

www.dergipark.gov.tr ISSN:2148-3736 El-Cezerî Fen ve Mühendislik Dergisi Cilt: 9, No: 1, 2022 (360-370)

El-Cezerî Journal of Science and Engineering Vol: 9, No: 1, 2022 (360-370) DOI :10.31202/ecjse.1002508



#### **Research Paper / Makale**

# Synthesis and Characterization of CaAl<sub>2</sub>O<sub>4</sub>: Dy<sup>3+</sup> and CaAl<sub>2</sub>O<sub>4</sub>: Sm<sup>3+</sup> Phosphor Powders

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Received/Gelis: 01.10.2021

Accepted/Kabul: 19.11.2021

Abstract: Calcium aluminate, CaAl<sub>2</sub>O<sub>4</sub> is efficient and well known host material for inorganic phosphors. Although this host structure is mostly doped with Eu<sup>2+</sup>, different types of rare earth ions have also been studied. In this study, attention was drawn to CaAl<sub>2</sub>O<sub>4</sub> type phosphors doped with Dy<sup>3+</sup> and Sm<sup>3+</sup> at different concentrations. Ca<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub>: Dy<sup>3+</sup><sub>x</sub> (x= 0.008, 0.012, 0.02, 0.03) and Ca<sub>1-y</sub>Al<sub>2</sub>O<sub>4</sub>: Sm<sup>3+</sup><sub>y</sub> (y= 0.008, 0.012, 0.02, 0.03) phosphors were synthesized as powder samples through the solid-state reaction method. After heat treatments, monoclinic CaAl<sub>2</sub>O<sub>4</sub> structure was confirmed for all rare earth doped samples by the XRD analysis. PL characteristics of samples depend on activator ion. The PL emission spectra of Dy<sup>3+</sup> doped powder samples show two strong bands at 484 nm and 577 nm which are attributed to a typical <sup>4</sup>F<sub>9/2</sub>  $\rightarrow$  <sup>6</sup>H<sub>15/2</sub> and <sup>4</sup>F<sub>9/2</sub>  $\rightarrow$  <sup>6</sup>H<sub>13/2</sub> transitions of Dy<sup>3+</sup> ions. Sm<sup>3+</sup> activated phosphors have the emission peaks at 565 nm, 604 nm, 649 nm, and 712 nm which are assigned to Sm<sup>3+</sup> transitions: <sup>4</sup>G<sub>5/2</sub>  $\rightarrow$  <sup>6</sup>H<sub>5/2</sub>, <sup>4</sup>G<sub>5/2</sub>  $\rightarrow$  <sup>6</sup>H<sub>7/2</sub>, <sup>4</sup>G<sub>5/2</sub>  $\rightarrow$  <sup>6</sup>H<sub>9/2</sub>, <sup>4</sup>G<sub>5/2</sub>  $\rightarrow$  <sup>6</sup>H<sub>11/2</sub>, respectively. The Commission International De IEclairage (CIE) 1976 chromaticity coordinates were evaluated from the emission spectra in two different rare earth ion doped phosphors, the values (u' = 0.21805, v' = 0.52537) and (u' = 0.36078, v' = 0.54567) were colors of yellow-orange and brick red, respectively. Consequently, synthesized Ca<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub>: Dy<sup>3+</sup><sub>x</sub> (x= 0.008) and Ca<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub>: Sm<sup>3+</sup><sub>y</sub> (y= 0.008) phosphors emitting in different color regions can be useful for LED's and display applications.

