

Preparation of $\text{GdCaAl}_3\text{O}_7$: Eu nanoparticles by a combustion method and their characterization

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$\text{GdCaAl}_3\text{O}_7$: Eu nanoparticles were synthesized using a metal nitrate solution with glycine as fuel. X-ray diffraction (XRD), a scanning electron microscope (SEM), a transmission electron microscope (TEM) and a photoluminescence spectrophotometer (PL) were used to characterize the products obtained. XRD patterns revealed that a pure $\text{GdCaAl}_3\text{O}_7$: Eu phase was formed by combustion of the metal nitrate solution in the presence of glycine at pH = 4. The appearance of spongy agglomerates indicates large amounts of exhaust gases and intense ignition of the powder obtained. SEM and TEM images showed that the agglomerates consisted of nanoparticles and 5-10 nm nanopores. An investigation of the chromaticity of the synthesized naophosphors showed that all samples synthesized at pH = 1 (after calcination), pH = 3 and pH = 4 have a red emission under 245 nm UV lighting. Furthermore, the synthesized sample at pH = 1 (after calcination) and the sample synthesized at pH = 4 have almost the same CIE chromaticity xy values.

Key words: Combustion, Nanostructure, Red phosphor, $\text{GdCaAl}_3\text{O}_7$: Eu, CIE xy chromaticity, Photoluminescence.

Introduction

Today, one of the most important challenges in display technology is to prepare a suitable red phosphor, which has acceptable light emission and good color co-ordinates [1]. In most of the applications involving oxide red phosphors, purity of color is a major problem. For example, plasma display panels (PDPs) which are the most promising candidate for large flat panel displays (FPD) do not generate a pure deep red color, because the CIE (Commission International De L'eclairage) chromaticity values of the most popularly used borate red phosphor for PDPs can not reach a standard value [1-2].

$\text{GdCaAl}_3\text{O}_7$ is in the class of stoichiometric oxides (the $\text{AA}'\text{B}_3\text{O}_7$ series) which has a layered-type structure. In this structure, Gd atoms are surrounded by oxygen, which induces a high degree of anisotropy. This anisotropic structure affects the magnetic and optical properties of the material [3]. Moreover, Eu and Tb dopants in the $\text{GdCaAl}_3\text{O}_7$ structure have a strong emission around 619 nm and 545 nm, respectively. These phosphors show a wide variety of colors with the same matrix, which are suitable red or green phosphors for display applications, particularly plasma display panels (PDPs) [4]. The $\text{GdCaAl}_3\text{O}_7$: Eu red phosphor has been synthesized by different methods such as sol-gel [5, 6] and a polymerized-complex [7].

Solution combustion is a well-known method for rapid synthesis of rare earth activated insulating materials at low temperatures (350-500 °C) and very short times (< 5 minutes). Although oxide phosphors synthesized by a combustion reaction have low-voltage cathodoluminescence efficiencies, hydrothermal, solid-state and combustion methods yield the same efficiencies at excitation voltages below 600 V [8]. Different structures of tricolor phosphors such as oxides, vanadates, borates, aluminates, etc., can be synthesized using a solution combustion method [9]. Recently, the feasibility of using a combustion process to synthesize $\text{GdCaAl}_3\text{O}_7$: Eu^{3+} has been considered. Mahakhode *et al.* used urea as a fuel for the combustion synthesis of $\text{GdCaAl}_3\text{O}_7$: Eu. Although the four Eu^{3+} peaks appeared in the green to red region of the emission spectrum, some additional peaks around 550 nm can be related to defect-related processes [10]. Therefore, experimental conditions such as temperature and the pH value of the metal nitrate mixture, which affect the luminescence properties, must be controlled.

