Combustion synthesis and spectroscopic properties of Ba$_2$Zn$_7$F$_{18}$:Eu$^{3+}$ phosphor

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Abstract. In the present work, a series of Ba$_2$Zn$_7$F$_{18}$:xmol% Eu$^{3+}$ (x =0.1,0.5,0.7,1.0,1.5) phosphors were synthesized by combustion method. The spectroscopic properties of synthesized phosphor were observed by photoluminescence and photometric characterization technique. The observed excitation spectra revealed two bands around 395nm and 466nm that was attributed to the $^7$F$_0$→$^1$L$_6$, and $^7$F$_0$→$^3$D$_2$, transition of trivalent europium ions, respectively. Under 395nm and 466nm excitation, the PL emission spectra shows several emission bands around at 580nm, 593nm and 613nm, which are ascribed due to $^5$D$_0$→$^7$F$_2$, $^5$D$_0$→$^7$F$_1$, and $^5$D$_0$→$^7$F$_{2}$ transition of Eu$^{3+}$ ions, respectively. The emission band of 613nm indicates the highest emission intensity compared to the other emission bands. The emission band revealed the highest emission intensity at 1mol% concentration of Eu$^{3+}$ ions. Further, a CIE chromaticity diagram was obtained, which is confirmed that red emission. The entire investigation and their outcomes revealed that the synthesized phosphors exhibit strong red emission, which can be applied in the lighting industry and display applications.

Keywords: Combustion method; Photoluminescence; CIE Coordinate

1. Introduction
In the current scenario, rare earth activated luminescent materials have attract more attention due to their advantages and applicability in various fields such as solid-state lighting, display devices, solar cell, TLD badges, fingerprint detection, plant growth, temperature sensor, medical applications, etc [1–4]. White LEDs are novel lighting technology in field of lighting applications. In the last few years, phosphor converted-WLEDs has grown popularity and it is already used commercially in various applications such as traffic lights, outdoor lighting, inside and outside lighting in airplane, vehicles, and transports, etc [5–7]. Due to their popularity, WLEDs will be utilized more broadly in the coming years and will prompt the development of new novel materials for commercial lighting. WLEDs can reduce energy dissipation in the field of lighting. Generally three ways are known for white light generation based on LEDs (i) yellow-emitting phosphor excited by blue-emitting diode (ii) combination of Red, Green and Blue (RGB) LED lights and (iii) By combination of RGB phosphor with near UV LEDs [8,9]. A combination of yellow emitting (YAG: Ce$^{3+}$) phosphors with a blue emission (InGaN) chip is used as commercial WLEDs, but this method faces some drawbacks such as lack of red emission, high correlated color temperature (CCT), and poor color rendering index (CRI), which hinders its
commercialization. Therefore, it should be advocated that researchers and scholars discover some new materials with higher quantum efficiency and thermal stability for LED lighting.

At present, many researchers and scholars are working in the field of luminescence, and have paid more attention to the synthesis and characterization of luminescence materials. Till date, various rare earth activated luminescent materials are investigated such as sulphate, borate, phosphate, tungstate, molybdate, vanadate, fluoride, chloride, aluminate, silicate etc [10]. In the present work, we have synthesized Eu$^{3+}$ doped fluoride phosphors via combustion synthesis route. They have demonstrated their potential in the field of light over the past years. They have gained immense popularity in the research community due to their low cost, easy availability, easy synthesis, high luminescence efficiency, low-phonon energy. They also exhibit excellent luminescence properties such as narrow bands in orange-red emission.

Currently, the combustion synthesis route has become a very popular synthesis approach for the preparation of luminescence materials and is used in about 65 countries. Over the years, this synthesis route has attracted research societies and industrialists due to its attractive features such as easy synthesis route, low-cost method, time saving, without special apparatus. With these benefits, combustion synthesis proves to be the best synthesis route for the industrial production of many inorganic materials. This synthesis can be divided into two phases: (i) self-diffusion high-temperature synthesis (ii) thermal explosion mode. The main disadvantage of this method is uncontrollable over phase and morphology, but in the last years, several luminescent materials have been reported, which are synthesized by the combustion method.

