Innovative Borohydride Synthesis Strategy to Fabricate Red ($YBO_3:Eu^{3+}$) and Green ($YBO_3:Tb^{3+}$) Nanophosphor with Improved Photoluminescence Characteristics

Shubham SRIVASTAVA[1+], Niroj Kumar SAHU[2], Shantanu Kumar BEHERA[1], Bibhuti Bhusan NAYAK[1#]

[1]Ceramic Engineering, National Institute of Technology Rourkela, India, [2]Centre for Nanotechnology Research, VIT University, India

[+]Presenter

[#]Corresponding author: bibhutib@gmail.com

The research endeavour on lanthanide ions doped YBO_3 nanophosphors is escalating with the availability of these borate hosts, which present incentives such as excellent UV absorbance, high thermal stability and exceptional optical damage threshold [Appl. Phys. Lett., 80, 1447 (2002)]. However, for preparation of this host, the use of boric acid (H_3BO_3) as a boron source is rampant [Small, 3, 438 (2007)]. Literature gives a plethora of evidences for use of excess H_3BO_3 in addition to difficulties encountered in formation of high temperature stable YBO_3 [J. Am. Ceram. Soc., 2008, 91, 591]. Different syntheses employed for YBO_3 fabrication aim towards improving colour purity and chromaticity. Our approach allows accomplishing this goal by means of a unique synthesis strategy for producing high temperature phase pure phosphors with better photoluminescence properties.

In this context, for the first time, innovative borohydride synthesis strategy using sodium borohydride ($NaBH_4$) has been explored to fabricate red (YBO_3: 5 mol % Eu^{3+}) as well as green (YBO_3: 5 mol % Tb^{3+}) phosphor. Moreover, phase-stability, microstructure and photoluminescence properties of these phosphors were studied in detail. The colour purity [R/O ratio: area under the curve of red ($^5D_0 \rightarrow {}^7F_2$ transition) to orange ($^5D_0 \rightarrow {}^7F_1$) emission] of red phosphor and CIE coordinates of both red and green phosphor are strongly dependent on the excitation wavelengths. The colour tuning from pink to reddish-orange for $YBO_3:Eu^{3+}$ and bluish-green to green for $YBO_3:Tb^{3+}$ is achieved by adjusting excitation wavelengths from near-VUV to UV. The findings of the study suggest that this borohydride method is better than the conventional boric acid based solid-state method. The follow up of the properties unanimously depicts that the use of $NaBH_4$ is virtuous for synthesizing nanophosphors and could be put to use in light emitting diodes and flat display technology.

Keywords: Phosphors; YBO_3; Borohydride, Colour purity; CIE coordinates.

INNOVATIVE BOROHYDRIDE SYNTHESIS STRATEGY TO FABRICATE RED ($YBO_3:Eu^{3+}$) AND GREEN ($YBO_3:Tb^{3+}$) NANOPHOSPHORS WITH IMPROVED PHOTOLUMINESCENCE CHARACTERISTICS

CONFERENCE RETURN SEMINAR

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Presented by: **Shubham Srivastava**
Ph.D. Scholar

Work being carried out under the guidance of
Dr. Bibhuti Bhusan Nayak and **Dr. Shantanu Kumar Behera**
Department of Ceramic Engineering
National Institute of Technology Rourkela
India

Properties and Importance of YBO_3 based systems

- Strong luminescence intensity
- High chemical stability
- Exceptional optical damage threshold
- Excellent VUV absorption

