**Synthesis and Characterization of Structural and Luminescent properties of long afterglow CaAl2O4: Eu2+, Nd3+, Dy3+ phosphors by solution – combustion technique.**

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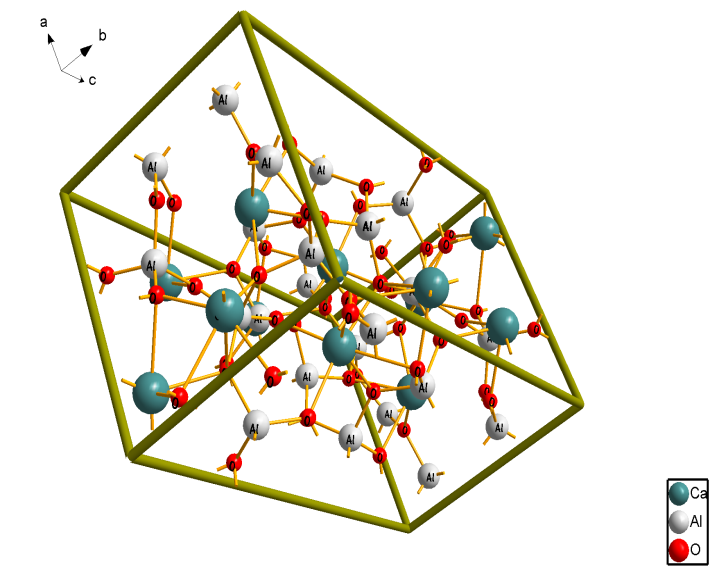
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**Abstract.**  Long afterglow calcium aluminate phosphors doped with Eu2+ and co-doped with Nd3+ and/or Dy3+ (CaAl2O4:Eu2+,Nd3+,Dy3+) were fabricated by urea-nitrate solution – combustion method at 500 °C. The effects of varying concentrations of Ca: Al and co-dopants molar ratio (Nd3+:Dy3+) on the structural and luminescent properties of the phosphor were investigated. It was observed that Ca : Al mass ratios greatly affect the crystalline structure of the material. The results of the X-ray diffraction (XRD) analysis reveal that the formation of several crystalline phases depends on the ratios of the host material. The XRD peaks show the presence of other phases such as Ca3Al2O6 and CaAl4O7 but the predominant phase formed was that of CaAl2O4. However it was found that the crystalline structure is generally not affected by the variation of the co-dopants concentration. PL studies revealed a general rise in intensity with an increase in the mole ratio of Ca : Al . The highest PL intensity was observed with 0.7% Ca. The initial luminescent intensity and rate of decay vary from each other when co-doped with various proportions of Nd3+ and Dy3+.

**1. Introduction**

Aluminates doped with rare earth ions have advantages of being highly stable, bright and versatile in industrial processes that are appropriate for lighting and display devices [1, 2]. Unlike other phosphors so far reported in the literature [3-5], in this study Eu2+, Dy3+ , Nd3+ and the host CaAl2O4 are added together to improve the luminescent properties of the phosphor. The solution-combustion synthesis method also has the merits of low temperature, low cost and time saving. Earlier studies explained the mechanism of persistent luminescence as being caused by the interplay of the rare earth ions with the host band structure and the lattice defects (Fig. 1(a)). The ability of the rare earth species to trap electrons/holes can be predicted from the positions of the 4f and 5d levels of the Eu2+ ion and the other R3+ ions in the host lattice structure [6], but the energy storage and luminescent mechanisms cannot be explained from the level locations alone [1]. The radiative transitions are highly affected by the crystal field components because the 5d orbital is exposed to the surrounding ion. Thus the structure of the host crystals strongly influences the wavelength of a maximum emission peak. This explains why for instance, Eu2+ -doped Ca and Sr aluminates show blue and green emissions, respectively [7]. CaAl2O4 has a tridymite type monoclinic structure (space group: P21/n (No. 14), Z: 12) [8], where [AlO4] tetrahedral construct a three-dimensional framework. Each aluminium ion is bonded to two oxygen ions [9]. The structure consists of channels built up of rings formed by six corner- sharing AlO4 tetrahedra and Ca2+ cations situated within the channels (Fig. 1(b)).



(a) (b)

Figure 1: (a). Persistent luminescence mechanism for CaAl2O4:Eu2+, R3+ materials. (b)structure of monoclinic CaAl2O4.

