



Preparation and Photoluminescence Study of Luminophore Activated Nonlinear Polycrystals of Sodium Lanthanum Borates for Lighting.

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Abstract

A unique way to contribute in the development of cutting edge technology of lighting and screen devices is to search for new or develop existing luminescent material of desired dimensions and composition suitable in technical aspect. In concern with this a promising non linear optical material; $\text{Na}_3\text{La}_2(\text{BO}_3)_3$ (NLBO) has a long range of transparency and exceptional stability with high damage threshold, pick up as a host material. A fine powder of polycrystalline samples of $\text{Na}_3\text{La}_{(2-x)}(\text{BO}_3)_3:x \text{Eu/Tb}$ ($0.01 \leq x \leq 0.07$ wt.mol %) has been synthesized by combustion synthesis, structure and phase of compound obtained confirm by powder XRD technique; Luminescent properties of RE added NLBO were investigated under UV light. An optimum concentration of $\text{Eu}^{3+}/\text{Tb}^{3+}$ ion in NLBO was search for the highly chromatic red emission line at 613 nm with lacks of inversion symmetry and efficient green emission at 546 nm. The results obtained shows close resemblance and suitability for further development and employ them in tricolor lamps (*w-LEDs*) and *screen printing* technology.

Keywords: Solution Combustion, Luminescence, *w-LEDs*, Luminophore, Phosphors.

1. Introduction

In the modern usage there is rapid and fast developments in the lighting and display devices, as a progressive aspects one technology is superiorly replace by the other. Nowadays, there is highly demand of 'cold light' and 'Flat panel display' which includes, white light-emitting diodes (*w-LEDs*) and Flat screen panel, these technologies have several advantages over conventional devices with advancement such as high definition resolution and brightness, least energy consumption, long lifetime, broad viewing angle and

operates over non pollution environment [1-3]. Therefore, a search of efficient host which produce red and green emission upon RE doped ion has begun, In this concern Lanthanide doped with RE ion (luminophore) compounds have played an outstanding role as phosphors in lighting, flat panel displays, optical telecommunication and as the active material in solid-state lasers [4-7].

The borates materials are available in variety of structures and have large band gap, high UV transparency and absorption. The borates coordinated with lanthanum ligands produce stable structure of the host materials. Lanthanides elements have abundant $4f$ electron configurations, when a lanthanide ion is incorporated into a host lattice, some well-localized energy states belonging to the $4f^n$ ground configuration and $4f^{n-1}5d$ excited configuration of Ln^{3+} are introduced between the valence and the conduction bands of the host. This will introduce excitation and emission spectra of the transitions occurring between the Ln^{3+} quasi-atomic levels [8-10].

This $NLnBO:RE^{3+}$ composition offers a replaceable Ln^{3+} site of cation for the doping with different rare earth ions such as Eu^{3+} and Tb^{3+} to produce efficient red and green emission within a single host, further the melting point of these metal coordinated borates are rather low therefore, polycrystalline materials can be obtained easily at relatively low temperature

In the present work, we report simple, efficient green synthesis of $NLnBO:RE^{3+}$ ($RE=Eu^{3+}/Tb^{3+}$) phosphors by solution combustion technique. The luminescent ions in the corresponding environment of NLBO crystal lattice was analyzed using Eu^{3+} ions as a probe. The luminescent properties of $NLBO:Ln^{3+}$ ($Ln =Eu^{3+}/Tb^{3+}$) phosphor, the luminescence mechanism and the concentration quenching of Ln^{3+} doped NLBO were also investigated.

2. Experimental

2.1 Combustion synthesis of $Na_3La_2(BO_3)_3:RE^{3+}$ ($RE =Eu^{3+}/Tb^{3+}$)

For the preparation of phosphors materials simple route of solution combustion technique was employed [11-14]. The colorimetric amounts of starting ingredients required were calculated on the basis of molar ratio in balanced inorganic reaction indicated in Table 1. The different steps involves in synthesis described schematically by using flow chart shown in Fig.1 Starting ingredients were uniformly mixed in an Agate Mortar by adding little amount of double distilled water and stirred, milky solution was obtained which then place on hot plate to get aqueous thick homogeneous solution. The aqueous solution was then transferred in to a preheated muffle furnace at $600^\circ C$, the solution boils, froths and ignites to burn with flame and obtained a voluminous, foamy substrate the entire combustion process was complete within 5 minutes. Following combustion, the foamy substrate crushed and grinded to obtain fine powder, which then annealed at $900^\circ C$ for about 2 hours and suddenly cooled to room temperature.

