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Luminescence Properties of $BaAl_2O_4:Eu^{2+}$ Phosphors

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Abstract - *$BaAl_2O_4$ phosphors activated by Eu^{2+} have been synthesized by a combustion method using urea as a fuel at a temperature of 600°C. Photoluminescence (PL) and thermoluminescence (TL) properties of UV-irradiated Eu^{2+}-activated barium aluminate were investigated. The PL spectrum shows one strong peak at 493 nm under 363 nm excitation. The observed emission peak at 493 nm attributed to transition $4f^6 5d^1 \rightarrow 4f^7$ of Eu^{2+}. Thermoluminescence (TL) studies were performed for different concentrations of Eu. Optimum intensity of photoluminescence was found for 0.05 mol% concentration of Eu. It was found that initially the peak TL intensity increases with increasing concentration of Eu^{2+} in the $BaAl_2O_4$ host, attains a maximum value for 0.02 mol% concentration and decreases with further increase in the doping concentration due to concentration quenching.*

Key Words: Luminescence Properties, Photoluminescence (PL), Thermoluminescence (TL), Combustion technique.

1. INTRODUCTION

The alkaline earth aluminates MAl_2O_4 are an important class of phosphorescence materials because of their high quantum efficiency in visible region [1], long persistence of phosphorescence, good stability, color purity and good chemical, thermal and radiation resistance [2-3]. Rare earth and non-rare earth inorganic phosphors are widely used in a variety of applications, such as light industry, radiation measurement, X-ray imaging technique and colour display [4]. Several aluminates are used as host for doping rare earth ions in luminescent applications. The luminescence in the visible region of Eu^{2+} doped alkaline earth aluminates $MAl_2O_4:Eu^{2+}$ (M = Ca, Ba, Sr) phosphor has found interest in recent years owing to their safe, chemically stable and very bright photoluminescence properties and several researchers have made extensive investigations concerning the next generation of displays and lighting devices [5–7]. The rare earth metal ion-doped calcium aluminate phosphors, because of their high quantum efficiency, anomalous long phosphorescence and good stability, have been studied in depth and used widely. In particular $BaAl_2O_4:Eu^{2+},Nd^{3+}$ has been considered as a useful violet phosphor in the application of luminous clocks and watches as well as potential outdoor night time displays [8]. Aluminates of Ca, Ba and Sr doped with Eu^{2+} activator ion possess safer, chemically stable and intense photoluminescence in visible light [9, 10] compared with the conventional sulfide-based phosphors. These properties make them useful in many applications, such as luminous paints in highway, airport, buildings and ceramic products, in textile, dial plate of glow watch, warning signs and the escape routes [11].

Recently many studies on phosphors with barium aluminate as a host based on their persistent luminescence and photoconductivity spectrum have been reported [12]. Many phosphors such as $CaAl_2O_4:Eu^{2+}$, Dy^{3+} [13] and $CaAl_2O_4$: Ce^{3+} [14] were developed for their photoluminescence and high chemical stability. Thermoluminescent materials are used as passive dosimeters in a wide range of radiological applications. Alkaline earth aluminate ceramics are important host materials that have been prepared and studied by several researchers for luminescence applications. Several reports dealing with the luminescence studies of $SrAl_2O_4$, $BaAl_2O_4$ and $MgAl_2O_4$ are available in the literature [15, 16]. However, there are very few researchers who reported $CaAl_2O_4$ as a TL material. In the present work, we report the thermoluminescence (TL) and photoluminescence (PL) properties of UV irradiated ($BaAl_2O_4:Eu^{2+}$) phosphor to find out its suitability in dosimetry applications. In this paper, a facile combustion process was chosen to prepare Eu^{2+}-doped $BaAl_2O_4$ phosphor. Thermoluminescence (TL) and photoluminescence (PL) properties of Eu^{2+}-doped $BaAl_2O_4$ phosphor have been investigated.

