# Photo-Luminescence study of $Ba_3Gd_{1-x}(BO_3)_3$ : X $Ce^{3+}$ phosphor

**S. P. Hargunani[1],R. P.Sonekar[1], V. R.Panse[2], Marta Michalska-Domanskais[3],N.S.Bajaj[4]**

[1]Department of Physics, G. S. College khamgaon, Dist: Buldana (M.S.), INDIA.

[*2]Department of Physics, Late B.S.Arts Prof.N.G.Sci & A.G.Comm College Sakharkherda, India-443202

[3] Institute of Optoelectronics, Military University of Technology, Poland.

[4]Department of Physics, Toshniwal Arts, Commerce & Science College

*[*2]Corresponding author's e-mail address: vshl.panse@gmail.com*

## Abstract

The polycrystalline powder sample of $Ce^{3+}$ activated barium gadolinium borate phosphors $Ba_3Gd_{1-x}(BO_3)_3$ : X $Ce^{3+}$($0.01 \leq X \leq 0.06$ ) are prepared by solution combustion. Formation of phosphor in desired crystalline phase confirmed by powder XRD characterization & FTIR. A SEM image shows the irregular grains with average particle size 2.5µm. The excitation spectrum consists of a single broad absorption band from 200 to 400 nm with the prominent excitation peak at 343 nm [$^2F_{5/2}$ to $^5D_1$ of $Ce^{3+}$ ions]. Strongest emission peak of 488nm [$^5D_1 \rightarrow {}^2F_{5/2}$] and weak of 501nm [$^5D_1 \rightarrow {}^2F_{7/2}$] wavelength which is of blue light is observed at 343nm UV light excitation. $Ba_3Gd_{1-x}(BO_3)_3$ : X $Ce^{3+}$ phosphor emits blue light under UV excitation. Maximum PL emission takes place at 3 mole percentage of $Ce^{3+}$. Concentration quenching for $Ce^{3+}$ ions is studied. Hence $Ba_3Gd_{1-x}(BO_3)_3$ : X $Ce^{3+}$ is new UV excited blue emitting phosphor useful for UV/Blue chip WLEDs.

## Keywords

Borate phosphor, Photoluminescence, Red emission, W- LED.

## 1. Introduction

The syntheses of compounds $M_3Ln(BO_3)_3$ M =Sr, Ba and Ln=La–Lu, Sc, Y have been reported in recent past years [1]. The spectroscopic properties of vacuum ultraviolet and x-ray excited $Ce^{3+}$ ion-activated $Ba_3Gd(BO_3)_3$ have been reported by Hong-bin Liang et.al. They studied luminescence properties of $Ce^{3+}$-doped barium gadolinium borate $Ba_3Gd(BO_3)_3$:$Ce^{3+}$ under vuv, uv, and x-ray excitations. $Ba_3Gd(BO_3)_3$:$Ce^{3+}$ is a poor x-ray phosphor. The dopant $Ce^{3+}$ is slightly larger than $Gd^{3+}$ but it will not distort the crystal lattice of $Ba_3Gd(BO_3)_3$ too seriously and is expected to replace $Gd^{3+}$ ions [2]. $Ba_3Gd(BO_3)_3$ doped with $Eu^{3+}$ ion was prepared by high temperature solid-state method and luminescence was studied by ZHOU Liya et.al. $Ba_3Gd(BO_3)_3$:$Eu^{3+}$ phosphor was effectively excited by the near ultraviolet (UV) light (396 nm) and blue light (466 nm). The main

