

Photo Luminescent Properties of Dysprosium-Dy³⁺ Doped Ba₃Y(BO₃)₃ Phosphor

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ABSTRACT

Ba₃Y_{1-x}(BO₃)₃:xDy³⁺ [0.005 ≤ x ≤ 0.03] phosphor is synthesized by solution combustion method. Photoluminescence in the range 400nm to 700nm is recorded which shows two major peaks at 485nm [⁴F_{9/2} – ⁶H_{15/2}], 575nm [⁴F_{9/2} – ⁶H_{13/2}] and minor peak at 622nm ⁴F_{9/2} – ⁶H_{11/2}. Under UV excitation of 349nm it shows white luminescence. Intensity ratio of Blue line of 485nm to yellow line of 575nm is calculated which also confirms the emission of near white light. The optimal doping concentration of Dy³⁺ in Ba₃Y_{1-x}(BO₃)₃ host matrix is found to be 2 mole percentage. The 1931-CIE color coordinates and the CCT value of phosphor is also calculated using McCamy empirical formula. All the results indicate that Dy³⁺ doped Ba₃Y_{1-x}(BO₃)₃ powder phosphor could be used as an efficient luminescent material for solid state lighting as well as NUV based w-LEDs.

Keywords:- Photoluminescence, White Light Emitting Diodes, Solution Combustion Synthesis

I. INTRODUCTION

Dy³⁺ ion has been extensively studied to generate white light in various hosts like oxides, silicates, aluminates, aluminoborates, aluminosilicates, nitrides, borates, etc. due to its two main emission bands the blue band (455–500 nm) due to the magnetic dipole transition and the yellow band (570–600 nm) due to the electric dipole transition. In most cases trivalent dysprosium ion (Dy³⁺)-doped phosphors shows intense blue (455–490nm) and yellow (570–590nm) emissions and generate white-light emission. As a result white light can be obtained by balancing the ratio of blue to yellow emissions. The yellow emission of Dy³⁺ is dependent to the local environment in crystal, and the blue emission of Dy³⁺ is not very sensitive to the local environment. Owing to the high sensitivity property to the local environment, Dy³⁺ can be used to probe the crystal structure of the

host lattice. A white light emission with proper correlated color temperature (CCT) and chromaticity coordinates can be achieved by suitable adjustment of the yellow/blue (Y/B) intensity ratio of Dy³⁺-doped phosphors. Because of this, Dy³⁺-doped host lattices can be developed as a single host phosphor as source of white light in light emitting diodes [1]. Poor color rendering index and high CCT are the drawbacks of blue InGaN LED chip and YAG:Ce³⁺ yellow phosphors used for white light emitting diodes. So research on new blue and yellow phosphors which balances the red component in white light emission is going on [2,3]. In recent years, many phosphors doped with Dy³⁺ have been reported, such as SrGa₂O₉:Dy³⁺ [4], LaB₃O₆:Dy³⁺ [5], KBaY(BO₃)₂:Ce³⁺, Dy³⁺ [6], Ba₂CaZn₂Si₆O₁₇:Dy³⁺ [7], Li₄CaB₂O₆:Dy³⁺ [8], Li₄CaB₂O₆:Dy³⁺ [9] etc.

II. METHODS AND MATERIAL

Powder samples of $Ba_3Y_{1-x}(BO_3)_3 \cdot xDy^{3+}$ [$0.005 \leq x \leq 0.03$] were synthesized by a modified exothermic solution combustion method. In the SCS, nitrate solution of A.R. grade [99.9% purity] precursors [$Ba(NO_3)_2, Y(NO_3)_3, H_3BO_3, Dy(NO_3)_3 \cdot xH_2O$] in the stoichiometric amount was used as an oxidizer while NH_2CONH_2 is a fuel for combustion [10,11]. In deionized water paste of all precursors is made and then kept in preheated furnace at $680^\circ C$. The paste boiled - ignited within a few minutes and develops a self-propagating yellow-orange flame for 4 to 5 minutes. To ensure the complete decomposition of chemicals and for proper phase of phosphor the crucible is kept in furnace for 20 minutes. After removing crucible from the furnace it cooled to room temperature and grinded into fine powder. The synthesized powder phosphor were post annealed at $950^\circ C$ for 3 hours in a muffle furnace in air.