In this work, we have synthesized Eu$^{3+}$ doped Ba$_2$Zn$_7$F$_{18}$ phosphors by combustion method and synthesized materials were characterized by photoluminescence techniques. The PL properties of synthesized materials demonstrate emission of light in the orange-red region. The results demonstrated that red emitting Ba$_2$Zn$_7$F$_{18}$:Eu$^{3+}$ phosphor, which is a promising red emitting phosphor for n-UV excitable w-LEDs.

2. Synthesis

A series of Ba$_{2-x}$Zn$_{7}$F$_{18}$:xmol%Eu$^{3+}$ (x =0.1,0.5,0.7,1.0,1.5) phosphors are synthesized via simple combustion route. During this synthesis urea is used as a fuel. For the preparation of the materials, Ba(NO$_3$)$_2$, N$_2$O$_5$Zn,6H$_2$O, NH$_4$F, Eu$_2$O$_3$ (AR/ACS grade with 99.0% purity) materials are used as starting materials. All the mentioned materials are weighed to stoichiometric ratios using a high sensitive monopan balance. The Oxidizer: Fuel ratio was calculated using propellant chemistry. The weighted amount of europium ions was dissolved in nitric acid, as europium is the form of oxide, and we need it as nitrate for synthesis. Further, all weighed samples were collected in the china dish. Then, all samples mixed together and crushed to form a paste in a mortar pestle. Then again mixture (paste) was transferred into china dish and it was kept in the vertical muffle furnace for firing at 525°C for 10-15min. Due to the exothermic process of combustion, large amounts of heat were released with high amount of gases. After 10 minute the flames become moist and the combustion reaction is complete. The obtained material was cooled to room temperature and ground gently using pestle and mortar. Further, the synthesized powder was calcinated at 500°C for 12 hours, which is necessary to remove water and other impurities from the samples. Here, table 1 shows list of starting materials with suppliers’ name and purity %, and table 2 shows stoichiometric ratio of starting materials.

| Sr. No. | Chemical name with Formula | Molecular Weight | Supplier | Purity % |
|---------|---------------------------|------------------|----------|----------|
| 1. | Barium Nitrate Ba(NO$_3$)$_2$ | 261.32 | Lobachemie, | 99% |
2. Zinc Nitrate (N$_2$O$_6$Zn.6H$_2$O) 297.48 Lobachemie, CAS No: 10022-31-8
3. Ammonium Fluoride 37.04 Labachemie, CAS No: 10196-18-6
4. Europium oxide (Eu$_2$O$_3$) 362 Lobachemie, CAS No: 1308-96-9

Table 2. The amount of reagents added in the synthesis methods

| Concentration of Eu$^{3+}$ | Ba(NO$_3$)$_2$ (gm) | N$_2$O$_6$Zn.6H$_2$O (gm) | NH$_4$F (gm) | Eu$_2$O$_3$ (gm) |
|-----------------------------|--------------------|--------------------------|-------------|------------------|
| 0 mol%                      | 7.027gm            | 4gm                      | 8.964       | 0gm              |
| 0.1mol%                     | 7.024gm            | 4gm                      | 8.964       | 0.001gm          |
| 0.5mol%                     | 7.009gm            | 4gm                      | 8.964       | 0.012gm          |
| 0.7mol%                     | 7.002gm            | 4gm                      | 8.964       | 0.017gm          |
| 1.0mol%                     | 6.993gm            | 4gm                      | 8.964       | 0.024gm          |
| 1.5mol%                     | 6.974gm            | 4gm                      | 8.964       | 0.036gm          |

