

# Synthesis and Characterization of Dy<sup>3+</sup> Activated Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub> Nanophosphors for Environment Friendly Lighting

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## ABSTRACT

In the present study Dy<sup>3+</sup> activated Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub> phosphors were synthesized by combustion synthesis. Formation of crystalline phases were identified by X ray diffraction (XRD) pattern and their photoluminescence (PL) properties were investigated using excitation and emission spectra under ultraviolet (UV) ray excitation ranging from 200 to 400 nm. When Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>:Dy<sup>3+</sup> phosphor was excited at 350 nm, the emission spectrum showed intense bands at 480 nm (blue) and 575 nm (yellow) emission due to Dy<sup>3+</sup> ions. The external morphology of Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub> phosphor has been studied by SEM. The results obtained showed that phosphors have the promising applications for solid state lighting and near-UV white light-emitting diodes (LEDs).

**Keywords:** Photoluminescence, Light-Emitting Diodes, Lamp Phosphor, Silicate

## I. INTRODUCTION

Rare earth-doped inorganic phosphors are widely used in variety of applications such as for the lamp industry, X-ray imaging, scintillators and for color display. Recently there has been a growing focus on research in the area of light-emitting diodes (LEDs) due to their many merits such as being environmental friendly, highly efficient and having a longer lifetime [1,2]. After a decade of intense research, phosphor-converted light-emitting diodes (pc-LEDs) have attracted worldwide attention owing to their high luminescence efficiency and variety wide range of applications, such as in flashlights, display backlighting, traffic signals, and especially for solid-state lighting. The huge potential market in home lighting encourages the rapid

development of pc-LEDs because of their advantages over the existing incandescent and fluorescent lamps in power efficiency, reliability, long lifetime, low energy consumption, and environmentally friendly characteristics [3]

Zhang reported the tunable bluish green to yellowish green Ca<sub>2</sub>(1-x)Sr<sub>2x</sub>Al<sub>2</sub>SiO<sub>7</sub>:Eu<sup>2+</sup> phosphors. Wu reported the Dy<sup>3+</sup> and Tb<sup>3+</sup> and co-doped Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub> phosphor and deliberated photoluminescence properties [4]. Li also reported the luminescent properties Sr<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>:Ce<sup>3+</sup>, Eu<sup>2+</sup> phosphors and discussed the possible application for near UV-excited white light-emitting diodes (w-LEDs) [5].

Silicate-based phosphors have increased enormous informative and commercial benefits since their rigid crystal structure, ample crystalline phase, multi-color emission and extraordinary luminous proficiency, and appropriate physical and chemical structures [6]. Therefore, it is necessary to continue the development of new PL materials with suitable silicate hosts and activators to expand the color range, and at the same time to contribute to a better understanding of the PL mechanism. Here in this work we have prepared many silicate-based phosphors doped with RE ions (RE=) as the significant constituents used in different optical application arenas.

The single doped  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Dy}^{3+}$  powders were synthesized by conventional combustion synthesis have reported in this work. And their detailed luminescence properties have been discussed and investigated systematically.

Zhang reported the tunable bluish green to yellowish green  $\text{Ca}_2(1-x)\text{Sr}_x\text{Al}_2\text{SiO}_7:\text{Eu}^{2+}$  phosphors. Wu reported the  $\text{Tb}^{3+}$  and  $\text{Dy}^{3+}$  doped  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  phosphor and deliberated photoluminescence properties [7]. Li also reported the luminescent properties  $\text{Sr}_2\text{Al}_2\text{SiO}_7:\text{Ce}^{3+}$ ,  $\text{Eu}^{2+}$  phosphors and discussed the possible application for near UV-excited white light-emitting diodes (*w*- LEDs) [8].

The host  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  belongs to the family of melilite compounds whose luminescence properties have been widely studied in various fields of solid state lighting Here in this work we have prepared many silicate-based phosphors doped with RE ions (RE= $\text{Dy}^{3+}$ ) as the significant constituents used in different optical application arenas.

## II. EXPERIMENTAL DETAILS

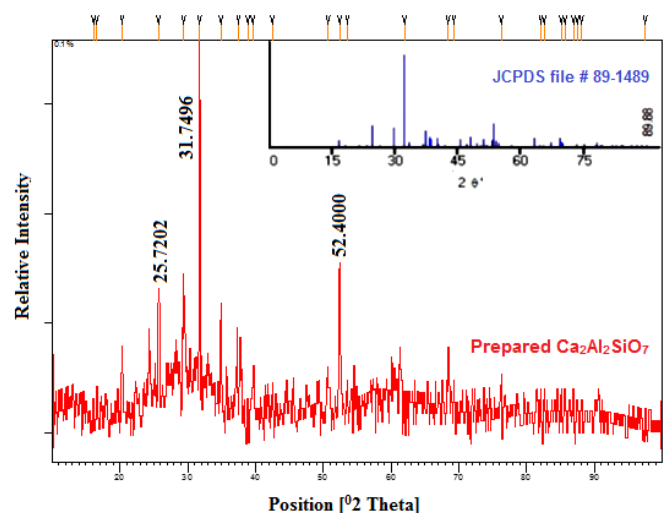
The series of rare earth-doped Gehlenite ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ) phosphor reported in this paper were synthesized using

