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Combustion synthesis and photoluminescence properties of $CaAl_2O_4 : Eu^{2+}$, Y^{3+} based long lasting nanophosphors

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Phosphorescent materials are known as long lasting materials including lanthanide atom doped nano particles which recently have found wide application field. Phosphorescent, classically, is the materials which have light emission in visible region of electromagnetic spectrum on removal of excitation effect such as radiation, electron beam, electrical field, temperature etc. A novel red long lasting phosphor $CaAl_2O_4 : Eu^{2+}$, Y^{3+} nano phosphors have been prepared using a combustion method. The crystallization, particle sizes and luminescence properties of the samples have been investigated systematically by using powder X-ray diffraction, scanning electron microscopy, luminescence spectrophotometer and FT-IR.

Key words: Long lasting phosphor, Luminescent.

Introduction

Ever since a report on long lasting green phosphorescence (> 50 h) from aluminate host lattices doped with rare-earth ions was published [1]. Rare earth doped phosphorescence materials, in fact, nowadays they have been widely used in the fields like fire control and emergency dealing, traffic and transportation, instruments and meters, building and upholstery, military establishment and low-brightness illuminance, etc, in the form of luminescent dope, as well as luminescent film, printing ink, plastic, ceramics, fibers, papers. [2].

Phosphorescence materials, rare earth element called nano particles lanthanides should be prepared long radiation and has a common usage area. Phosphorescence, as a classic, excitation effects (radiation, electron beam, electric field, temperature, etc.) disappear after the radiation in the visible region which is the name given to materials. After glow long lasting phosphorescence materials, usually sulfur, oxide, silicate, aluminate, alumina silicate, phosphate, etc… structure with crystal structures are substances.

Long persistent phosphors can light up for a long time in the darkness after irradiation with sunlight or artificial light. Eu^{2+} doped alkaline earth aluminates $MAl_2O_4 : Eu^{2+}$ (M: Ca, Sr, Ba) phosphors with strong photoluminescence at the blue-green visible region have been studied extensively by many researchers. The rare earth metal ions doped calcium aluminate phosphors, because of their high quantum efficiency, anomalous long phosphorescence and good stability, have been studied in depth and used widely [3].

Phosphorescence materials are usually produced by classical synthesis method (solid-state), but these methods have several disadvantages. High reaction temperatures are energy intensive and thus increase the production costs. This process often results in poor homogeneity. Additionally size distribution of the powder which affects luminescence efficiency. Grinding process in order to reduce particle size introduces chemical contamination that also has a role in luminescence efficiency [4].

Combustion synthesis is a novel powder processing technique that can produce ceramic pigments. These methods a low temperature synthesis technique that offers a unique synthesis route via highly exothermic redox reaction between metal nitrates and an organic fuel to produce ceramic pigments [5]. These processes are characterized by high temperature, fast heating rates and short reaction time. Some other advantages of combustion synthesis are; use of relatively simple equipment, formation of high-purity products, stabilization of metastable phases and formation of virtually any size and shape products [6].

In this paper, combustion synthesis is applied to prepare the $CaAl_2O_4 : Eu^{2+},Y^{3+}$ phosphor nanometer powders at the first time. It was performed by rapidly heating aqueous solution containing stoichiometric quantity of corresponding metal nitrates and urea at 400 °C. This process lasted for about 5 min. and in voluminous powder.

Experimental

The starting materials were $Al(NO_3)_3 9H_2O$, $Ca(NO_3)_2$ $4H_2O$, $Eu(NO_3)$, $Y(NO_3)$, H_3BO_3, $CO(NH_2)_2$. According

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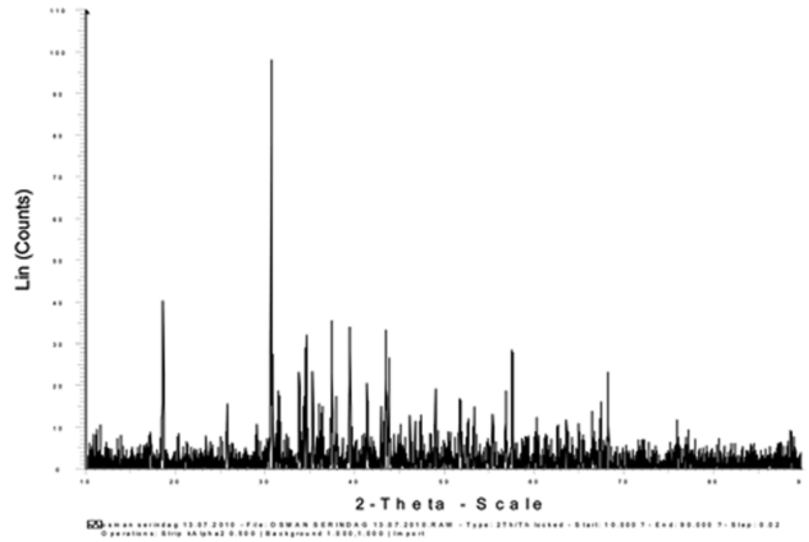