**Keywords**: CaAl<sub>2</sub>O<sub>4</sub>, Dy<sup>3+</sup>, Sm<sup>3+</sup>, solid state reaction method, LED phosphors

# CaAl<sub>2</sub>O<sub>4</sub>: Dy<sup>+3</sup> ve CaAl<sub>2</sub>O<sub>4</sub>: Sm<sup>+3</sup> Işıldar Tozlarının Üretimi ve Karakterizasyonu

Öz: Kalsiyum alüminat, CaAl<sub>2</sub>O<sub>4</sub>, inorganik fosforlarda oldukça işlevsel ve iyi bilinen bir konut malzemedir. Bu konut yapıdaki fosforlar çoğunlukla Eu<sup>2+</sup> ile katkılanmakla birlikte farklı tipte nadir toprak iyonları da çalışılmıştır. Bu çalışmada CaAl<sub>2</sub>O<sub>4</sub> tipindeki konut yapı, Dy<sup>3+</sup> ve Sm<sup>3+</sup> ile farklı konsantrasyonlarda katkılanmıştır. Ca<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub>: Dy<sup>+3</sup><sub>x</sub> (x= 0.008, 0.012, 0.02, 0.03) ve Ca<sub>1-y</sub>Al<sub>2</sub>O<sub>4</sub>: Sm<sup>+3</sup><sub>y</sub> (y= 0.008, 0.012, 0.02, 0.03) fosforları toz numuneler halinde katı-hal tepkimesi yöntemiyle sentezlenmişlerdir. Isli işlemlerden sonra XRD analizi yapılarak nadir toprak iyonları katkılı fosfor tozları monoklinik CaAl<sub>2</sub>O<sub>4</sub> yapısında indislenmiştir. Fotolüminesans özellikler katkı iyonuna bağlı olarak belirlenmiştir. Dy<sup>+3</sup> katkılı fosforlara ait 484 nm ve 577 nm iki belirgin pik, <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>15/2</sub> ve <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub>: Dy<sup>+3</sup> geçişlerine aittir. Sm<sup>3+</sup> katkılı fosforlara ise 565 nm, 604 nm, 649 nm, and 712 nm'deki pikler <sup>4</sup>G<sub>5/2</sub> → <sup>6</sup>H<sub>5/2</sub>, <sup>4</sup>G<sub>5/2</sub> → <sup>6</sup>H<sub>7/2</sub>, <sup>4</sup>G<sub>5/2</sub> → <sup>6</sup>H<sub>9/2</sub>, <sup>4</sup>G<sub>5/2</sub> → <sup>6</sup>H<sub>11/2</sub>: Sm<sup>+3</sup> geçişleri ile ilgilidir. Commission International De IEclairage (CIE) 1976 renklilik diyagramından faydalanılarak fosfor tozlarına ait ışıma dalga boylarına bağlı olarak belirlenen (u' = 0.21805, v' = 0.52537) ve (u' = 0.36078, v' = 0.54567) koordinatlarına göre sırasıyla Dy<sup>+3</sup> iyonları sarı-turuncu bölgede, Sm<sup>+3</sup> iyonları ise kiremit kırmızısı renk bölgelerinde ışımaların oluştuğunu göstermiştir. Sonuç olarak iki farklı alternatif nadir toprak iyonu ile katkılanan CaAl<sub>2</sub>O<sub>4</sub> fosforlarının LED'lerde ve görüntü oluşturma uygulamalarında değerlendirilmeleri mümkündür.

Anahtar Kelimeler: CaAl<sub>2</sub>O<sub>4</sub>, Dy<sup>+3</sup>, Sm<sup>+3</sup>, katı hal tepkimesi yöntemi, LED fosforları

How to cite this article

Bu makaleye atıf yapmak için

*Karacaoglu, E., "CaAl<sub>2</sub>O<sub>4</sub>: Sy<sup>+3</sup> ve CaAl<sub>2</sub>O<sub>4</sub>: Sm<sup>+3</sup> Işıldar Tozlarının Üretimi ve Karakterizasyonu" El-Cezerî Fen ve Mühendislik Dergisi 2022, 9 (1); 360-370. ORCID ID: 0000-0003-3883-7343* 

Karacaoglu, E., "Synthesis and Characterization of CaAl<sub>2</sub>O<sub>4</sub>: Dy<sup>3+</sup> and CaAl<sub>2</sub>O<sub>4</sub>: Sm<sup>3+</sup> Phosphor Powders" El-Cezerî Journal of Science and Engineering, 2022, 9 (1); 360-370.

