{}^4M_{15/2},{}^6P_{7/2}$), 363 nm ($^6H_{15}\rightarrow{}^4I_{11/2}$), 383 nm ($^6H_{15}\rightarrow{}^4I_{13/2}$, $^4F_{7/2}$), 425 nm ($^6H_{15}\rightarrow{}^4G_{11/2},$), 451 nm ($^6H_{15}\rightarrow{}^4I_{15/2}$). The emission spectra of CAS: Dy^{3+} show narrow lines at wavelength 478 nm, 575 nm, 664 nm, correspond to the transitions $^4F_{9/2}\rightarrow{}^6H_J$ (J = 15/2, 13/2, 11/2) of Dy^{3+} ion. However, their emission intensity is weaker than that of CAS: Ce^{3+}. PLE spectra of CAS: Dy^{3+} (1.0 mol%) and PL spectra of CAS: Ce^{3+} (0.5 mol%) showed that there is an overlap between the emission band of Ce^{3+} ion and the excitation spectra of Dy^{3+} ion. It could indicate the energy transfer from Ce^{3+} ion to Dy^{3+} ion in the lattice CAS.

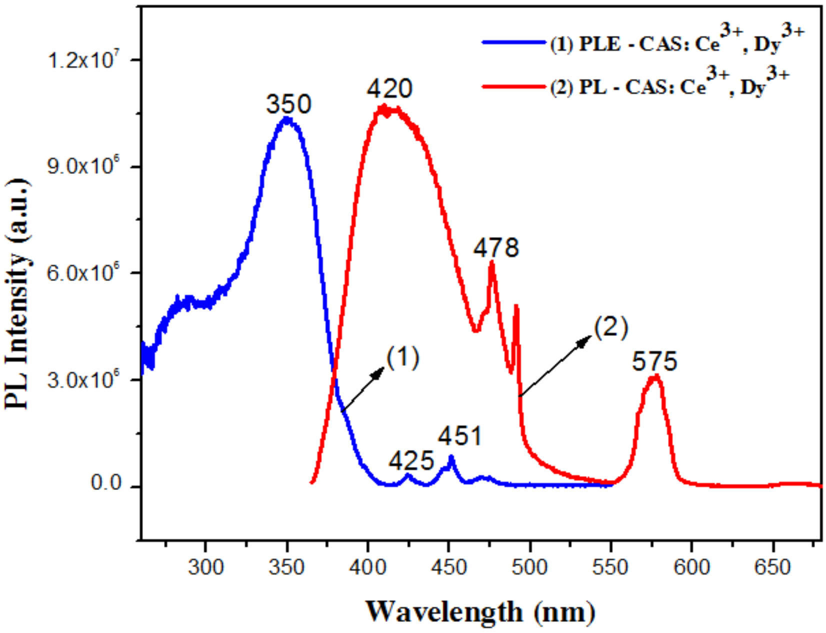

Fig. 3. PLE spectra of CAS: Ce^{3+} (0.5 mol%), Dy^{3+} (1 mol%) (λ_{em} = 575 nm) and PL spectra of CAS: Ce^{3+} (0.5 mol%), Dy^{3+} (1 mol%), λ_{ex}=350 nm

Fig. 3 show the PLE spectra of CAS: Ce^{3+}, Dy^{3+} (line 1) monitored at 575 nm ($^4F_{9/2}\rightarrow{}^6H_{13/2}$ emission Dy^{3+}), consists of the excitation bands of Ce^{3+} and Dy^{3+} ions, indicating that beside to f-f absorption transition of Dy^{3+} ion, the absorption of Ce^{3+} ion also contributes greatly to the emission of Dy^{3+} ion. The contribution to the direct excitation of Dy^{3+} ion is negligible, mainly due to the absorption of Ce^{3+} to generate emission of Dy^{3+} ion via energy transfer from Ce^{3+} ion to Dy^{3+} ion. The result proves that the emission efficiency of Dy^{3+} ion is rather high in the CAS co-doped with Ce^{3+} and Dy^{3+} ions.