III. RESULTS AND DISCUSSION

3.1 XRD:-The formation of the phosphor in desired crystallographic phase was determined by powder XRD recorded by X-ray diffraction using the Cu-K α wavelength ($\lambda = 1.54060 \text{ \AA}$) and scanning in the 2θ range from $20^\circ - 80^\circ$. Figure (1) shows the powder XRD pattern of the phosphor $Ba_3Y_{1-0.02}(BO_3)_3 \cdot 0.02Dy^{3+}$. It is in agreement with standard pattern given in ICSD File NO. 39744 and standard JCPDS file no 51-1849. This host crystal compound has two phases i.e. low temperature phase α - $Ba_3Y(BO_3)_3$ and high temperature β - $Ba_3Y(BO_3)_3$ [12]. XRD pattern of synthesized phosphor matches with the standard low temperature phase. Few extra peaks at 68.92° and 75.94° are present in the XRD. Low temperature α - $Ba_3Y(BO_3)_3$ phosphor possess hexagonal crystal structure with the space group $P6_3 cm$ (No.185) [13]. All B^{3+} are co-ordinated with three O^{2-} forming the BO_3^{3-} triangles. Y and Ba

sites are separated by parallel planes constructed by BO_3^{3-} anion group. All Ba sites has the 9 co-ordination number. All Y^{3+} ions has the 6 co-ordination number. As shown in figure (2) crystal structure comprised of isolated BO_3 triangles; YO_6 octahedral and BaO_4 polyhedral. $Ba_3Y(BO_3)_3$ possess layer structure of BO_3 triangles [14]. Cell parameters are $a=b=9.419 \text{ \AA}$; $c=17.590 \text{ \AA}$; $V=1352.67 \text{ \AA}^3$.

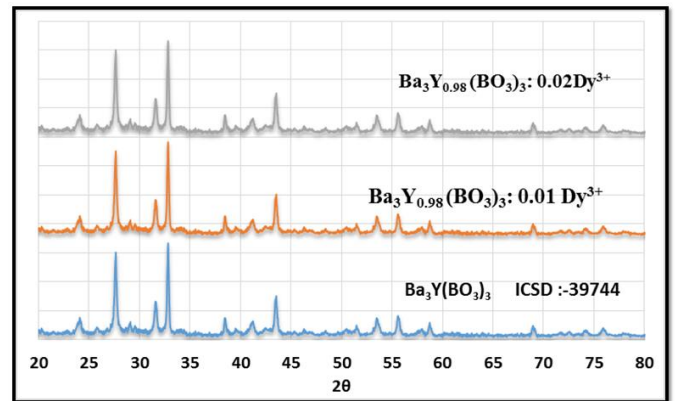
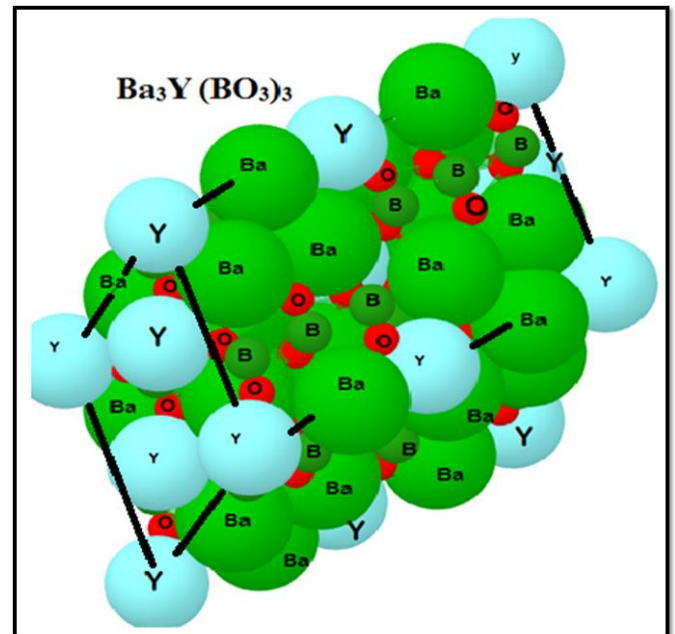