emission peaks are at 611 and 616 nm , it was red emitting phosphor [3]. Cerium trivalent ion has only one 4f electron and only single discrete 4f energy level shielded by the completely filled $5S^2$, $5P^6$orbital. General emission of $Ce^{3+}$ has doublet character with wavelength difference approximately 40nm. Broad emission band is due to inter-configurationally $5d^1$-$4f^1$ allowed transition of $Ce^{3+}$. For blue luminescence $Ce^{3+}$ ions is worthy to use in phosphors. For the important point of application, each proper mono-color-blue LED phosphor must meet the following necessary conditions. (1) The phosphor must show higher thermal stability. (2) The phosphor must efficiently absorb the 340nm - 400nm excitation energy. (3) The CIE coordinates of the phosphor are close to the NTSC standard values. $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) is one kind of reported commercial blue phosphor used in fluorescent lamps, because of its efficient blue emission [11]. $Ca_2B_5O_9Cl:Eu^{2+}$, is another suitable Blue-Emitting Phosphor for n-UV Excited Solid-State Lighting [12]. $Ca_2Pb_3(PO_4)_3Cl : Ce^{3+}$ is recently reported blue emitting lamp phosphor [13]. $Sr_{1-x}Ca_xLu_2O_4:Ce^{3+}$ is blue phosphor for high CRI white LEDs [14-15].

## 2. Experimental

Phosphors were prepared by the solution combustion synthesis [4,5]. Stoichiometric amounts of high purity starting materials, $Ba(NO_3)_2$ (A.R.), $H_3BO_3$ (A.R.), $CO(NH_2)_2$ (A.R.), $Gd(NO_3)_3.6H_2O$ (A.R.), $Ce(NO_3)_3.6H_2O$ as given in table (1) are used for phosphor preparation. All chemicals from Merck of AR grade of (99.99%) purity. 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 $100^oC$ for about 30 min and the paste was then transferred directly to a pre-heated Muffle furnace, maintained at temperature $680^oC$, for combustion. Following the combustion, the resulting foamy samples was crushed to obtain fine particles and then annealed for 3 h at temperature $950^oC$. As prepared Borate phosphor material was characterized by powder XRD, SEM, PL and FT-IR techniques. Surface morphology and elemental analysis of the calcined powder sample was observed by scanning electron microscopy [SEM:Model JSM6100 (Jeol)].

***Table 1*** *Merck -AR grade chemicals used for synthesis*

| **$Ba_3Gd_{0.97}(BO_3)_3 : 0.03\ Ce^{3+}$** | | | | | |
|---|---|---|---|---|---|
| Precursors | **$Ba(NO_3)_2$** | **$Gd(NO_3)_2$** | **$H_3BO_3$** | **$NH_2CONH_2$** | **$Ce(NO_3)_3.6H_2O$** |
| Molar ratio | **3** | **0.96** | **3** | **7.45** | **0.04** |
| Weight in gm | **7.8405** | **1.08388** | **1.853** | **4.4744** | **0.194028** |

## 3. Results and Discussion

### *3.1. X-ray diffraction*

Powder X-ray diffraction measurementsof $Ba_3Gd_{0.970\ 0.03}Ce^{3+}$ $(BO_3)_3$ phosphor were taken on a RigakuMiniflex II X-ray Diffracto-meter and compared with JCPDS No.(52-1327) as shown in figure 1-A.The maximum peaks matches with the standard pattern. The additional peaks are present in recorded pattern are due to impurities. Sharp peaks in XRD pattern are due to large crystallite size. X-ray pattern of $Ba_3Gd(BO_3)_3$ matches with the X-ray pattern of low temperature phase of $Ba_3Y(BO_3)_3$ [1,2].Space group of phosphor $Ba_3Gd(BO_3)_3$ is R3(148) and cell parameters are a = 13.06, c=9.552. V= 1412.42 $A^{o3}$. A detailed structure description of $Ba_3Gd(BO_3)_3$ was not found in literature. Bing Han *et.al*. in his work mentioned that $Ba_3Gd(BO_3)_3$ is isomorphic with *H*-$Ba_3Y(BO_3)_3$ for the following three reasons: (i) The powder XRD patterns of $Ba_3Gd(BO_3)_3$ and *H*-$Ba_3Y(BO_3)_3$ are similar. (ii) The ionic radii of $Gd^{3+}$ [$R$Gd$_{(III)}$] = 93.8 pm are close to that of $Y^{3+}$ [$R$Y$_{(III)}$]=90.0 pm in six fold coordination. (iii) It was found that the unit cell parameters [$a$=13.067(3)Å, $c$=9.552(3)Å, trigonal, $R_3$] of $Ba_3Gd(BO_3)_3$ are similar with that [$a$=13.028(2) Å, $c$ =9.4992(2) Å, trigonal, $R_3$] of *H*-$Ba_3Y(BO_3)_3$[2]. In ahigh temperature phase, a *H*-$Ba_3Y(BO_3)_3$ with a trigonal system having a space group of $R(3)$, $Z$ = 6, which consistsof $YB_6O_{18}$ unit with polyhedral of $BaO_6$ and $BaO_8$as shown in figure 1-B [16 ].