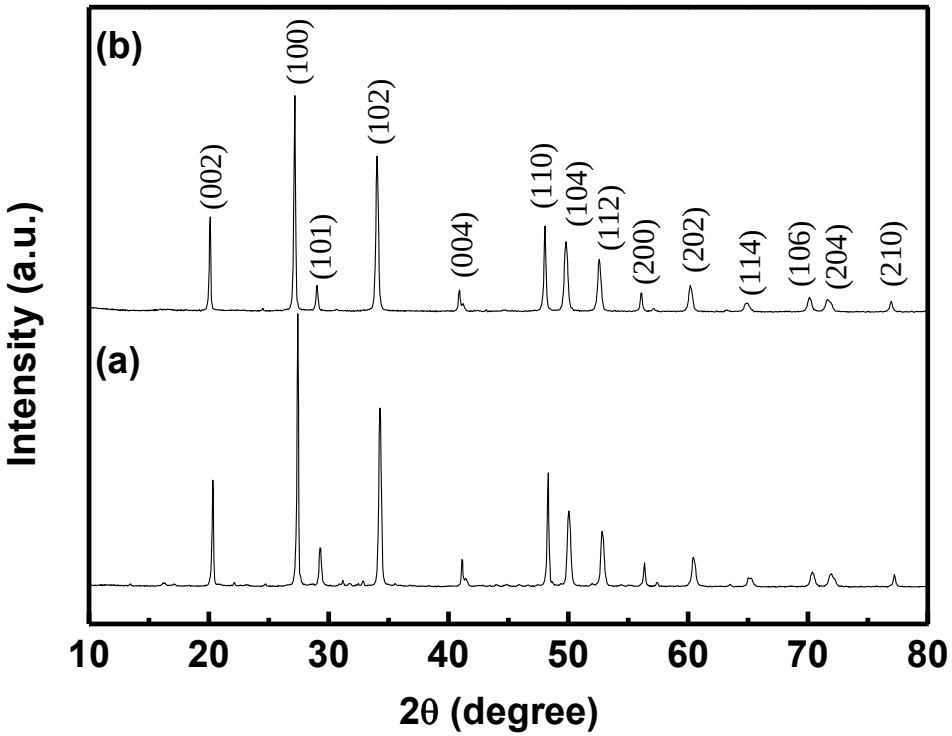
Methodology

Conventional solid state method and Borohydride based gelation-precipitation route were used to prepare the requisite phosphors.

Objective

Development of high temperature stable phase pure $YBO_3:Eu^{3+}$ and $YBO_3:Tb^{3+}$ phosphor nano material using a unique borohydride synthesis strategy with an improvement in the photoluminescence characteristics

Phase analysis

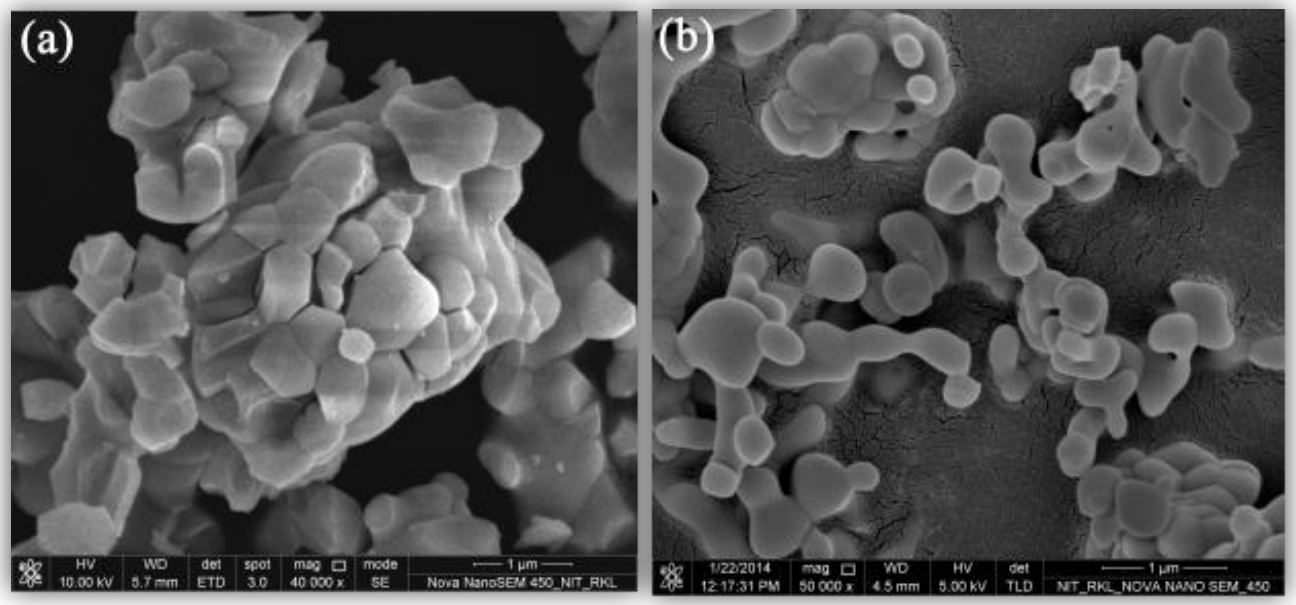


XRD patterns of calcined (1200 °C) $YBO_3:Eu^{3+}$ powders prepared using (a) conventional solid-state and (b) borohydride method.

