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Combustion synthesis, characterization and luminescence properties of barium aluminate phosphor

A.H. Wako[1,*], F.B Dejene[1], H.C Swart[2]

(1. Department of Physics, University of the Free State (Qwaqwa Campus), Private Bag X13, Phuthaditjhaba 9866, South Africa; 2. Department of Physics, University of the Free State, P.O. Box 339, Bloemfontein 9300, South Africa)

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Abstract: The blue-green emitting Eu^{2+} and Nd^{3+} doped polycrystalline barium aluminate ($BaAl_2O_4:Eu^{2+},Nd^{3+}$) phosphor, was prepared by a solution-combustion method at 500 ºC without a post-annealing process. The characteristic variation in the structural and luminescence properties of the as-prepared samples was evaluated with regards to a change in the Ba/Al molar ratio from 0.1:1 to 1.4:1. The morphologies and the phase structures of the products were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), while the optical properties were investigated using ultra-violet (UV) and photoluminescence (PL) spectroscopy, respectively. The XRD and TEM results revealed that the average crystallite size of the $BaAl_2O_4:Eu^{2+},Nd^{3+}$ phosphor was about 70 nm. The broad-band UV-excited luminescence of the phosphors was observed at λ_{max}=500 nm due to transitions from the $4f^65d^1$ to the $4f^7$ configuration of the Eu^{2+} ion. The PL results indicated that the main peaks in the emission and excitation spectrum of phosphor particles slightly shifted to the short wavelength due to the changes in the crystal field due to the structure changes caused by the variation in the quantity of the Ba ions in the host lattice.

Keywords: $BaAl_2O_4:Eu^{2+},Nd^{3+}$; persistence luminescence; Eu^{2+} and Nd^{3+} doping; rare earths

Rare earth doped aluminates form a group of luminescence materials which exhibit high stability, brightness, and versatile industrial processing characteristics suitable for manufacture of lighting and display devices[1,2]. They exhibit high quantum efficiency in the visible region[3]. The Eu^{2+} doped solid state materials usually show strong broad band luminescence with a short decay time of the order of some tens of nanoseconds[4]. The very short decay time and strong intensity of the luminescence arise from the allowed states of the electronic transitions both in the excitation and emission. The luminescence is very strongly affected by changes in the structure of the host and can range from the ultraviolet to the red region of the electromagnetic spectrum. The high intensity emission of Eu^{2+} finds important industrial applications in, for example, the tricolour low pressure mercury fluorescence lamps. The discovery of the plasma display panel (PDP) and light-emitting diode (LED) has contributed significantly to comprehensive studies for large-scale flat panel display and lighting devices[5]. Plasma display panels (PDPs), are gaining considerable popularity because of its obvious merits, such as a fast response, a wide viewing angle, large screen, low energy consumption and high scalability[6].

Eu^{2+} and Nd^{3+}-doped alkaline earth aluminate phosphors exhibit afterglow which is visible to the naked eye for longer duration after exposure to a fluorescent light or sunlight. The synthesis of oxide phosphors has been achieved by a variety of methods. The solution-combustion process is very simple, safe, energy saving and takes only a few minutes. The technique makes use of the heat energy from the redox exothermic reaction at a relatively low igniting temperature between metal nitrates and urea as fuel. In the present work, $BaAl_2O_4:Eu^{2+},Nd^{3+}$ materials were prepared with different Ba/Al molar ratios and constant Eu^{2+} and Nd^{3+} concentrations. The effects of this on the stability, homogeneity and structure as well as persistence luminescence were presented and discussed based on the analyses of the X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) imaging as well as photoluminescence spectroscopy (PL) studies.

1 Experimental

1.1 Synthesis

$BaAl_2O_4:Eu^{2+},Nd^{3+}$ phosphors were synthesized using the solution-combustion method under atmospheric pressure without any post treatment. The starting raw materials used in the experiment included various proportions of analytical pure grade $Ba(NO_3)_2$, $Al(NO_3)_3\cdot9H_2O$, $Eu(NO_3)_3\cdot5H_2O$, $Nd(NO_3)_3$, and urea

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* **Corresponding author:** A.H. Wako (**E-mail:** wakoah@qwa.ufs.ac.za; **Tel.:** +27-51-4012926)

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$(CO(NH_2)_2)$. No flux was added. The precursors were prepared with different Ba/Al molar ratios of 0.1:1, 0.4:1, 0.7:1 and 1.4:1, respectively. The doping concentrations of both Eu^{2+} and Nd^{3+} were kept constant at 0.2 mol.%. A minimum amount of distilled water together with excess amount of urea was added and then thoroughly mixed at room temperature using a magnetic stirrer for 15 min without heating to obtain uniform aqueous solutions. The solutions were introduced into a muffle furnace previously maintained at 500 °C. Dehydration occurred as the solution boiled and decomposed letting off large amounts of gases (CO_2, NO_2 and NH_4). The mixture then frothed and swelled enormously into foam. Spontaneous ignition and smouldering occurred which gradually led to an explosion rupturing the foam with a flame that glows to incandescence producing white foamy and voluminous $BaAl_2O_4:Eu^{2+},Nd^{3+}$. The foam was taken out of the muffle furnace, cooled then milled resulting in a dry, usually crystalline, fine white oxide powders of $BaAl_2O_4:Eu^{2+},Nd^{3+}$. The whole combustion process took about 5 min. The powders were stored in glass sample bottles for characterization.