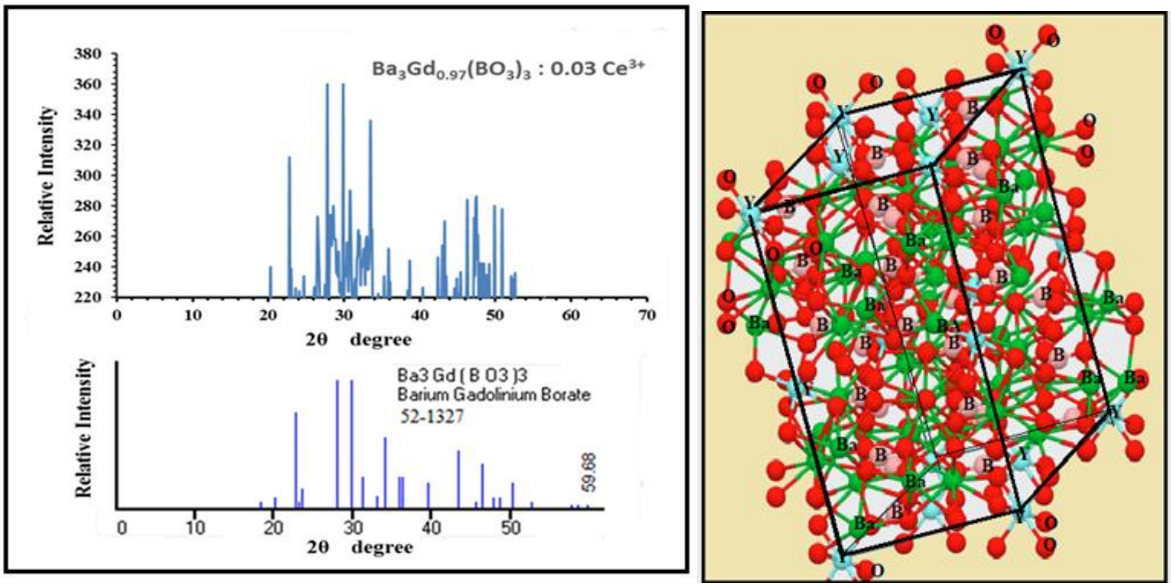


***Figure 1-A:****XRD-pattern of sample****1-B:****Structural unit of $Ba_3Y(BO_3)_3$ with six fold coordination of $Y^{3+}$ ions [17]*

### *3.2. SEM*

SEM study was carried out to examine the surface morphology of the prepared phosphor. The SEM images of $Ba_3Gd_{1-0.03}(BO_3)_3$:$0.03Ce^{3+}$ phosphors are shown in Figure 2. It was

observed that the microstructure of the phosphor consist of irregular grains with agglomerate phenomena. The average size of synthesized phosphor particles is about 50 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 nearly same as seen in surface morphology. SEM shows the image of polycrystalline particles and XRD measurements reflect the crystalline domain size. It indicates that solution combustion synthesized phosphor has sharp surface morphology as well as crystalline grains.

