

Modified Route of Combustion Synthesis and Photoluminescence of (Y,Gd)Al₃(BO₃)₄:Eu³⁺ Phosphors for PDPs applications.

J. T. INGLE¹, R.P.SONEKAR^{2#}, S.K.OMANWAR³, YUHUA WANG⁴

¹ Department of Physics, J.D. Institute of Engineering & Technology, Yavatmal, India.

² Department of Physics, G. S. Science, Arts & Commerce College, Khamgaon, India.

³ Department of Physics, S.G.B.Amravati University, Amravati, India.

⁴ Department of Materials Science, School of Physical Science and Technology, Lanzhou University, Lanzhou, P.R.China. e-mail:sonekar_rp@yahoo.com

Abstract

The high luminescent (Y,Gd)Al₃(BO₃)₄:Eu³⁺ phosphor with improved the color purity and high intensity of red phosphor for plasma display panel was reported. The phosphor was prepared by a modified and simple solution combustion technique. The synthesis is based on the exothermic reaction between the fuel (Urea) and Oxidizer (Ammonium nitrate). The heat generated in reaction is utilized for auto-combustion of precursors. The photoluminescence (PL) spectra were investigated under 147 nm (VUV) excitation, The Optimized composition (Y_{0.55}Gd_{0.35})Al₃(BO₃)₄:0.10Eu³⁺ phosphors showed a strong red emission around 615 nm. This is due to Eu³⁺ substituted for Y³⁺ occupied the non-centrosymmetric position, energy transfer from Y to Gd observed and Al³⁺ doped ion will increase the electric dipole ⁵D₀→⁷F₂ transition of Eu³⁺ in the crystal structure of (Y,Gd)Al₃(BO₃)₄:Eu³⁺. It can be concluded that combustion synthesis technique can successfully employed to produce promising red phosphor for plasma display panels (PDPs) applications.

Keywords: Combustion synthesis, phosphors, PDPs applications.

Introduction

In the cutting edge development of display technology, inorganic phosphors have been studied extensively for use in display panel applications of various types, such as plasma display panel (PDP), vacuum fluorescent display (VFD), and field emission display (FED) [1]. Recently, phosphors(Y,Gd)Al₃(BO₃)₄ has been focused due to their good thermal and chemical stability. (Y,Gd)Al₃(BO₃)₄ is known to have rhombohedral symmetry with the space group R32, where rare earth ions are at the center of distorted trigonal prism, being in non-centrosymmetric sites[2]. The major emission peak for Eu³⁺ activator in non-centrosymmetric site is the forced electric dipole ⁵D₀→⁷F₂ transition. Hence, Eu³⁺ ion is doped into (Y,Gd)Al₃(BO₃)₄ lattices to obtain a red phosphor with excellent colorimetric characteristics[3,4].(Y,Gd)Al₃(BO₃)₄:Eu³⁺ phosphors are synthesized using solid-state reaction methods[5,6], which require very high temperature and prolonged heating to obtain pure phase. In the last few years, various improved wet-chemical methods, such as sol-gel[7,8], combustion[9], the thermal decomposition[10] and spray pyrolysis [11] methods, have been developed to prepare the

phosphors, which have some advantages, for example, fine homogeneity, high reactivity of starting materials, as well as lower sintering temperatures, etc. Among the wet chemical routes, solution combustion synthesis is an attractive technique due to its advantages such as low-processing cost, energy efficiency and high production rate. The auto-combustion of fuel-nitrate route applied in the present work is used to prepare highly reactive and homogeneous powders, and it involves a low temperature initiated combustion process which makes use of the heat energy liberated by the exothermic anionic oxidation-reduction between citrate and nitrate ions [12-18].

Experimental techniques

Combustion synthesis of phosphors

The samples were prepared by a simple route of solution combustion technique. The starting ingredients $Y(NO_3)_3 \cdot 6H_2O$, $Gd(NO_3)_3 \cdot 6H_2O$, $Eu(NO_3)_3 \cdot 6H_2O$, (IRE Ltd.), $Al(NO_3)_3 \cdot 6H_2O$, H_3BO_3 , NH_4NO_3 & $NH_2-CO-NH_2$ (S D Fine AR) were used. The stoichiometric amounts of the ingredients required were calculated from multiplier of coefficient in balanced chemical reaction listed in table 1. Ingredients were thoroughly mixed in an Agate Mortar, adding little amount of double distilled water and obtained an aqueous homogeneous solution. The aqueous solution was then transferred in to a china basin and introduced in to preheated muffle furnace maintained at $550^\circ C$. The solution boils, foams and ignites to burn with flame and obtained a voluminous, foamy powder. The entire combustion process was over in about 5 minutes following the combustion, the resulting fine powders were annealed in a slightly reducing atmosphere suddenly cooled to room temperature.

