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Luminescence studies of a combustion-synthesized blue–green $BaAl_xO_y$:Eu^{2+},Dy^{3+} nanoparticles

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ABSTRACT

Blue–green emitting $BaAl_xO_y$:Eu^{2+},Dy^{3+} phosphor was synthesized by the combustion method. The influence of various parameters on the structural, photoluminescence (PL) and thermoluminescence (TL) properties of the phosphor were investigated by various techniques. Phosphor nanocrystallites with high brightness were obtained without significantly changing the crystalline structure of the host. In the PL studies, broad-band excitation and emission spectra were observed with major peaks at 340 and 505 nm, respectively. The observed afterglow is ascribed to the generation of suitable traps due to the presence of the co-doped Dy^{3+} ions. Though generally broad, the peak structure of the TL glow curves obtained after irradiation with UV light was non-uniform with suggesting the contribution to afterglow from multiple events at the luminescent centers. Further insight on the afterglow behavior of the phosphor was deduced from TL decay results.

1. Introduction

Aluminate phosphors are most promising luminescent materials for various applications, which include their current and potential use in high definition television (HDTV), plasma display panels (PDP), cathode ray tubes (CRT) and field emission displays (FED) [1,2]. Among these luminescent materials, rare-earth doped phosphors have been outstanding due to their technological importance and are widely used in color displays and fluorescent lamps [3]. Research geared towards meeting these goals usually aim at producing luminescent materials having characteristics such as fine phosphor particles with a spherical morphology, homogeneous composition and good surface properties [4,5]. The possibility of tuning the emission of Eu^{2+} ions spanning the whole visible light region [6] has been of great motivation to further study the luminescence of Eu^{2+}, which can be significantly enhanced by co-doping with trivalent rare earth ions such as Dy^{3+} ions [7]. On the other hand, the remarkable properties expected of materials produced on the nanoscale can greatly advance the prospects of utilizing nanocomposites in various luminecence devices to improve performance, which differ from those of bulky materials [8]. In spite of the prospective improvement in the long afterglow properties of $BaAl_xO_y$:Eu^{2+},Dy^{3+} [9,10], Eu^{2+},R^{3+} co-doped barium aluminates have not been adequately investigated [11,12].

This paper reports the results of the synthesis and characterization of $BaAl_2O_4$:Eu^{2+},Dy^{3+} powder samples, which were prepared by a combustion synthesis technique. The combustion synthesis technique provides a very attractive route for making both simple and complex phosphor materials. It is an extremely time- and energy-efficient process. The effects on the structure, homogeneity and persistent luminescence are presented and discussed based on the analyses of the x-ray powder diffraction, SEM imaging, photoluminescence and thermoluminescence investigations. The high brightness luminescence intensity and long persistence characteristics of the synthesized $BaAl_xO_y$:Eu^{2+},Dy^{3+} phosphor are encouraging for practical applications.

2. Experimental

2.1. Synthesis

Eu^{2+} doped and Dy^{3+} co-doped $BaAl_2O_4$ phosphor was prepared by conventional solution combustion reaction method. $Ba(NO_3)_2$ (A.R.), $Al(NO_3)_3 \cdot 9H_2O$ (A.R.), $Eu_2(NO_3)_3$(4N), CH_4N_2O were used as starting materials. A homogeneous, thick white solution was obtained after thoroughly milling the precursor mixture in a mortar using a pestle. The solution was then introduced into a muffle furnace maintained at 500 °C. The final fine $BaAl_xO_y$:Eu^{2+},Dy^{3+} powder products were easily formed by grinding the resulting foamy froth from the combustion ash in a pestle and mortar.

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2.2. Characterization

2.2.1. Microstructure and structural analysis

The microstructure and elemental composition of the $BaAl_2O_4:Eu^{2+},Dy^{3+}$samples were performed on a Shimadzu model ZU SSX-550 Superscan scanning electron microscope (SEM) coupled with an energy dispersive x-ray spectrometer (EDS). An x-ray diffractometer (Bruker D8 diffractometer, Bruker Corporation of Germany, operating at 40 kV and 40 mA, and using $CuK_\alpha = 1.5406$ Å) with a scan step of 0.02° in 2θ and a scan speed of 4°/min, was employed for the analysis of crystalline phases. The divergence slit (DS), scatter slit (SS) and receiving slit (RS) were 1°, 1° and 0.15 mm, respectively.

2.2.2. Photoluminescence (PL) and thermoluminescence (TL) measurements

The photoluminescence (PL) measurements were done at room temperature on a Cary Eclipse fluorescence spectrophotometer (Model: LS 55) with a built-in 150 W xenon lamp as the excitation source. Each sample was loaded into a circular holder and excited with 340 nm radiation.

The TL glow curves of the $BaAl_2O_4:Eu^{2+},Dy^{3+}$ phosphors were recorded using a PC based Thermoluminescence Reader system (TL 1009I) with PMT type 9924 supplied by M/s Nucleonix Systems Pvt. Ltd., India. In the thermoluminescence measurements, a UV source kept at a fixed distance of 5 cm above the sample, was used as an excitation source. Samples of mass 30 mg were used in all the measurements. The TL glow curves of the $BaAl_2O_4:Eu^{2+},Dy^{3+}$ phosphors were recorded with a thermoluminescence system with a linear heating rate of 6 °C s^{-1} in the temperature range between 25 and 300 °C. Each time the readout was made twice with the second reading considered to be the background. The background reading was subsequently subtracted from the first read-out. In-reader annealing was carried out at 300 °C for 30 min for all the samples to erase any residual signal.