# 1. Introduction

 $Eu^{2+}$  activated alkaline earth aluminates have remarkable photoluminescence (PL) effect in from blue to green region light emission. When these phosphors are co-doped with another rare-earth ion provide long persistence. The luminescence lifetime of  $Eu^{2+}$ -doped and RE-ion co-doped phosphors can be up to 16 hours. The long persistence is attributed to the thermal activation of holes from traps followed by the emission related  $Eu^{2+}$ . MAl<sub>2</sub>O<sub>4</sub> (M: Ca, Sr, Ba) based phosphors provide bright, long-lasting PL, chemically stable, and safe compared to the well-known and studied sulfide-based systems. These features make them beneficial in many applications, such as luminous paints in buildings, factories, highway, ceramics, airport, and, in glow watches, escape and warning signs, and the textiles. Moreover, phosphors have been used as efficient materials for generating assorted emission colors in the process up to the present which have many applications in display devices and solid-state lighting, etc [1-3].

Calcium aluminate based (CaAl<sub>2</sub>O<sub>4</sub>, Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>, Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>, etc.) materials have been extensively studied and found new applications in the field of advanced ceramics as catalysts, optical ceramics, structural and dental ceramics. Eu<sup>2+</sup>-doped and Nd<sup>3+</sup> or Dy<sup>3+</sup> co-doped calcium aluminates particularly show violet/blue emission and persistent luminescence for up to 10 hours at room temperature. Among the calcium aluminates, the CaAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup> phosphors possess an emission peak at about 440 nm that allows using it as a blue emitting material in optical memories, high-energy detectors, electronic displays, and image storage etc [4].

With the developing light technology, especially in recent years, phosphors for white-light-emitting diodes (w-LEDs) have drawn attraction to researchers due to their properties such as energy savings, efficiency, low production cost, long service life, and environmental and health safe. They are also replacing the traditional light emitting materials, i.e., fluorescent, and incandescent lamps. Essentially, practicable w-LEDs are produced using tricolor phosphors which are excited by near-UV. From this point of view, the development of inorganic phosphors has been developed due to their potential in acquiring w-LEDs and other luminescent devices for new generation [5-6]. Among other rare-earth ions, the Sm<sup>3+</sup> and Dy<sup>3+</sup> ions could be chosen to be an alternative activator for many inorganic phosphors for emitting orange-red and white light for fabricating w-LEDs [7-8].

In the present research, concentration studies of  $CaAl_2O_4$ -based phosphors doped with  $Sm^{3+}$  and  $Dy^{3+}$  separately was successfully synthesized by solid state reaction method.  $CaAl_2O_4$ :  $Sm^{3+}$  and  $CaAl_2O_4$ :  $Dy^{3+}$  phosphors were investigated in detail as influence of  $Dy^{3+}$  and  $Sm^{3+}$  dopant concentrations in the luminescence behavior. PL characteristics were measured by excitation, emission, and decay time with respect to  $Sm^{3+}$  and  $Dy^{3+}$  doping concentrations.

# 2. Experimental Methods 2.1 Materials and Synthesis

Powder samples of  $Ca_{1-x}Al_2O_4$ :  $Dy_{x}^{3+}$  (x= 0.008, 0.012, 0.02, 0.03) and  $Ca_{1-y}Al_2O_4$ :  $Sm_{y}^{3+}$  (y= 0.008, 0.012, 0.02, 0.03) phosphors have been synthesized through the solid-state reaction technique under open atmosphere at high temperature (1300 °C-3 hours) heat treatment process. The compositions of phosphor powders in appropriate quantities were weighed using high purity chemicals:  $Al_2O_3$  (Reynolds, 99.99%), CaCO<sub>3</sub> (Alfa Easer, 99.5%), Dy<sub>2</sub>O<sub>3</sub> (Aldrich, 99.99%), Sm<sub>2</sub>O<sub>3</sub> (Aldrich, 99.9%) and H<sub>3</sub>BO<sub>3</sub> (Fisher Chemical, ≥99.5%). The raw materials were weighed stoichiometrically. Before the firing process, batches were dry mixed homogeneously in agate mortar. After weighing and milling, the differential thermal analysis (DTA) and thermogravimetric (TG) analyzes at a heating rate of 10 °C/min in an inert argon atmosphere from room temperature to 1500 °C were implemented to specify the oxidation and decomposition process of the reaction