XRD Analysis and particle morphology

S.No.	Product	Corresponding reaction with balanced molar ratios of precursors
1.	$(Y_{1-x-y}, Gd_y)Al_3(BO_3)_4 \cdot zEu^{3+}$	$(1-x-y)Y(NO_3)_3 \cdot 6H_2O + yGd(NO_3)_3 \cdot 6H_2O$ $+ 3Al(NO_3)_3 + 4H_3BO_3 + 5CO(NH_2)_2 + 4.5 NH_4NO_3$ $+ zEu(NO_3)_3 \cdot 6H_2O \xrightarrow[\Delta]{550^\circ C} (Y_{0.55}, Gd_{0.35})Al_3(BO_3)_4 \cdot 0.10Eu^{3+} + \text{Gaseous products}$ $(H_2O, NH_3 \text{ and } NO_2),$ $x=0.55, y=0.35, z=0.10$

Characterization of samples

The X-ray diffraction (XRD) pattern of prepared host samples were recorded on Rigaku MiniFlex diffractometer with Scan speed 2.00 deg./min . The morphology of the phosphor particles were studied by using Hitachi model S-4800 type-2 field emission scanning electron microscope. VUV PL spectra were

measured by FLS-920T fluorescence spectrophotometer with a VM-504-type vacuum monochromator using a deuterium lamp as the lighting source. The excitation spectrum can be corrected by sodium salicylate, whose quantum efficiency is almost constant in this region. All the measurements were performed at room temperature. The emission spectrum were tested under 147 nm excitation.

Result and Discussion

Figure 1 shows the powder XRD patterns of host lattice $(Y,Gd)Al_3(BO_3)_4$ calcinated at 900 °C for about 2 hour is match with ICDD Card no. 00-052-0232 corresponds to the formation of pure and mono-phase phase of this phosphor having rhombohedral symmetry with the space group R32, with unit cell parameter of $a=b=9.295 \text{ \AA}$, $c=7.243 \text{ \AA}$ and interfacial angles $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$ where rare earth ions are at the center of distorted trigonal prism, being in non-centrosymmetric sites [2]. This is most favorable aspects as Eu^{3+} doped ion takes complete site of Y^{3+} this may due to comparable ionic radii of Y^{3+} and Eu^{3+} .

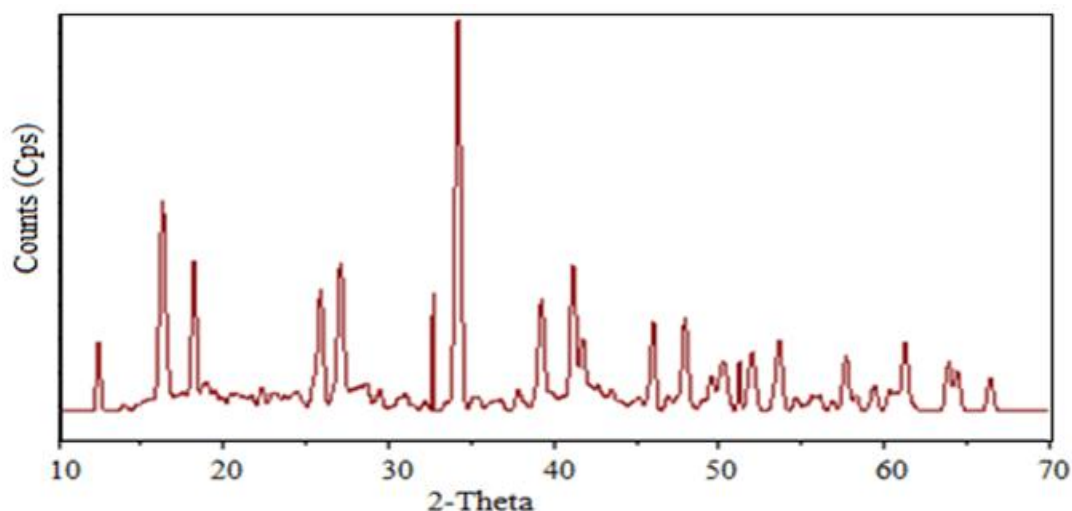


Figure 1: XRD pattern of $(Y,Gd)Al_3(BO_3)_4$ (ICDD Card no. 00-052-0232)

Solution combustion process can achieve the in depth mixing of reactants on the atomic level, leading to an increase in reaction rate and a decrease in synthesis temperature [19]. Figure 2 shows average particle size of the phosphor particles is about 1 μm particles with regular morphology with some agglomeration.