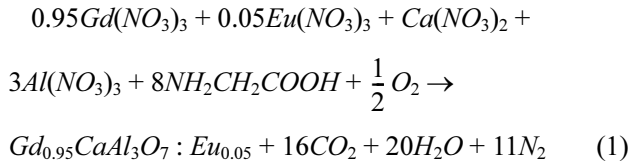
In this paper, combustion synthesis of a $\text{GdCaAl}_3\text{O}_7$: Eu red nanophosphor with glycine is reported. The effect of the pH value on the combustion reaction, structure and morphology of $\text{GdCaAl}_3\text{O}_7$: Eu phosphors is also investigated.

Experimental

Calcium and aluminum nitrates, europium (Eu_2O_3) and gadolinium (Gd_2O_3) oxides and glycine were of analytical grade. Initially, Eu_2O_3 and Gd_2O_3 were dissolved in hot

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dilute nitric acid. Metal nitrate solutions of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3$ and $\text{Gd}(\text{NO}_3)_3$ were also dissolved in distilled water. The above four metal nitrate solutions were mixed with each other in a 250 ml beaker under vigorous stirring. The fuel to oxidizer (F/O) ratio was calculated based on the following stoichiometric equation:



Initially, the pH value of the metal nitrate solutions was adjusted to 1-4. Then, stoichiometric amounts of glycine fuel were added. The final solution was converted to a gel by heating up to 80-90 °C. The beaker was transferred into a microwave oven (Samsung, Korea, 900 W, 2.45 GHz frequency) to complete the combustion reaction. All experiments were performed at a maximum power of microwave for 50 seconds. The samples are summarized in Table 1.

The structures of the powders obtained were characterized by X-ray Diffraction (XRD) (D-500 Siemens, Karlsruhe, Germany). The morphology of the particles and agglomerates were also investigated by a scanning electron microscope (SEM) (LEO 1455VP Oxford, UK), and a transmission electron microscope (TEM) (Zeiss, Em 900). The luminescent properties of the powders obtained were characterized using a photoluminescence spectrophotometer (PL (Perkin-Elmer LS5)).

Results and Discussion

Fig. 1 shows XRD patterns of $\text{GdCaAl}_3\text{O}_7 : \text{Eu}$ samples synthesized at different pH values. Actually, no phase can be distinguished for the as-synthesized Gd1 sample indicating the amorphous nature of the product. As the pH was increases to 3, some peaks appear which cannot be assigned to a $\text{GdCaAl}_3\text{O}_7$ structure or other oxide phases in the Gd_2O_3 - CaO - Al_2O_3 system (Gd3 sample). The XRD pattern of the Gd4 sample indicates the formation of a pure gadolinium calcium aluminum oxide ($\text{GdCaAl}_3\text{O}_7$, JCPDS No. 050-1808) and disappearance of the previous peaks occurs. This is because of the higher densities of energy delivered to the mixture at higher pH values. Moreover, the increase of the pH value promotes glycine

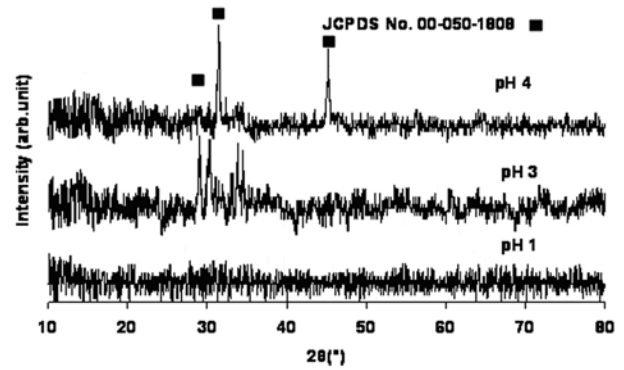


Fig. 1. XRD patterns of the sample synthesized at different pH values.