3. Results and Discussion

3.1. XRD measurement

The confirmation phase formation were analyzed by XRD measurement. The XRD pattern synthesized materials were analyzed by Rigaku miniflex X-ray diffractometer with 0.02°/sec scanning rate. The XRD diffraction pattern of the synthesized undoped phosphors shows all diffraction peaks are well matched with the standard ICDD reference code: 98-004-0925, as shown in Figure 1. Standard ICDD reference code: 98-004-0925 (Ba$_2$Zn$_7$F$_{18}$) selected from the international database for material structures. No additional diffraction peak observed. The results indicated that synthesized phosphor have high crystalline nature and excellent homogeneity. Ba$_2$Zn$_7$F$_{18}$ host lattice possesses crystallizes in the triclinic space group of P-1(2).
Photoluminescence (PL) properties

Photoluminescence (PL) is the process of light emission after from any form of matter after the absorption of photons. In the PL process, energy release in the form of photons (light), this energy relates with the distinction in energy levels between the excited state and the balance state [11]. PL is a useful method for the study and characterization of electronic structure both intrinsic and extrinsic, of semiconducting and semi-insulating materials. In the present work, PL properties of the synthesized phosphor were analyzed using SHIMADZU RF-5301 PC Spectrofluorophotometer with Xe non-lamp of 150 W at room temperature. For the powder sample slit width fixed at 1.5nm.

The PL excitation spectra of the synthesized sample are shown in Figure 2, which is observed in the range of 350nm to 500nm. The excitation spectrum revealed that synthesized Ba$_{1.99}$Zn$_7$F$_{18}$:1mol%Eu$^{3+}$ phosphor exhibits several excitation band, which are consist around at 366nm, 386nm, 395nm and 466nm. The observed sharp excitation peaks are resulted due to transition from $^7F_0$ energy level of Eu$^{3+}$. As can see from the figure, 395nm and 466nm peaks are sharp and intense, these peaks are attributed due to $^7F_0$$\rightarrow$$^5L_6$, and $^7F_0$$\rightarrow$$^5D_2$, transition of Eu$^{3+}$ ions [12]. The investigation confirmed that synthesized Ba$_{1.99}$Zn$_7$F$_{18}$:1mol%Eu$^{3+}$ phosphor can be excited by NUV and blue LED chip for pc-WLEDs [13]. The 395nm and 466nm excitation peaks are the most intense peak in the spectrum, so we are consider these two peaks for further analysis.
Figure 2. PL excitation spectra of the synthesized Ba$_{1.99}$Zn$_7$F$_{18}$:1mol%Eu$^{3+}$ phosphor monitored at 613nm

Figure 3 demonstrate that PL emission spectra and concentration curve of the synthesized Ba$_{2-x}$Zn$_7$F$_{18}$:xmol%Eu$^{3+}$ (x = 0, 1, 0.5, 0.7, 1.0, 1.5) phosphors. Emission spectra can be shown in the Figure 2 (I) and (III) under 395nm and 466nm, respectively, which is investigated in the range of 540nm to 640nm. Both emission spectra consist three emission band around at 580nm, 593nm and 613nm, which are attributed due to $^5D_0 \rightarrow ^7F_J$ ($J = 0, 1, \text{and} 2$) transitions of Eu$^{3+}$ ions [14]. As we can clearly see from figure 3 that the nature of the emission bands are the same for each concentration of Eu$^{3+}$ ions and both excitation wavelengths. No change in the position of peaks was observed, only the intensity of PL emission changed with the concentration of Eu$^{3+}$ ions. Figure 3 (II) shows the variation in intensity with concentration of Eu$^{3+}$ ions, which is also known as concentration quenching curve. This curve initially shows increase in the intensity of emission with an increase in the concentration of Eu$^{3+}$ ions, consistently up to 1mol%. Furthermore, emission intensity decreases beyond the concentration of 1mol% Eu$^{3+}$ ions. This may be possible due to concentration quenching [15]. From figure 2 we are clearly seen that 613nm emission peak is most intense emission peak, which is arose due to hypersensitive transition of electric dipole (ED) transition. This is strongly influenced by the environment around Eu$^{3+}$ ions. The other emission peak at 593nm arose due to magnetic-dipole (MD) transition of Eu$^{3+}$ ions. It is insensitive to the environment of the crystal region. As per the literature, if the intensity of the MD transition is higher than the ED transition, Eu$^{3+}$ ions occupy the inversion symmetry site and the synthesized materials show red-orange emission. On the other hand, if the ED transition is higher than the MD transition, Eu$^{3+}$ ions occupy the crystallographic site without inversion symmetry and the synthesized material show red coloured emission [14,16,17]. PL emission results of Ba$_2$Zn$_7$F$_{18}$:Eu$^{3+}$ phosphor revealed high intensity at ED transition, which confirms that Eu$^{3+}$ ions occupied the crystallographic site without inversion symmetry and the sample shows emission of red color.
Figure 3. PL Emission spectra of Ba$_{2-x}$Zn$_x$F$_{18}$:xmol%Eu$^{3+}$ (x =0.1,0.5,0.7,1.0,1.5) phosphor monitored at 395nm and 466nm (II) Variation in emission intensity with concentration of Eu$^{3+}$ ions

