Luminescence study of UV-C to UV-A converting Sr$_3$Y$_{1-x}$(BO$_3$)$_3$:xPb$^{2+}$ (x = 3, 4, 5, 6, 7 mole %) phosphor

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Abstract:

The polycrystalline powder sample of Pb$^{2+}$ activated strontium yttrium borate phosphor Sr$_3$Y$_{1-x}$(BO$_3$)$_3$:xPb$^{2+}$ (x = 3, 4, 5, 6, 7 mole %) is prepared by solution combustion technique. Formation of phosphor in the desired crystalline phase is confirmed by powder XRD characterization & FTIR. SEM images of the synthesized phosphor show the irregular grains with average particle size 5 μm. Luminescence properties of the synthesized phosphor are investigated at room temperature. The PL excitation spectrum consists of a single broad absorption band from 200 to 350 nm with the prominent excitation peak at 270 nm [$^1S_0$ to $^3P_1$ of Pb$^{2+}$ ions]. Photoluminescence is recorded in the range 300nm to 700nm. Strongest luminescent peak of 376 nm wavelength monitored at 276nm is observed. The shape of PL band is same at all concentrations of dopant and intensity of emission increases up to 0.07 mole of Pb$^{2+}$ and then decreases. Sr$_3$Y$_{1-x}$(BO$_3$)$_3$:xPb$^{2+}$ phosphor convert UV-C light into UV-A light and it’s Stokes shift is 10442 cm$^{-1}$.

keywords:- UV-A, Borate phosphor, Combustion, Luminescence

1. Introduction:

UVA1 (340-400 nm) radiation used in phototherapy is effective in clearing or controlling a variety of skin diseases like atopic dermatitis, scleroderma, cutaneous T-cell lymphoma, urticariapigmentosa, lupus erythematus, extragenital lichen scleroses, Granuloma Annulare. (1). High-dose UVA1 has also been observed to help: hypertrophic scars and keloids, dyshidrotic eczema (pompholyx), prurigonodularis (2). UV radiations in the range 360nm to 390nm are also used in UV cured resin, ink, adhesives, paintings, clear coat, Glue. Most of the UV-A emitting phosphors are based on Silicates, Fluorides, Aluminates or Phosphate. Few borate based phosphors, as UV-A emitter have been studied till now and listed in table [1]. Inorganic borates could be excellent host materials because of their variety of structure type, large electronic band gap, transparency to a wide range of wavelengths, high optical damage threshold and high optical quality (3). A large number of borate compounds are transparent over a wide spectral range, beginning from VUV and extending into IR, which makes borate compounds important for opto-electronic materials or as phosphors (4). In the present work, we report the UV-A emitting borate phosphor Sr$_3$Y$_{1-x}$(BO$_3$)$_3$:xPb$^{2+}$. 
Given Inorganic borate phosphors were prepared by the solution combustion synthesis technique. This method was accidentally discovered in 1988 in the lab of Prof. Patil in India (15). It is an exothermic reaction and occurs with the evolution of heat and light. Such a high temperature leads to formation and crystallization of phosphor materials. For phosphor particle preparation, combustion synthesis method is promising technique due to its ability to produce fine size of particles without high temperature annealing and extra steps such as grinding or milling (16) (17).

Stoichiometric amounts of high purity starting materials, SrNO$_3$ (A.R.), Pb(NO$_3$)$_2$ (high purity 99.9%), H$_2$BO$_3$ (A.R.), CO(NH$_2$)$_2$ (A.R.), Y(NO$_3$)$_3$ (A.R.) are used for phosphor preparation. The starting materials with little amount of double distilled water were mixed thoroughly in agate mortar to obtain a homogeneous solution. Excess water was removed by heating the samples at temperature 70°C for about 30 min on magnetic stirrer and the solution was then transferred directly to a pre-heated Muffle furnace, maintained at temperature 650°C, for combustion. Following the combustion, the resulting foamy samples was crushed to obtain fine particles and then annealed for 3 h at temperature 800°C.
3. Results & Discussion

The prepared materials were characterized by powder XRD, SEM, PL and FT-IR techniques. Powder X-ray diffraction measurements were taken on a RigakuMiniflex II X-ray Diffractometer and compared with ICSD files. Surface morphology and elemental analysis of the calcined powder sample was observed by scanning electron microscopy [SEM: Model JSM6100 (Jeol) ]. PL and PLE measurements at room temperature were performed on a Hitachi F-7000 spectro- fluorometer with spectral resolution of 2.5 nm. FTIR of sample was done on F.T. Infra-Red Spectrophotometer Model RZX (Perkin Elmer).

3.1. XRD

Powder XRD pattern of the synthesized phosphor was recorded by X-ray diffraction using the Cu-Kα wavelength (λ= 1.54060 Å) and scanning in the 2θ range from 20°–80°. Figure [1] shows the powder XRD pattern of the phosphor Sr3Y(BO3)3. The powder XRD pattern of synthesized phosphor agrees with standard pattern given by ICSD File NO. 246230. Space group is R-3; crystal system is trigonal (hexagonal axes); unit cell parameters a=b=17.7025 Å c= 9.8830 Å.