Table 1. The molar ratios of ingredients used in the synthesis and corresponding balanced chemical reactions

S.N.	Product	Corresponding reaction with balanced molar ratios of precursors
1.	$\text{Na}_3\text{La}_2(\text{BO}_3)_3:\text{Eu}^{3+}$	$3\text{Na}(\text{NO}_3) + (2-x) \text{La}(\text{NO}_3)_3 + 3\text{H}_3\text{BO}_3 + 4\text{CO}(\text{NH}_2)_2 + 2 \text{NH}_4\text{NO}_3 + x \text{Eu}(\text{NO}_3)_3 \xrightarrow{550^\circ\text{C}} \text{Na}_3\text{La}_2(\text{BO}_3)_3:\text{Eu}^{3+} + \text{Gaseous products } (\text{H}_2\text{O}\uparrow, \text{NH}_3\uparrow \text{ and } \text{NO}_2\uparrow)$
2.	$\text{Na}_3\text{La}_2(\text{BO}_3)_3:\text{Tb}^{3+}$	$3\text{Na}(\text{NO}_3) + (2-y) \text{La}(\text{NO}_3)_3 + 3\text{H}_3\text{BO}_3 + 4\text{CO}(\text{NH}_2)_2 + 2 \text{NH}_4\text{NO}_3 + y \text{Tb}(\text{NO}_3)_3 \xrightarrow{550^\circ\text{C}} \text{Na}_3\text{La}_2(\text{BO}_3)_3:\text{Tb}^{3+} + \text{Gaseous products } (\text{H}_2\text{O}\uparrow, \text{NH}_3\uparrow \text{ and } \text{NO}_2\uparrow)$

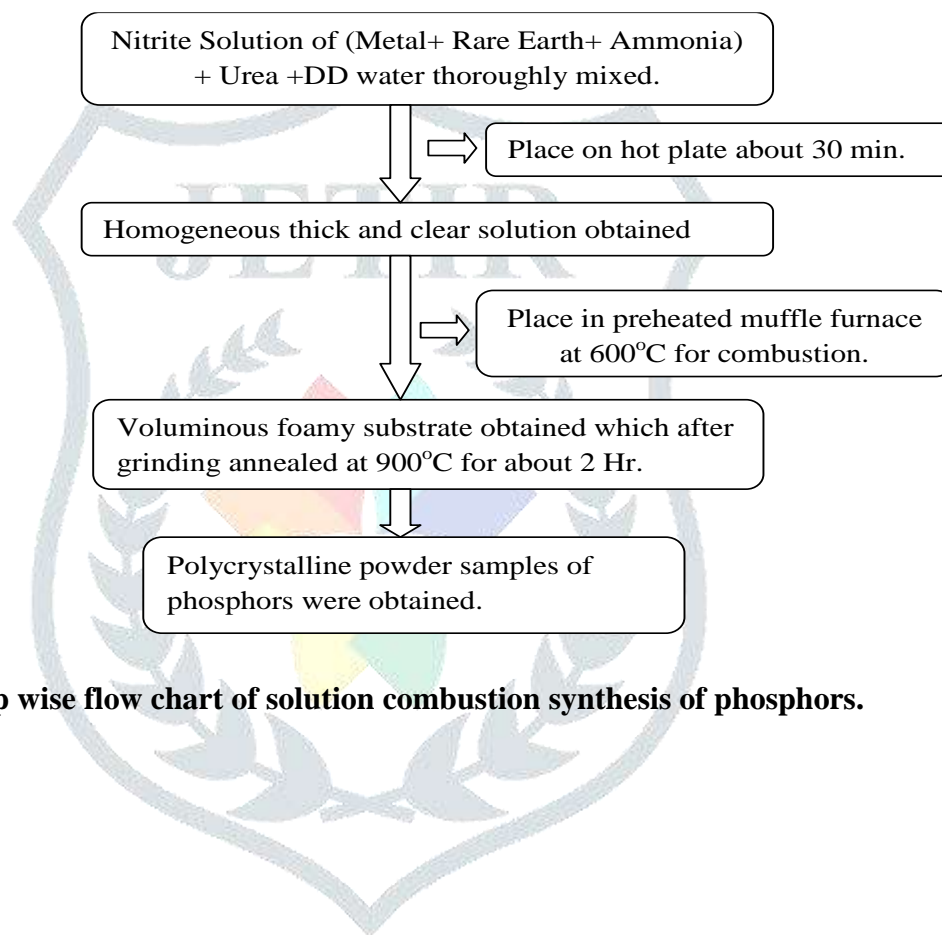


Fig. 1 Step wise flow chart of solution combustion synthesis of phosphors.

