Synthesis and Photoluminescence in Garnet-type $CaLa_2Al_4SiO_{12}:Dy^{3+}$ Phosphor for Optical Applications

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Abstract

The series of xDy^{3+} doped $CaLa_2Al_4SiO_{12}$ garnet-structured phosphors were synthesized by conventional combustion method. The prepared materials were studied using various techniques such as x-ray powder diffraction for crystal structure and phase, photoluminescence for optical properties, scanning electron microscopy (SEM) for morphological studies, and energy dispersive spectroscopy analyses for the existence of elements in the prepared materials. The excitation and emission of the prepared garnet-type phosphor were recorded at 351 nm in the transition from $^6H_{15/2} \rightarrow {}^6P_{7/2}$ and 584 nm in the transition from $^4F_{9/2} \rightarrow {}^6H_{13/2}$. The concentration quenching obtained at 7.0 mol.% of dysprosium ions. This phosphor has potential application in w-LED and other optical devices.

Keywords: Photoluminescence; $CaLa_2Al_4SiO_{12}$; Garnet; Dysprosium.
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Introduction

Efficient lighting devices based on the light emitting diode have attracted great attention in recent time. The solid-state lighting devices are considered as the energy saving light emitting devices than incandescent bulbs [1]. In order to increase the colour stability and life time, the garnet-type phosphor is used in white light emitting devices (w-LEDs) [2]. The luminescence immunoassays is an example of the many uses for garnet-structure phosphor, which are used in a variety of industries, including clinical studies, environmental surveillance, food hygiene, and pharmaceutical testing [3]. The garnet-type phosphors are mostly used in the industry related to optoelectronics [4]. We mostly used various kinds of highly efficient lighting devices now days because of their luminescence efficiency. Among them, phosphor converted light emitting diodes are used [5]. In order to increase quantum yield and luminous intensity, we are choosing garnet-type phosphor. Dy^{3+} doped garnet phosphor uses in the fields of lighting devices as w-LEDs.

The trivalent dysprosium ions are the best dopant with emission in blue and yellow regions [6]. The $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions cause blue and yellow emissions respectively to appear when dysprosium trivalent ions are doped with phosphor [7]. By doping dysprosium trivalent ions (Dy^{3+}) in a suitable phosphor for the proper and pure white lighting devices should be obtained by improving the yellow-blue intensities [8]. As the garnet silicate phosphor host are favourable due to their thermal and chemical equilibrium stabilities [9].

Haipeng *et al*. have prepared garnet-silicate phosphor like $BaY_2Al_4SiO_{12}$, $SrY_2Al_4SiO_{12}$, $CaY_2Al_4SiO_{12}$ and $MgY_2Al_4SiO_{12}$ by solid state reaction synthesis method [10]. In our earlier work we have synthesized $LiCa_3MgV_3O_{12}:Nd^{3+}/Yb^{3+}$ [12], $LiCa_3MgV_3O_{12}$ activated with Er^{3+} [11] and $LiCa_3ZnV_3O_{12}:Nd^{3+}$ [13]. The garnet type phosphor CLASG has high chemical and thermal stability. The emission spectrum was obtained about greenish yellow in visible region while irradiating the material by UV or near-UV radiation [14].

In this paper, we have studied the novel garnet-structured $CaLa_2Al_4SiO_{12}:Dy^{3+}$ phosphor first time. The major applications of this phosphor are optoelectronic devices as solid-state lighting and illumination [15].

Experimental

Materials and synthesis

Pristine $CaLa_2Al_4SiO_{12}$ and $CaLa_2Al_4SiO_{12}:xDy^{3+}$ prepared by using simple combustion method. Calcium Nitrate ($Ca(NO_3)_2$, MERCK), Aluminium Nitrate ($Al(NO_3)_3$, MERCK), Silicon Oxide (SiO_2, MERCK), Lanthanum Oxide (La_2O_3, MERCK), and Dysprosium Oxide (Dy_2O_3, MERCK) mixed with Urea & Glycine as fuel in stoichiometric ratio. We used glycine as fuel for lanthanum oxide and dysprosium oxide and urea as fuel for rest of the nitrates [16].