- **Phase pure 10 mol % Eu^{+3}-doped YBO_3 powder calcined at 1200 °C was prepared and its XRD pattern was compared with the solid state derived phosphor with same europium concentration.**
- **Crystallite size of borohydride synthesized $YBO_3:Eu^{3+}$ phosphor was found to be 47 nm, which was smaller than the solid-state derived phosphor (62 nm).**

S. Srivastava et al., *RSC Adv.*,2015, 5, 11009-11012

Morphological Analysis



FESEM micrographs of calcined (1200 °C) YBO_3: Eu^{3+} powders

- **For solid state route, clustering of polyhedral crystals form irregular shaped particles of size 5 microns**
- **YBO_3:Eu^{3+} phosphor prepared by borohydride route exhibits particles which may have been formed due to high temperature induced coarsening of finer spherical crystallites**

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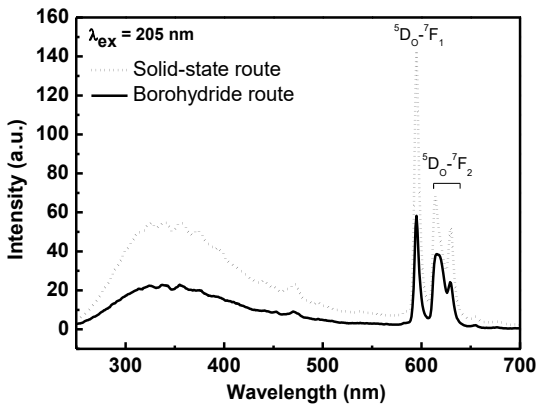
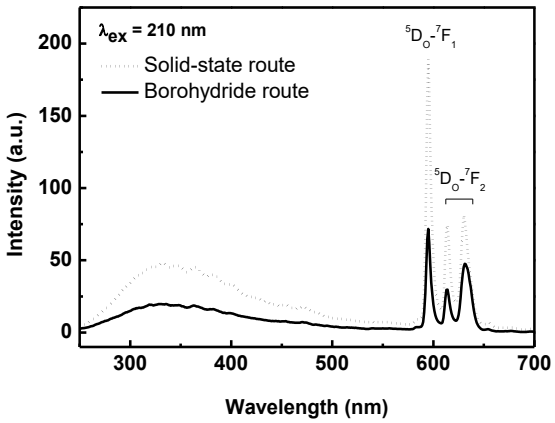
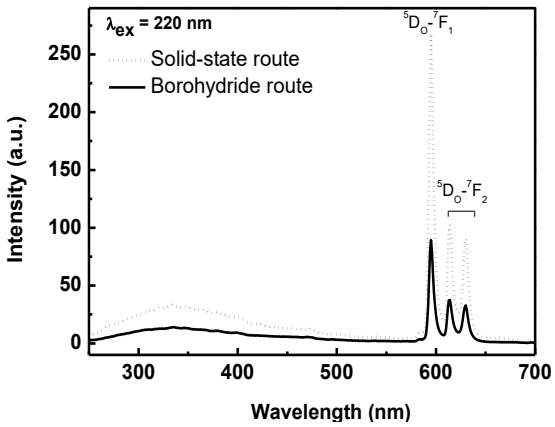
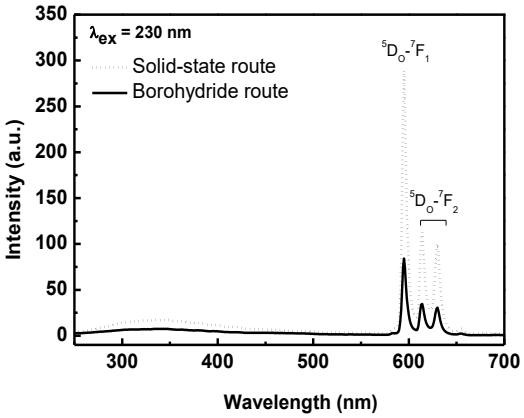
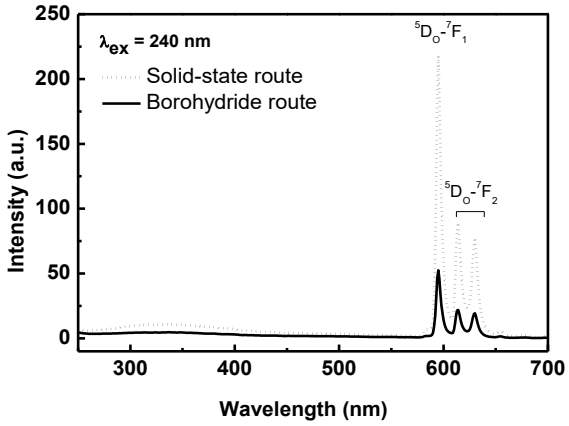
Contrasting PL emission spectra of bulk phosphor and nanophosphor











