

Enhancement of phosphorescence of BaAl₁₂O₁₉:Eu phosphor due to Dy, Nd co-activators

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This paper reports the preparation of BaAl₁₂O₁₉:Eu²⁺ and BaAl₁₂O₁₉:Eu²⁺, (RE=Dy³⁺, Nd³⁺) phosphors synthesized by a combustion method. The samples were characterized by X-ray powder diffraction, photoluminescence (PL) and phosphorescence decay curve. The PL spectra was recorded when the powders were excited by UV light at room temperature showed broad blue emission, this emission can be ascribed to 4f⁶5d¹ to 4f⁷ transition of the Eu²⁺ ions. More ever, small shift in wavelength was observed between the doped and co-doped phosphors. The phosphorescence characteristic was studied using the decay curves. The effect of Dy³⁺ and Nd³⁺ doping on enhancing the photoluminescence intensity and phosphorescence decay curve of BaAl₁₂O₁₉:Eu²⁺ is discussed.

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1. Introduction

Divalent europium is the most significant one of rare-earth ions widely investigated and applied in the field of long-lasting phosphorescence (LLP) materials [1]. Eu²⁺ is an important activator for luminescent materials. The luminescence of Eu²⁺ activated phosphors usually results from the ground 4f⁷ levels to the excited 4f⁶5d configuration. Since the 4f–5d transitions are electric-dipole allowed, the absorption and emission of Eu²⁺ are characterized as very efficient broad bands in many hosts [2]. Moreover, it is well known that the 5d wave function has a large spatial extension; its transition line is usually broadened, and it depends on the surroundings of the Eu²⁺ ions. Thus, the different crystal-lattice environment is a critical parameter for determining the optical properties of the Eu²⁺ ions [3]. Eu²⁺-doped BaAl₂O₄ emits green light [4], Eu²⁺-doped BaAl₁₂O₁₉ excited by ultraviolet light shows a very wide emission band from blue to green light region [5], and so on. Smets and Kutty et al. [6,7] have pointed out that BaAl₁₂O₁₉ matrix not only provides a site to Eu²⁺ ions, which the blue emission originates from Eu²⁺ ions on Ba²⁺ sites in mirror plane, but that the green emission is caused by the presence of aluminium vacancies. The mechanism is considered to include the photoionization of the Eu²⁺ ion and a subsequent transfer of the electrons to traps formed by the lattice defects as oxide ion vacancies and possibly also the auxiliary RE³⁺ ion co-dopants. The thermal bleaching of the electrons from the traps followed by the process reverse to the storage of the excitation energy leads to the Eu²⁺ emission [8]. This paper reports the preparation of Eu doped and Dy/Nd co-doped BaAl₁₂O₁₉ by combustion method. Photoluminescence (PL) and decay time measurements were carried out. Powder XRD measurement were performed to investigate the phase and crystallinity of the

material. The phosphorescent behavior of the phosphor is discussed based on the evaluation of decay characteristics.

2. Experimental

The phosphor BaAl₁₂O₁₉:Eu²⁺ and BaAl₁₂O₁₉:Eu²⁺, (RE=Dy³⁺, Nd³⁺) with varying concentration of Eu, Nd and Dy was prepared by the combustion method. All the starting materials employed in the experiment are of Merck-analytical grade. The starting materials are Ba(NO₃)₂, Al(NO₃)₃ .9H₂O, Eu₂O₃, Dy₂O₃, Nd₂O₃ and Urea (NH₂CONH₂, Merck) was used as fuel. Dy₂O₃, Nd₂O₃ and Eu₂O₃ are converted in to nitrate form by mixing of appropriate amount of dilute nitric acid. All the mixtures were mixed according to stoichiometric ratio. For these stoichiometric compositions of the metal nitrates as oxidizers and urea (fuel) were calculated using the total oxidizing and reducing valencies of the components, which serve as a numerical coefficient so that the equivalence ratio is unity and the heat liberated during combustion is at a maximum. Weighted quantities of each nitrates and urea are added to it and the mixture is crushed together for ½ hour to form a thick paste. The resulting paste is transferred into a vertical furnace maintained at 550 °C. The process being highly exothermic continues and the liberated gases swell the mixture into large volume. Large exothermicity results into a flame changing the mixture into gaseous phase. Flame temperature as high at 1600 °C converts the vapour phase into mixed aluminates. The paste melted, underwent dehydration, and finally decomposed with the evolution of gases (oxides of nitrogen and ammonia). The mixture frothed and swelled, forming a foam that ruptured with a flame. The combustion process was completed in less than 5 min. The flame persists for about 30 seconds final product obtained is in the fluffy form, which is used for the further

