Synthesis and luminescence behavior of $\text{Ba}_2\text{SiO}_4:\text{Dy}^{3+}$ phosphors in presence of charge compensator ions

Ganesh Ram Banjare¹*, D.P. Bisen¹, N. Brahme¹, Chitrkant Belodhiya¹, A.K. Upadhyay²

¹SoS in Physics & Astrophysics, Pt. Ravishankar Shukla University, Raipur (C.G.) India 492010
²Department of Physics, Government Engineering College, Raipur (Chhattisgarh) India 492015

*Corresponding author’s e-mail address: banjare.ganesh@rediffmail.com, dpbsen@rediffmail.com

Abstract: A series of dysprosium ($\text{Dy}^{3+}$) doped barium ortho-silicate ($\text{Ba}_2\text{SiO}_4$) phosphors were synthesized by conventional Solid State reaction technique. In order to find out the phase purity and crystal structure, characterization of the prepared powder samples was done by X-ray diffraction (XRD) method. FTIR method confirms the presence of all elemental compositions. Photoluminescence (PL) properties were studied. The PL spectra was observed to study the effect of concentration of $\text{Dy}^{3+}$ ion and it is found that the prepared phosphors show two strong emission peaks in the blue and yellow region at 478 nm and 573 nm, respectively, when excited by the near-ultraviolet (UV) of wavelength 348 nm. The critical distance between the $\text{Dy}^{3+}$ ions was calculated using Blasse’s equation. Effect of monovalent ion $\text{K}^+$ was examined as a charge compensator ion and observed that co-doping of charge compensator ion enhances the luminescence intensity. Chromaticity coordinates of the phosphor are found near to white light region, which confirms their applicability in solid state lighting applications; especially in white-LEDs.

Keywords: PL, charge compensator ion, LEDs.

1. Introduction
Phosphor materials play a key role in recent technologies; especially in lighting and display devices. They have outstanding chemical and physical properties as well as a stable crystal structure. Thus, a lot of attention has been drawn towards the study of phosphor materials because of their usefulness in the various fields such as Field Emission Displays (FEDs), sensors, Plasma Display Panels (PDP), X-ray imaging systems, optical fibres and white light emitting diodes (WLEDs). Among all these applications, WLEDs is considered to be the next generation lighting systems over the traditional lamps due to its reliability, long lifetime, high brightness, eco-friendly, and low power consumption properties [1-4]. It has been proved that Ultraviolet (UV) pumped phosphor converted WLEDs exhibit high Color Rendering Index (CRI) as well as high chromatic stability [5]. At the present time,
phosphor based WLED was highly useful and a number of approaches have been developed for the emission of white light through LEDs.

In the different oxide based phosphor materials, silicates are of great interest as a host for their high chemical, physical stability and stable crystal structure [6]. In this context, rare earth doped alkaline earth ortho-silicates such as SrCa$_{1-x}$SiO$_4$: xEu$^{3+}$, Sr$_2$SiO$_4$: xSm$^{3+}$, Sr$_2$Ba$_2$SiO$_4$:Eu$^{2+}$, Ba$_{1.55}$Ca$_{0.45}$SiO$_4$: (Eu$^{2+}$, Mn$^{2+}$) are popular commercial phosphors for WLEDs [7]. Recently, Dy$^{3+}$ doped alkaline earth ortho-silicate phosphors were fascinated because of their high absorption efficiency in UV area, outstanding spectroscopic behavior, simple chemical compositions and single luminescence center [8]. Therefore, it’s a huge demand for today’s scenario to synthesis new novel efficient white light emitting phosphor. With this motivation, we choose barium ortho-silicate i.e. Ba$_2$SiO$_4$ as a host due to its high quantum efficiency properties and lower harmfulness for the environment as well as health [9, 10].

In this paper, white light emitting phosphor materials Ba$_2$SiO$_4$: Dy$^{3+}$ is synthesized by high-temperature solid-state reaction method and its photoluminescence properties are investigated. The main aim of this work is to improve the luminescence intensity of the phosphor materials by the incorporation of K$^+$ ion as charge compensator ion. The chromatic behavior of the prepared phosphors was studied in detail.