Fig. 1. X-ray diffraction patterns of $CaAl_2O_4 : Eu^{2+},Y^{3+}$ phosphor.

to the chemical composition of $CaAl_2O_4 : Eu^{2+},Y^{3+}$, the stoichiometric of start materials $Al(NO_3)_3 9H_2O$, $Ca(NO_3) 4H_2O$, was dissolved into deionized water together with a certain amount of $CO(NH_2)_2$ in a 100 ml beaker. Eu^{2+} and Y^{3+} solutions were prepared. The two solutions were mixed together in another beaker. Then, a flux, H_3BO_3, was added into the solution and stirred for about 3 h at 70 °C. The beaker containing aqueous solution was inserted in a muffle furnace maintaining its temperature 600 °C.

The white voluminous foamy fine powder phosphor can be obtained in 3-5 min by combusting the precursor mixture in a muffle furnace at the temperature of 400-600 °C. Initially, the solution boiled and underwent dehydration, followed by decomposition with the evolution of large amounts of gases (oxides of carbon, nitrogen and ammonia). Then, spontaneous ignition occurred and underwent smouldering combustion with enormous swelling, producing white foamy and voluminous ash. The voluminous and foamy combustion ash can be easily milled to obtain the phosphor powders [3].

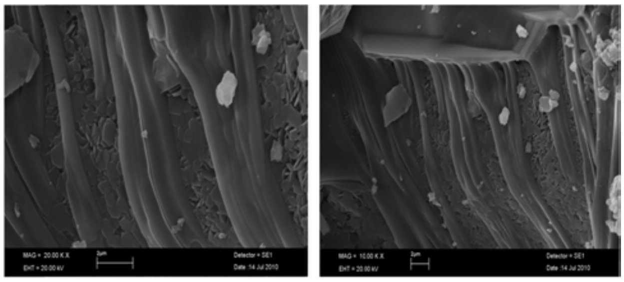


Fig. 2. SEM imagesof $CaAl_2O_4 : Eu^{2+},Y^{3+}$ phosphor.

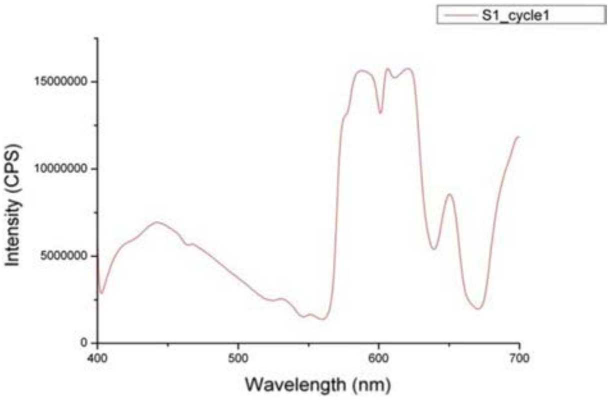


Fig. 3. Excitation spectra of the $CaAl_2O_4 : Eu^{2+}, Y^{3+}$ phosphor.

Results and Discussion

Combustion process is an exothermic reaction, which occurs with evaluation of light and heat. Combustion is simply expressed by a well-known reaction, burning of carbon in presence of oxygen:

$$C+O_2 \rightarrow CO_2 + \text{heat}$$

Here carbon is reducer and oxygen is oxidizer. Therefore, for any combustion process reducer and oxidizer are required. This combustion takes place only if ignited. For the combustion synthesis of oxides, metal nitrates or ammonium nitrate are employed as oxidizer and urea is employed as a reducer [12]. When the stoichiometric amount of metal nitrates and urea ignited at 600 °C combustion takes place. Formation of oxides by the combustion process is represented by a theoretical equation assuming complete combustion takes place:

$$6Al(NO_3)_3 + 3Ca(NO_3)_2 + 20NH_2CONH_2 \longrightarrow 3CaAl_2O_4 + 20CO_2 + 32N_2 + 40H_2O$$

Formation of these phosphors has been characterized by powder XRD. Fig. 1 shows the representative powder XRD pattern for the $CaAl_2O_4 : Eu^{2+},Y^{3+}$. It is reported that besides $CaAl_2O_4$ it was found that a pure