2. EXPERIMENTAL

In figure (1) the flow chart for a quick material screening and material elaboration illustrated. Analytical grade barium nitrate Ba $(NO_3)_2$, aluminum nitrate Al $(NO_3)_3.9H_2O$, Europium oxide Eu_2O_3 and urea CO $(NH_2)_2$ were used as the staring materials. According to the stoichiometry the starting materials were weighted. First of all Eu_2O_3 was converted into Eu $(NO_3)_3$ by mixing Eu_2O_3 into 2 ml of dil. HNO_3. Then weighed quantities of each nitrate and urea were mixed together and crushed into mortar for 1 hour to form a thick paste. The resulting paste was transferred to crucible and introduced into a vertical cylindrical muffle furnace maintained at 600°C initiating temperature. Initially the mixture boils and undergoes dehydration followed by decomposition with the evolution of large amount of gases (oxides of carbon, nitrogen and ammonia). The process being highly exothermic continues and the spontaneous ignition occurs. The solution underwent smoldering combustion with enormous swelling, producing white foamy and voluminous ash. The foamy product can easily be milled to obtain the precursor powder.

Flow chart

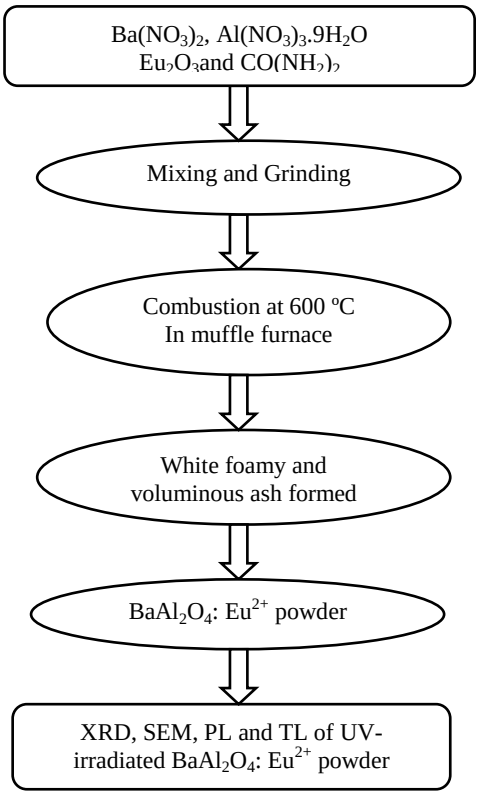

Fig. 1: Flowchart for the preparation and characterization of $BaAl_2O_4$: Eu^{2+} phosphor

The crystalline structure of the synthesized samples was investigated by X-ray diffraction analysis (XRD model D2 PHASER, Bruker AXS) using Cu/Kα radiation (λ = 1.54060Å). Data have been collected by step scanning 2θ from 10° to 80° and 9.6 s swept time at each step at room temperature. In order to study the surface morphology of phosphor scanning electron micrograph (SEM) was taken on a JOEL-JSM-6390A analytical scanning electron microscopy. Photoluminescence (PL) was recorded using fluorescence spectrophotometer (Shimadzu RF-5301 XPC). For thermoluminescence (TL) measurement, samples were irradiated with UV radiation by ultra violet lamp operating at 230 V – 50 Hz (emitting 365 nm) for different time of interval. A routine TL setup (Nucleonix TL 1009I) was used for recording TL glow curve. Absorption spectrum was recorded using Shimadzu UV-1700 UV- visible spectrophotometer. For the measurement of TL spectra of sample interference filters of different wavelength were used.

3. RESULTS AND DISCUSSIONS

3.1 X-ray diffraction analysis

The XRD pattern of the prepared $BaAl_2O_4$:Eu^{2+} synthesized by solution combustion process at initiating temperature of 600°C is shown in fig. 2. All the diffraction peaks in figure 2 are in good agreement to the pure hexagonal phase structure of $BaAl_2O_4$ phosphors. Calculated lattice parameters are: a = 8.700, b = 8.0920, c = 15.19100 and β = 90.170. The XRD pattern matched well with that reported for $BaAl_2O_4$ (JCPDS File No. 00-73-0202). Furthermore, a small amount of doped rare earth ions has almost no effect on $BaAl_2O_4$ phase composition.