Figure 2: FE-SEM micrograph $(Y,Gd)Al_3(BO_3)_4:Eu^{3+}$

Photoluminescence of $(Y,Gd)Al_3(BO_3)_4:Eu^{3+}$

The optimization of $(Y,Gd)Al_3(BO_3)_4:Eu^{3+}$ was carried out for the best luminescence performance. VUV PL spectra for $(Y_{0.55},Gd_{0.35})Al_3(BO_3)_4:Eu^{3+}$ under 147 nm is depicted in figure 3. Shows intense radiation line peaking at 615nm due to $^5D_0 \rightarrow ^7F_2$ electric dipole transition, and the other emission peaks are 593nm, 705 nm ascribed to $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_4$ magnetic dipole transition of Eu^{3+} respectively. The result indicates that most of the Eu^{3+} is located at sites without inversion symmetry, the CIE Co-ordinates of prominent emission line was found to be (0.67,0.31)[20] and chromatic point is shown in Figure 4 .

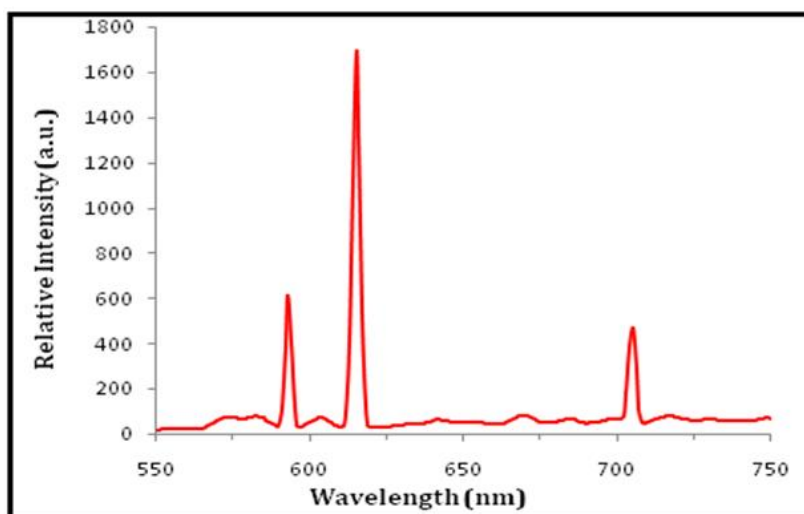


Figure 3 :PL Emission Spectra of $(Y,Gd)Al_3BO_4:Eu^{3+}$ 147 nm.