investigations. Some corresponding methods were used to characterize the prepared phosphor. The prepared host lattice was characterized for their phase purity and crystallinity by X-ray powder diffraction (XRD) using PAN-analytical diffractometer (Cu-K α radiation) at a scanning step of 0.010, continue time 20s, in the 2θ range from 10^0 to 80^0 ; the average crystallite size was calculated from the broadening of the X-ray line (311) using Scherer's equation. The photoluminescence measurement of excitation and emission were recorded on the Shimadzu RFPC5301 Spectrofluorophotometer. The same amount of sample 2 gm was used for each measurement. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm.

3. Result and discussion

3.1. XRD phase analysis

In order to explore the crystal phase structure, the XRD phase analysis was adopted. The typical XRD patterns of BaAl₁₂O₁₉ phosphor are shown in Fig. 1 is well matched with standard JCPDS file no 026-0135. The small amount of doped rare earth ions has virtually no effect on phase structures.

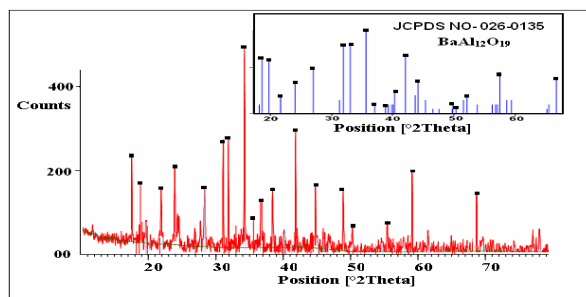


Fig. 1. XRD of BaAl₁₂O₁₉ host.

3.2. Photo-luminescence and phosphorescence properties of BaAl₁₂O₁₉:Eu²⁺

Photoluminescence studies were carried out on the prepared phosphor compositions. All the phosphor compositions exhibit blue emission when excited by UV light. The appearance of blue emission indicates that the matrix retain the parent phosphor host. The activator ion Eu is in divalent Eu²⁺, blue emission state. Fig. 2 and 3 shows the excitation and emission spectra of BaAl₁₂O₁₉:Eu²⁺. At room temperature, both the emission and excitation are broad bands. The excitation spectra shows a broad band from 270 to 400 nm corresponding to the crystal field splitting of the Eu²⁺ d-orbital. The emission spectra has a symmetrical broad band centered at 447 nm, which is attributed to the typical 4f⁶5d¹ → 4f⁷ transition of Eu²⁺. This is corresponding to the f-d transition of Eu²⁺. The 5d energy level of Eu²⁺ and the

lower level of 4f state overlap, so the electrons of the 4f state can be excited to the 5d state. The broad luminescence of Eu²⁺ is due to the 4f⁶5d¹ → 4f⁷ transition, which is an allowed electrostatic dipole transition. However, the wavelength of the emission peak is not influenced by the Eu²⁺ concentration. It is known that the emission of Eu²⁺ ion in the crystalline phase generally shows a broad emission band due to 4f⁶5d¹ → 4f⁷ transition. When the phosphor is doped with 1 mole % Eu, the intensity of observed excitation spectra reaches the maximum value. The phosphors exhibit blue emission when excited by UV light. This indicates that the matrix has one of the parent phosphor host. The activator ion Eu is in the divalent (Eu²⁺, blue emission) rather than the trivalent (Eu³⁺, red emission) state.