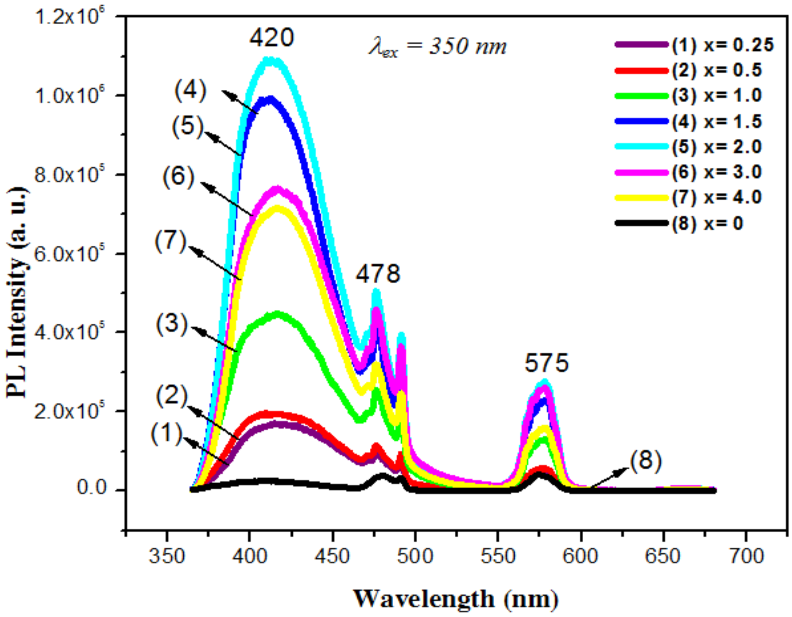

Fig. 4. PL Spectra of CAS co-doped with Ce^{3+} (x mol%), Dy^{3+} (1 mol%), λ_{ex} = 350 nm

To better understand the energy transfer mechanism from Ce^{3+} ion to Dy^{3+} ion in CAS: Ce^{3+}, Dy^{3+}. The PL spectra of CAS: Ce^{3+}(x mol%), Dy^{3+} (1 mol%) with x = 0.25, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 mol% and the concentration of Dy^{3+} ion 1 mol% have investigated in Fig. 4. The results show that when x = 0 mol% the emission intensity of CAS: Dy^{3+} is weak and only characteristic peaks of Dy^{3+} ions in the host could be observed. The broad band with maximum emission at 420 nm was attributed by Ce^{3+} ions, narow lines ranging from 450 to 600 nm, which was attributed by the transitions of Dy^{3+} ion. The PL spectra do not change peak shape and position when concentration of Ce^{3+} ions varies. The PL intensity of both Ce^{3+} and Dy^{3+} ions increases when the concentration of Ce^{3+} ion increases. The result confirms that there is an energy transfer from Ce^{3+} to Dy^{3+} in CAS: Ce^{3+}, Dy^{3+}. The emission intensity of Dy^{3+} ions increases with the increasing concentration of Ce^{3+} ions and reaches a maximum when x = 2 mol%, later the emission intensity decreases.

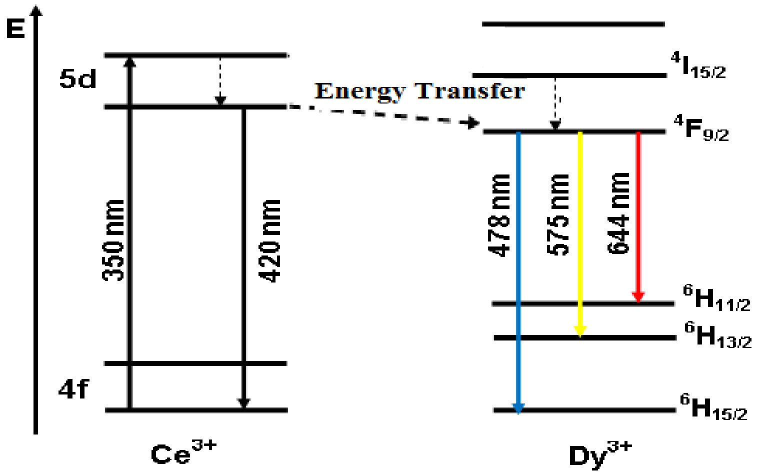

Fig. 5. Energy transfer mechanism from Ce^{3+} ion to Dy^{3+} ion in CAS.

The energy level diagram of Ce^{3+}, Dy^{3+} ions and The energy transfer Ce^{3+} to Dy^{3+} in CAS: Ce^{3+}, Dy^{3+} phosphor upon excitation radiation λ_{ex}=350 nm is illustrated in Fig. 5. The electrons are excited from the ground state 4f to the excited state 5d of Ce^{3+} ion and non-radiatively relaxed to the lowest state of the 5d level. Subsequently, the transition of electron from 5d state to 4f state formed broad band emission of Ce^{3+}ion. At the same time, amount electrons transferred from 5d state of Ce^{3+} ion to $^4F_{9/2}$ excitation state of Dy^{3+} ion, later transited to ^6H_J ground state of Dy^{3+} ion to generate the emission.