2. Synthesis and characterization

A series of trivalent dysprosium (Dy$^{3+}$) doped barium ortho-silicate namely Ba$_{2-x-y}$SiO$_4$: xDy$^{3+}$, yK$^+$ phosphors (x = 1.0, 2.0, 3.0, 4.0 and 5.0 %) were prepared by high temperature solid-state reaction method in presence of charge compensator ion K$^+$ (y = 1.0, 2.0, 3.0, 4.0 and 5.0 %). BaCO$_3$, SiO$_2$, Dy$_2$O$_3$, Dy$_2$O$_3$, and K$_2$CO$_3$ were used as raw materials; all of the analytical grades (A.R.) with 99.9 % purity were utilized for the synthesis of phosphor under study. H$_3$BO$_3$ was used as a flux. Stoichiometric proportions of all raw materials were ground using an agate mortar and pestle for 3 hand transferred into alumina crucible, further kept into muffle furnace. Thereafter, mixed materials were fired at 1200°C for 4 h in air. The final products in powder forms were ground again, yielding the resulting powder form of the phosphors.

X-ray diffraction (XRD) measurements were carried out for the phase identification in powder samples using Bruker D8 Advance X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54$ Å, 40 kV, 40 mA) at room temperature. For functional group identification Fourier transform infrared (FTIR) measurements have been performed using Shimadzu IRAffinity-1 Fourier Transform Infrared Spectroscopy. The photoluminescence (PL) spectra (excitation & emission) of the phosphors samples were carried out by using a Shimadzu, RF-5301 PC spectrofluorophotometer.

3. Results and discussions

3.1 XRD analysis

To identify the crystal structure and phase purity of the prepared samples, X-ray diffraction (XRD) technique was used. The XRD pattern of the Ba$_{1.94}$SiO$_4$: 0.03Dy$^{3+}$, 0.03K$^+$ phosphors being represented in figure 1. It was observed that all the peaks are well-matched with the JCPDS # 70-2113. No extra peaks are present in the pattern, which confirms the single phase of the Ba$_{1.94}$SiO$_4$: 0.03Dy$^{3+}$, 0.03K$^+$ phosphor. The single phase of the prepared samples indicates that dopant Dy$^{3+}$ and co-dopant K$^+$ are fully dissolved into the host matrix. The powder samples shows an orthorhombic type crystal structure with the space group Pmcn,(62) and the cell parameters were determined to be $a = 5.80$ Å, $b = 10.20$ Å, $c = 7.50$ Å with $\alpha = \beta = \gamma = 90^\circ$. The position of atoms with the occupancy factors is listed in Table 2 [11]. Fig.2 (a) shows the tetrahedral structure of SiO$_4$ whereas fig. 2 (b) represents within a distance of 3.2 Å, both the sites namely Ba1 and Ba2 sites, are coordinated by ten and nine oxygen atoms, respectively.
Figure 1. XRD pattern of Ba$_2$SiO$_4$ phosphor.

Figure 2. (a) tetrahedral structure of SiO$_4$ (b) coordination structure of Ba$_2$SiO$_4$ phosphor.

Table 1. Some important parameters of Ba$_2$SiO$_4$ phosphor.

| Parameters         | Ba$_2$SiO$_4$ |
|--------------------|---------------|
| Phase structure    | Orthorhombic  |
| Lattice type       | Primitive     |
| Space group        | Pmcn(62)      |
| Cell parameters    |               |
| a                  | 5.80 Å        |
| b                  | 10.20 Å       |
| c                  | 7.50 Å        |
| α = β = γ          | 90°           |
| Radiation          | CuKα 1        |
| Wavelength         | 1.54060 Å     |
Table 2. The position of atoms and occupancy factors.