An important result of our present work is that we have developed obvious blue emission in the BaAl₁₂O₁₉:Eu²⁺ phosphors. The sample was excited at 328 nm and phosphorescence lifetime decay at 447 nm is shown in Fig. 4. The lifetime decay curves have been analyzed by curve fitting and they can be fitted successfully based on the following exponential equation [9].

$$I = A_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$

Where I is phosphorescence intensity; A_0 , A_1 and A_2 are constants, t is time, and τ_1 , τ_2 are luminescent lifetime for exponential components, respectively. The decay curve exhibits an initial growth and then decay, which could be fitted into a bi-exponential. The fitting result indicates that decay times monitored at 447 nm in BaAl₁₂O₁₉:Eu²⁺ phosphor. The two observed phosphorescence decay constants are associated with slow and fast decay components having the value $\tau_1 = 8.38 \mu\text{s}$ and $\tau_2 = 1.93 \mu\text{s}$ respectively. The short excited-state decay time of BaAl₁₂O₁₉:Eu²⁺ can be explained by the fact that the 4f⁶5d¹ → 4f⁷ transition of Eu²⁺ is parity allowed. The phosphorescence from the aluminates is believed to be caused by the 4f-5d transition of the Eu²⁺ ions in the crystals and this behavior is based on the thermal activation of holes from traps followed by the emission of Eu²⁺ [10, 11]. Such electron transitions have been reported to be affected by the electrical environment around the Eu²⁺ ions. Significant and varied values of τ_1 and τ_2 clearly indicate the concentration of shallow and deeper traps. It shows that the sample by combustion method has shorter decay times and so deeper trap density. It is known that the bigger the value of decay time is, the slower the decay speed and the better the afterglow properties are. These parameters further confirm that the decay processes of these phosphors behave in terms of a double exponential decay model. At first it acts on the first exponential, with the decay time extending, the afterglow decay acts on the second exponential.

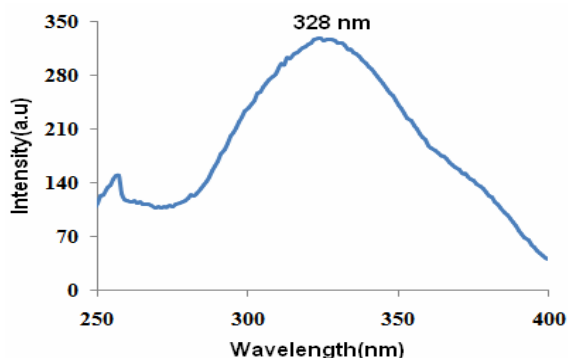


Fig. 2. Excitation spectra of $BaAl_{12}O_{19}:Eu$ under emission 447 nm.

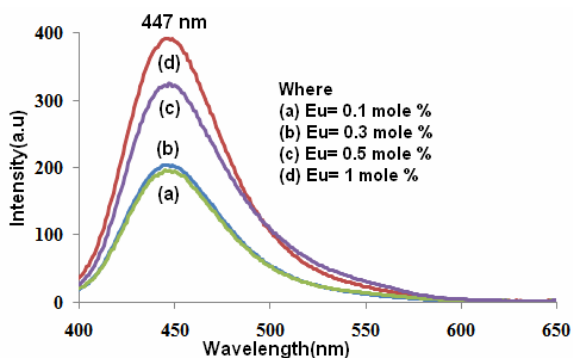


Fig. 3. Emission spectra of $BaAl_{12}O_{19}:Eu$ under excitation 328 nm.

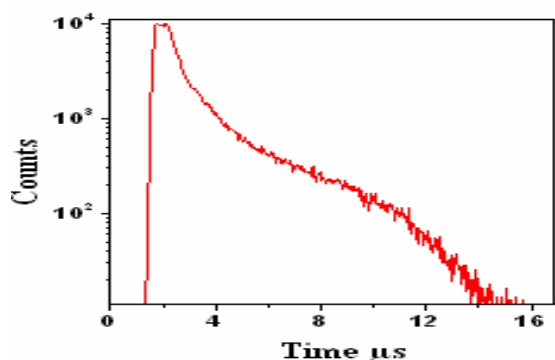


Fig. 4. Phosphorescence decay curve of $BaAl_{12}O_{19}:Eu$.