3.3. CIE Chromaticity

The CIE chromaticity diagram is very useful for confirmation the exact emission color and color purity of the synthesized materials. The CIE chromaticity coordinates are directly calculated by intensity of emission using the OSRAM SYLVANIA color calculator. Figure 4 shows CIE diagram of the Ba$_{1.99}$Zn$_{0.01}$F$_{18}$:1mol%Eu$^{3+}$ phosphor monitored at 395nm and 466nm. The CIE coordinates for the Ba$_{1.99}$Zn$_{0.01}$F$_{18}$:1mol%Eu$^{3+}$ phosphor are found in the red region around A = (0.6144, 0.3850) and B = (0.4952, 0.4050), which are excited from 395nm and 466nm excitation, respectively. These results indicated that this synthesized red emitting phosphor have potential application in the field of lighting.

Figure 4. CIE Chromaticity Coordinate of the synthesized Ba$_{1.99}$Zn$_{0.01}$F$_{18}$:1mol%Eu$^{3+}$ phosphor monitored at 395nm and 466nm excitation

4. Conclusion

In the present work, a series of Ba$_{2-x}$Zn$_x$F$_{18}$:xmol%Eu$^{3+}$ (x =0.1,0.5,0.7,1.0,1.5) phosphors were synthesized via combustion method using urea as a fuel. The XRD pattern of the synthesized material
showed that the material has been successfully synthesized and the combustion method is the easiest synthesis route for the preparation of luminescent materials. Photoluminescence properties have been measured under near UV and blue excitation. The emission spectra shows strong sharp emission peak around 613nm, due to the \( ^5\text{D}_0 \rightarrow ^7\text{F}_2 \) transition of Eu\(^{3+} \) ions. The PL emission results of Ba\(_2\)Zn\(_2\)F\(_{18}\)Eu\(^{3+}\) phosphor revealed high intensity at ED transition, which confirms that Eu\(^{3+} \) ions occupied the crystallographic site without inversion symmetry and the sample shows emission of red color. The red color emission under 395nm and 466nm is confirmed by the CIE diagram, which shows the coordinates in the red region around A (0.6144, 0.3850) and B (0.4952, 0.4050) for the 395nm and 466nm excitations. All these results indicate that synthesized red emitting phosphor have potential application in the field of lighting, it may be useful for the future studies.

5. References

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Acknowledgement

One of the authors, Yatish R. Parauha, is thankful to the Department of Science and Technology (DST), India for financial support through INSPRIRE fellowship (INSPRIRE Code - IF180284). One more author, SJD, is thankful to the Department of Science and Technology (DST), India (Nano Mission) (Sanction Project Ref. No. DST/NM/NS/2018/38(G), dt.16/01/2019) for financial assistance.