the combustion method. This is a simple, cheap technology for aluminosilicate based materials, as other techniques require long reaction times and high temperatures to achieve the desired phase purity. For the synthesis of the  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Dy}^{3+}$  phosphor, we selected  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (99.9%),  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (99.9%),  $\text{SiO}_2$  (99.9%),  $\text{NH}_2\text{CONH}_2$ ,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Dy}_2\text{O}_3$ . All materials were taken in stoichiometric ratio, Details experimental details of the combustion methods and its advantages have been discussed previously by Pawde et al.[9]

## III. RESULT AND DISCUSSION

### 3.1 X-ray diffraction pattern and structural behavior of $\text{Ca}_2\text{Al}_2\text{SiO}_7$ phosphor

The phase purities of  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  phosphor was checked by powder X-ray diffraction (XRD) using a PAN-analytical diffractometer with  $\text{CuK}\alpha$  radiation (1.5405 Å) operating voltage at 40 kV, 30 mA and scan step time at 10.3377s. The XRD pattern of the resulted material is shown in figure 1 It is found that the obtained diffraction peaks of the phosphor prepared at 550 °C are in well match with the standard JCPDS standard file no. 89-1489.

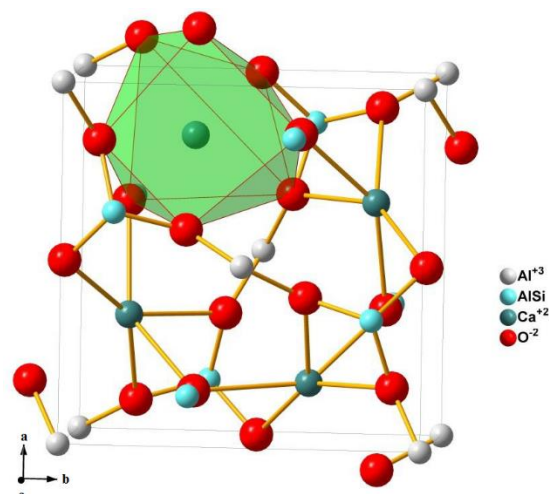


**Figure 1 :** The XRD pattern of the  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  phosphor

**Peak List : Table 3.1 Peak list of XRD data**

Pos. [ $^{\circ}$ Th.]	Height [cts]	FWHM [ $^{\circ}$ Th.]	d-spacing [ $\text{\AA}$ ]	Rel. Int. [%]
16.1014	1.73	0.2856	5.50021	5.43
16.6125	2.91	0.2448	5.33212	9.16
20.3157	5.88	0.3264	4.36776	18.52
<b>25.7202</b>	<b>11.24</b>	<b>0.2448</b>	<b>3.46090</b>	<b>35.37</b>
29.4436	8.86	0.4080	3.03117	27.89
<b>31.7496</b>	<b>31.77</b>	<b>0.2856</b>	<b>2.81608</b>	<b>100.00</b>
34.8964	9.20	0.2448	2.56901	28.94
37.5069	3.99	0.9792	2.39598	12.57
38.8160	2.13	0.2448	2.31813	6.70
39.6139	4.91	0.4896	2.27326	15.46
42.5244	3.10	0.2856	2.12416	9.75
50.7274	3.41	0.4896	1.79824	10.72
<b>52.4000</b>	<b>14.05</b>	<b>0.2856</b>	<b>1.74471</b>	<b>44.22</b>
53.5433	2.93	0.2856	1.71012	9.23
61.9871	1.53	0.2448	1.49590	4.81
68.4339	4.79	0.4896	1.36984	15.06
69.2768	2.70	0.2448	1.35522	8.51
76.2084	3.41	0.2856	1.24827	10.72
82.0617	3.30	0.3264	1.17340	10.40
82.5825	2.65	0.2448	1.16732	8.33
85.0512	2.69	0.2448	1.13963	8.45
85.6288	3.29	0.4488	1.13342	10.35
86.8495	3.47	0.2856	1.12060	10.94
87.4429	2.25	0.4080	1.11451	7.08
88.0730	2.34	0.2448	1.10816	7.36
97.5293	1.89	0.3264	1.02432	5.93