| Name of atoms | x      | y      | z      | Sites | Occ. |
|---------------|--------|--------|--------|-------|------|
| Ba1           | 0.2499 | 0.0872 | 0.1608 | 4c    | 1    |
| Ba2           | 0.2499 | 0.6955 | -0.0085| 4c    | 1    |
| Si            | 0.2498 | 0.4198 | 0.2283 | 4c    | 1    |
| O1            | 0.0197 | 0.3480 | 0.3051 | 8d    | 1    |
| O2            | 0.0197 | 0.3480 | 0.3051 | 8d    | 1    |
| O3            | 0.0251 | 0.4157 | 0.0130 | 4c    | 1    |

3.2 Fourier Transform Infrared Spectroscopy (FTIR) Spectroscopy

The functional compositions of the synthesized phosphors were identified by FTIR spectroscopy. Fig. 3 shows the transmittance spectrum of the Ba1.94SiO4:0.03Dy3+, 0.03K+ phosphor, which was recorded in the range of wave number 400 – 4000 cm⁻¹. The FTIR spectrum of the observed powder sample shows following six prominent bands which are located around (i) 3641.6 cm⁻¹ (ii) 1408.08 cm⁻¹ (iii) 972.12 cm⁻¹ (iv) 491.85 cm⁻¹ (v) 432.05 cm⁻¹ and (vi) 391.55 cm⁻¹. The absorption band around 3641.6 cm⁻¹ ascribes the presence of hydroxyl group in the prepared phosphor. Thereafter, C=O in carbonyl functional group which have an anti-symmetric stretching vibrations shows a strong peak at 1408.08 cm⁻¹. The next broadband lying in the region 900–1200 cm⁻¹, and the single peak at 972.12 cm⁻¹ assigned due to the Ba²⁺ ions. The band centred at 491.85 cm⁻¹ are combinations of a number of contributions of the asymmetric stretching modes due to the presence of silicates (SiO₄). The vibrations of the monovalent ion were found to produce a broad IR absorption band centred on 391.55 cm⁻¹.

Figure 3. FTIR spectroscopy of the Ba₂SiO₄: Dy³⁺, K⁺ phosphor.
3.3 Photoluminescence (PL) studies

Photoluminescence behaviors of the prepared phosphors were inspected. The excitation and emission spectra (see figure 4 a) were recorded in the wavelength range 200 – 700 nm at room temperature. The excitation spectra exhibit five excitation peaks centered at 295 nm, 325 nm, 352 nm, 364 nm and 390 nm. The sharp peaks are obtained due to 4f – 4f transition of Dy$^{3+}$ ion. The sharp peaks originated from the ground energy state to higher energy state corresponding to following transitions $^6H_{15/2} \rightarrow ^4P_{5/2}$, $^6P_{3/2}$, $^6P_{5/2}$, $^4I_{15/2}$ except the first peak. Among all these peaks, the peak at 352 nm is more dominant over the others. Z. Ci et al reported the suitable wavelength range from 350 nm to 410 nm for the strong absorption of ideal luminescent materials [12]. In this study, the obtained absorption matches with the emission of commercially available NUV and blue LED chips light. Thus, it is observed that the prepared sample can be effectively excited by near-ultraviolet (n-UV) and blue light.

The emission spectra of Ba$_{1.97}$SiO$_4$: 0.03Dy$^{3+}$ phosphors under the n-UV excitation at the wavelength 352 nm corresponding to $^6H_{15/2} \rightarrow ^4P_{5/2}$ transition are shown in fig. 4 (a). Two emission peaks were occurred at 476 nm (blue region) and 573 nm (yellow region), upon the n-UV excitation of 352 nm, which is a typical emission characteristic of Dy$^{3+}$ion. From figure 4 (a), it is clear that the intensity of emission peak at the blue region is stronger than emission obtained at the yellow region. The strong blue emission occurs due to $^4F_{9/2} \rightarrow ^6H_{15/2}$ transition (magnetic dipole transition), which represents the presence of Dy$^{3+}$ ion in a high symmetric site. However, the yellow emission is obtained as a result of the hypersensitive transition at 577 nm and which is electric dipole transition related to $^4F_{9/2} \rightarrow ^6H_{13/2}$ transition. In this case, the PL intensity highly depends on the host matrix. Indeed, the hypersensitive transition is strongly influenced by the nearby atmosphere of activator i.e. Dy$^{3+}$ ion [13]. From figure 4 (a), it is clear that the intensity of emission peak at the blue region is stronger than emission obtained at the yellow region. Thus, it is analyzed that Dy$^{3+}$ ion present in the higher symmetry site with an inversion centre, whereas for yellow emission, dopants(Dy$^{3+}$) located at lower symmetry site with no inversion center [14].

