Luminescence study of UV-C to UV-A converting $Sr_3Y_{1-x}(BO_3)_3:xPb^{2+}$ (x = 3,4,5,6,7 mole %) phosphor

Sanjay P. Hargunani[1]*, Rajkumar P. Sonekar[1], Shriniwas K. Omanwar[2]

[1] *Department of Physics, G.S. College Khamgaon, Dist: Buldana (M.S.) India.*
[2] *Department of Physics, S.G.B. Amravati University, Amravati, (M.S.) India*

Abstract:

The polycrystalline powder sample of Pb^{2+} activated strontium yttrium borate phosphor $Sr_3Y_{1-x}(BO_3)_3:xPb^{2+}$ (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. $Sr_3Y_{1-x}(BO_3)_3:xPb^{2+}$ phosphor convert UV-C light into UV-A light and it's Stokes shift is $10442cm^{-1}$.

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 erythematous, 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 $Sr_3Y_{1-x}(BO_3)_3:xPb^{2+}$.

Table 1 Spectroscopic properties of Pb^{2+} doped Phosphors

Pb^{2+} DOPED HOST	λ_{exc}	λ_{em}	STOKE'S SHIFT	REFERENCES
Pb^{2+}-doped $Sr_2B_2O_5$	289nm	370nm	7575 cm^{-1}	(5)
$NaSr_{4-x}Pb_x(BO_3)_3$ $(0.005 \le x \le 0.03)$	289nm	370nm	7574cm^{-1}	(6)
$KCa_4(BO_3)_3$	260nm	335nm	8756cm^{-1}	(7)
$Sr_{(1-x)}Pb_xB_4O_7$ and	270nm	307nm	4464cm^{-1}	(8)
$Sr_{(1-x)}Pb_xB_2O_4$	276nm	365nm	8454cm^{-1}	
$LiSr_{4-x}Pb_x(BO_3)_3$	284nm	328nm	4723cm^{-1}	(9)
$Ba_{2-x}Pb_xBe_2B_2O_7$	284nm	396nm	9959cm^{-1}	(10)
$Li_4Sr_{1-x}Pb_xCa(SiO_4)_2$	249nm	290nm	5678cm^{-1}	(11)
$NaSr_{4-x}Pb_x(BO_3)_3$	291nm	368nm	7190cm^{-1}	(12)
$LiSr_4(BO_3)_3$	290nm	325nm	3832cm^{-1}	(13)
$Sr_3Y_{1-x}(BO_3)_3{:}xPb^{2+}$.	270nm	376nm	10442cm^{-1}	This work
$Sr_{2-x}Pb_xMg(BO_3)_2$ and	260nm	330nm	8159cm^{-1}	(14)
$Ba_{2-x}Pb_xMg(BO_3)_2$	293nm	381nm	7883cm^{-1}	

2. Experimental Details

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_3BO_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 70^0C for about 30 min on magnetic stirrer and the solution was then transferred directly to a pre-heated Muffle furnace, maintained at temperature 650^0C, for combustion. Following the combustion, the resulting foamy samples was crushed to obtain fine particles and then annealed for 3 h at temperature 800^0C

TABLE 1: Molar concentration of ingredients

$$3[Sr(NO_3)_2]+ x[\ Pb(NO_3)_2\ ] + (1-x)Y(NO_3)_3 + 3H_3BO_3 + CO(NH_2)_2 \xrightarrow{780\ ^{o}C}$$

$$Sr_3\,Y_{1-x}\,(BO_3\,)_3{:}xEu^{3+} + \text{Gaseous products}$$

$Sr(NO_3)_2$	$Pb(NO_3)_2$	$Y(NO_3)_3$	$3H_3BO_3$	$CO(NH_2)_2$
6.3486	**0.0669**	**1.13**	**1.855**	**4.80**

3. Results & Discussions

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- flurometer 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 $Sr_3Y(BO_3)_3$. 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.