Figure [1] X-ray diffraction $Ba_3Y_{1-0.02}(BO_3)_3 \cdot 0.02Dy^{3+}$



3.2 SEM-EDS:-

SEM micrographs of $Ba_3Y(BO_3)_3 \cdot 0.02Dy^{3+}$ given in figure(3) shows that powder phosphor is made of a network of agglomerated irregular particles. The surface consists of voids due to large gaseous matter that escaped due to high exothermicity during combustion process. SEM micrographs of $Ba_3Y(BO_3)_3 \cdot 0.02Dy^{3+}$ powder phosphors were

recorded at 20KV X 10000; 20KV X 20000; 20KV X 30000; 20KV X 55000 magnifications. Elemental composition of powder phosphor is studied using EDS along with SEM. EDS Spectrum given in figure(4) confirms the presence of Barium (Ba), Yttrium(Y), Boron(B), Oxygen(O), and Dysperium (Dy) elements.

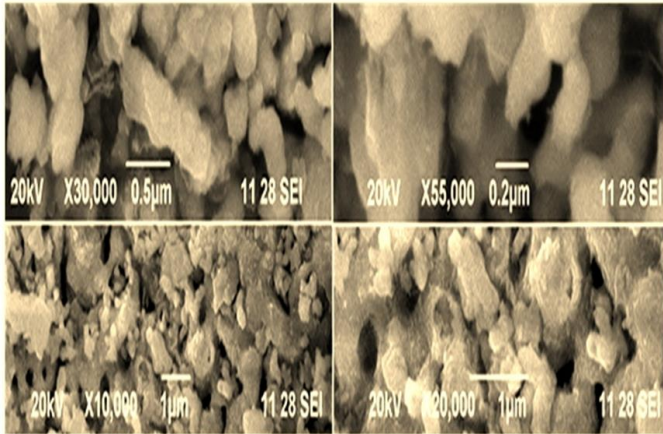


Figure 2 SEM images of $Ba_3Y(BO_3)_3:0.02Dy^{3+}$ at different resolution

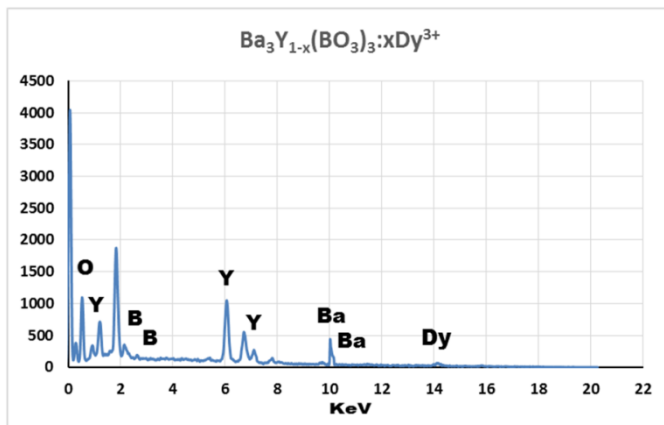


Figure 3 EDS of $Ba_3Y(BO_3)_3:0.02Dy^{3+}$

3.3 FTIR:- To confirm the coordination environment of B-O in $Ba_3Y(BO_3)_3$ structure, the IR spectra of $Ba_3Y(BO_3)_3$ were recorded at room temperature & shown in Figure(5). The FTIR spectrum exhibit broad absorptions in the $650 - 1600 \text{ cm}^{-1}$ range. All the bands in the $1200 - 1600 \text{ cm}^{-1}$ range correspond to the stretching of the B-O bonds of BO_3 units. The bands in the region of $800 - 1200 \text{ cm}^{-1}$ correspond to the B-O bond stretching of tetrahedral BO_4 units. All the bands below 800 cm^{-1} correspond to the B-O-B bending vibrations of borate networks. The peak at

$3300-3500 \text{ cm}^{-1}$ corresponds the stretching mode of O-H are also absent. The absence of peaks in $1500- 2000 \text{ cm}^{-1}$ indicates the complete residual of nitrate and organic matter. Comparing the FTIR spectra of $Ba_3Y(BO_3)_3$ and that of $Ba_3Y(BO_3)_3:0.02Dy^{3+}$, $Ba_3Y(BO_3)_3:0.03Dy^{3+}$, $Ba_3Y(BO_3)_3:0.04Dy^{3+}$, it was observed that there is no change in the FTIR spectrum structure, and only difference in intensity was observed. It can be concluded that incorporating different dopant ions in the $Ba_3Y(BO_3)_3$ host matrix did not influence the main structure or form any type of bonds in the development of the powder phosphors, which is in agreement with the XRD spectra.