- **Luminescence intensity corresponding to the solid state method is high for all cases, which is in striking contrast with the behavior of the particles prepared using borohydride route**

- **This is ascribed to small sized phosphor particles of the latter route**

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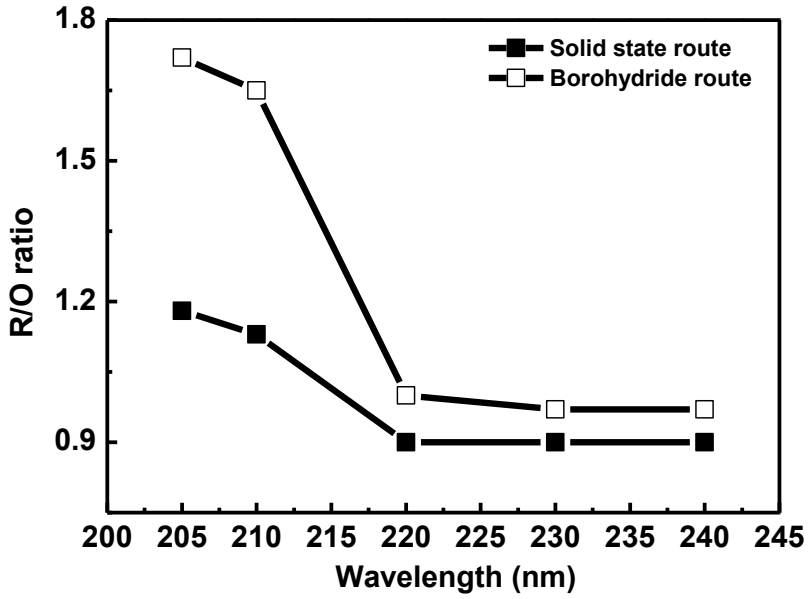
Determination of Colour Purity (R/O ratio)



- **R/O ratio of solid state is less than the values observed for precipitation method at different excitation wavelengths**
- **Higher R/O ratio (1.72) for near VUV wavelength (205 nm) in borohydride derived phosphor depends on the contribution of $^5D_0 \rightarrow {}^7F_2$ transition, which is more prominent and may be owing to highly disordered surface with lower site symmetry**
- **Contribution of both $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transition lead to a decrease in R/O ratio in UV range (220 to 240 nm).**