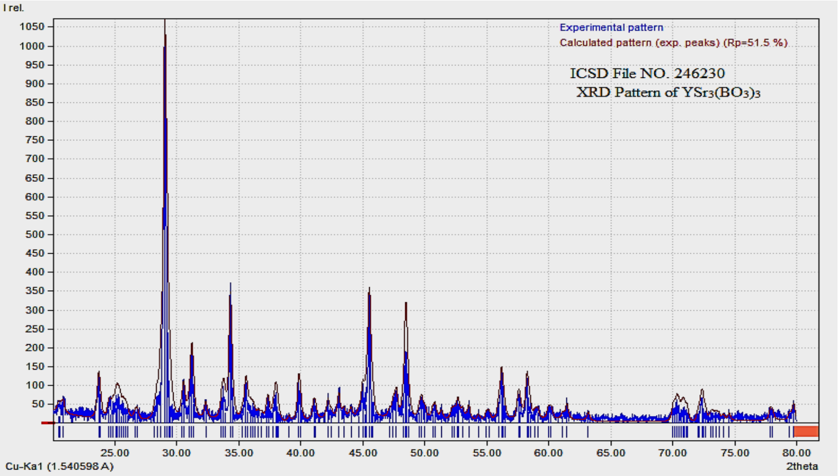

Figure 1 XRD Pattern of YSr3(BO3)3

3.2. FTIR

The FT-IR spectra of $Sr_3Y_{1-0.03}(BO_3)_3{:}0.03Pb^{2+}$ 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 $[BO_3]^-$ 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 $[BO_3]^-$ 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.

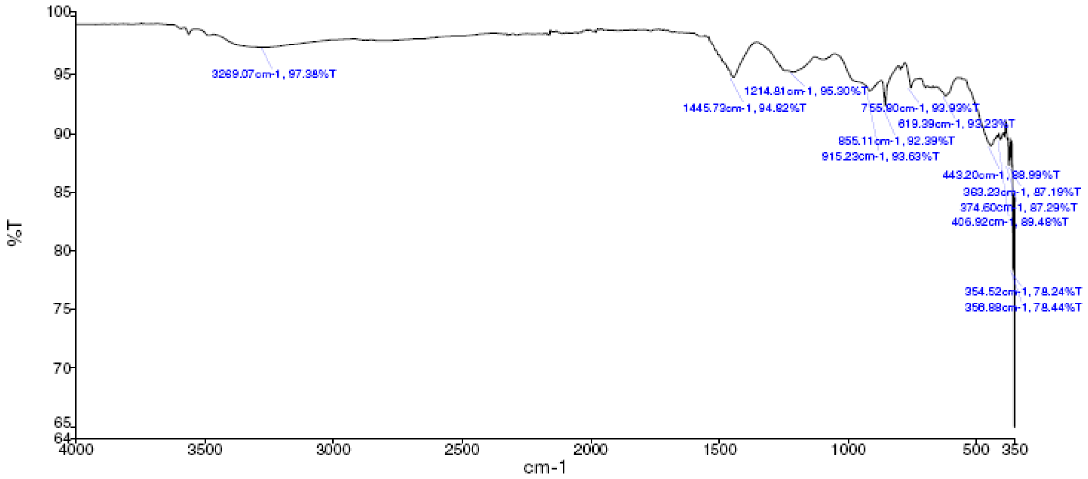

Figure 2 FT-IR spectra of $Sr_3Y_{1-0.03}(BO_3)_3{:}0.03Pb^{2+}$ at room temperature

3.3. SEM

The morphology of sample was studied using Scanning electron microscopy. The SEM images of $Sr_3Y_{1-0.03}(BO_3)_3{:}_{0.03}Pb^{2+}$ 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.