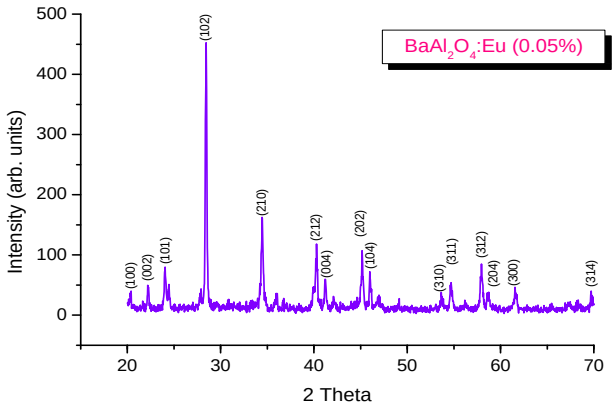

Fig. 2: X-ray diffraction (XRD) pattern of $CaAl_2O_4$:Eu^{2+} (0.05 mol %) phosphor.

3.2 Surface Morphology

To investigate the surface morphology of synthesized phosphor SEM study was carried out. Figure (3) shows the SEM micrograph of the sample reflects the foamy and agglomerate particle nature of the powder. The foamy structure of hexagonal $BaAl_2O_4$: Eu^{2+} reflects the inherent nature of the reaction. Urea enhances combustion and this process results in crystal facets growing in different directions. The surface of the powder shows lots of voids and pores, which may be formed by the evolved gases during combustion. The non-uniform and irregular shapes of the particle can be attributed to the non-uniform distribution of temperature and mass flow in the combustion flame.

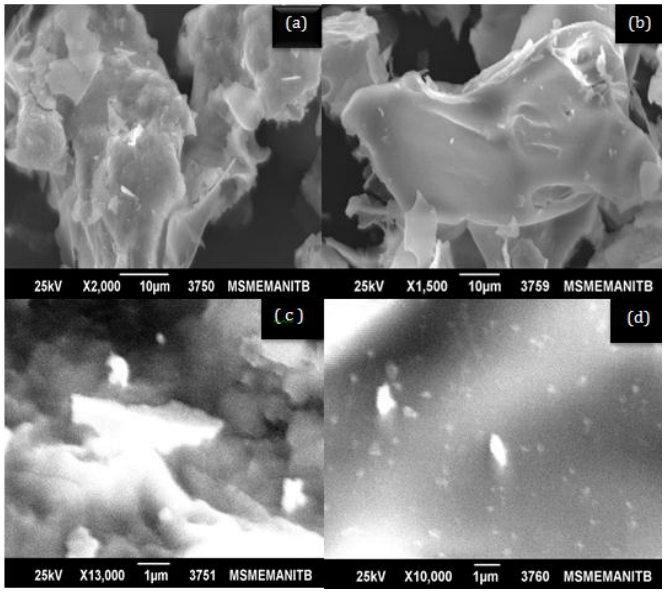

Fig. 3: SEM photograph of BaAl2O4: Eu2+ (0.05 mol %) phosphor.

3.3 Photoluminescence (PL) Studies

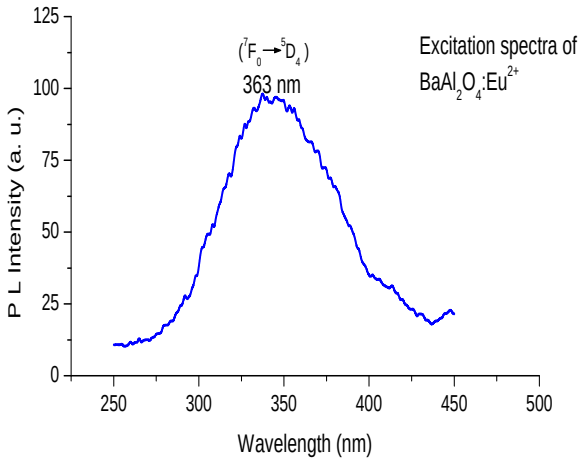

Fig. 4(a): Excitation spectra of $BaAl_2O_4:Eu^{2+}$ phosphor with 363 nm excitation