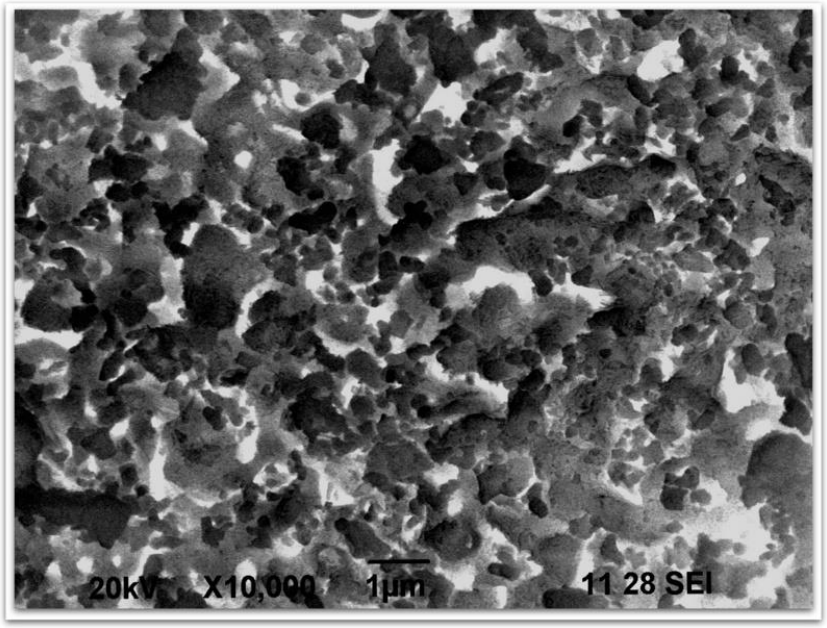


***Figure 2****: SEM Image of phosphor host.*

### *3.3. PL and PLE Study*

The PLE of $Ba_3Gd_{0.97}(BO_3)_3 : 0.03Ce^{3+}$ phosphor is shown in figure (3). It is recorded on F-7000 FL spectrophotometer with scan speed 240 nm/min, excitation-emission slit width 1nm. $Ce^{3+}$ is all-round candidate for phosphor materials and it does not have any 4f-4f transition. It shows only 4f-5d type inter configurationally transition in borate host [8,9,10]. Photoluminescence excitation is broad band in region 240nm to 400nm with shoulder peak at 343nm due to transition from $^2F_{5/2}$to$^5d_1$ level of activator ion in host lattice.