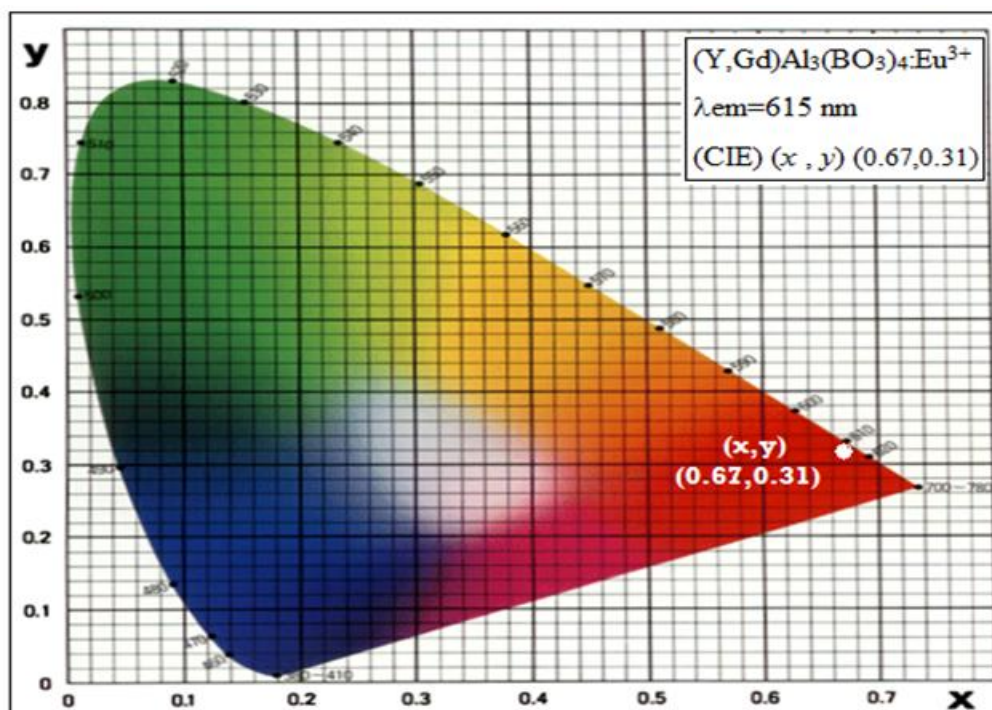


Figure 4: CIE Chromatic points & spectral locus of XY-Coordinates of wavelength $(Y,Gd)Al_3(BO_3)_4:Eu^{3+}$

Conclusion

Simple and modified route of solution combustion synthesis was successfully employed for the preparation of Yttrium aluminum borate host phosphors. The prepared sample were characterized by powder XRD, particle size by FE-SEM. The VUV photoluminescence shows intense and purity of red component at 615 nm, suitably applied in PDP and other flat panel display devices.

References

- [1] J.H.In,H.C.Lee,M.J.Yoon,,K. Lee,J.W. Lee Journal of Supercritical Fluids, (2007), 40, 389.
- [2] A.D.Mills, Inorganic Chemistry, (1962), 1, 960.
- [3] H.You,G. Hong,X.Zeng, C.Kim,C.Pyun,B. Yu,H. Bae. Journal of Physics and Chemistry of Solids, (2000), 61, 1985.
- [4] X.Li ,Yuhua Wang,Materials Chemistry and Physics, (2007),101, 191.
- [5] K.G.Lee,B.Y.Yu,C. Pyun,S. Mho, Solid State Comm. (2002),122, 485.
- [6] D.Liu,D. He,K.Kang,C. Liu,S. Li . Journal of Rare Earths, ,(2004),22,133.
- [7] H.Yang,Z.Ren,Y.Cui,L.Yu, J. Mater.Sci., (2006), 41, 4133.
- [8] B.Yan,C.Wang,Solid State Sciences, (2008),10, 82.
- [9] C.Yang,Y.Pan,,Q. Zhang,Materials Science and Engg. (2007),B,137, 195.
- [10] X.Li,Y.Wang,Y. Hao,L.Wang Journal of the Electrochem.Soc., (2006),153, G807.
- [11] L.Wang,X. Liu,Z.Quan,D.Kong ,J.Yang, J. Lin. J.of Lumin., (2007),122-123, 36.



- [12] R.P. Sonekar, S.K. Omanwar, S.V. Moharil, S.M. Dhopte, P.L. Muthal, V.K. Kondawar, Opt. Mater. (2007), 30 (4), 622.
- [13] R.P. Sonekar, S.K. Omanwar, S.V. Moharil, P.L. Muthal, S.M. Dhopte, V.K. Kondawar, J. Lumin, (2009), 129, 624.
- [14] R.P.Sonekar, S. K.Omanwar & S. V. Moharil, Indian J Pure & Appl Phy (2009),47, 441.
- [15] J.T.Ingle, R.P.Sonekar, P.A.Nagpure and S.K.Omanwar, International Journal of Current Research (2013), 5, 529.
- [16] J. T. Ingle, A. B. Gawande, R. P. Sonekar, P. A. Nagpure, and S. K. Omanwar, AIP Conf. Proc. (2013),1536, 895.
- [17] J.T. Ingle, A.B. Gawande, R.P. Sonekar, S.K. Omanwar, Yuhua Wang, Lei Zhao Journal of Alloys and Compounds (2014), 585, 633.
- [18] J. T. Ingle, R. P. Sonekar, S. K. Omanwar, Yuhua Wang, and Lei Zhao, Lei Zhao, Combust. Sci. Technol.,(2014), 186, 1.
- [19] J.Zhou, Y.H.Wang, B. Liua and Y. Lu, J.Alloys Comds, (2009),484, 439.