There are three different Ca2+ sites in the CaAl2O4 lattice: one (Ca3) is nine-coordinated and two of them (Ca1 and Ca2) are six-coordinated [10]. Doped Eu2+ ions prefer nine-coordinated Ca2+ sites (rCa: 1.18 Å) to two six-coordinated ones (rCa: 1.0 Å), because larger spaces are necessary for the substitution of Eu2+ ions (rEu: 1.30 Å) due to the difference in ionic size. The average Ca–O distances 2.42 Å and 2.43 Å for the six-coordinated Ca2+ ions are clearly shorter compared to that of the nine-coordinated ones (2.78 Å) [11]. By doping with Eu2+ ions, CaAl2O4 powders exhibit a strong blue emission around 440 nm when excited with 320 nm [12]. CaO–Al2O3 systems easily degenerate into multi-phased compounds with slight deviation from the exact stoichiometric composition and firing temperature which makes it difficult to obtain CaAl2O4 single phase. So the synthesis conditions, such as host elements, dopant concentration and temperature are very important to the formation of single phase. However, in spite of many previous studies, a thorough investigation has so far not been carried out. This study focuses on the blue emitting persistent luminescence, CaAl2O4:Eu2+,Nd3+,Dy3+ phosphor of which CaAl2O4:Eu2+,Nd3+ is already in commercial use.

**2. Experimental**

***2.1 Synthesis***

CaAl2O4:Eu2+,Nd3+,Dy3+ phosphors were synthesized using the solution - combustion method. The starting raw materials used in the experiment include various proportions of analytical pure grade Ca(NO3)2.4H2O, Al(NO3)3.9H2O, Eu(NO3)3.5H2O, Nd(NO3)3, Dy(NO3)3, urea ( CH4N2O) and boric acid ( H3BO3). The raw materials were weighed according to the chemical composition of CaAl2O4: Eu2+, Nd3+,Dy3+, dissolved in 10 ml of de-ionized water and thoroughly mixed using a magnetic stirrer for 15 minutes without heating to obtain a uniform solution. In the first group, eight samples were prepared without flux. The Al concentration was kept constant at 1.5 mass % for all the prepared solutions. Varying concentrations; 0.1, 0.4, 0.5, 0.6, 0.7, 0.8, 1.0, and 1.5 mass % of Ca were taken. The second set consist of five samples used to study the influence of variation of co-dopants, Nd3+ and Dy3+ molar ratio on the structural and luminescent properties of the CaAl2O4:Eu2+ phosphor. The samples were mixed in the mass ratios 0:1, 0.25:0.75, 0.5: 0.5, 0.75:0.25 and 1:0 of Nd3+: Dy3+. The solutions were then poured into China crucibles and placed one at a time in a muffle furnace pre-heated at 5000C. Combustion time was 5–6 min per sample. White voluminous foam was obtained by combusting the mixture at temperatures of 400–500°C. Initially, the solution boiled and underwent dehydration, followed by decomposition releasing large amounts of gases (oxides of carbon, nitrogen and ammonia). Then, spontaneous ignition and smoldering occurred which gradually led to an explosion with enormous swelling. When taken out of the muffle furnace and cooled down, voluminous foam was obtained, which was a mixture of the incomplete combustion compound CaAl4O7 and the complete combustion compound CaAl2O4. The voluminous foam was milled to obtain the fine, white powders. The powders were stored in transparent sample glass bottles for characterization.

***2.2 Characterization***

The synthesized products were characterized by X-ray diffraction (XRD) using a Bruker D8 X-ray diffractometer operating at 40 kV and 4 mA using Cu Kα = 0.15406 nm. The morphologies were investigated using a Shimadzu model ZU SSX-550 Super scan Scanning Electron Microscope (SEM) and an Energy Dispersive X-ray Spectrometer (EDS). The decay curves, excitation and emission spectra were measured using a Cary Eclipse fluorescence spectrophotometer model: LS- 55 with a built-in 150W xenon flash lamp as the excitation source.

**3. Results and discussion**

***3.1 The influence of the Ca: Al mass ratio on structure.***

Scanning electron microscopy (SEM) study was carried out to investigate the surface morphology and crystalline sizes of the synthesized phosphor powder. Figure 2 shows the representative SEM micrograph taken for the 0.4% Ca sample. As can be seen, the surfaces of the foam display many cracks and pores formed by the escaping gases during the combustion reaction. The material also presented agglomeration and the grain size of the sample got bigger. This tends to reduce the luminescent properties when the sample is ground.