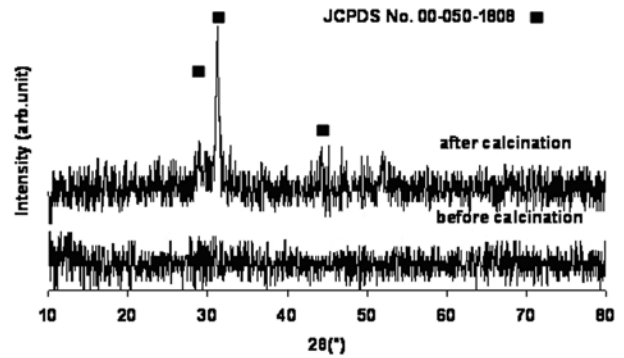


Fig. 2. XRD patterns of the samples obtained at pH = 1 with and without calcination

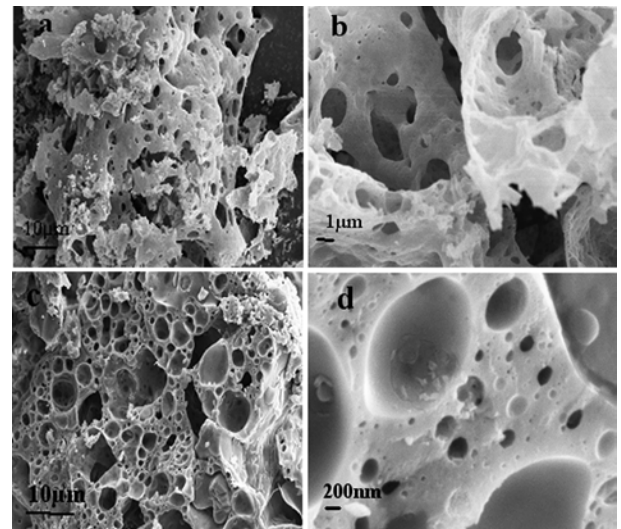


Fig. 3. SEM images of $\text{GdCaAl}_3\text{O}_7 : \text{Eu}$ (a-b) Gd1, (c-d) Gd4 samples at various magnifications.

Table 1. The pH values and calcination conditions of phosphors

name	pH values of metal nitrate solutions	Calcination (temperature, time)
Gd1	1	-
Gd2	1	(900 °C, 1 h)
Gd3	3	-
Gd4	4	-

decomposition and causes the more rapid ignition of the mixture, which provides higher temperatures for the reaction [11]. The Gd4 sample has an average crystallite size of about 26 nm (by the Scherrer equation). The amorphous structure of the Gd1 sample changes to $\text{GdCaAl}_3\text{O}_7$ after 1 hour calcination at 900 °C (Gd2). XRD patterns of the calcined sample are shown in Fig. 2.

Fig. 3 shows the SEM images of samples obtained at

different pH values. When the ignition of the metal nitrate solution with nitrogen-based fuels starts, localization of the heat on the particle boundaries results in a semi-sintered morphology of particles [12]. The_Gd1 sample (Fig. 3(a) and (b)), has a larger particle size. It is evident that the low intensity of ignition at pH = 1 suppresses the formation of a spongy-like structure. However, in the case of the Gd4 sample (Fig. 3(c) and (d)), formation of a porous foamy-like morphology and the presence of nano to micro pores are related to the enhancement of the combustion reaction at pH = 4 and the increase of the combustion reaction gases. Deganello *et al.* [13] have also reported that the intensity of the combustion reaction increases with the pH. Consequently, the formation of foamy particles with a large amount of micro to nano pores can be related to the above mentioned intensification of reaction.

Calcination as an effective process is also investigated. SEM images of Gd1 and Gd2 samples are shown in Fig. 4. Lenka *et al.* [14] showed that two exothermic reactions occur during the heat treatment: a weak exothermic peak related to the combustion reaction, and oxidation of residual reactants and carbonaceous matters at a higher temperature. When the first reaction is completed, the intensity of the second reaction decreases. Moreover, the intensity of the ignition decreases at lower pH values. Therefore, an imperfect porous morphology is formed (Fig. 4(a)). The calcination process completes the combustion reaction; hence, the foamy structure shown in Fig. 4(b) is formed after calcination.