3. Characterization of samples

3.1 XRD

Fig.2, Shows the powder XRD patterns of Non linear polycrystalline powder phosphor of host lattice, $\text{Na}_3\text{La}_2(\text{BO}_3)_3$. The diffraction peaks observed in pattern can be exactly assigned to pure phase and match with (JCPD.15-1884). $\text{Na}_3\text{La}_2(\text{BO}_3)_3$ crystallizes in an orthorhombic unit-cell with space group $\text{Amm}2(38)$. No noticeable extra diffraction peaks observed which indicates that Ln^{3+} ions (Eu^{3+} , Tb^{3+}) were completely replace and takes lattice site of La^{3+} ion this may due to their similar ionic radii.

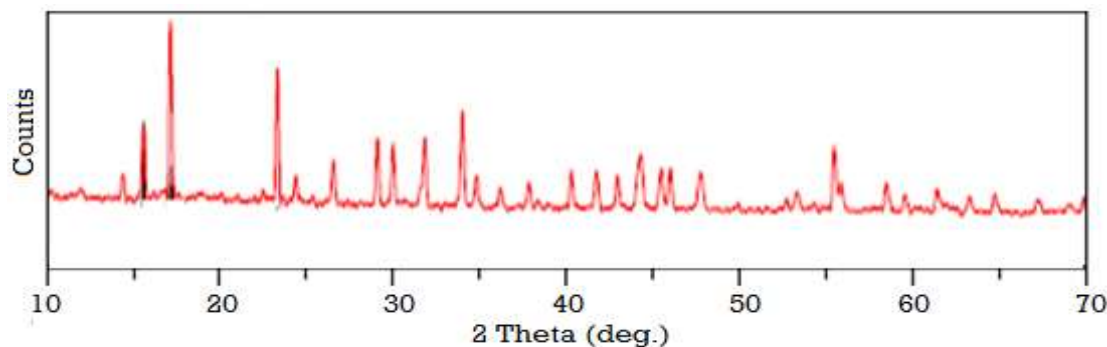


Fig.2 XRD Pattern of host lattice $\text{Na}_3\text{La}_2(\text{BO}_3)_3$ (JCPD file No.15-1884)

3.2 Crystal structure of $\text{Na}_3\text{La}_2(\text{BO}_3)_3$ (NLBO)

The $\text{Na}_3\text{La}_2(\text{BO}_3)_3$ crystallized in to orthorhombic system, space group $\text{Amm}2(38)$, with lattice parameters $a = 5.1580 \text{ \AA}$, $b = 11.350 \text{ \AA}$, $c = 7.3230 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $Z = 2$, $V = 428.71 \text{ \AA}^3$

The structure of NLBO crystal could be described as a three-dimensional framework. It is made up of isolated BO_3 triangles held together by the $\text{La}(1)\text{O}_9$, $\text{Na}(1)\text{O}_6$, $\text{Na}(2)\text{O}_8$, and $\text{Na}(3)\text{O}_6$ polyhedron).

3.3 Particle Morphology

The particle morphology and grain size of the phosphors particles were analysed using Hitachi model S-4800 type-2 FE-SEM. It is well establish fact that fine size and regular morphology of particles leads to an efficient photoluminescence, Fig.4 shows FE-SEM Images of $\text{Na}_3\text{La}_2(\text{BO}_3)_3 : (\text{Eu}/\text{Tb})$ average particle size and particle morphology showing flossy and densely agglomerates plane with a particle size about $2\text{-}3 \mu\text{m}$, sample particles densely agglomerate with regular hexagonal elongated rod like structure shape at post heated temperature around 900°C . The sizes of particles are suitable for high energy UV absorption and subsequent emission from exterior part of phosphors atoms.