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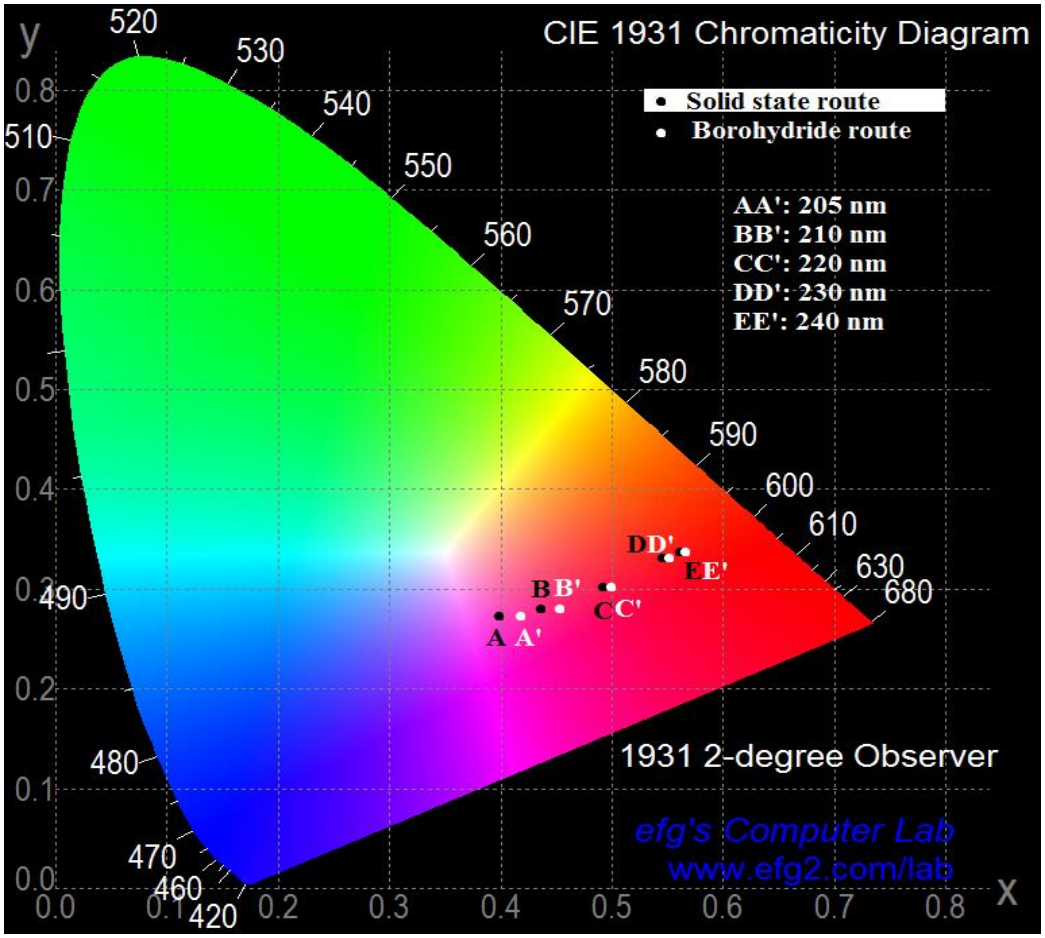
Chromaticity Coordinates



- **Colour tuning from pink to reddish orange is possible for $YBO_3:Eu^{3+}$ phosphors by changing the excitation wavelengths from near VUV to UV range due to the contribution of the host and the activator.**

- **Borohydride derived YBO_3: Eu^{3+} phosphor shows better chromaticity than solid-state derived phosphor**

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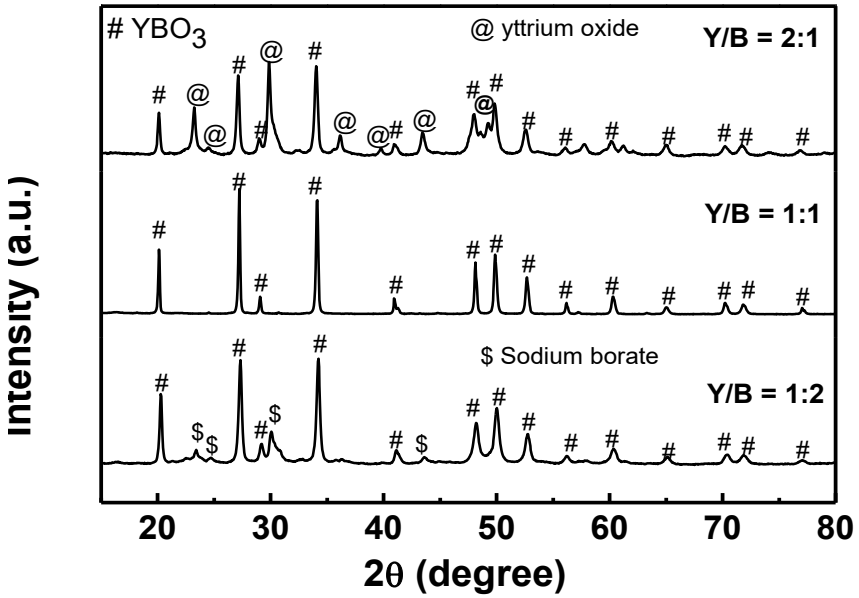
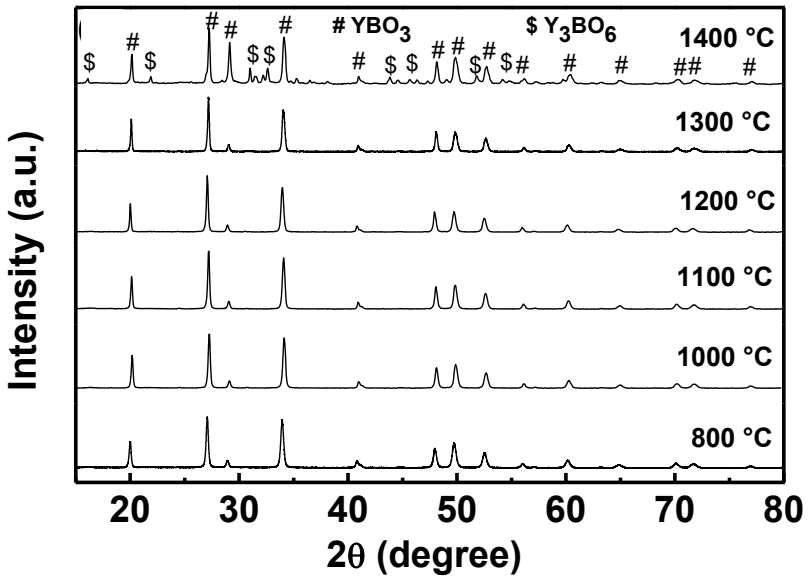
Thermal stability (formation of parasitic Y_3BO_6 phase at higher temperature)