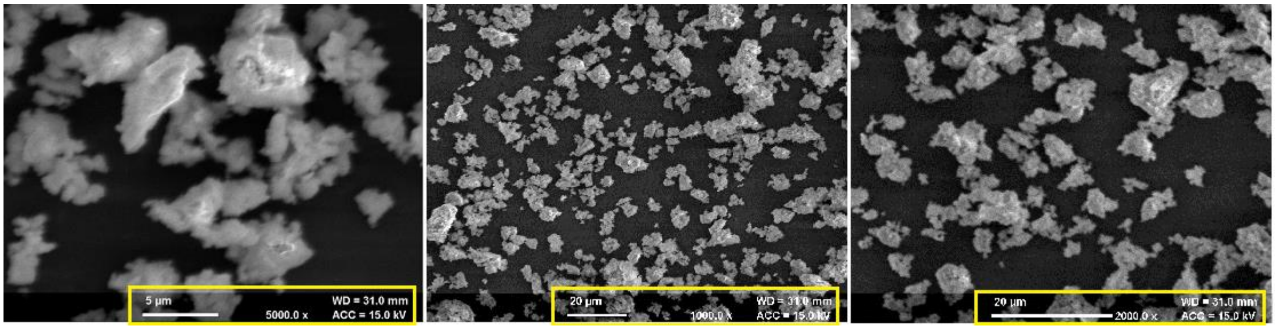

Figure 3 SEM Images at different Resolution

3.4 Photo-Luminescence Study

The PL and PLE of $Sr_3Y_{1-0.03}(BO_3)_3{:}0.03Pb^{2+}$ 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 $Sr_3Y_{1-0.03}(BO_3)_3{:}0.03Pb^{2+}$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 $^1S_0$ to the excited state $^3P_1$

of Pb^{2+} ions. At 270nm excitation, $Sr_3Y_{1-0.03}(BO_3)_3$:$0.03Pb^{2+}$ 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 $Sr_3Y_{1-0.03}(BO_3)_3$:$0.03Pb^{2+}$ 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_3Y $(BO_3)_3$. 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.