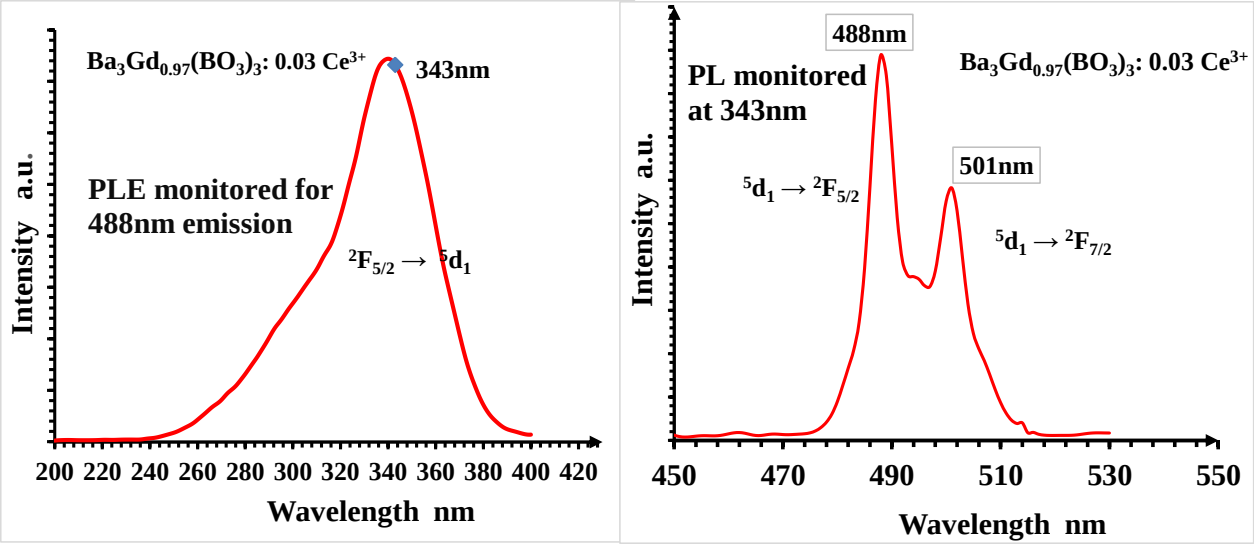


***Figure 3*** *PLE of $Ba_3Gd_{0.97}(BO_3)_3$ : 0.03 $Ce^{3+}$* ***Figure 4*** *PL of $Ba_3Gd_{0.97}(BO_3)_3$ : 0.03 $Ce^{3+}$*

The PL of $Ba_3Gd_{0.97}(BO_3)_3$ : 0.03 $Ce^{3+}$ phosphor monitored at 343nm excitation is shown in figure (4). PL recorded in range 450nm to 530nm shows two peaks at 488nm and 501nm. 488nm peak is due to $^5d_1$ to $^2F_{5/2}$ and 501nm peak is due to$^5d_1$ to $^2F_{7/2}$ transition of activator in crystal environment. $Ce^{3+}$ ion shown the two characteristic lines. Intensity of 501nm is less than 488nm line. 488nm lies in blue region of spectrum. So it is NUV excited blue emitting phosphor. The photoluminescence study is carried out at room temperature.

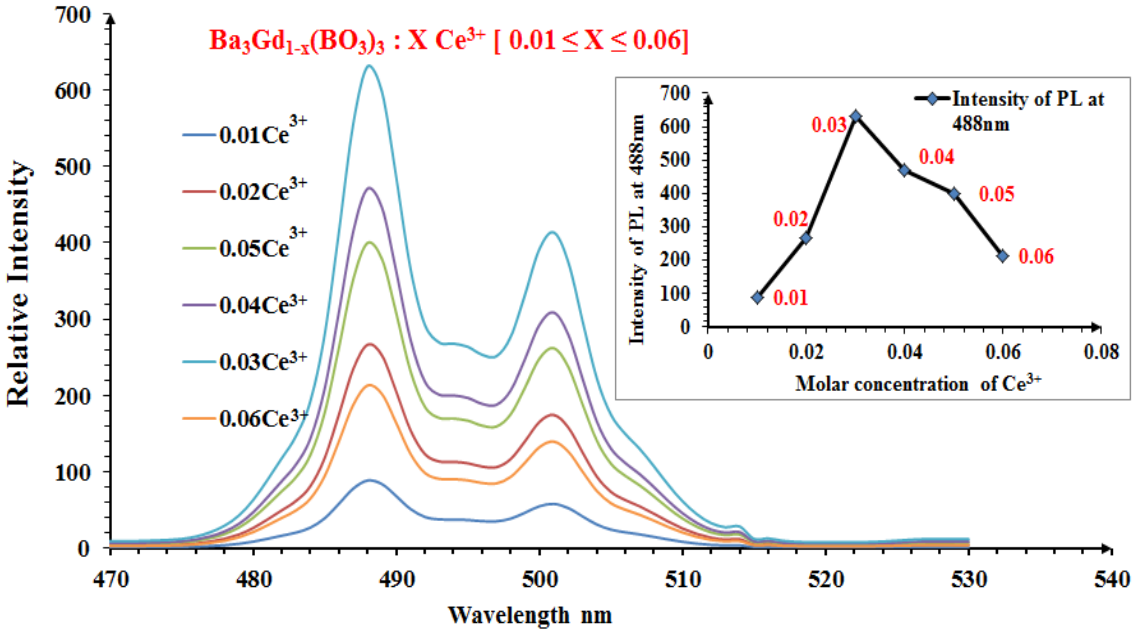


***Figure 5*** *PL of host phosphor at different concentration of dopant $Ce^{3+}$And embedded Concentration quenching Curve*