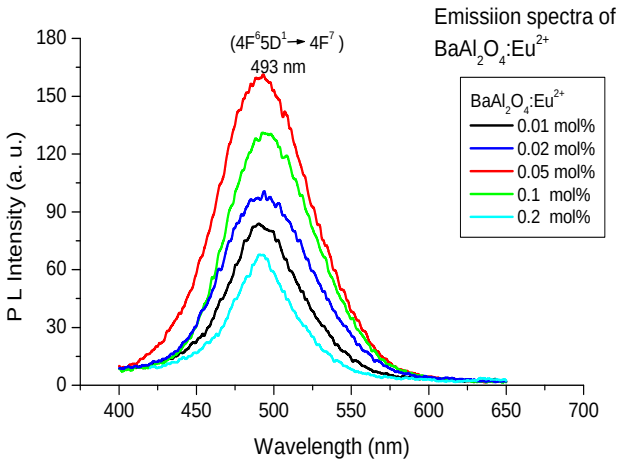

Fig. 4(b): Emission spectra of $BaAl_2O_4:Eu^{2+}$ phosphor for different doping concentration

Fig. 4(a) shows the excitation spectra of $BaAl_2O_4$: Eu^{2+} phosphor. In excitation spectra a broad peak centered at 363 nm is observed which attributed to transition $^7F_0 \rightarrow {}^5D_4$. Figure 4(b) shows the photoluminescence emission spectra of $BaAl_2O_4$: Eu^{2+} (0.01, 0.02, 0.05, 0.1 and 0.2 mol %) phosphors. The emission spectra of $BaAl_2O_4$: Eu^{2+} phosphor show one strong peak at 493 nm under 363 nm excitation. The observed emission peak at 493 nm is due to the transition of Eu^{2+} from excited state of $4f^65d^1$ configuration to the ground state $^8S_{7/2}$ of $4f^7$ configuration. Optimum intensity of photoluminescence was found for 0.05 mol% concentration of Eu^{2+}.

3.4 Thermoluminescence (TL) Studies

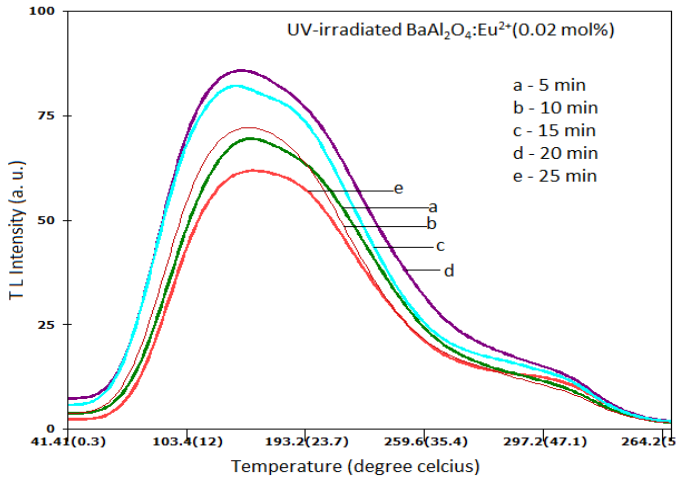

Fig. 5(a) TL glow curve of $BaAl_2O_4:Eu^{2+}$ (0.02 mol %) phosphor for different UV exposure time

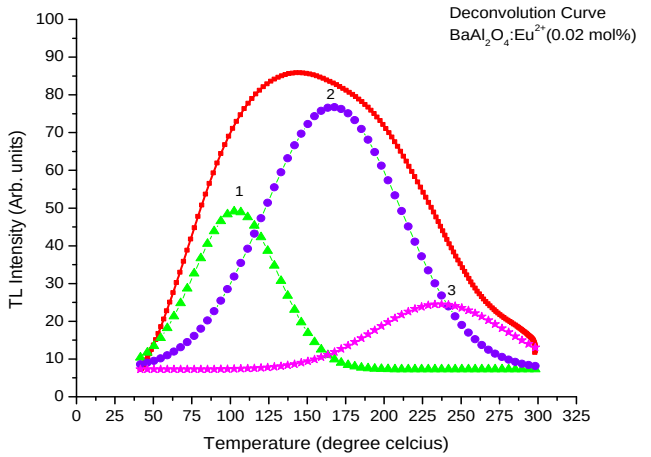

Fig 5(b): Deconvolution curve of $BaAl_2O_4:Eu^{2+}$ (0.02 mol %) phosphor for 20 min UV exposure time