materials. The pre-heating step was carried out considering thermal analysis. Powder sample compositions placed in alumina crucibles were sintered in an atmosphere-controlled tube furnace. Fourier transform infrared (FTIR) spectra of the host material,  $CaAl_2O_4$  was recorded in a Shimadzu IRPrestige-21 to identify the formation of the chemical bond. The particle morphologies and size distributions of powders were observed by scanning electron microscopy (SEM) (Hitachi 8230). Phase identifications were conducted by X-ray diffraction (XRD) operated at 40 kV and 40 mA (Cu-K $\alpha$  radiation,  $\lambda = 1.541$  A) (Panalytical X'Pert PRO Alpha-1) in a step-scan mode (0.02°/2 $\theta$ ). The photoluminescence (PL) and decay (luminescence lifetime) characteristics of phosphors were measured on a spectrofluorometer (Photon Technology International (PTI), QuantaMasterTM 30).

# 3. Results and Discussion 3.1. Thermal analysis (TG/DTA)

Fig. 1 shows the reactions with single-step decomposition mechanism of the undoped  $CaAl_2O_4$  batch composition that did not include  $H_3BO_3$  flux. During the heat treatment, the reaction of CaO and  $Al_2O_3$  begins, following the decomposition of  $CaCO_3$  into CaO.



**Figure 1.** Thermogravimetric analysis (a) and DTA/TG patterns (b) of undoped CaAl<sub>2</sub>O<sub>4</sub> batch composition.

The decomposition reaction of calcium carbonate and sintering process of CaO and  $Al_2O_3$  effectuates the solid-state reaction. Considering the TG curve, there's immediate weight loss within the temperature range of 650–850 °C caused by the decomposition of calcium carbonate. The striking weight loss at about 815 °C, the endothermic peak is marked on the DTA curve. The TGA result (Fig. 1a) also helps to clarify how the decomposition of CaCO<sub>3</sub> is completed up to 900 °C and it happens fast. The total weight loss at the end of the process is around 21.6% which is similar each other for TGA and DTA/TG results. The formation of CaAl<sub>2</sub>O<sub>4</sub> phase is seen on DTA curve as endothermic peak at 1395 °C. Therefore, calcination process at 900 °C for 3 hours and reaction temperature about 1400 °C are necessary formation of CaAl<sub>2</sub>O<sub>4</sub>. Considering these results, it was necessary to add H<sub>3</sub>BO<sub>3</sub> to this system to reduce the reaction temperature and shorten the process. In addition, it has been revealed in previous studies that boric acid contributes positively to the luminescence characteristic and provides an improvement in the luminous intensity [1,9].

# 3.2. Fourier Transform Infrared (FTIR) Spectroscopy

Fig. 2 shows the FTIR spectra that provides the functional groups and structures of the undoped  $CaAl_2O_4$ .



When the peaks marked in the FTIR spectra are examined; the bands at 570, 540, 447 and 412 cm<sup>-1</sup> are due to the stretching vibrations of metal oxides which are Al–O, Ca–O and Ca–O–Al bonds. Stretching vibrations of AlO<sub>4</sub> tetrahedrons are pointed at 840, 802, 775 and 721 cm<sup>-1</sup>. The absorption bands of AlO<sub>6</sub> clusters in the range of 680–500 cm<sup>-1</sup> are seen at 682, 632, 570 and 540 cm<sup>-1</sup>. Hereby the significant bands of CaAl<sub>2</sub>O<sub>4</sub> are identified in the spectra [7,10].