The morphology of the primary particles in the loose packed agglomerates was evaluated by TEM. Fig. 5 shows

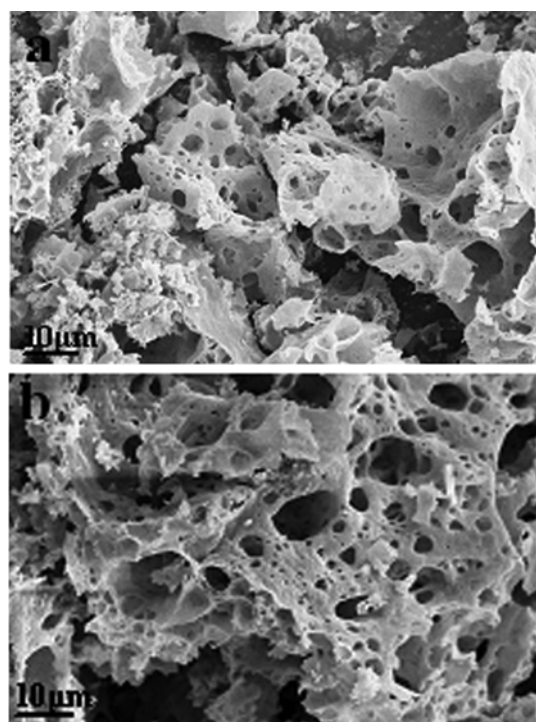


Fig. 4. SEM images of $\text{GdCaAl}_3\text{O}_7$:Eu (a) Gd1 (b) Gd2 samples.

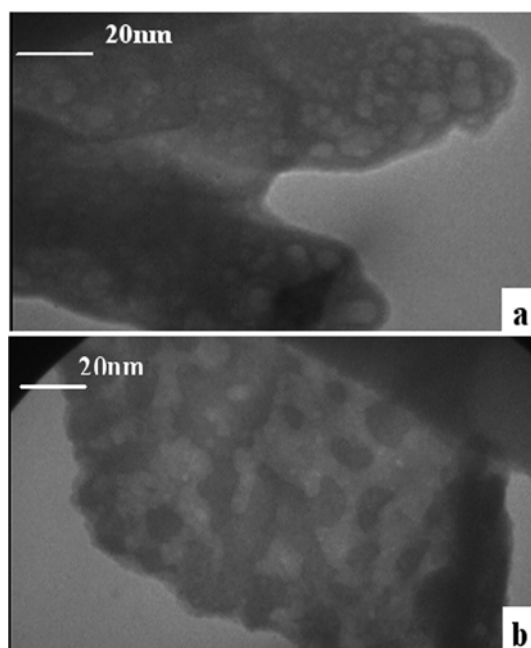


Fig. 5. TEM images (different magnifications) of the Gd4 sample.

the porous agglomerates consist of primary particles and 5-10 nm nanopores. In addition, primary particles are surrounded by a porous structure, which indicates that the ignition of the combustion reaction has been initiated homogeneously. Moreover, morphology of Gd2 sample obtained after calcination step is shown in Fig. 6. The spongy structure of the agglomerates consists of more uniform pores (in size and shape) due to the two-step combustion (the initial combustion reaction and the combustion during calcination) mentioned earlier.