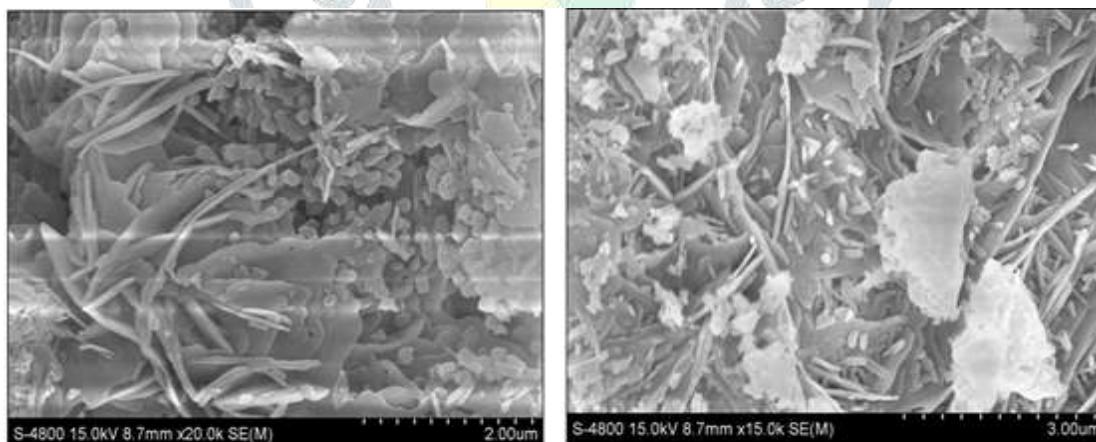


Fig. 4 FE-SEM micrograph of (a) $\text{Na}_3\text{La}_2(\text{BO}_3)_3:\text{Eu}^{3+}$ (b) Tb^{3+}

4. Results and Discussion

4.1 Photoluminescence of $\text{Na}_3(2-x)\text{La}(\text{BO}_3)_3:x\text{Eu}^{3+}$

PL and PLE measurements were performed on a Hitachi F-7000 spectrofluorometer equipped with a 450W Xenon lamp in the range $200\text{--}650 \text{ nm}$.

The UV PL investigation of $\text{Na}_3(2-x)\text{La}(\text{BO}_3)_3:x\text{Eu}^{3+}$ ($x = 0.03, 0.05, 0.07 \text{ wt. mol } \%$) phosphor is shown in Fig.5, excitation spectrums contain a double hump broad band peaking at 222 and 234 nm . The strong band

corresponds to the charge transfer band (CTB) of $\text{Eu}^{3+}\text{-O}^{2-}$. Emission spectrum under near UV 234 nm excitation consists of an intense red line at 613 nm corresponding to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ electric dipole transition of Eu^{3+} . The other emission lines observed at 594 nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$) and 627 nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$) are comparatively weak, which indicates that the Eu^{3+} ion occupies its favorable non-centrosymmetric position in this host lattice.

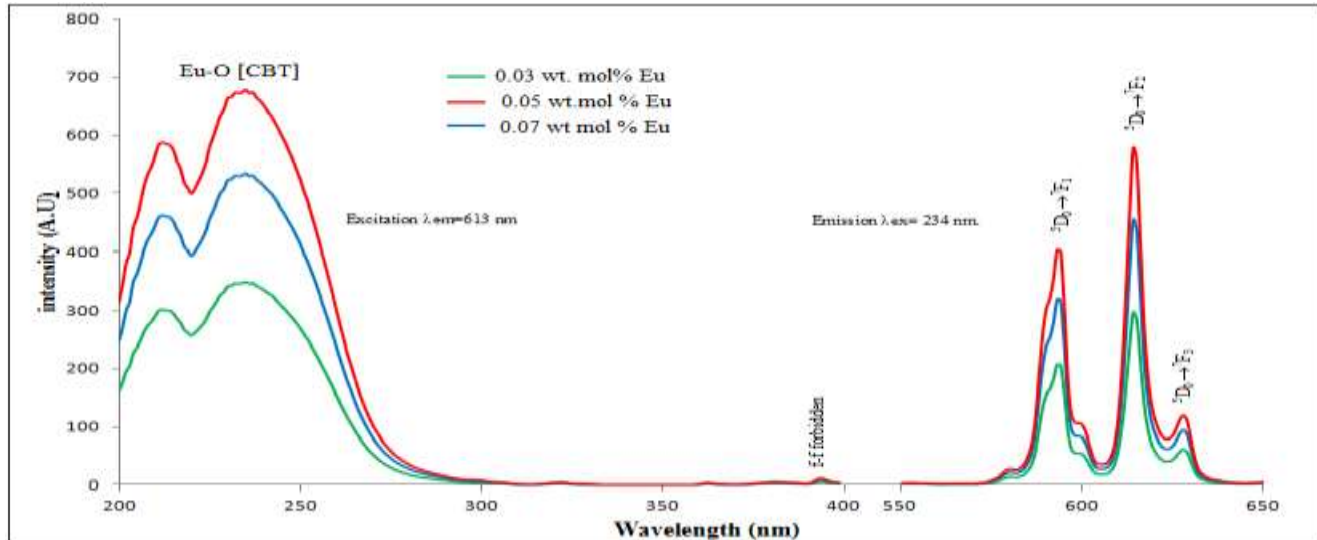


Fig.5 PL and PLE spectrum of $\text{Na}_3\text{La}_2(\text{BO}_3)_3:\text{Eu}$

4.3 Luminescence in $\text{Na}_3\text{La}_2(\text{BO}_3)_3:\text{yTb}^{3+}$

Tb^{3+} ion is used as a green emitting center in a variety of commercial phosphors [14-15]. The electronic configuration of Tb^{3+} ion is $4f^8$ the absorption is usually due to allowed f-d transition, from excited state of $4f^75d^1$ configuration, the electron loses energy to lattice and comes to ${}^5\text{D}_j$. ${}^5\text{D}_3 \rightarrow {}^7\text{F}_j$ emission is in UV and blue region while ${}^5\text{D}_4 \rightarrow {}^7\text{F}_j$ emission is predominantly green.