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Figure 2: SEM micrographs for 0.4% Ca sample.

Figures 3(a and b) show the powder XRD pattern for the CaAl2O4:Eu2+, Nd3+, Dy3+. Several phases are easily observable. Analysis of these diffractive peaks reveal that 0.5% Ca and 0.6% Ca favour pure monoclinic phase [fig 3(a)] while higher concentrations of calcium; 0.8% Ca, 1.0% Ca and 1.5% Ca seem to favour the formation of cubic phase [fig 3(b)]. Both phases are matching with the JCPDS data file (no. 23-1036). Weak diffraction peaks of CaAl4O7 compound formed due to incomplete combustion were also observed. The calculated lattice parameters for the monoclinic crystal system were a=8.6942Å, b=8.0930Å, c=15.2097Å and β=90.17° while for the cubic system was a=11.9868Å.

Figure 3: (a) Monoclinic and (b) cubic phase of CaAl2O4:Eu2+,Nd3+,Dy3+ phosphors.

***3.2 The effects of Ca : Al mass ratio on photoluminescence properties.***

Figure 4 (a) shows the excitation spectrum of the phosphor. There is an excitation peak at around 325 nm in the excitation spectrum (λem = 440 nm), which is in conformity with the absorption of the host CaAl2O4. It’s known that CaAl2O4 has a broad band excitation spectrum ranging from 250 to 340 nm. This means that in a broad range (λex ≤360 nm), CaAl2O4:Eu2+, Dy3+, Nd3+ phosphor can be activated to produce long persistence. As can be seen in Fig. 4(b), the emission spectrum (λex = 325 nm) shows a broad band from the 4f65d1 to the 4f7 configuration of the Eu2+ ions at about 440 nm, which is consistent with the literature.[25]. Energy levels are located between excited state 4f65d1 and ground state 4f7 of Eu2+, and there is the energy gap (ET) between the energy levels and the excited state energy level. When the material is excited, some of the Eu2+ excitation electrons get stored in the trap energy level through the relaxation process. When the excitation stops, the electrons stored up in the trap energy level obtain energy through thermal agitation at room temperature, overcome the energy level gap between the trap energy level and the excited state energy level, return to the excited state, then transit back to the ground state and emit light energy. From the decay of figure 4(c),It can be seen that the samples show quite long time especially when the powder was efficiently activated by using 0.7% Ca. In general all the PL results show 0.7% Ca as the optimal concentration for the excitation, emission and decay characteristics.

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**Figure.4:** (a) Excitation, (b) emission (c) decay characteristics of the phosphors dependence on Ca : Al mass ratio (d) emission intensities of the varying Nd3+ : Dy3+co-dopant ratio.

***3.3 The effects of co-dopants mass ratio (Nd3+:Dy3+) on the photoluminescence properties.***

Figure 4(d) shows the emission intensities of the CaAl2O4:Eu2+,Nd3+,Dy3+ phosphors while the phosphors are excited at a wavelength of 325 nm. Within the scope of content ratio 0.75:0.25, Nd3+ and Dy3+ ions seem to improve the luminescent properties of the phosphors CaAl2O4:Eu2+,Nd3+,Dy3+. The peak wavelength of the phosphor does not vary with the doped Nd3+:Dy3+. This implies that the crystal field, which affects the 5d electron states of Eu2+, is not significantly changed by the variations in the co-dopants. When the phosphor is doped with Nd3+ and Dy3+, Ca2+ ions are replaced by Nd3+ and Dy3+ ions. But Ca2+ ions and Nd3+/Dy3+ ions are different resulting in unequal replacement. This causes more trap energy level and the depth of the energy level becomes deeper. Otherwise, Nd3+ seems to possess the correct affinity toward to the electrons more than Dy3+ in the energy level.

**4. Conclusion**

The phosphor CaAl2O4:Eu2+, Nd3+, Dy3+ can be prepared by solution-combustion method. The influences of the quantity of mixed Nd3+, Dy3+ and varying concentrations of Ca: Al on the phosphor were studied. The analytical results indicate that the broad emitted band of the CaAl2O4:Eu2+, Nd3+, Dy3+ is observed in the blue region (λ max = 440 nm) due to transitions from the 4f65d1 to the 4f7 configuration of the Eu2+ ion. It may serve as a promising material for use as a lamp phosphor in the blue region. Furthermore, the solution- combustion method is cost-effective, saves energy and time.

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