3.3.1 Influence of concentration of Dy$^{3+}$ ion

Varying concentrations of Dy$^{3+}$ ions (1.0 – 5.0 %) were employed into the host. Initially, the luminescence intensity increases with the concentration and optimum occurred for 3.0 mol % of Dy$^{3+}$. Further increment of Dy$^{3+}$ ion results in the reduction in PL intensity due to concentration quenching. Thus, x = 3.0 % is identified as critical concentration. According to Blasse, the critical distance (Rc) for Ba$_{2-x}$SiO$_4$: xDy$^{3+}$ can be calculated using the following equation

$$Rc = 2 \left[ \frac{3V}{4\pi x_c Z} \right]^{1/3}$$

Where V is the volume of the unit cell, x$_c$ represents the critical concentration of the activator ion, and Z is the number of cations per unit cell. Here Z = 4, V = 387.233 Å$^3$ and x$_c$ = 0.03 for Ba$_{1.97}$SiO$_4$: 0.03Dy$^{3+}$ phosphor. Consequently, the critical distance (Rc) of activator ion (Dy$^{3+}$) was calculated by the formula (1) and obtained 24Å. The critical distance value determines interaction types between the activator ions on the basis of according to Dexter’s theory, which is expressed as:

$$\frac{I}{X} = k \left( 1 + \alpha(x) \right)^{-\frac{\theta}{3}}$$

$\theta = 6, 8$ and 10 then d – d, d – q and q – q are the corresponding interactions [15]. In this study, the value of $\theta$ is 8.37, which is determined by fitting the plot between log (I/X) and log (x) as shown in
The value 8.37 is nearly equivalent to 8 determined the d–q interaction type between activator ions. Thus, it’s concluded that PL emission intensity is influenced by the concentrations of Dy$^{3+}$ ions. In this study, it is investigated that introduction of Dy$^{3+}$ ion into the host, replaces Ba$^{2+}$ because the ionic radii of Dy$^{3+}$ (91.2 pm) are less than Ba$^{2+}$ (135 pm). Due to this replacement, charge imbalance (obtained due to the presence of Dy$^{3+}$ ion in the symmetry site) creates defects, which is responsible for non–radiative transition. This transition reduces the PL intensity. Hence, the improvement of PL intensity is necessary.

Figure 4. (a) PL excitation and emission spectra of Ba$_{2-x}$SiO$_4$: xDy$^{3+}$ phosphors.

Figure 4. (b) PL emission spectra of Ba$_{2-x}$SiO$_4$: xDy$^{3+}$ (x = 1.0, 2.0, 3.0, 4.0 and 5.0 %) phosphors.
3.3.2 Effect of charge compensator ion K⁺
Doping of trivalent Dy³⁺ ions substitutes divalent Ba²⁺ sites will responsible in the formation of excess positive charge in the host. The excess charge resulting in the distortion of crystal structure and sample will become unstable; perturbed the total charge neutrality of the system [16]. The major effect of the above result is nothing but a reduction in PL intensity due to charge imbalance. In order to remove the above drawback, K⁺ ions were incorporated into Ba₁.⁹⁷SiO₄: ₀.₀₃Dy³⁺ phosphor.