Fig. 5(a) shows comparative study of the TL glow curve of $BaAl_2O_4:Eu^{2+}$ (0.02mol %) phosphor as a function of UV exposure time. It is seen that the TL glow curves have a principal broad peak centered at 145.6°C for 20 min exposure time and the TL intensity decreases with increasing exposure time. For study of TL parameters deconvoluted curve shown in Fig. 5(b). TL glow curve consists of three peaks around 103.66°C, 166.66°C and 236.28°C.

Fig (6) shows the variation in peak TL intensity as a function of Eu concentration in $BaAl_2O_4$ host lattice. All solids contain imperfections in the form of impurities and intrinsic defects. Upon excitation of suitable radiation these imperfections capture electrons/holes whose radiative recombination can be studied by the technique of Thermoluminescence (TL). Each TL peak is associated with certain trapping levels

whose intrinsic parameters may be retrieved by analyzing the TL data. Fig (6) shows the variation in peak TL intensity as a function of Eu concentration in $BaAl_2O_4$ host lattice. It is clear that Peak TL intensity increases with increasing the concentration of activator (Eu) and attains a maximum value for 0.02 mol% concentration of Eu and decreases for higher concentrations of Eu. The drop in Peak TL intensity for higher doping concentration of Eu can be explained by the fact that the trapping probability is reduced if the density of the activator ion is increased due to the statistical reduced spatial distance between the activator ions and the excitons formed after band absorption.

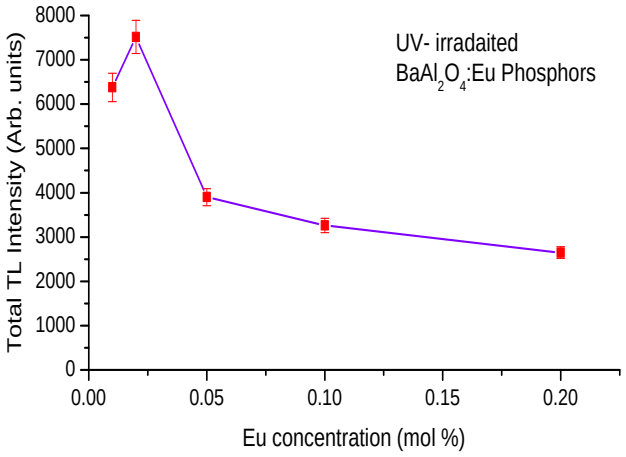

Fig. 6: Concentration Vs total TL intensity curve of $BaAl_2O_4:Eu^{2+}$ phosphor for UV-dose

Fig (7) shows the TL emission spectra of $BaAl_2O_4$: Eu^{2+} (0.02mol %) phosphor. TL emission spectra have two peaks around 440 nm and 520 nm which are in accordance with PL spectra. The peak at 440 nm and 520 nm is attributed to $4f^6 5d^1 \rightarrow 4f^7$ transition of Eu^{2+} ion [16]. The similarity in TL and PL spectra reveals that the same luminescence centre may be responsible for both.

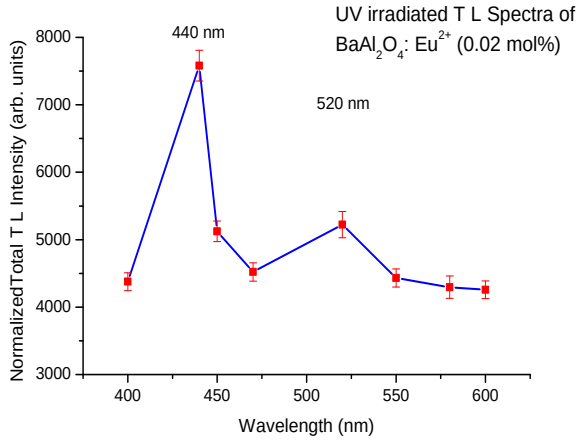

Fig. 7: TL spectra of $BaAl_2O_4:Eu^{2+}$ (0.02 mol %) phosphor

3.5 Calculation of TL kinetics parameters:

Table 1: TL kinetics parameter as calculated by Chen's formula

Shape factor(μ_g), activation energy (E) and frequency factor (s^{-1}) for UV-irradiated $BaAl_2O_4$: Eu^{2+} (0.02 mol %) phosphor