3.3 Photo-luminescence and phosphorescence properties of $BaAl_{12}O_{19}:Eu^{2+}$, (RE = Dy^{3+} , Nd^{3+})

The excitation and emission spectra of $BaAl_{12}O_{19}:Eu^{2+}$, Dy^{3+} is shown in Fig. 5 and 6. The excitation and emission spectra of $BaAl_{12}O_{19}:Eu^{2+}$, Nd^{3+} is shown in Fig. 7 and 8. These two phosphors showed strong absorption in the UV band and emitted a blue light when they were illuminated by UV light. When Dy^{3+} and Nd^{3+}

are co-doped in the phosphors, the shape of the excitation and emission spectra remains, but the excitation and emission intensity are increased. Both these emissions located at 449 nm (excited at 328 nm), which is attributed to the typical $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} . However, no special emission peaks of Eu^{3+} were observed in Fig. 6 and Fig. 8. This means that Eu^{3+} in the crystal matrix has been completely reduced to Eu^{2+} . The small shift of the emission maximum for the co-doped samples is attributed to changes of crystal field strength around Eu^{2+} ions, when Dy^{3+} and Nd^{3+} ions are also introduced. The outer 5d orbital of the Eu^{2+} can be influenced by the crystal field in a large extent. Therefore the $4f^65d$ energy value can be spread into a continuous band, the emission spectra are shown with a broad band. The result shows that ion Eu is only luminescent centre in the phosphors while ion Dy and Nd does not contribute to luminescence in this work.

The special Dy^{3+} emission peak is not present, which maybe ascribed to the function of the hole or electron traps and energy transporting of Dy^{3+} [12]. The emission intensity of phosphors increases with increasing Dy^{3+} concentration and the maximum intensity approaches at $Dy = 0.5$ mole %, then concentration quenching takes place. Concentration quenching may occur because the excitation energy migrates about a large number of centers before being emitted. In this case, the energy transfer occurs from one activator to another until an energy sink in the lattice is reached. When the Dy ion concentration is over 0.5 mole %, the emission intensity value is decreased and when the Nd ion concentration is over 0.3 mole %, the emission intensity value is decreased, both these concentration quenching is shown in Fig. 9.

With respect to Dy^{3+} and Nd^{3+} it induces the formation of the holes trap levels and can prolong the phosphorescence. There are two sites available for incorporating Dy^{3+} and Nd^{3+} in $BaAl_{12}O_{19}$ lattice are Ba^{2+} sites or Al^{3+} . Ionic radius of Al^{3+} (0.0530 nm) are small. But for Ba^{2+} (0.142 nm) it is comparable in size to Dy^{3+} (0.103 nm) and Nd^{3+} (0.112 nm) [13,14]. Therefore, the Dy^{3+} and Nd^{3+} can occupy the Ba^{2+} sites in the lattices. But the special Dy^{3+} and Nd^{3+} emission peaks are not present, which may be ascribe to that Dy^{3+} and Nd^{3+} worked as the hole traps and produce the phosphorescence.

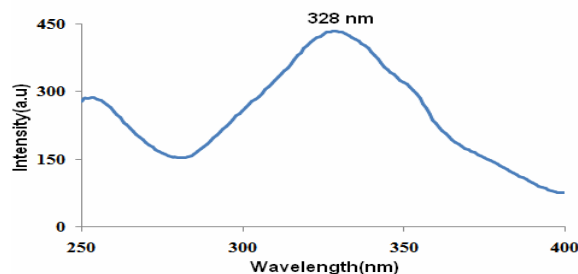


Fig. 5. Excitation spectra of $BaAl_{12}O_{19}:Eu:Dy$ under emission 449 nm.