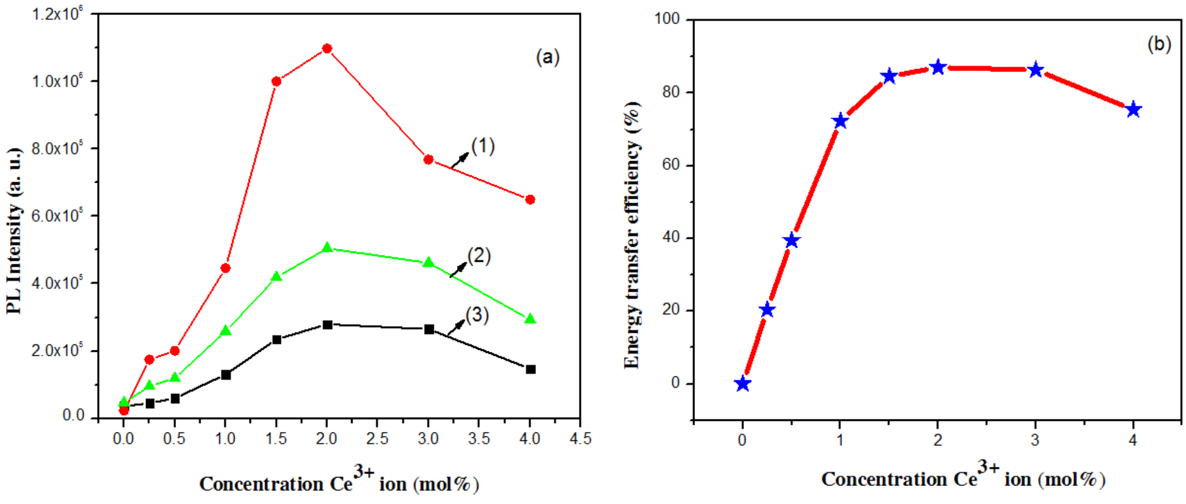

Fig. 6. The dependence of PL intensity (peak at 420 (1), 478 (2) and 575 nm (3)) (a) and the energy transfer efficiency from Ce^{3+} to Dy^{3+} (b) on the concentration of Ce^{3+} ion

Fig. 6 (a) shows the variation of the emission intensities of Ce^{3+} ion and Dy^{3+} ion versus the Ce^{3+} concentration. The observed variations of the emission intensity of the Ce^{3+} and Dy^{3+} ions indicate that the energy transfer process occurred from Ce^{3+} to Dy^{3+}. Thus, the energy transfer efficiency from Ce^{3+} ion to Dy^{3+} ion can be calculated by using the following formula [7]:

$$\eta = 1 - \frac{I_{S0}}{I_S}$$

Where, η is the energy transfer efficiency, I_{S0} is the intrinsic luminescence intensity of an activator (here is Dy^{3+}) in the absence of a sensitizer, I_S the luminescence intensity of Dy^{3+} in the presence of a sensitizer (here is Ce^{3+}). From Fig. 6 we can see that the luminescence intensity of Dy^{3+} ion reaches a maximum when the concentration of Ce^{3+} ion is about 2 mol%. The calculation result shows that the sample CAS: Ce^{3+} (2 mol%), Dy^{3+} (1 mol%) has the highest energy transfer efficiency value of 87% as show in Fig. 6(b).

4. Conclusion

Ce^{3+} and Dy^{3+} ions doped $Ca_2Al_2SiO_7$ phosphors were prepared by the solid-state reaction. Photoluminescence of CAS: Ce^{3+} shows an asymmetric broad band peaking at 420 nm, due to the transition from the 5d excited state to the $^2F_{5/2}$ and $^2F_{7/2}$ ground states. The PL spectra of CAS: Dy^{3+} shows narrow lines at wavelength 478 nm, 575 nm, 664nm correspond to the state transitions $^4F_{9/2} \rightarrow {}^6H_J$ (J = 15/2, 13/2, 11/2). The energy transfer from Ce^{3+} ion to Dy^{3+} ion appears in the Ce^{3+} ion and Dy^{3+} ion co-doped phosphor CAS: Ce^{3+}, Dy^{3+}. The highest energy transfer efficiency is optimal when doping concentration is about 2.0 mol% Ce^{3+} and 1.0 mol% Dy^{3+}.

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