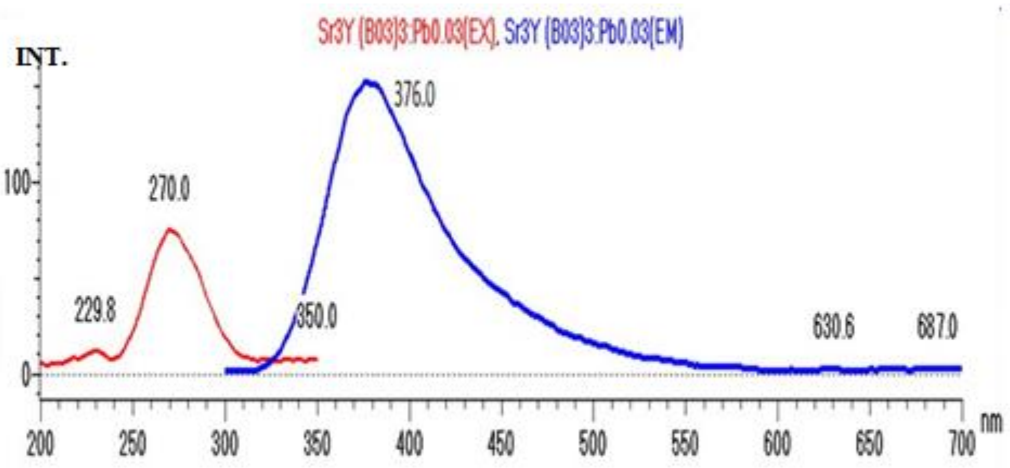

Figure 4 PL and PLE of $Sr_3Y_{1-0.03}(BO_3)_3$:$0.03Pb^{2+}$

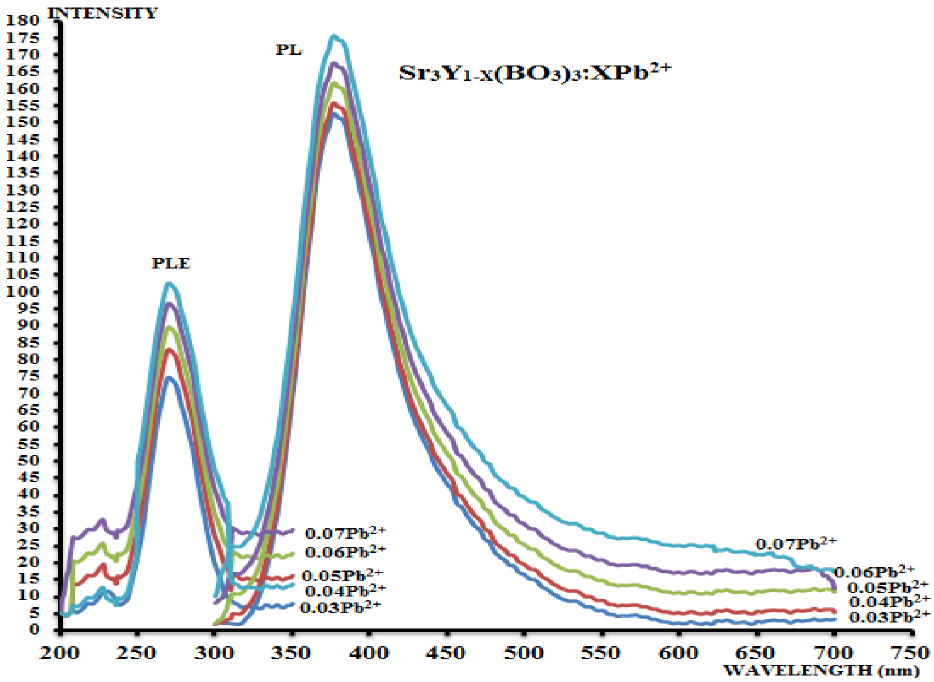

Figure 5 PL and PLE of $Sr_3Y_{1-x}(BO_3)_3:xPb^{2+}$

3.5 CIE-Chromacity

Figure [7] shows the Commission International del Eclairage (CIE) chromaticity coordinates diagram of the $Sr_3Y_{1-0.03}(BO_3)_3:0.03Pb^{2+}$ phosphor at 376nm. The chromaticity coordinates of the phosphor $Sr_3Y_{1-0.03}(BO_3)_3:0.03Pb^{2+}$ 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 $Sr_3Y_{1-0.03}(BO_3)_3:0.03Pb^{2+}$ phosphor has 376nm UV-A emission under UV-C light at 270 nm. This means that the $Sr_3Y_{1-x}(BO_3)_3:X\ Pb^{2+}$ phosphor could be a good UV-A phosphor candidate for solid-state lighting and Phototherapy applications.

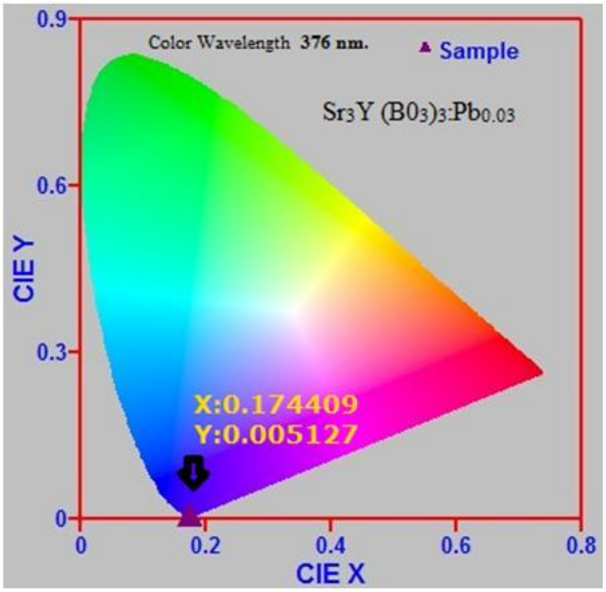

Figure 6 CIE diagram of Sr3Y1-0.03(BO3)3:0.03Pb2+

4. Conclusion

$Sr_3Y_{1-x}(BO_3)_3$: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

1. ***J. Krutmann, W. Czech, T. Diepgen.*** *s.l. : J. Am. Acad. Dermatol, 26 (1992) 225.*

2. Efficacy of Ultraviolet A1 Phototherapy in Recalcitrant Skin Diseases. ***Suh KS, Kang JS, Baek JW, Kim TK, Lee JW, Jeon YS, Jang MS, Kim ST.*** *s.l. : Ann Dermatol. , 2010 Feb 22(1):1-8. Englis. https://doi.org/10.5021/ad.2010.22.1.1.*

3. . ***L. Wu, X.L. Chen, Y. Zhang, Y.F. Kong, J.J. Xu, Y.P. Xu.*** *s.l. : J. Solid State Chem, 179 (2006) 1219.*

4. Synthesis and photoluminescence of inorganic borate host red emitting VUV phosphor YCaBO4:Eu3+. ***Ingale J T, Gawande Atul.*** *s.l. : AIP Conference Proceedings 1536, 895 (2013), 03 June 2013. Volume 1536, Issue 1 > 10.1063/1.4810517.*

5. Investigation of luminescence properties of Pb2+-doped Sr2B2O5. s.l. : The American Ceramic Society WILEY ONLINE Int J Appl Ceram Technol, 6 February 2018. 10.1111/ijac.12881.