XRD patterns of calcined (800°C) pure YBO_3 prepared by varying Y:B ratio

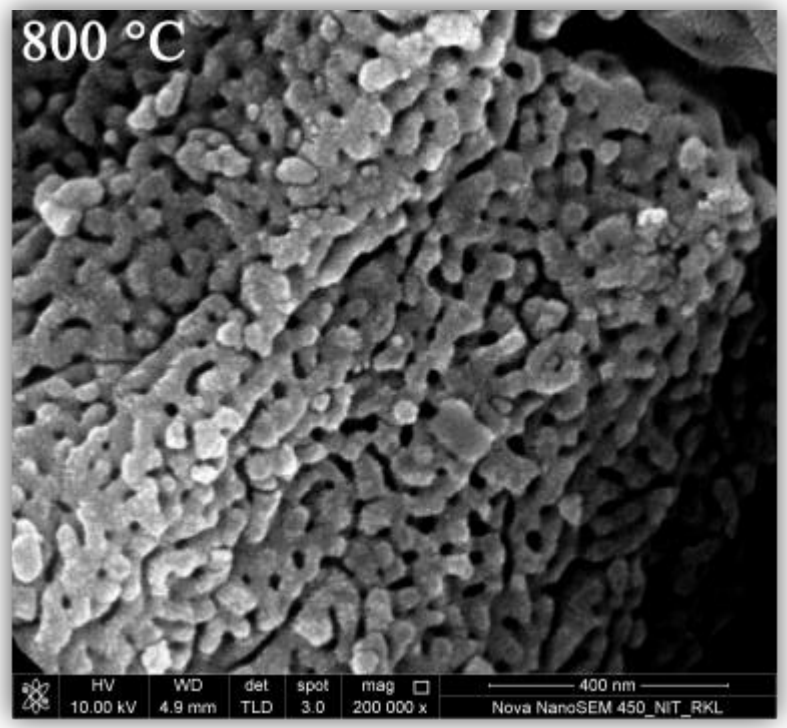


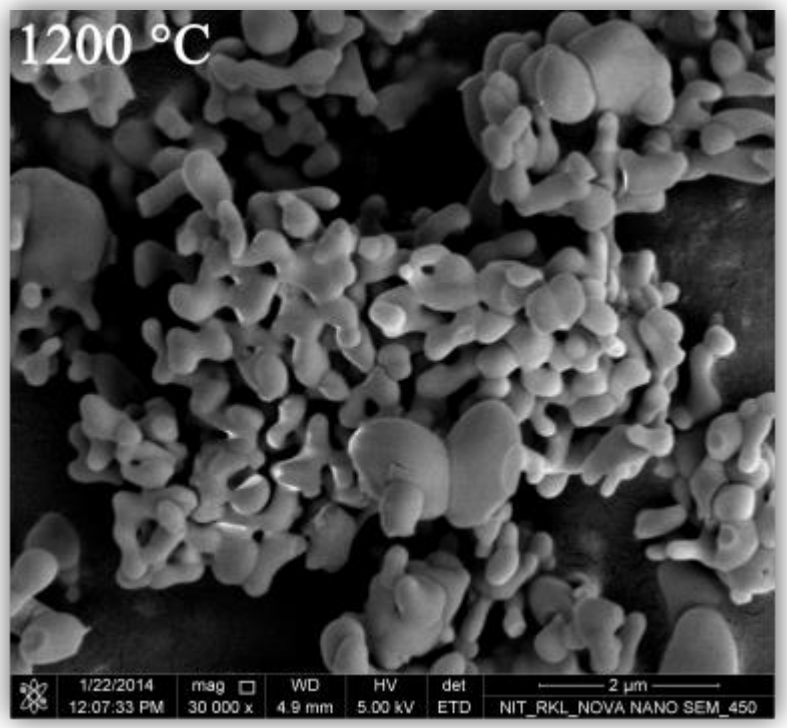
XRD patterns of pure YBO_3 (Y:B ratio 1:1) heat-treated at different temperatures.

- **Either excess of 'B' or 'Y' in the samples having Y:B ratio of 1:2 or 2:1 indicates the formation of some additional impurity phases along with YBO_3.**
- **Borohydride synthesized YBO_3 is stable up to 1300°C and the formation of Y_3BO_6 phase is detected at 1400 °C.**
- **This value is higher than a few preceding reports which concerned with the formation of Y_3BO_6 phase**