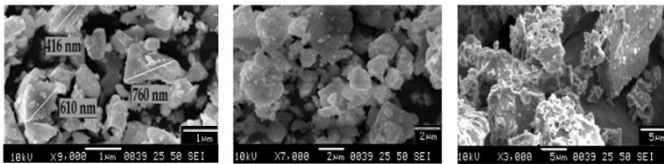
The XRD pattern of aforesaid sample did not indicate presence of the constituents like  $\text{Ca}(\text{NO}_3)$ ,  $\text{Al}(\text{NO}_3)$  or  $\text{NH}_4\text{H}_2\text{PO}_4$  and other likely phases which are direct confirmation for the formation of desired compound. The reported crystal structure of  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  phosphor has been distinguished in  $P421m$  space group with tetragonal crystalline phases [10]. The crystallographic planes with unit cell parameters  $a = 7.694 (1) \text{ \AA}$ ,  $c = 5.077 (1) \text{ \AA}$ , and atomic no  $Z=2$ . From figure 1 it is concluded that the peaks at 25.7202 (35.37 %), 31.7496(100.00 %), 52.4000 (44.22 %) are well matched with peaks in standard JCPDS file No. 89-1489 which confirms the formation of  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  phosphor. Figure 2 indicated the representative crystal structure of  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  [11].



**Figure 2 :** representative crystal structure of  $\text{Ca}_2\text{Al}_2\text{SiO}_7$

### 3.2 SEM (Scanning Electron Microscope) characterization of $\text{Ca}_2\text{Al}_2\text{SiO}_7$ phosphor

Figure 3.3 shows micrograph of the  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  phosphor powder. It is detected that the phosphor powder is composed of asymmetrical particles of a few  $\mu\text{m}$  in size, which are essentially made from accumulation of considerably smaller particles of a submicron size. The particles retain foamy morphology made from highly agglomerated crystallites. When the phosphor was synthesized by combustion synthesis the particles growth took place quickly forming bigger size particles. The particles shape has fixed boundary and the average particle size is increased to about 1-5  $\mu\text{m}$ .  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  phosphors clearly show that the grains are asymmetrical shaped with an average crystallite size in sub-micrometer range of 1 -5  $\mu\text{m}$  seen in SEM images. Additionally high magnification study indicated that grains are tetragonal shaped which is in good agreement with obtained XRD data. From Figure 3 it is concluded that particles are unselective in appearance, composing of different sizes as observed in submicron range 416 nm, 610 nm, 760 nm, 870 nm and 891 nm which are measured under 1  $\mu\text{m}$  resolution.

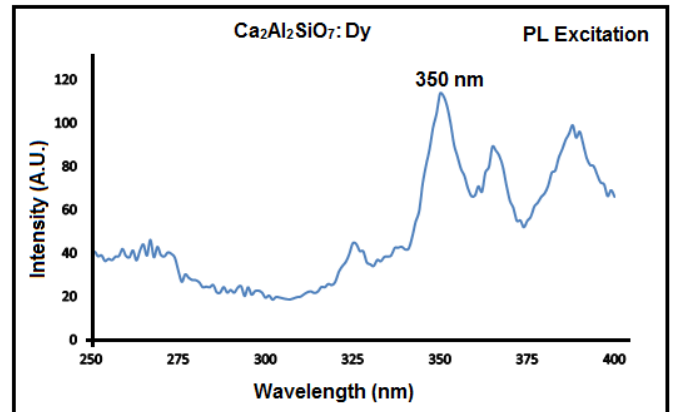


**Figure 3 :** SEM micrograph of the  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  phosphor

### 3.3 Photoluminescence properties of $\text{Dy}^{3+}$ activated $\text{Ca}_2\text{Al}_2\text{SiO}_7$ phosphor

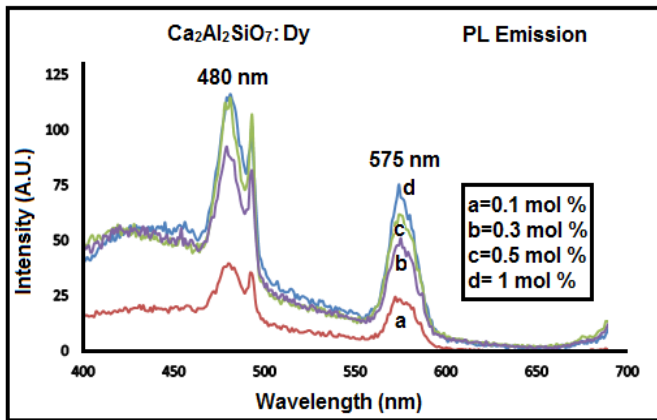
The excitation spectra of  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Dy}^{3+}$  phosphor monitored at around 575nm is shown in figure 4. The excitation spectrum monitored at yellow emission from  $\text{Dy}^{3+}$  ions indicates several bands in wavelength region of 300 - 400 nm, which are due to excitation of f-f shell transitions of  $\text{Dy}^{3+}$  [12]. The several peaks at 350 nm, 365 nm and 390 nm, correspond to the transitions from the ground state  $^6\text{H}_{15/2}$  to the excited states;  $^4\text{P}_{7/2}$ ;  $^4\text{P}_{3/2}$

and  $^4\text{F}_{7/2}$  respectively [13, 14].The maximum PL intensity of the excitation wavelength is located at 350 nm which is a characteristics of solid state lighting and suitable NUV excited LEDs, consequently it was chosen for the PL investigation in the present study.