6. Synthesis and Photoluminescence Properties of Pb2+ Doped. ***A. O. Chauhana1, K. A. Koparkar1, N. S. Bajaj2, S. K. Omanwar1.*** *s.l. : AIP, 2016. 1728, 020470 (2016); doi: 10.1063/1.4946521.*

7. Synthesis and PL study of UV emitting phosphor KCa4(BO3)3:Pb2 þ. ***A.B. Gawande a, 1, R.P. Sonekar b,n, S.K. Omanwar a.*** *s.l. : Journal of Luminescence Elsevier, 23 January 2014. 10.1016/j.jlumin.2014.01.044.*

8. Photoluminescence in Pb2 þ activated SrB4O7 and SrB2O4 phosphors. ***A.B. Gawande, J.T. Ingle, R.P. Sonekar, S.K. Omanwar.*** *s.l. : Journal of Luminescence Elsevier, 149 (2014) 236–239. 10.1016/j.jlumin.2014.01.007.*

9. A novel UV-emitting phosphor: LiSr4(BO3)3: Pb2+. ***Pekgözlü, İlhan.*** *s.l. : Journal of Luminescence Elsevier, 2013, pp. 93–95.*

10. Synthesis and photoluminescence properties of Pb2+ doped. ***Pekgözlü, Ilhan.*** *s.l. : optik Elsevier GmbH., 2015, pp. 1368-1371.*

11. Synthesis and photoluminescence properties of Li4SrCa(SiO4)2: M (M: Pb2 þ and Bi3 þ). ***İlhan Pekgözlü a, n, Ertuğrul Erdoğmuş a, Mükremin Yılmaz b.*** *s.l. : Journal of Luminescence Elsevier B.V., 2015, pp. 160-163.*

12. A novel UV-emitting phosphor: NaSr4(BO3)3: Pb2 +. ***Pekgözlü, İlhan.*** *s.l. : Journal of Luminescence,Elsevier B.V., 2016, pp. 182-185.*

13. Synthesis and PL study of UV emitting phosphor LiSr4(BO3)3:Pb2+. ***A. O. Chauhan*, N. S. Sawala, C. B. Palan, S. K. Omanwar.*** *s.l. : International Journal of Luminescence and applications, 2015, Vol. Vol5 (4), pp. 465-467 . 2277 – 6362.*

14. Photoluminescence properties of Pb2 þ doped M2Mg(BO3)2 (M¼Sr, Ba). ***Ayhan Mergen a, _Ilhan Pekg.*** *s.l. : Journal of Luminescence Elsevier B.V, 2013, Vol. 134, pp. 220-223.*

15. Combustion synthesis. ***TArunaSambandanEkambaram, Kashinath CPatilSinganahally.*** *2, s.l. : Current Opinion in Solid State and Materials Science, April 1997, Vol. 2. 10.1016/S1359-0286(97)80060-5.*

16. Combustion synthesis of borate phosphors. ***Thakare, D. S., et al., et al.*** *2, s.l. : Optical Materials ELSEVIER, 08/2007, Vol. 29. .*

17. UV-emitting phosphors: synthesis, photoluminescence and applications. ***Moharil, D. S. Thakare S. K. Omanwar P. L. Muthal S. M. Dhopte V. K. Kondawar S. V.*** *3, s.l. : physica status solidi Wiley, 20 January 2004, Vol. 201.*

18. The luminescence properties of Sr3Gd(BO3)3: Tb3+ phosphors under. ***ZHAO WenYu1, 2, GAO SongWei3, AN ShengLi2,3*, FAN Bin1 & LI SongBo.*** *34, s.l. : material science chinees science bulletin, Vol. 57, pp. 4513-4516.*

19. Br. J. Dermatol. ***R.A. Sheehan-Dare, M.J. Goodfield, N.R. Rowell,.*** *121-65, 1989 .*