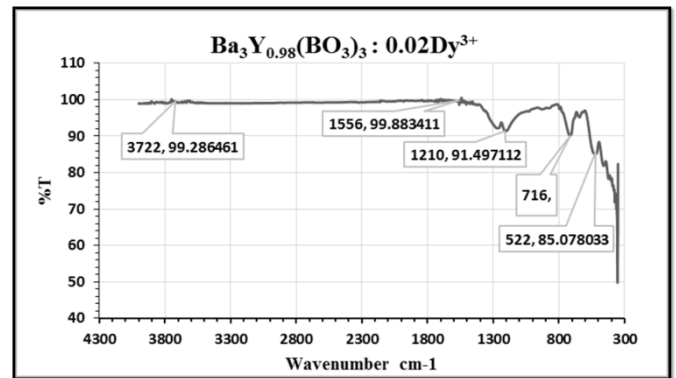


Figure 4 FTIR of $Ba_3Y(BO_3)_3:0.02Dy^{3+}$

3.4 Photo-Luminescence study:-

PL-PLE spectra of $Ba_3Y_{0.98}(BO_3)_3:0.02Dy^{3+}$ phosphor was measured at room temperature and shown in figure(6). PLE spectra monitored at 485nm luminescence exhibit intense absorption peak for 349nm because of ${}^6H_{15/2} \rightarrow {}^6F_{9/2}$ transition of Dy^{3+} in host crystal. PLE spectra also shows less intensity multiple peaks at 324nm, 364nm and 387nm. PL spectra was measured in the range 450nm -680nm for 349nm near UV excitation. In PL three major peaks was present at 485nm, 575nm and 622nm. ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ magnetic dipole transition of Dy^{3+} independent of surrounding crystal field produce blue emission line at 485nm. Crystal field hypersensitive ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ electric dipole transition of Dy^{3+} produce yellow line at 575nm. Disordered crystal field transition ${}^4F_{9/2} \rightarrow {}^6H_{11/2}$ of Dy^{3+} produce near red

spectral line at 622nm. Ratio of intensities of 485nm to 575nm spectral line is 1.28, which results in near white light emission from the material. So $Ba_3Y_{0.98}(BO_3)_3:0.02Dy^{3+}$ phosphor is NUV excited white light emitting phosphor.

According to Judd-Ofelt theory when Dy^{3+} take low symmetry local site without inversion symmetry in host crystal the ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ electric dipole transition resulting in yellow emission will be dominant in PL spectra [15]. In this phosphor blue emission at 485nm which is independent of Dy^{3+} surrounding crystal field is prominent. Yellow emission line decide the color correlated temperature of phosphor and generate white light. The effect of Dy^{3+} concentration on photo luminescent property of $Ba_3Y_{1-x}(BO_3)_3:xDy^{3+}$ is shown in figure (7). At all concentrations of Dy^{3+} position of PL peaks is at the same wavelength and only intensity changes. At 2mole% weight of Dy^{3+} intensity of PL-PLE line is maximum and above it intensity decreases i.e. concentration quenching occurs. Figure (8) shows concentration quenching curve. As concentration of Dy^{3+} increases the probability of non radiative energy transfer among them increases leading to decrease in PL intensity. Critical distance R_c among Dy^{3+} ions will decide the type of interaction i.e. an exchange, radiation reabsorption or multipole-multipole leading to concentration quenching.