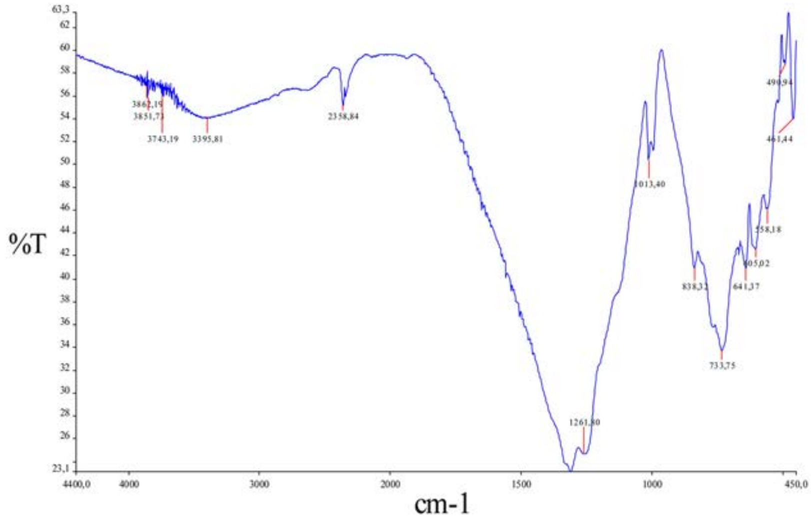


Fig. 4. FT-IR spectra of the $CaAl_2O_4$: Eu^{2+}, Y^{3+} phosphor.

monoclinic phase of parent $CaAl_2O_4$ is dominant in the XRD pattern (JCPDS-23-1036). The results proved that all phosphor samples prepared in this work are almost single $CaAl_2O_4$ phase, and the little amount of co-doped rare earth ions have almost no effect on the $CaAl_2O_4$ phase composition.

Fig 2. the morphology of the powders was observed with a scanning electron microscope. The microstructure of these samples reflects the inherent nature of the combustion process. The non uniform and irregular shapes of the particles as shown can be attributed to the non- uniform distribution of temperature and mass flow in the combustion flame [7]. The precursor powder shows the irregular to hexagonal particles with surfaces lots of cracks, voids and pores formed by escaping various gases like COx, NOx and NH_3 during the combustion of precursor nitrates and fuels [8].

The excitation spectra of Eu^{2+} activated $CaAl_2O_4$ synthesized by combustion method at 600 ºC. Excitation wavelength 390 nm. The characteristic red emission due to Eu^{3+} is observed in the region 605-625 nm. Fig. 3. shows emission spectrum of Eu^{3+}-activated $CaAl_2O_4$. It shows very broad peak covering entire region from 575 to 630 nm [12].

The FT-IR spectra of the samples are shown in Fig. 4. the broad peak at 3400 cm^{-1} is typical of the O-H stretching vibration. The mid-IR stretching and bending modes of tightly bound tetrahedral AlO_4 units are considerably strong and have relatively high frequencies (578-937 cm^{-1}). The absorption bands at 733, 641 and 461 cm^{-1} are attributed to the stretching vibration of Ca-O bond.

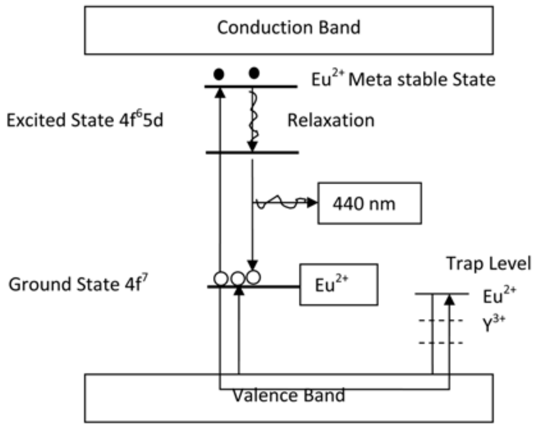
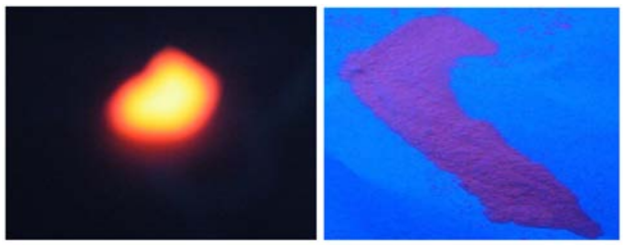


Fig. 5. Schematic graph of mechanism of long afterglow photoluminescence of $CaAl_2O_4$-based phosphors [9].



(a) (calcined 1000 °C), (b) (combustion, 600°C)

Fig. 6. Color images of $CaAl_2O_4$: Eu^{2+}, Y^{3+}.

Conclusions

$CaAl_2O_4$:Eu^{2+}, Y^{3+} phosphor has been synthesized by the combustion method. XRD patterns show the phase formation of $CaAl_2O_4$ with some impure phases. XRD analysis shows that the prepared compositions retain the monoclinic phase of $CaAl_2O_4$. The Eu^{2+} luminescence, in general, varies from UV to red, depending upon the host lattice. It is generally agreed that the phosphorescence of Eu^{2+} in most of hosts is believed to be caused by the 4f 5d transition [13, 14]. This fundamental work might be important in developing new luminescent devices applicable for luminescent film, printing ink, plastic, ceramics and other fields. The combustion synthesis is found to be a simple method for the preparation of phosphor. This method lowers the cost and can save energy, and can be operated easily. Combustion synthesis technique is faster than other methods of synthesis such as co-precipitated sulphates, oxalates, sol-gel, and spray decomposition processes.

Acknowledgments

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