S. Srivastava et al., *Dalton Trans.*,2015,44,7765-7769

Morphological studies

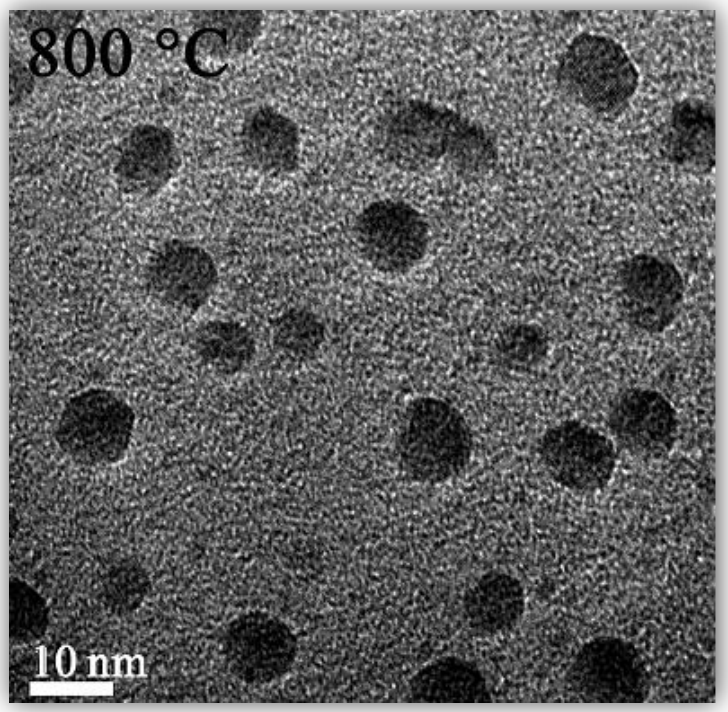


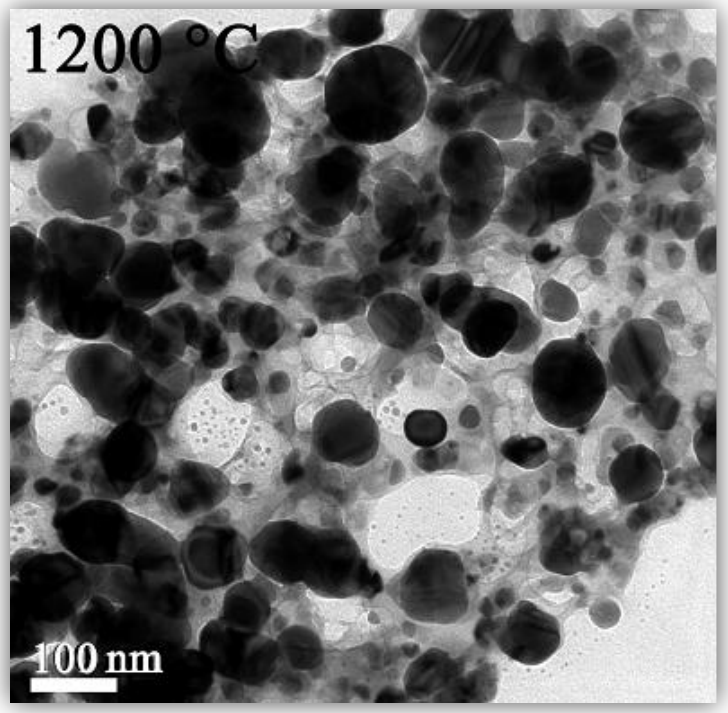


- **800° C calcined Eu^{3+}-doped YBO_3 particles (size ~ 50 nm) well-connected**
- **Average particle size ranging from 200 nm to 1.5 µm was observed for the phosphor calcined at 1200° C**