### *3.4. CIE Chromaticity Diagramof $Ba_3Gd_{0.97}(BO_3)_3$ : 0.03 $Ce^{3+}$*

Figure (6) shows the Commission International del Eclairage (CIE) chromaticity coordinates diagram of the $Ba_3Gd_{0.97}(BO_3)_3$ : 0.03 $Ce^{3+}$ phosphor at 488nm. The chromaticity coordinates of the phosphor $Ba_3Gd_{0.97}(BO_3)_3$ : 0.03$Ce^{3+}$for fixed concentration of $Ce^{3+}$ at 488 nm was computed using LEDTUNING. NL Software [https://www.ledtuning.nl/en/cie-convertor][11-12-13]. CIE Chromaticity co-ordinates for $Ba_3Gd_{0.97}(BO_3)_3$ : 0.03$Ce^{3+}$at PL wavelength 488nm are X = 0.05467, Y = 0.2541. It comes in blue region of CIE Chromaticity diagram and is indicated by black circle in figure(6). CCT value is 122321 kelvin and Delta uv is 0.1402.

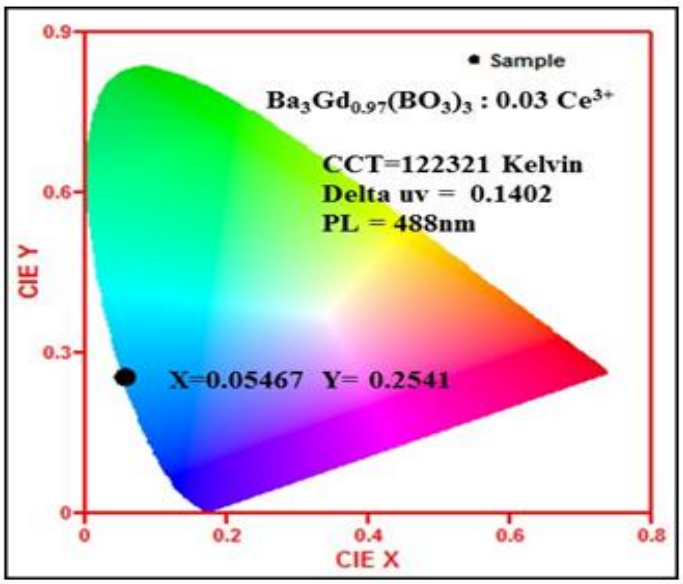


***Figure 6*** *CIE chromaticity of $Ba_3Gd_{0.97}(BO_3)_3$ : 0.03 $Ce^{3+}$*

## 4. Conclusions

The $Ba_3Gd_{1-x}(BO_3)_3$ : X $Ce^{3+}$polycrystalline phosphor was synthesized by solution combustion method . XRD confirmed the phase & formation of compound and it matches withstandard JCPDS file number 52-1327. SEM shows the average size of synthesized phosphor particles was about 2.5 µm and good crystalline. Phosphor shows broadexcitation band from 200 to 400 nm with prominent peak at 343 nm.PLE for characteristic emissionwavelength 488 nm was found to be 343 nm. At 343 nm, UVlight excitation $Ba_3Gd_{1-x}(BO_3)_3$ : X $Ce^{3+}$ phosphor emits blue light.

**Acknowledgements**

Author S.P.Hargunani is thankful to the Chairman of FIST-DST project SGB Amravati University Amravati, for providing XRD facility to this work and also thankful to Dr. R.P. Sonekar, Head Physics Dept., Dr. D S Talwankar, Head research center, G.S. Science,Arts and Commerce College Khamgaon, for providing synthesis facility.