In fig.6 the major emission peaks of Tb^{3+} originates from ${}^5\text{D}_4 \rightarrow {}^7\text{F}_j$ ($J=3, 4, 5, 6$) these lines emission intensity, among the emission lines from the ${}^5\text{D}_4$ state, the most prominent emission, ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ peaking at 546 nm is undoubtedly due to a magnetic dipole transition and is allowed which results in a green color with excellent purity.

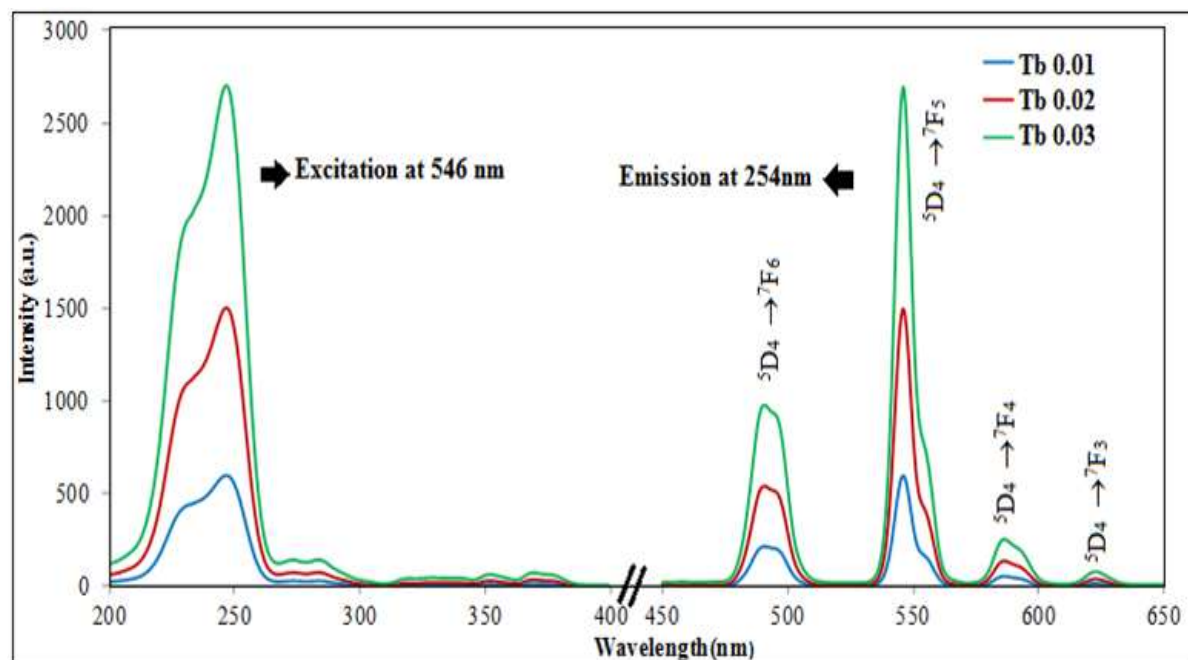


Fig.6 PL and PLE spectrum of $\text{Na}_3\text{La}_2(\text{BO}_3)_3: \text{Tb}$

5. Conclusion

In conclusion, simple route of solution combustion with green synthesis approach was successfully employed for the preparation of Non linear polycrystalline sodium lanthanum borate phosphors i.e $\text{Na}_3\text{La}_2(\text{BO}_3)_3:\text{RE}^{3+}$ ($\text{RE} = \text{Eu}^{3+}/\text{Tb}^{3+}$). The technique is simple, time saving and low cost. Photoluminescence properties of $\text{Na}_3\text{La}_2(\text{BO}_3)_3:\text{Eu}^{3+}$ under near UV(235nm) radiation shows excellent and efficient pure red emission at 613 nm. Under identical exposure of radiations at 254 nm $\text{Na}_3\text{La}_2(\text{BO}_3)_3:\text{Tb}^{3+}$ shows green emission, both these results are in favors to develop and employ them for tri-color lamp and PC converted *w-LEDs*.

6. References

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