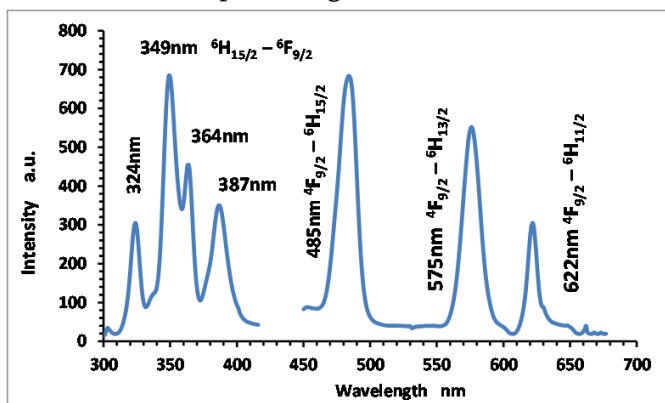


Figure 5 PL-PLE of $Ba_3Y_{0.98}(BO_3)_3:0.02Dy^{3+}$

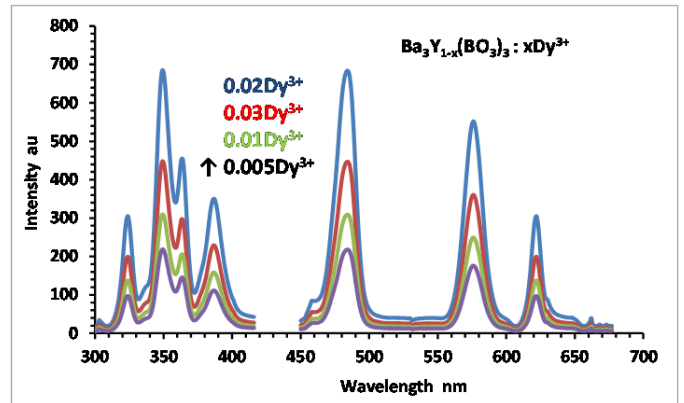


Figure 6 PL-PLE OF $Ba_3Y_{1-x}(BO_3)_3:xDy^{3+}$

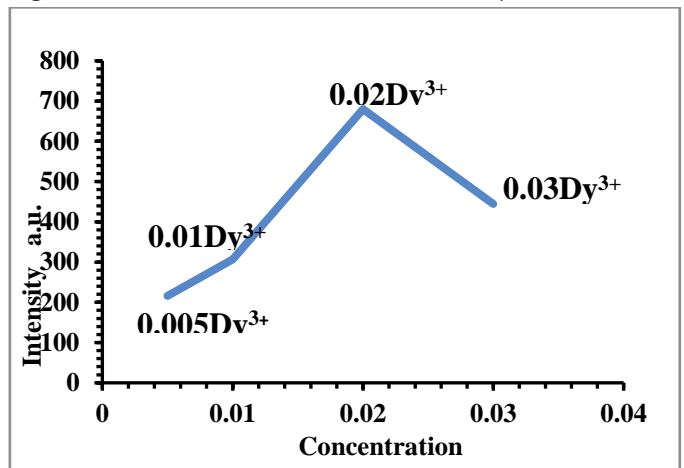


Figure 7 Concentration quenching curve of $Ba_3Y_{1-x}(BO_3)_3:xDy^{3+}$

3.5 CIE-Chromaticity Diagram:-The Commission International de l'Eclairage (CIE-1931) chromaticity is an important system for checking colors of phosphors [16]. Figure (9) shows 1931-CIE chromaticity co-ordinates diagram of phosphor $Ba_3Y_{1-x}(BO_3)_3:xDy^{3+}$. The 1931-CIE co-ordinates of $Ba_3Y_{0.98}(BO_3)_3:0.02Dy^{3+}$ phosphor are $X=0.410, Y=0.380$ and lie in the white region but away from ideal same intensity white light illumination ($X=0.333, Y=0.333$). CIE- co-ordinates of $0.005Dy^{3+}$ and $0.03Dy^{3+}$ doped phosphor are the yellowish-white region. $0.04Dy^{3+}$ and $0.01Dy^{3+}$ phosphor are in radish-white region of 1931-CIE diagram. The color quality of white light in terms of color correlated temperature (CCT) is given by the McCamy empirical formula [17].

$$CCT = -437n^3 + 3601n^2 - 6861n + 5514.31$$

Where n is the inverse slope line having value, $n = (X - X_e) / (Y - Y_e)$. Here (X, Y) are CIE-co-ordinates and $(X_e = 0.332, Y_e = 0.186)$ co-ordinates of epicenter.

Lamps with CCT value below 3200K are considered as Warmth sources and having value more than 4000K are considered Cool sources of light in appearance. For each phosphor CCT value and CIE- co-ordinates are given in table (1).