# 3.3. X-Ray Diffraction (XRD)

Fig. 3 shows the XRD patterns of  $Ca_{1-x}Al_2O_4$ :  $Dy_{x}^{3+}$  (x= 0.008) and  $Ca_{1-y}Al_2O_4$ :  $Sm_{y}^{3+}$  (y= 0.008) phosphors which were selected because of optimal PL measurement results (Fig. 3). These phosphor powders were prepared with H<sub>3</sub>BO<sub>3</sub> flux.



**Figure 3.** XRD patterns of  $Ca_{1-x}Al_2O_4$ :  $Dy_{x}^{3+}(x=0.008)$  and  $Ca_{1-y}Al_2O_4$ :  $Sm_{y}^{3+}(y=0.008)$  phosphor powders.

Compared XRD patterns of two phosphors which were selected based on photoluminescence analyzes among rare earths doped at different concentrations, match the powder diffraction file (JCPDS Card #00-062-0217) for the CaAl<sub>2</sub>O<sub>4</sub> monoclinic structure [7,11], verifying that solid-state reaction synthesis process was successful. Secondary phases do not cause any significant diffraction peaks prominent at the doping amount of rare earths. Ionic radii of  $Dy^{3+}$  (1.03 Å) [12] and  $Sm^{3+}$  (1.08 Å) [13] are close to Ca<sup>2+</sup> (1.12 Å), based on this their substitutions do not noticeably alter the crystal's lattice parameter.

## 3.4. Scanning Electron Microscopy (SEM)

Fig. 4 shows the SEM images of Ca<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub>:  $Dy_{x}^{3+}$  (x= 0.008) and Ca<sub>1-y</sub>Al<sub>2</sub>O<sub>4</sub>:  $Sm_{y}^{3+}$  (y= 0.008) selected phosphor powders.



Figure 4. SEM images of  $Ca_{1-x}Al_2O_4$ :  $Dy^{3+}_x$  (x= 0.008) (a) and  $Ca_{1-y}Al_2O_4$ :  $Sm^{3+}_y$  (y= 0.008) (b) phosphor powders.

Surface morphology and particle size distributions of phosphor powders are examined with electron microscopy. Fig. 4 shows representative SEM images of  $Dy^{3+}$  (a) and  $Sm^{3+}$  activated  $CaAl_2O_4$  powder, respectively. Both powders have irregularly shaped and broken particles with sharp corners, and nearly regular size distributions. Particle agglomeration also become evident as seen in the figures.

#### 3.5. Photoluminescence (PL)

PL study of  $CaAl_2O_4:Dy^{3+}$  and  $CaAl_2O_4:Sm^{3+}$  phosphors with varying  $Dy^{3+}$  and  $Sm^{3+}$  dopant concentration (0.8–3 mol%) were carried out to attain the dopant concentration with the highest PL emission intensity. Figs. 5 and 6 show the compared PL excitation and emission spectra of phosphors depending on dopant concentrations.

Fig. 5(a) shows the excitation spectra of  $Dy^{3+}$ -doped  $CaAl_2O_4$  samples, measured at  $\lambda_{emission} = 577$  nm. The excitation peaks are marked at 326 nm ( ${}^{6}H_{15/2} \rightarrow {}^{6}P_{3/2}$ ), 350 nm ( ${}^{6}H_{15/2} \rightarrow {}^{6}P_{7/2}$ ), 389 nm ( ${}^{6}H_{15/2} \rightarrow {}^{4}I_{13/2}$ ) and 425 nm ( ${}^{6}H_{15/2} \rightarrow {}^{4}G_{11/2}$ ) that belongs the transitions of  $Dy^{3+}$ . The peak centered at 296 nm is owing to the charge transfer from  $O^{2-}$  to  $Dy^{3+}$ . The emission spectra were obtained exciting with a wavelength of 350 nm for the  $Ca_{1-x}Al_2O_4$ :  $Dy^{3+}_{x=0.8-3\%}$  phosphor powders (Fig. 5(b)). The PL emission spectra show two strong bands at 484 nm and 577 nm, and two minor bands were observed at 667 nm and 757 nm. The major emission band is attributed to a typical  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$  and  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$  transitions of  $Dy^{3+}$  ions [7,14,15].