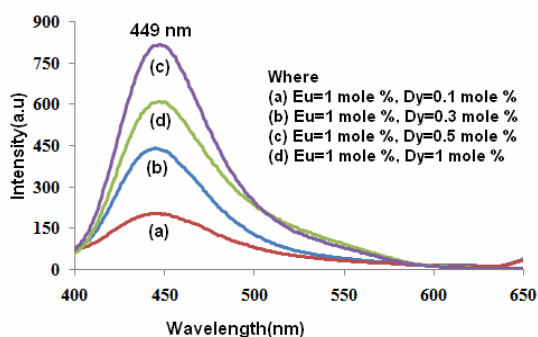


Fig. 6. Emission spectra of BaAl₁₂O₁₉:Eu:Dy under excitation 328 nm.

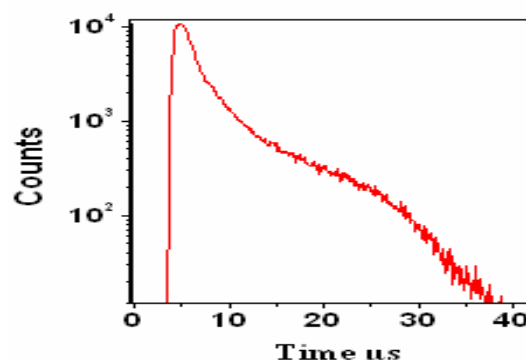


Fig. 10. Phosphorescence decay curve of BaAl₁₂O₁₉:Eu:Dy.

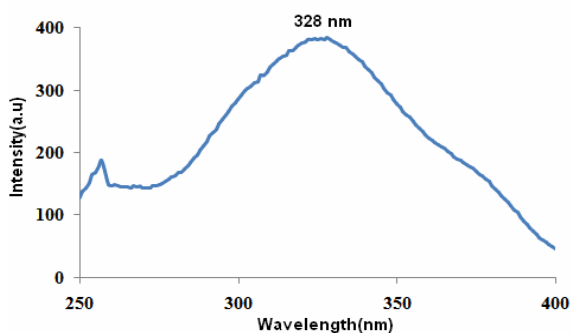


Fig. 7. Excitation spectra of BaAl₁₂O₁₉:Eu:Nd under emission 449 nm.

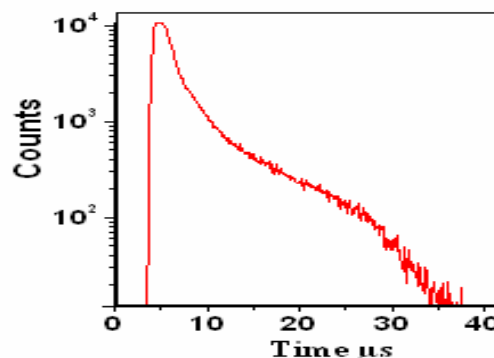


Fig. 11. Phosphorescence decay curve of BaAl₁₂O₁₉:Eu:Nd.

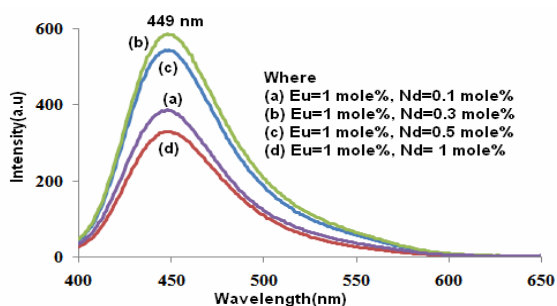


Fig. 8. Emission spectra of BaAl₁₂O₁₉:Eu:Nd under excitation 328 nm.