Table 1 CCT value and CIE- co-ordinates of synthesized phosphor

$Ba_3Y_{1-x}(BO_3)_3:xDy^{3+}$	CIE-Co-ordinates (X,Y)	CCT
0.005 Dy^{3+}	(0.430,0.395)	3043.877892
0.01 Dy^{3+}	(0.420,0.340)	2688.035948
0.02 Dy^{3+}	(0.410,0.380)	3309.475983
0.03 Dy^{3+}	(0.410,0.350)	3018.699669
0.04 Dy^{3+}	(0.398,0.425)	3885.047021

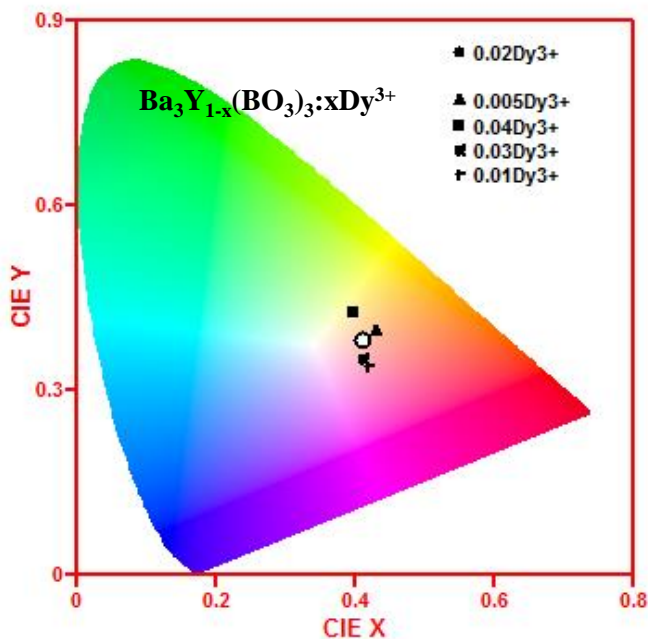


Figure 8 CIE-Chromaticity diagram of $Ba_3Y_{1-x}(BO_3)_3:xDy^{3+}$

IV. CONCLUSION

$Ba_3Y_{1-x}(BO_3)_3:xDy^{3+}$ phosphors doped with different concentrations of Dy^{3+} ions were prepared by the solution combustion method in air. The crystalline structure, excitation, emission properties of the

phosphors were characterized by XRD and photoluminescence spectrophotometry, respectively. The PLE spectrum shows that $Ba_3Y_{1-x}(BO_3)_3:xDy^{3+}$ powder phosphor exhibit a strong peak at 349 nm which is acceptable wavelength for w-LEDs. Upon 349 nm excitation, this phosphor shows peaks at 485 nm (blue), 575 nm (yellow) and 622 nm (red). The optimal doping concentration of Dy^{3+} in $Ba_3Y_{1-x}(BO_3)_3$ host matrix was found to be $x = 0.02$. The 1931-CIE color coordinates for $Ba_3Y_{1-x}(BO_3)_3:xDy^{3+}$ ($x = 0.02$) phosphor is calculated by LED tuning software to be (0.410,0.380) which falls near the white region with the CCT value of 3309.475983 K. All the results indicate that Dy^{3+} doped $Ba_3Y_{1-x}(BO_3)_3$ powder phosphor could be used as an efficient luminescent material for solid state lighting as well as NUV based w-LEDs.

V. REFERENCES

- [1]. Shrivastava, Ravi, Jagjeet Kaur, and VikasDubey. "White light emission by Dy^{3+} doped phosphor matrices: A short review." *Journal of fluorescence* 26, no. 1 (2016): 105-111.
- [2]. Y. Narukawa, J. Narita, T. Sakamoto, T. Yamada, H. Narimatsu, M. Sano, T. Mukai, Recent progress of high efficiency white LEDs, *Phys. Status Solidi A*. 204 (6) (2007) 2087-2093.
- [3]. Z.G. Xia, Q.L. Liu, Progress in discovery and structural design of color conversion phosphors for LEDs, *Prog. Mater Sci.* 84 (2016) 59-117.
- [4]. Lai, Junan, Zhangwen Long, JianbeiQiu, Dacheng Zhou, Junhe Zhou, Congcong Zhu, Songhan Hu, Ke Zhang, and Qi Wang. "Warm white light emitting from single composition $SrGa_2O_{19}: Dy^{3+}$ phosphors for AC-LED." *Journal of the American Ceramic Society* 103, no. 1 (2020): 335-345.
- [5]. Wu, Xiao, Chuanxing Jiang, Zijian Liang, Qiang Wang, Junqin Feng, Daoyun Zhu, Shengbiao Pan, Zekai Lin, Defu Tan, and Zhongfei Mu.