The excitation spectrum of the Ca<sub>1-y</sub>Al<sub>2</sub>O<sub>4</sub>: Sm<sup>3+</sup><sub>y=0.8-3%</sub> were measured at  $\lambda_{emission}$ = 604 nm and there are other peaks shown in the insets of Fig. 6(a). The excitation spectrum is composed of the peaks at 320 nm (<sup>6</sup>H<sub>5/2</sub>  $\rightarrow$  <sup>4</sup>G<sub>11/2</sub>), 347 nm (<sup>6</sup>H<sub>5/2</sub>  $\rightarrow$  <sup>4</sup>K<sub>17/2</sub>), 365 nm (<sup>6</sup>H<sub>5/2</sub>  $\rightarrow$  <sup>4</sup>H<sub>7/2</sub>), 377 nm (<sup>6</sup>H<sub>5/2</sub>)

 $\rightarrow$  <sup>6</sup>P<sub>7/2</sub>), 407 nm (<sup>6</sup>H<sub>5/2</sub>  $\rightarrow$  <sup>4</sup>F<sub>7/2</sub>) (max. peak), 445 nm (<sup>6</sup>H<sub>5/2</sub>  $\rightarrow$  <sup>4</sup>G<sub>9/2</sub>) and 482 nm (<sup>6</sup>H<sub>5/2</sub>  $\rightarrow$  <sup>4</sup>M<sub>15/2</sub>). Sm<sup>3+</sup>-doped samples were investigated at  $\lambda_{\text{excitation}}$ = 407 nm to search on their light emission properties (Fig. 6(b)).



**Figure 5.** Comparative excitation and emission spectra of  $Ca_{1-x}Al_2O_4$ : Dy<sup>3+</sup><sub>x=0.8-3%</sub>.



**Figure 6.** Comparative excitation and emission spectra of  $Ca_{1-y}Al_2O_4$ : Sm<sup>3+</sup><sub>y=0.8-3%</sub>.

The sample  $Ca_{1-x}Al_2O_4$ :  $Sm^{3+}_{x=0.8}$  shows emission peaks at 565 nm, 604 nm, 649 nm, and 712 nm which are assigned to  $Sm^{3+}$  transitions:  ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$ ,  ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ ,  ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ ,  ${}^4G_{5/2} \rightarrow {}^6H_{11/2}$ , respectively. This study shows that with the increasing amount of  $Sm^{3+}$  until 0.8 mol %, the emission intensity increases but decreases with increasing the  $Sm^{3+}$  over 0.8 mol % that is due to the concentration quenching affect. The results obtained in this research are in accord with previous studies [7,13,14,16].

The Commission Internationale dÉclairage (CIE) Chromaticity color diagram and coordinates of  $Ca_{1-x}Al_2O_4$ :  $Dy^{3+}_{x=0.8\%}$  and  $Ca_{1-y}Al_2O_4$ :  $Sm^{3+}_{y=0.8\%}$  phosphor powders are shown in Fig. 7.

The colors from the CIE Chromaticity color diagram gives a yellow-orange and brick red colors of  $Dy^{3+}$  and  $Sm^{3+}$  doped phosphor powders, respectively.



**Figure 7.** CIE Chromaticity color diagram and coordinates of  $Ca_{1-x}Al_2O_4$ :  $Dy^{3+}_{x=0.8\%}$  and  $Ca_{1-y}Al_2O_4$ :  $Sm^{3+}_{y=0.8\%}$  phosphor powders.