Characterization

Excitation and emission spectra were recorded employing a fluorescence spectrophotometer (Hitachi Make F-7100). The phase was determined using the X-ray powder diffraction technique (Rigaku Miniflex, Cu-Kα wavelength 0.154059 nm). The surface study and compositional details were optimized using a FE-SEM JEOL, JSM-6500F.

Results and Discussion

X-Ray Diffraction

Figure 1(a) represent XRD pattern and Figure 1(b) refined XRD pattern of garnet-type phosphor.

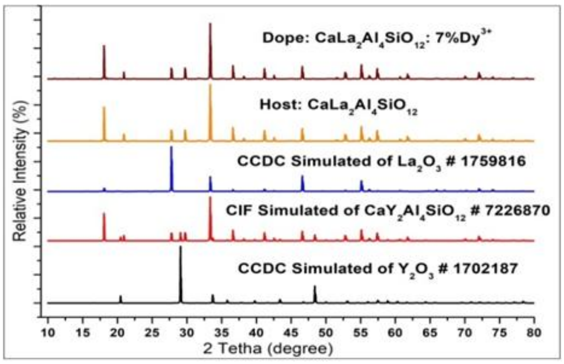

Figure 1: (a) The representation of XRD pattern of $CaLa_2Al_4SiO_{12}$, the comparison of XRD patterns of prepared un-doped and doped garnet materials with CIF simulated file #7226870, #1702157 for Y_2O_3 and #1759816 for La_2O_3.

All XRD peaks were indexed to cubic structure having space group Ia-3d. As the novel phosphor $CaLa_2Al_4SiO_{12}$ the conformation of the crystallographic structure were possible by matching the standard XRD pattern of $CaY_2Al_4SiO_{12}$, La_2O_3 and Y_2O_3 with standard CIF #7226870, CCDC #1759816 and CCDC #1702187. The details of the structural parameters and Wyckoff symbols are shown in Table 1. The lattice parameters (a = b = c=12.00062 A°) with relative error 0.09 % with calculated value [17]. Figure 1(a) shows that there was no effect due to doping in the garnet-structure phosphor.

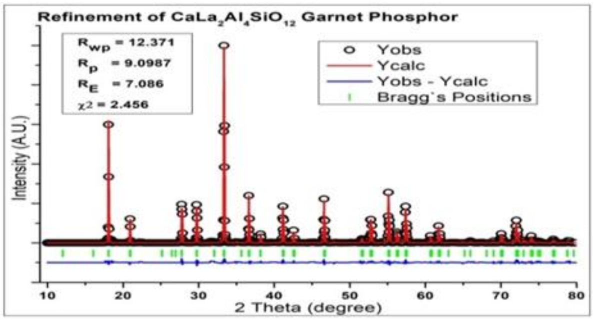

Figure 1: (b) The representation of refined XRD pattern of $CaLa_2Al_4SiO_{12}$.

Table 1: Details of phase identification of XRD data with Rietveld refinement.

Compound	$CaLa_2Al_4SiO_{12}$	
Crystal structure type	Cubic structure	
Space group	Ia-3d (230)	
Translational Lattice -parameters (a = b = c) in Å	12.00062 Å	
Volume of unit cell $(nm)^3$	1728.27 $Å^3$	
Chi^2	3.425	
R_p	9.0987	
R_{wp}	12.371	
Expected R_w	7.086	
Wyckoff symbols		
Ions	**Symbols**	**Occupancy**
Ca^{2+}	24c	1/3
La^{3+}	24c	2/3
Al^{3+}	16a	1
$Al1^{3+}$	24d	2/3
Si^{4+}	24d	1/3
O (for Ia-3d)	96h	1

Morphology and EDX

Figure 2 depicts FESEM images of the materials with different magnification. This technique is useful to investigate the grain size and surface study. To examine elemental composition of the material, it's characterized by EDX technique. Figure 3 show all elements are present with desired composition. The energy dispersive peaks are shown the host materials Ca, La, Al, Si and O as well as dopant Dy^{3+} ions.

Photoluminescence

Figure 4 (a) shows excitation spectrum of $CaLa_2Al_4SiO_{12}:0.07Dy^{3+}$. The excitation spectrum is obtained at the wavelength of 351 nm with emission wavelength 584 nm.