![Figure 1 XRD Pattern of YSr3(BO3)3](image)

3.2. FTIR

The FT-IR spectra of Sr3Y1-0.03 (BO3)3:0.03Pb2+ recorded at room temperature is shown in Figure [2]. The strong bands observed above 1100 cm⁻¹ should be assigned to the B-O stretching mode of the triangular [BO3]⁻ groups, while the bands with maxima at about 700-800 cm⁻¹ should be attributed to the B-O out of plane bending, which confirms the existence of the [BO3]⁻ groups (18). The absence of peaks in 1500- 2000 cm⁻¹ indicates the complete combustion of nitrate and organic matter. The peak at 3300-3500 cm⁻¹ corresponds the stretching mode of O-H are also absent.
3.3. SEM

The morphology of sample was studied using Scanning electron microscopy. The SEM images of Sr$_3$Y$_{1-0.03}$(BO$_3$)$_3$:0.03Pb$^{2+}$ phosphors are shown in figure [3]. It was observed that the microstructure of the phosphor consisted of irregular grains with agglomerate phenomena. The average size of synthesized phosphor particles is about 5–20 µm. The results show that phosphors have a good crystallinity and a relatively low sinter temperature. Average crystalline size by Scherrer formula is in 42.2 nm which is different than as seen in surface morphology. It is because SEM shows the image of polycrystalline particles and XRD measurements reflects the crystalline domain size.

![Figure 3 SEM Images at different Resolution](image1.jpg)

3.4 Photo-Luminescence Study

The PL and PLE of Sr$_3$Y$_{1-0.03}$(BO$_3$)$_3$:0.03Pb$^{2+}$ phosphor is shown in figure [4]. It is recorded on F-7000 FL spectrophotometer with scan speed 240 nm/min, excitation-emission slit width 1nm. The excitation spectrum of Sr$_3$Y$_{1-0.03}$(BO$_3$)$_3$:0.03Pb$^{2+}$ consists of a single broadband absorption ranging from 200 to 350 nm with the peaks at 229.8nm and 270nm. The strongest absorption peak is at 270 nm, which may be due to the electronic transitions from the ground state $^1$S$_0$ to the excited state $^3$P$_1$.
of Pb$^{2+}$ ions. At 270nm excitation, Sr$_3$Y$_{1.03}$(BO$_3$)$_3$:0.03Pb$^{2+}$ exhibit a broad emission band in the range 350–700 nm, which originates from the $^3P_1 \rightarrow ^1S_0$ electronic transitions of Pb$^{2+}$ ions. Strongest emission peak has 376nm wavelength which is hardly visible purple UV-A light. So at 270nm UV-C light excitation Sr$_3$Y$_{1.03}$(BO$_3$)$_3$:0.03Pb$^{2+}$ phosphor emits UV-A light of 376nm. Stokes shift is 10442cm$^{-1}$. Large Stoke’s shift (8000-10000 cm$^{-1}$) are usually indicative of excited state reaction, most often excited state photon transfer. Due to single peak in photoluminescence spectra it is believed that the Pb$^{2+}$ ions have taken only one site in Sr$_3$Y (BO$_3$)$_3$. Activator ion Pb$^{2+}$ ion occupy the Y$^{2+}$ site in phosphor. We studied the PL properties with different doping concentrations of Pb$^{2+}$ activator ion and is shown in figure (5). The shape of PL band is same and intensity of emission increases up to 0.07 mole of Pb$^{2+}$ and then decreases. The Luminescence of Pb$^{2+}$ depends upon the site occupied by Pb$^{2+}$, crystal structure of host lattice.
3.5 CIE-Chromacity

Figure [7] shows the Commission International del Eclairage (CIE) chromaticity coordinates diagram of the Sr$_3$Y$_{1-x}$(BO$_3$)$_3$:0.03Pb$^{2+}$ phosphor at 376nm. The chromaticity coordinates of the phosphor Sr$_3$Y$_{1-0.03}$(BO$_3$)$_3$:0.03Pb$^{2+}$ for fixed concentration of Pb$^{2+}$ at 376 nm was computed using LEDTUNING. NL Software [https://www.ledtuning.nl/en/cie-convertor]. The chromaticity coordinates are used in ‘GO-CIE’ CIE plot utility software developed by Organic material laboratory of IIT Roorkee for 1931 CIE CHROMATICITY diagram [http://faculty.iitr.ac.in/~krjt8fcy/gocie.html]. For 376 nm the coordinates obtained were X = 0.174409, Y = 0.005127, which fall at the border of blue region in the CIE 1931 chromaticity diagram and shown as radish triangle shaped spot. As seen in the PL spectra, the Sr$_3$Y$_{1-0.03}$(BO$_3$)$_3$:0.03Pb$^{2+}$ phosphor has 376nm UV-A emission under UV-C light at 270 nm. This means that the Sr$_3$Y$_{1-x}$(BO$_3$)$_3$:X Pb$^{2+}$ phosphor could be a good UV-A phosphor candidate for solid-state lighting and Phototherapy applications.
Figure 6 CIE diagram of Sr3Y1-0.03(BO3)3:0.03Pb2+

### 4. Conclusion

Sr$_3$Y$_{1-x}$(BO$_3$)$_3$:X Pb$^{2+}$ (X= 0.03,0.04,.0.05,0.06,0.07 Mole Pb$^{2+}$) is UV-C to UV-A down conversion phosphor useful for medical and industrial application. Broadband PL in 300nm to 700nm with high intensity luminescent peak 376nm monitored at 276nm is important result of these study.

### References


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