**References**

1. Wang, De-Yin, Teng-Ming Chen, and Bing-Ming Cheng. *Inorganic chemistry* 51, no. 5 (2012): 2961-2965.
2. Han, Bing, Hong-bin Liang, Hui-hong Lin, Jiu-ping Zhong, Qiang Su, Pieter Dorenbos, M. DanangBirowosuto, Guo-bin Zhang, and Yi-bing Fu. *Journal of applied physics* 101, no. 11 (2007): 113530.
3. Liya, Zhou, Junli Huang, Yi Linghong, Gong Menglian, and Shi Jianxin. *Journal of Rare Earths* 27, no. 1 (2009): 54-57.
4. Simura, Rayko, TatsushiYagi, Kazumasa Sugiyama, Takayuki Yanagida, and Akira Yoshikawa. "*Journal of crystal growth* 362 (2013): 145-148.
5. Pan, Shangke, Jianyu Zhang, and Jianguo Pan. *Optical Materials* 76 (2018): 178-183.
6. Palaspagar, R. S., R. P. Sonekar, and S. K. Omanwar. *AIP Conference Proceedings*, vol. 1536, no. 1, pp. 807-808. American Institute of Physics, 2013.
7. Hargunani, S. P., R. P. Sonekar, HarmanpreetKaur, J. G. Mahakhode, and Samikha B. Dhoble. "Combustion synthesis of Ba3Y1-xSm3+ x (BO3) 3 asred-light emitting phosphors for indoor plant cultivation applications." In *Journal of Physics: Conference Series*, vol. 1913, no. 1, p. 012016. IOP Publishing, 2021..
8. Hargunani, Sanjay P., Rajkumar P. Sonekar, Ritesh S. Palaspagar, PranitaPatil, and Shriniwas K. Omanwar. *Macromolecular Symposia*, vol. 387, no. 1, p. 1800184. 2019.
9. X. Zhang and M. Gong, *Industrial & Engineering Chemistry Research ACS,* vol. 54, p. 7632−7639, 2015.
10. JiayueSuna, YiningSuna, J. Lai, Z. Xiab and HaiyanDua, *Journal of Luminescence,* vol. 132, no. 11, pp. 3048-3052, November 2012,.
11. Wang, Z. L., KokWaiCheah, Hoi Lam Tam, and M. L. Gong. *Journal of Alloys and Compounds* 482, no. 1-2 (2009): 437-439.
12. Zhang, Xinmin, Hong Chen, Weijia Ding, Hao Wu, and Jongsu Kim. *Journal of the American Ceramic Society* 92, no. 2 (2009): 429-432.
13. Panse, V. R., and S. J. Dhoble. *Optik* 219 (2020): 165107.
14. Zhou, Yipeng, Yunsheng Hu, Ronghui Liu, Yuanhong Liu, WeidongZhuang, Min Cao, TongyuGao, JunhangTian, Yanfeng Li, and Guantong Chen. *Journal of Rare Earths* (2020).
15. N.S.Kokode, V.R.Panse, S.J.Dhoble, J.of advanced material letter 2015,6(7),616-619.

16. Wang, De-Yin, Teng-Ming Chen, and Bing-Ming Cheng. "Host sensitization of Tb3+ ions in tribarium lanthanide borates Ba3Ln (BO3) 3 (Ln= Lu and Gd)." *Inorganic chemistry* 51, no. 5 (2012): 2961-2965.
17. Qiao, Xuebin, and Hyo Jin Seo. "Phase transition, structural and spectroscopic properties of Ba3Y (BO3) 3 phosphor." *Journal of Alloys and Compounds* 637 (2015): 504-508.
18. Hargunani, Sanjay Prakash, RajkumarPandurangSonekar, Anoop Singh, AjitKhosla, and SandeepArya. "Structural and spectral studies of Ce3+ doped Sr3Y (BO3) 3 nano phosphors prepared by combustion synthesis." *Materials Technology* (2020): 1-12.