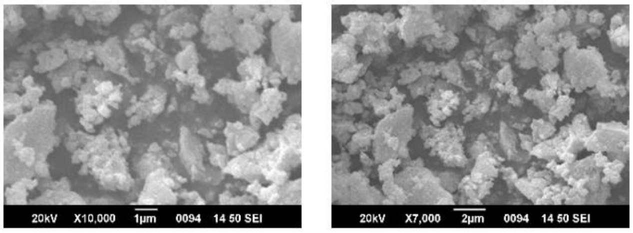

Figure 2: SEM images of as-prepared garnet phosphor $CaLa_2Al_4SiO_{12}:Dy^{3+}$.

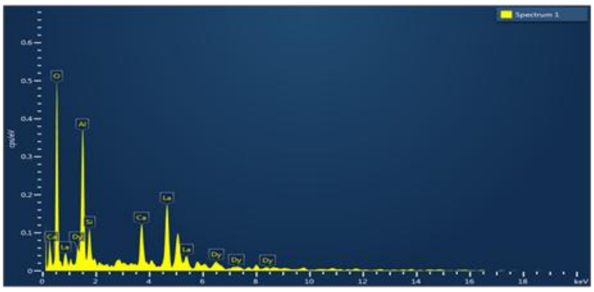

Figure 3: Energy Dispersive X-ray Spectrum of $CaLa_2Al_4SiO_{12}:Dy^{3+}$.

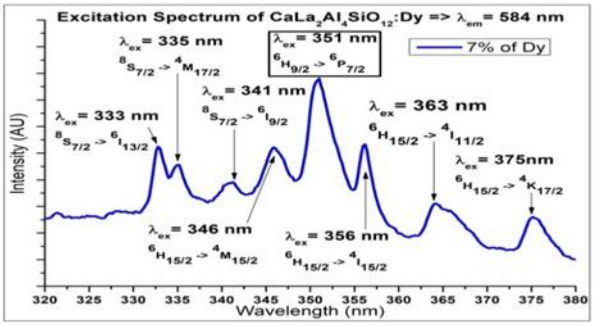

Figure 4 (a): Excitation spectrum of garnet-type phosphor $CaLa_2Al_4SiO_{12}:Dy^{3+}$ is observed at 584 nm.

The electronic transition for the excitation is observed from $^6H_{15/2} \rightarrow {}^6P_{7/2}$. There was serval peaks obtained at wavelengths 333, 335, 341, 346, 351, 356, 363 and 375 nm.

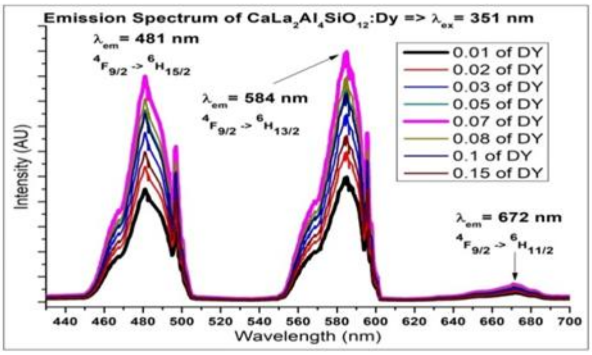

Figure 4 (b): Emission spectrum of garnet-type phosphor $CaLa_2Al_4SiO_{12}:xDy^{3+}$ (x = 0.01, 0.02, 0.03, 0.05, 0.07, 0.08, 0.10, 0.15) is excited by 351 nm.

Figure 4 (b) depicts the emission spectrum of the garnet-type phosphor. The PL profile and position of the peaks does not change during the exciting at 351 nm [19]. The prepared material is useful for near UV, green and yellow LEDs.

Conclusion

Using conventional combustion reaction, a series of single phase Dy^{3+}-doped $CaLa_2Al_4SiO_{12}$ garnet phosphors were prepared. The single-phase crystallography was examined by XRD result. The most intense peak was obtained at 584 for $CaLa_2Al_4SiO_{12}$:7%Dy^{3+} in transition from $^4F_{9/2} \rightarrow {}^6H_{13/2}$. By FESEM and EDX, the materials were characterized surface study and chemical composition investigation respectively. The prepared materials were suitable in yellow colour lighting devices and w-LEDs.

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