Fig. 7 shows the PL spectra obtained of the $\text{GdCaAl}_3\text{O}_7$: Eu samples synthesized at different pH values. The main advantage of the combustion reaction is its one-step production of the products without any further calcination [10]. The ignition of the metal nitrate solution at pH 1 is weak and the powder obtained has a black color, which can be related to the incomplete combustion reaction. Although UV cannot excite this sample, increasing the intensity of ignition in Gd3 and Gd4 samples, causes the formation of fine white $\text{GdCaAl}_3\text{O}_7$: Eu nanoparticles, which emit sharp red light. When Eu^{3+} is well doped in the structure, an emission at 580-630 nm is observed in the PL spectrum. The peaks at 595 nm and 615 nm can be assigned to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions, respectively. The electric dipole $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is stronger than the magnetic dipole $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition, consequently, Eu^{3+} ions occupy more non-inversion symmetric sites of Gd^{3+} [4]. The appearance of the weak peak at 570 nm indicates the formation of strong crystal field of $\text{GdCaAl}_3\text{O}_7$ [5]. Sharp red emission indicates that $\text{GdCaAl}_3\text{O}_7$: Eu is suitable for display phosphors [10]. According to Fig. 7, Gd2 and Gd4 samples show almost similar curves. However, the Gd3 sample has a different trend. Comparing the three PL spectra shows that the

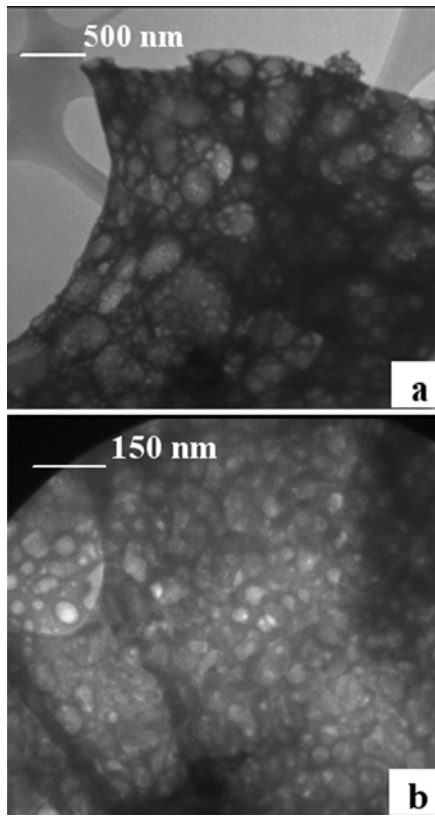


Fig. 6. TEM images (different magnifications) of the Gd2 sample.

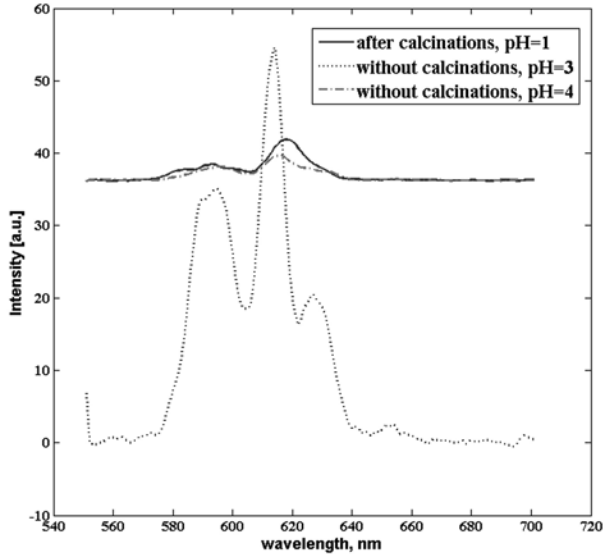


Fig. 7. Emission spectra for the $\text{GdCaAl}_3\text{O}_7:\text{Eu}$ samples synthesized at different pH values (excited at 254 nm).

dominant wavelength of the Gd3 sample is about 10 nm smaller than the other two. Moreover, it can be seen that the Gd2 and Gd4 samples have a significantly higher intensity than Gd3. This can be related to impure structure of structure.