The luminescent decay curves of the Ca<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub>:  $Dy_{x=0.8-3\%}^{3+}$  and Ca<sub>1-y</sub>Al<sub>2</sub>O<sub>4</sub>:  $Sm_{y=0.8-3\%}^{3+}$  phosphors, irradiated by 350 nm and 407 nm light at room temperature, respectively are shown in Fig. 8 (a-b).



Figure 8. The luminescent decay curves of the  $Ca_{1-x}Al_2O_4$ :  $Dy^{3+}_{x=0.8-3\%}$  (a) and  $Ca_{1-y}Al_2O_4$ :  $Sm^{3+}_{y=0.8-3\%}$  (b) phosphors.

The luminescent decay curves of the Ca<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub>: Dy<sup>3+</sup><sub>x=0.8-3%</sub> (Fig. 8a) and Ca<sub>1-y</sub>Al<sub>2</sub>O<sub>4</sub>: Sm<sup>3+</sup><sub>y=0.8-3%</sub> (Fig. 8b) phosphors show the optimal lifetimes while they are doped 0.8 mol% of Dy<sup>3+</sup> and Sm<sup>3+</sup> separately. The lifetimes of phosphors can be calculated using the equation given below, where *I* is the phosphorescence intensity, A1 and A2 are constants, *x* is time, and t<sub>1</sub> and t<sub>2</sub> (t=  $\tau$ ) are decay times for the exponential components, respectively.

$$I = A1 \exp(-x/t_1) + A2 \exp(-x/t_2)$$
(1)

The values of the decay times for the phosphors are shown in the inset of Fig. 8(a-b), and based on the above analysis, the sequence of lifetime is in the order 0.008 > 0.012 > 0.02 > 0.03 mol% of both Dy<sup>3+</sup> and Sm<sup>3+</sup> ions doping.

According to the PL studies, maximum PL characteristics were obtained when 0.8 mole percent Dy and Sm were added to both  $CaAl_2O_4$ :  $Dy^{3+}$  and  $CaAl_2O_4$ :  $Sm^{3+}$  phosphors. Then, these two phosphor powders, which give maximum PL intensity, were physically mixed in equal proportions in a bottle to obtain the luminescence properties of 2 different rare earth ions at the same time and to investigate their evaluability in LED technology. PL excitation and emission (Fig. 9) and decay curve (Fig. 10) of mixed phosphor powder were investigated.



**Figure 9.** PL excitation and emission spectra of mixtures of CaAl<sub>2</sub>O<sub>4</sub>:  $Dy^{3+}_{x}$  (x= 0.8 mol%) and CaAl<sub>2</sub>O<sub>4</sub>: Sm<sup>3+</sup><sub>y</sub> (y= 0.8 mol%) phosphor powders which have different emission characteristics depending on excitation wavelengths.

The PL excitation and emission properties of  $CaAl_2O_4$ :  $Dy^{3+}$  and  $CaAl_2O_4$ :  $Sm^{3+}$  powders obtained by physically mixing showed both the  $Dy^{3+}$  and  $Sm^{3+}$  two dopant ions.



**Figure 10.** Decay curves and luminescence lifetimes of mixture of  $CaAl_2O_4$ :  $Dy^{3+}$  and  $CaAl_2O_4$ :  $Sm^{3+}$  phosphor powders as a function of different excitation wavelengths.

When this powder is excited at 350 nm, the PL characteristic of the  $Dy^{3+}$  dopant is the dominant peak, while the characteristic of the Sm<sup>3+</sup> ion is in the foreground when excited at 405 nm. Under both excitations, the mixed phosphor powder also has the PL properties of both ions which are at 485 nm (Dy<sup>3+</sup>), 569 nm (Sm<sup>3+</sup>), 575 nm (Dy<sup>3+</sup>), 605 nm (Sm<sup>3+</sup>), 650 nm (Sm<sup>3+</sup>), 701/719 nm (Sm<sup>3+</sup>) and 758 nm (Dy<sup>3+</sup>).