3. Results and discussion

3.1. Morphology and structural analysis

Fig. 1 shows the SEM micrographs used to study the microstructures of the $BaAl_xO_y:Eu^{2+},Dy^{3+}$ powders. An inspection of the morphology of the as-synthesized powder samples reveal that the phosphor powders are characterized by flakes up to 10 μm diameter. The surface of the powder samples shows voids and pores formed by the escaping gases during the combustion process. The wide particle-size distribution as well as irregular shapes of the particles is probably due to the non-uniform distribution of temperature and mass flow in the combustion wave.

The EDS spectra of the sample with 10:7 $Eu^{2+}:Dy^{3+}$ molar ratio (Fig. 2) shows the expected chemical components in the phosphor. The XRD spectra displayed in Fig. 3 give a clear indication of the formation of particles in the nano range. The spectrum shows the expected hexagonal crystalline phase for the nanopowders. The main diffraction peaks index well with the card file (JCPDS: 17-0306) in agreement with other reports [13,14]. Values between 30 and 40 nm were obtained from crystallite size estimation based on the Scherrer analysis.

3.2. Photoluminescence analysis

Fig. 4 is a display of the excitation spectra while the emission spectra are shown in Fig. 5. The photoluminescence spectra exhibit different shapes and broadband peaks. It is known that different host structures and crystallographic distortions will influence the crystal field environment of rare earth ions in the host structure [15]. Since the crystal field splitting varies considerably depending upon the host material, the spectral position

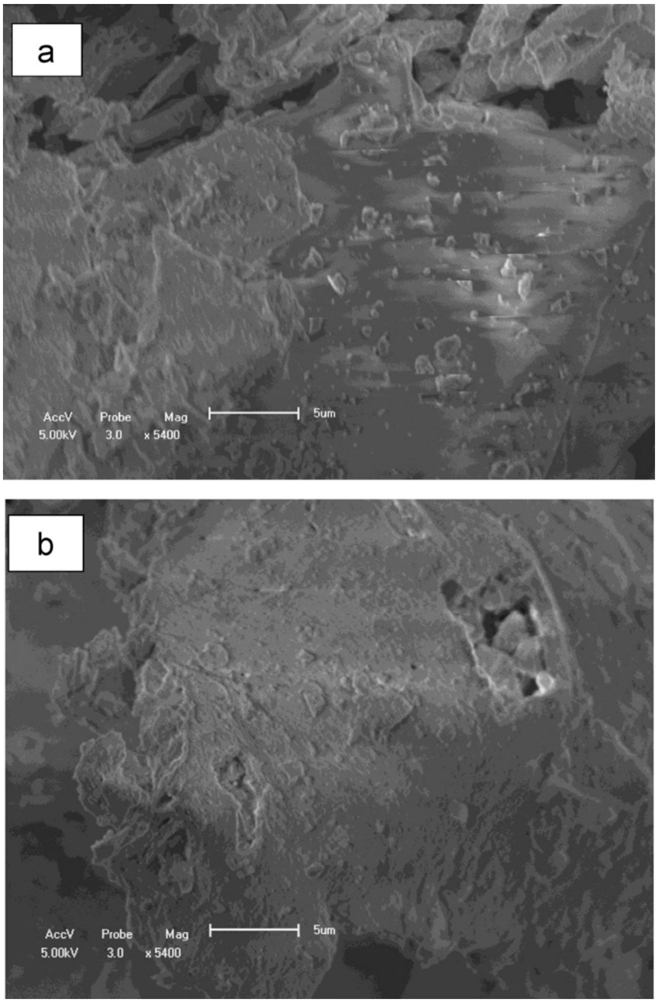

Fig. 1. (a) 5400 × magnification, SEM micrographs of as-synthesized $BaAl_xO_y:Eu^{2+},Dy^{3+}$ with $Eu^{2+}:Dy^{3+}$ ratio = 1:2. (b) [10,000 × magnification] 0% CH_4N_2O.

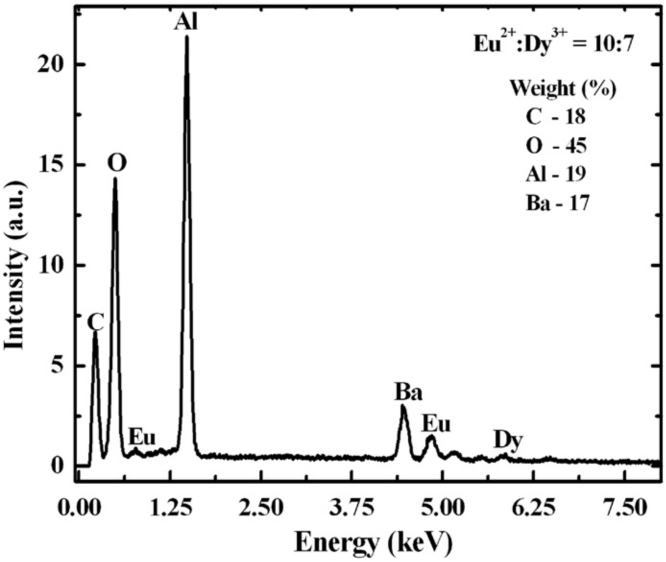

Fig. 2. EDS spot analysis results for the $BaAl_xO_y:Eu^{2+},Dy^{3+}$ powder sample with 10:7 $Eu^{2+}:Dy^{3+}$ molar ratio.