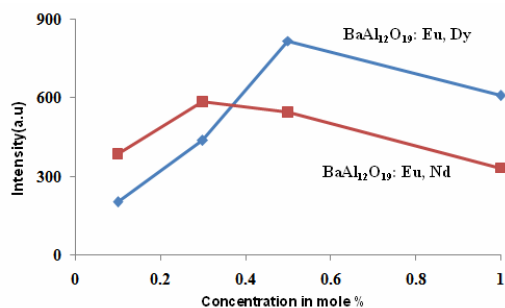


Fig. 9. Concentration quenching of BaAl₁₂O₁₉:Eu, RE (Dy, Nd) phosphors.

The phosphorescent lifetime decay curves of BaAl₁₂O₁₉:Eu²⁺, (RE= Dy³⁺, Nd³⁺) have been analyzed by curve fitting and they can be fitted successfully based on the exponential equation [9].

$$I = A_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$

Where I is phosphorescence intensity; A_0 , A_1 and A_2 are constants, t is time, and τ_1 , τ_2 are luminescent lifetime for exponential components, respectively. The decay curve exhibits an initial growth and then decay, which could be fitted into a bi-exponential. In BaAl₁₂O₁₉:Eu²⁺, Dy³⁺ phosphor we get two observed decay constants having the phosphorescence lifetime of $\tau_1 = 19.55 \mu\text{s}$ and $\tau_2 = 2.53 \mu\text{s}$ respectively as shown in Fig. 10. Also Fig. 11 indicates the phosphorescence lifetime of BaAl₁₂O₁₉:Eu²⁺, Nd³⁺ having lifetime $\tau_1 = 12.35 \mu\text{s}$ and $\tau_2 = 2.17 \mu\text{s}$. It has been observed that there is increase in the phosphorescence lifetime of these doubly doped phosphors when compared with doped phosphors. The enhancement of phosphorescence behavior for this doubly doped phosphor is because of the sensitizer ion Dy³⁺ and Nd³⁺. As already known, the luminescent decay time for the transitions between 4fn→4fn levels is typically in the range of μs to ms. The phosphorescence observed in our phosphors could

be attributed to energy exchange processed between traps and emission states resulting from Eu, Dy and Nd doping. Although the decay process of luminescence is very complicated, it is certain that long decay times can be attributed to traps with different deepness. The Dy³⁺ incorporation creates deep traps in the energy band gap of the host material. These traps are in the form of hole-trapping levels near the valence band. Therefore, when the excitation but not for the Dy³⁺. In fact the Dy³⁺ doping in the phosphor creates the deep trapping levels [15]. It is to be mentioned here that the dysprosium Dy³⁺ ions possess relatively large electron–phonon interactions with the oxide matrices like lead-based glasses for the IR luminescence. It is understood that the sensitizer ion Nd³⁺ acts as traps of holes and the trap levels lie near the valence band. Electron–hole pairs are produced in Eu²⁺ ions when excited by the excitation light source and the Nd³⁺ traps capture some of the free holes moving in the valence band. When the excitation source is cut off, some holes captured by the Nd³⁺ traps are thermally released slowly and relaxed to the excited state of Eu²⁺, finally returning to the ground state of Eu²⁺ accompanied with the emission of light. Mechanism of the long persistence is due to the holes trapped–transported–detrapped process [16–17].

4. Conclusions

In summary, we have observed phosphorescence in all the phosphors. These phosphors might be prepared within several minutes, using the entitled combustion method, leading to reduction in fast synthesis of aluminates. A very broad emission is observed in all the phosphors. The photoluminescence intensity of the BaAl₁₂O₁₉:Eu²⁺ phosphor is increased as the concentration of co-dopant increases in the host matrix. The co-doping of Dy³⁺ and Nd³⁺ ion allows for considerable increase phosphorescence lifetime of the doped Eu²⁺ ions. The Dy³⁺ co-doped BaAl₁₂O₁₉:Eu²⁺ phosphor revealed a excellent phosphorescence characteristic, indicating that a deeper trap center was formed in the phosphor by the doping of trivalent Dy ions. Such phosphorescent phosphor with good chemical stability will find potential application in the field of emergency lighting, safety indication and energy economized materials.

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