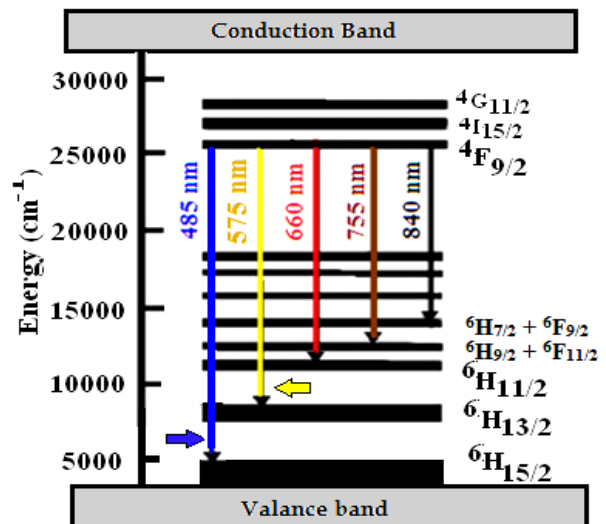
**Figure 4 :** Excitation spectrum of  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Dy}^{3+}$  phosphor

The emission spectra were measured between 400–700 nm. Two emission bands peaked at 480 nm and 575 nm are observed as shown in figure 5. The blue emission at 480 nm is related to  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$  magnetic dipole transition, the yellow emission at 575 nm is ascribed to  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$  electric dipole transition [15].These yellow and the blue emission transitions are the predominant transitions. The  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$  transition is hypersensitive ( $\Delta L=2$ ;  $\Delta J=2$ ), and it can be influenced by its microscopic environment so their intensity strongly depends on the host. The influence of divergent crystal field surrounding has been observed on the luminescent intensity.



**Figure 5 :** Emission spectrum of  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Dy}^{3+}$  phosphor

Incorporation of activator ions can influence photoluminescence characteristics of a phosphor; evidently the addition of Dy ion into  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  host increased the crystallinity which affects the particle size as well complexity of host material. The electronic transitions of  $\text{Dy}^{3+}$  involve only redistribution of electrons within the inner 4f sub-shell. The Photoluminescence study of  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Dy}^{3+}$  reveals that fluorescence intensity ratio increases gradually. Usually, a low doping gives weak luminescence, but excess doping can cause quenching of luminescence. A series of  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Dy}^{3+}$  phosphor with various  $\text{Dy}^{3+}$  concentrations ( $x=0.1, 0.3, 0.5$  and  $1\text{ mol } \%$ ) were prepared and the effect of doped  $\text{Dy}^{3+}$  concentration on the emission intensity was investigated. With increasing concentration of  $\text{Dy}^{3+}$  ions the photoluminescence intensity increased gradually up to  $1\text{ mol } \%$   $\text{Dy}^{3+}$  ion which was maximum among all the concentrations. Nevertheless the position of emission bands is not manipulated by the variation in incorporation of  $\text{Dy}^{3+}$  ions. Energy level transitions of  $\text{Dy}^{3+}$  ions is shown in figure 6 below.



**Figure 6 :** Energy level transitions of  $\text{Dy}^{3+}$  ions.

#### IV. CONCLUSION

In the present study, calcium aluminum silicate ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ) based phosphate phosphors activated with rare earth ions  $\text{Dy}^{3+}$  prepared by combustion synthesis and confirmed by XRD are reported. An average crystallite size is found out to be in sub-micrometer range of  $200\text{-}800\text{ nm}$  from SEM study. The PL spectroscopic characterizations of the prepared phosphors were performed using excitation and emission spectra. Photoluminescence spectra of rare earth activated  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  silicate based phosphor shows emission at  $400\text{-}700\text{ nm}$  when excited between  $200\text{-}400\text{ nm}$ . The obtained results suggests that this phosphor might be useful for the blue and orange light. The most efficient concentration of  $\text{RE}^{3+}$  for the maximum emission intensity is  $1\text{ mol } \%$ . The entire results suggests that the prepared phosphors could be the potential phosphors for possible applications in the field of solid state lighting and Light emitting diodes (LED).

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