Considering the decay curve and lifetime results, because of the excitation of the mixed phosphor powder at both 350 nm and 400 nm, the powder mixture yielded more effective results when excited at 400 nm. Therefore, even if the  $Dy^{3+}$  and  $Sm^{3+}$  doped  $CaAl_2O_4$  powders are mixed in equal amounts, the decay curve/luminescence lifetime properties dominate depending on the  $Sm^{3+}$  powders.

The Commission Internationale dÉclairage (CIE) Chromaticity color diagram and coordinates of  $Ca_{1-x}Al_2O_4$ :  $Dy^{3+}_{x=0.8\%}$  and  $Ca_{1-y}Al_2O_4$ :  $Sm^{3+}_{y=0.8\%}$  mixed phosphor powders are shown in Fig. 11.



Figure 11. CIE Chromaticity color diagram and coordinates of  $Ca_{1-x}Al_2O_4$ :  $Dy^{3+}_{x=0.8\%}$  and  $Ca_{1-y}Al_2O_4$ :  $Sm^{3+}_{y=0.8\%}$  mixed phosphor powders.

The colors from the CIE Chromaticity color diagram corresponds to a yellow-orange and brick red colors of  $Dy^{3+}$  and  $Sm^{3+}$  doped phosphor powders, respectively.

## 2. Conclusions

In this study, yellow-orange and brick red color emitting  $CaAl_2O_4$ :  $Dy^{3+}$  and  $CaAl_2O_4$ :  $Sm^{3+}$  phosphors at different  $Dy^{3+}$  and  $Sm^{3+}$  dopant concentrations were synthesized via solid state reaction method. Powder XRD patterns confirm the formation of single phase monoclinic  $CaAl_2O_4$  structure after heat treatments and well matched with JCPDS 00-062-0217. Irregularly shaped and broken particles with sharp corners, and nearly regular size distributions were observed from SEM studies. The excellent yellow-orange and brick red emission properties and the estimated CIE 1976 chromaticity coordinates (u', v') were also obtained. It was optimized that the highest PL intensity is for the doping of each rare-earths 0.8 mol% Dy and Sm. The PL characteristic of the sample which is physically mixed in equal proportions in powder form, is also investigated and it has PL emissions of both  $Dy^{3+}$  and  $Sm^{3+}$  dopant ions depending on excitation wavelengths. Therefore,  $Ca_{1-x}Al_2O_4$ :  $Dy^{3+}_{x=0.8\%}$  and  $Ca_{1-y}Al_2O_4$ :  $Sm^{3+}_{y=0.8\%}$  phosphors and mixed in equal proportions in powder

form of samples are promising materials for LEDs applications and displays. In addition to similar studies in the literature on this subject, Dy and Sm ions doped phosphor powders, which were studied for weight concentrations, were physically mixed in equal amounts and homogeneously. Although the mixture obtained has the radiation characteristics provided by both dopant ions when excited with both 350 nm and 405 nm, especially the Sm ion dopant showed more dominant characteristic peaks. Although the results obtained in this study are compatible with the limited number of studies in the literature, dopant concentrations were chosen to contribute to the literature and dominant and distinctive luminescence properties were revealed.

## Acknowledgments

Erkul Karacaoglu acknowledges TUBITAK–2214-A International Doctoral Research Fellowship Programme for supporting a portion of this research to be conducted at the Georgia Institute of Technology. Special thanks to Losego Research Group members in the School of Materials Science and Engineering at the Georgia Institute of Technology for helping with everything including laboratory uses.

## **Authors Contributions**

EK prepared all samples at Georgia Institute of Technology, School of Materials Science and Engineering, Ceramics Laboratory. The XRD, DTA/TG, FT-IR and SEM analysis were carried out at Georgia Institute of Technology. PL properties were analyzed at Karamanoglu Mehmetbey University, Metallurgy and Materials Engineering department.

#### **Competing Interests**

The author declares that he has no competing interests.

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