- "Photoluminescence properties of LaB₃O₆: Dy³⁺ phosphors for white light-emitting diodes." *Optik* (2020): 164877.
- [6]. Han, Bing, Yazhou Dai, Jie Zhang, Beibei Liu, and Hengzhen Shi. "Development of near-ultraviolet-excitable single-phase white-light-emitting phosphor K₂BaY (BO₃)₂: Ce³⁺, Dy³⁺ for phosphor-converted white light-emitting diodes." *Ceramics International* 44, no. 12 (2018): 14803-14810.
- [7]. Annadurai, G., S. Masilla Moses Kennedy, and V. Sivakumar. "Synthesis of novel Dy³⁺ activated Ba₂CaZn₂Si₆O₁₇ phosphors for white light-emitting diodes." *Luminescence* 33, no. 3 (2018): 521-527.
- [8]. Kumar, Vinay, Vivek K. Singh, J. Sharma, O. M. Ntwaeaborwa, and H. C. Swart. "Synthesis and photoluminescence study of a single dopant near white light emitting Li₄CaB₂O₆: Dy³⁺ nanophosphor." *Journal of Alloys and Compounds* 688 (2016): 939-945.
- [9]. Li, Panlai, Zhiping Yang, Zhijun Wang, and Qinglin Guo. "White-light-emitting diodes of UV-based Sr₃Y₂(BO₃)₄: Dy³⁺ and luminescent properties." *Materials Letters* 62, no. 10-11 (2008): 1455-1457.
- [10]. Mimani, T., and K.C. Patil. 2001 "Solution combustion synthesis of nanoscale oxides and their composites." *Materials Physics and Mechanics (Russia)* 4, no. 2 134-137.
- [11]. Bajaj, N. S., and S. K. Omanwar. 2012 "Combustion synthesis and luminescence characteristic of rare earth activated LiCaBO₃." *Journal of Rare Earths* 30, no. 10: 1005-1008.
- [12]. Hargunani, Sanjay P., Rajkumar P. Sonekar, Ritesh S. Palaspagar, Pranita Patil, and Shriniwas K. Omanwar. "Blue Luminescent Phosphor Sr₃Y_{1-x}(BO₃)₃: xBi³⁺ for WLED Applications." In *Macromolecular Symposia*, vol. 387, no. 1, p. 1800184. 2019.
- [13]. Hargunani, S. P., R. S. Palaspagar, R. P. Sonekar, and S. K. Omanwar. "Photo-luminescence study of red borate phosphor Sr₃Y_{1-x}(BO₃)₃: xEu³⁺." In *AIP Conference Proceedings*, vol. 2104, no. 1, p. 030027. AIP Publishing LLC, 2019.
- [14]. Kuang, Jinyong, and Yingliang Liu. "White-emitting long-lasting phosphor Sr₂SiO₄: Dy³⁺." *Chemistry letters* 34, no. 4 (2005): 598-599.
- [15]. Nagpure, I. M., V. B. Pawade, and S. J. Dhoble. "Combustion synthesis of Na₂Sr (PO₄)₂: Dy³⁺ white light emitting phosphor." *Luminescence* 25, no. 1 (2010): 9-13.
- [16]. Maggay, Irish Valerie B., and Wei-Ren Liu. "Novel red-emitting Ba₃Y (BO₃)₃: Bi³⁺, Eu³⁺ phosphors for N-UV white light-emitting diodes." *Journal of nanoscience and nanotechnology* 18, no. 1 (2018): 3-10.
- [17]. Kumar, Vinay, Vivek K. Singh, J. Sharma, O. M. Ntwaeaborwa, and H. C. Swart. "Synthesis and photoluminescence study of a single dopant near white light emitting Li₄CaB₂O₆: Dy³⁺ nanophosphor." *Journal of Alloys and Compounds* 688 (2016): 939-945.