To have a better comparison between the Gd2 and Gd4 samples, the PL spectra of these two samples are shown in Fig. 8. According to these spectra, the dominant wavelengths

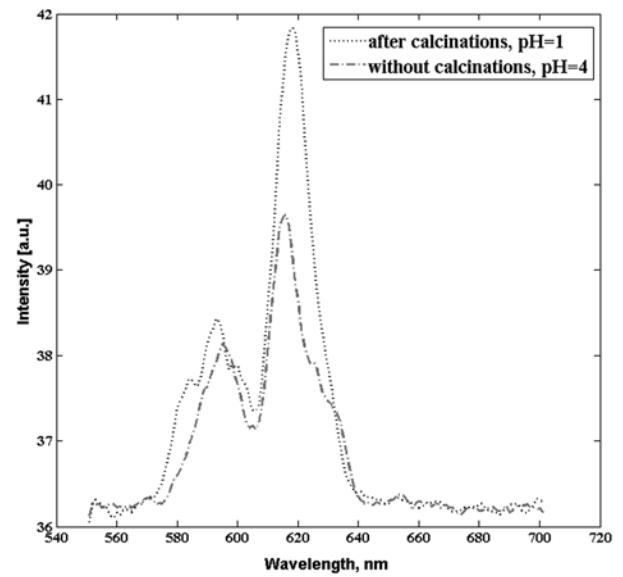


Fig. 8. Emission spectra for the synthesized Gd2 and Gd4 samples.

Table 2. xy CIE chromaticity values of Gd2-4 samples

sample	x	y
Gd2	0.5745	0.4247
Gd3	0.6323	0.3673
Gd4	0.5737	0.4254

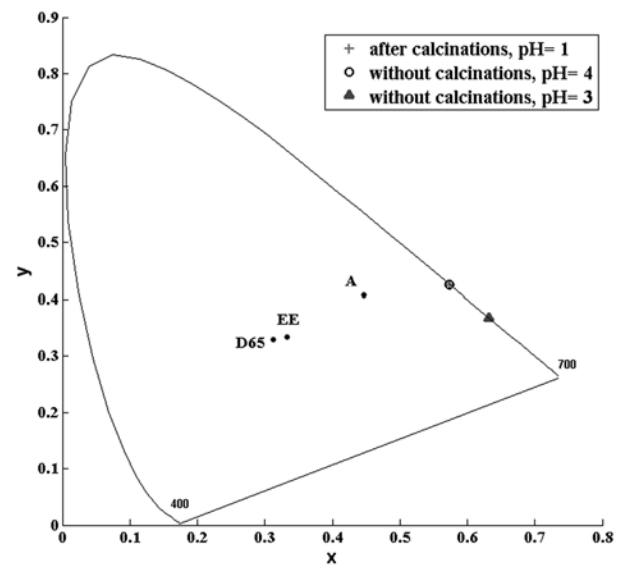


Fig. 9. xy CIE chromaticity coordinates of the samples synthesized at different pH values.

of the samples are almost similar; however the Gd2 shows a sharper peak and higher intensity values.

The CIE xy value of each nanophosphor is given in Table 2. Fig. 9 shows the xy chromaticity coordinates of the three samples in a CIExy chromaticity diagram. The coordinates of three CIE standard illuminants including D65, EE (equal energy) and A are indicated. As Fig. 9 illustrates, the Gd2 and Gd4 samples have the same

coordinates. Moreover, the Gd3 sample is further from them.

Conclusions

$\text{GdCaAl}_3\text{O}_7$: Eu^{3+} nanoparticles were synthesized by a one-step combustion reaction of metal nitrate precursors. Evaluation of the structures revealed that an increase in the pH value of the metal nitrate solution causes the complete formation of the $\text{GdCaAl}_3\text{O}_7$ structure. The Gd1 (pH = 1) sample needs further calcination to obtain the desired structure. The powders obtained were semi-sintered and hardly agglomerated. The average crystallite size and particle size of the spongy agglomerates were on the nanoscale. The phosphors gave a sharp red emission around 590-630 nm under UV light exposure. The Gd3 sample has some extra peaks and its dominant wavelength was higher than the others were, however the intensity of its emission peaks is about two times inferior to the Gd2 and Gd4 samples. The Gd2 and Gd4 samples have almost the same chromaticity xy values; however the Gd1 sample shows higher emission.

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