Peak number	τ	δ	ω	Shape Factor μ_g =δ/ω	Activation Energy E (eV)	Frequency factor S
Peak 1	23	16.34	40	0.63	0.41	2.02×10^8
Peak 2	41.66	44.34	86	0.36	0.52	6.3×10^{14}
Peak 3	32.75	33.19	65.94	0.5	1.14	1.5×10^{10}

The TL parameters can be determine by most popular Chen's method [17] in which the shape or geometrical properties of the peak is considered for determining the kinetic parameters. If the temperature corresponding to maximum TL intensity is Tm and T1 and T2 are the temperatures on either side of Tm corresponding to half intensity, τ (= Tm-T1) is the half width at the low temperature side of the peak, δ (= T2-Tm) is the half width toward the fall off side of the glow peak, ω (= T2-T1) is the total half width then the geometrical shape or symmetry factor is defined as μ = δ/ω (μ = 0.42 for first order and 0.52 for second order) and the general relation for activation energy given by Chen is

$$E\alpha = C\alpha\,[kT2m/\alpha] - b\alpha\,(2kTm) \quad \ldots (1)$$

The frequency factor is given by the relation

$$s = \frac{\beta E}{kT_m^{\,2}}\, exp\left(\frac{E}{kT_m}\right)[1+ (b\text{-}1)2kT_m/E]^{-1} \quad \ldots (2)$$

Where, β is the heating rate.

The kinetic parameters calculated by Chen method is given in table 1. For the calculation of various TL parameters such as shape factor, activation energy, frequency factor etc. we choose deconvoluted curve fig 5(b). The order of kinetics is determined by the symmetry factor μ, Chen proposed that one should also consider the shift in location of maximum TL intensity for determination of symmetry factor. For first order kinetics there is no shift in the location of maximum TL intensity for different dose value, but for non-first order TL glow peak the maximum TL intensity tends to shift towards higher temperature for smaller dose. This shift may also be resulted owing to presence of smaller satellite peaks. The glow curve for smaller dose consists of mainly two peaks for smaller dose but it converges to single peak when TL intensity becomes large.

4. CONCLUSIONS

$BaAl_2O_4:Eu^{2+}$ phosphors were successfully synthesized by a combustion method; Thermoluminescence (TL) and Photoluminescence (PL) of $BaAl_2O_4:Eu^{2+}$ were studied. The XRD pattern of synthesized $BaAl_2O_4:Eu^{2+}$ phosphor matched

well with standard data. The observed emission spectra of $BaAl_2O_4:Eu^{2+}$ phosphor shows one strong peak at 493 nm under 363 nm excitation. The observed emission peak at 493 nm is due to the transition of Eu^{2+} from excited state of $4f^65d^1$ configuration to the ground state $^8S_{7/2}$ of $4f^7$configuration. PL intensity is optimum for 0.05 mol% concentration of Eu. A TL spectrum was observed around 440 nm. TL intensity is optimum for 0.02 mol% concentration of Eu^{2+}.

We observed that thermoluminescence (TL) intensity depends on the concentration of RE impurity comprises with the host materials. It is seen that initially, TL intensity increases with increasing the activator concentration accomplish a maximum value for a particular concentration and then decreases with further increase in the activator concentration. With increase in the concentration of RE ions, more luminescence centres can be generated and hence the thermoluminescence (TL) intensity is increased. Although, the TL glow peak intensity cannot be expected to increase indefinitely with dopant concentration, because the rate of formation of active centres by occupying the holes during irradiation may be fading suddenly and concentration quenching is occurred.

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