1.2 Characterization

The structure and phase purity of the phosphor samples was checked with a Bruker-AXS D8 Advance X-ray diffractometer (Bruker Corporation of Germany) operating at 40 kV and 4 mA using Cu Kα=0.15406 nm. The morphologies of the phosphor powders were obtained by using a Shimadzu Superscan SSX-550 SEM coupled with an energy dispersive X-ray spectrometer (EDS) for elemental composition. For analysis of molecular bonding, binding energy, chemical and valence state of the samples, XPS was done using a PHI 5000 Versa probe — scanning XPS microprobe. Absorption spectra were recorded using a Perkin Elmer Scan-Lambda 950 UV-Vis spectrophotometer. The PL excitation and emission spectra were measured at room temperature using a Cary Eclipse luminescence spectrometer (model LS-55) with a built-in 150 W xenon flash lamp as the excitation source and a grating to select a suitable excitation wavelength.

2 Results and discussion

2.1 XRD analysis

Fig. 1 shows the XRD pattern of different phases of $BaAl_2O_4$ along with the (hkl) values for the various peaks recorded from the $BaAl_2O_4:Eu^{2+},Nd^{3+}$ samples with varying Ba/Al concentrations. Non-stoichiometric Ba/Al molar ratio were selected in order to investigate how the different phases formed by a shortage or excess of Ba ions as compared to Al ions would affect the luminescence properties of the phosphors. The results of X-ray phase analysis of the as-prepared powders at 500 ºC revealed that several crystalline phases are formed depending on the ratio of these main components of the host[7]. The patterns could separately be indexed to the various hexagonal systems of the $BaAl_2O_4$ and the lattice parameters were in agreement with the JCPDS data 072-0387 and 075-0707. It is observed that the peaks for hexagonal $BaAl_2O_4$ with space group $P6_322$ began to appear distinctly producing the highest intensity for samples with Ba/Al molar ratio of 0.7:1. Impurity phases including Eu_2O_3, Ba_3Al_5, and Ba_7Al_{10} could be identified. These impurities are attributed to the unreacted reagents that could be present in the as-prepared phosphor. Line broadening features are characteristics of samples exhibiting smaller particle size, indicating that the phosphor nanocrystallines can be prepared in a far low temperature (about 500 °C). It is well known that broadening occurs in the diffraction rings as the particle size of the powders

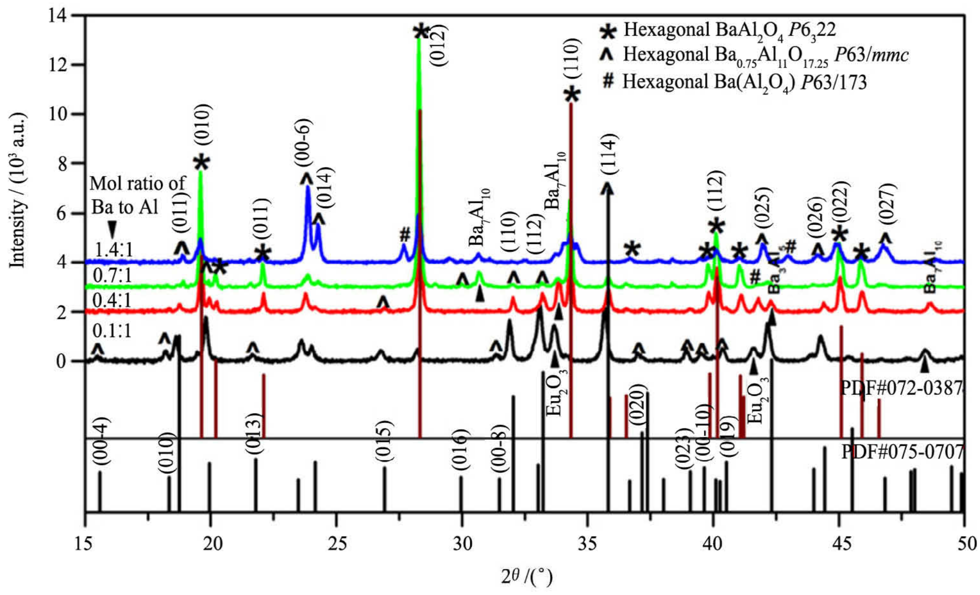

Fig. 1 Effect of varying Ba:Al molar ratios on the XRD structure of the $BaAl_2O_4:Eu^{2+},Nd^{3+}$ phosphor as compared with JCPDS #72-0387 and 075-0707 of hexagonal $BaAl_2O_4$