It can be seen very clearly from the fig. 5 (a) that introduction of K⁺ ion enhances the PL intensity because the K⁺ ion reduces the lattice distortion and nullify the excess positive charge. In this case, two Ba²⁺ (ionic radius = 135 pm) site is substitutes by one Dy³⁺ ion (ionic radius = 91.2 pm) and one K⁺ ion (ionic radius = 138 pm) [17]. Thus, it is investigated that due to the same size of the ionic radius, K⁺ ion easily replaces the Ba²⁺ site. Here, K⁺ ions are used as charge compensator ion. This is an important approach to enhance the luminescence intensity. Table 3 shows the relative PL intensity without K⁺ ion and with K⁺ ions. The PL intensity enhanced 1.75 times due to charge compensator ion (K⁺ ion). Fig. 5 (b) represents the PL emission spectra for different concentration of K⁺ (1.0 – 5.0 %) ions in the Ba₁.⁹⁷SiO₄: ₀.₀₃Dy³⁺ phosphor and maximum obtained for 3.0 mol % i.e. Ba₁.⁹⁷SiO₄: ₀.₀₃Dy³⁺, ₀.₀₃K⁺ phosphor.

| S. No. | Wavelength (nm) | PL intensity (without K⁺ ion) (arb. Unit) | PL intensity (with K⁺ ion) (arb. Unit) |
|-------|----------------|-----------------------------------------|---------------------------------------|
| 1.    | 476            | 221                                     | 387                                   |
| 2.    | 573            | 194                                     | 340                                   |
Figure 5. (a) PL excitation and emission spectra of $\text{Ba}_{2-x-y}\text{SiO}_4$: $x\text{Dy}^{3+}$ phosphors in presence of $y\text{K}^+$ ion.

Figure 5. (b) Emission spectra of $\text{Ba}_{1.97}\text{SiO}_4$: 0.03$\text{Dy}^{3+}$ phosphors for varying concentration of $\text{K}^+$ ion (1.0, 2.0, 3.0, 4.0, and 5.0 %)
Figure 6. (a) Effect of concentrations of Dy$^{3+}$ ions on PL intensity.

Figure 6. (b) Plot log (x) Vs log (I/x)

3.4 CIE coordinates
The CIE chromaticity coordinates of Ba$_{1.94}$SiO$_4$: 0.03Dy$^{3+}$, 0.03K$^+$ powders are calculated (see fig. 7). The values of chromaticity coordinates of the BOS powder were about (0.29, 0.31), which is very near to the typical value (0.33, 0.33) of white light. Therefore, this value directed the high color stability and color saturation behavior of the phosphor. Hence, Ba$_{1.94}$SiO$_4$: 0.03Dy$^{3+}$ phosphor in presence of charge compensator ion (K$^+$) is a suitable candidates for solid state lighting and puts potential applicability in white light areas.
4. Conclusion

Dysprosium (Dy\textsuperscript{3+}) doped alkaline (barium) ortho-silicate (Ba\textsubscript{2}SiO\textsubscript{4}) phosphors in the presence of K\textsuperscript{+} ions were prepared via a high – temperature solid-state reaction route. The analysis of XRD patterns reveals the formation of single-phase crystal structure of the phosphor. The identified phase structure was orthorhombic, which is confirmed through JCPDS # 70-2113. All peaks are well-matched with this JCPDS file. Chemical compositions were identified by transmittance spectrum by FTIR analysis, which confirms the presence of Ba\textsubscript{2}SiO\textsubscript{4}: Dy\textsuperscript{3+}, K\textsuperscript{+} phosphors. The maximum PL intensity was obtained for 3.0 mol% of Dy\textsuperscript{3+}. The two PL emission peaks occur at 476 nm and 573 nm related to \textsuperscript{4}F\textsubscript{9/2} \rightarrow \textsuperscript{6}H\textsubscript{15/2} and \textsuperscript{4}F\textsubscript{9/2} \rightarrow \textsuperscript{6}H\textsubscript{13/2} transitions when excited by 352 nm. The critical distance between dopants (Dy\textsuperscript{3+} ions) was calculated by using blasses equation and obtained 24Å. The Rc determines the dipole – quadrupole interaction between activator ions. K\textsuperscript{+} ions are used as charge compensator ion; which enhances the luminescence intensity as well as crystallinity. Incorporation of K\textsuperscript{+} ions enhances the PL intensity 1.75 times as compare to obtained with Dy\textsuperscript{3+} doping only. The CIE color coordinates were calculated (0.29, 0.31), which is very near to the standard value (0.33, 0.33). Thus, it is concluded that the synthesized phosphor is a fruitful candidate for white light applications (especially wLEDs).

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