S. Srivastava et al., *Dalton Trans.*,2015,44,7765-7769

TEM Analysis

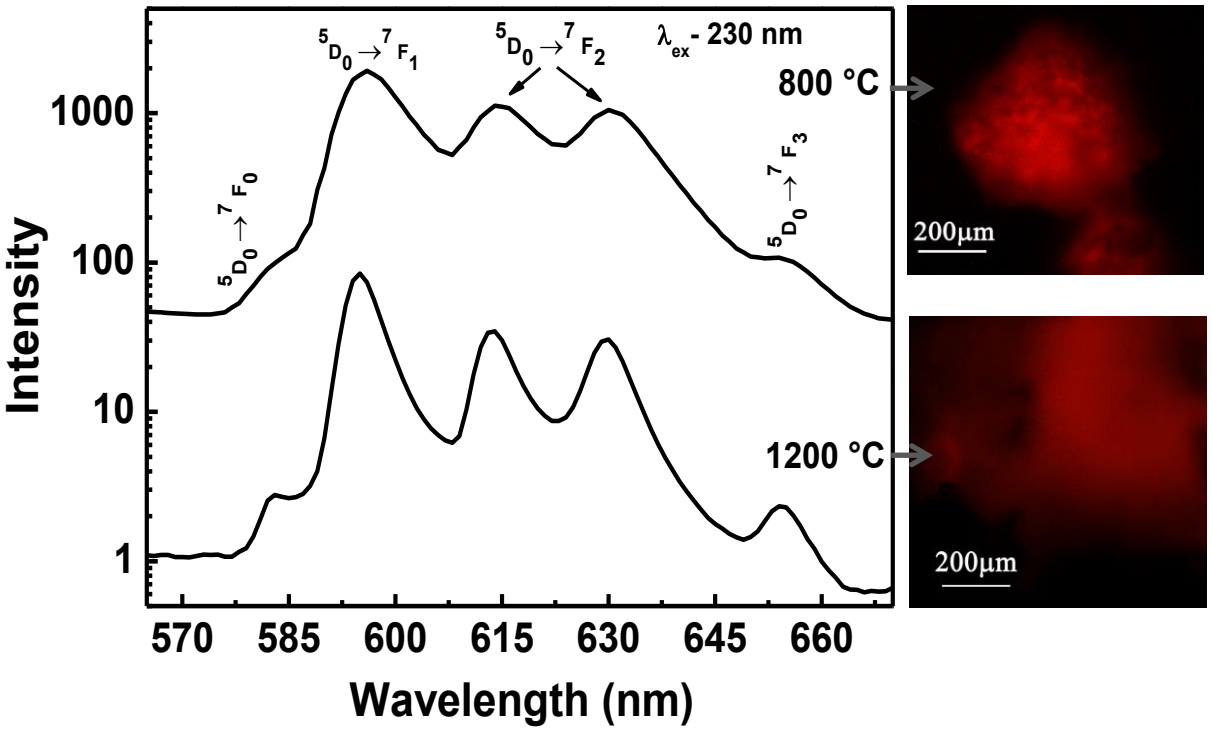




- **The average particle size of YBO_3: Eu^{3+}, calcined at 800 °C was found to be around 8-10 nm**
- **Average particle size was in the range of 30-100 nm when calcined at 1200°C**

S. Srivastava et al., *Dalton Trans.*,2015,44,7765-7769

Photoluminescence Studies

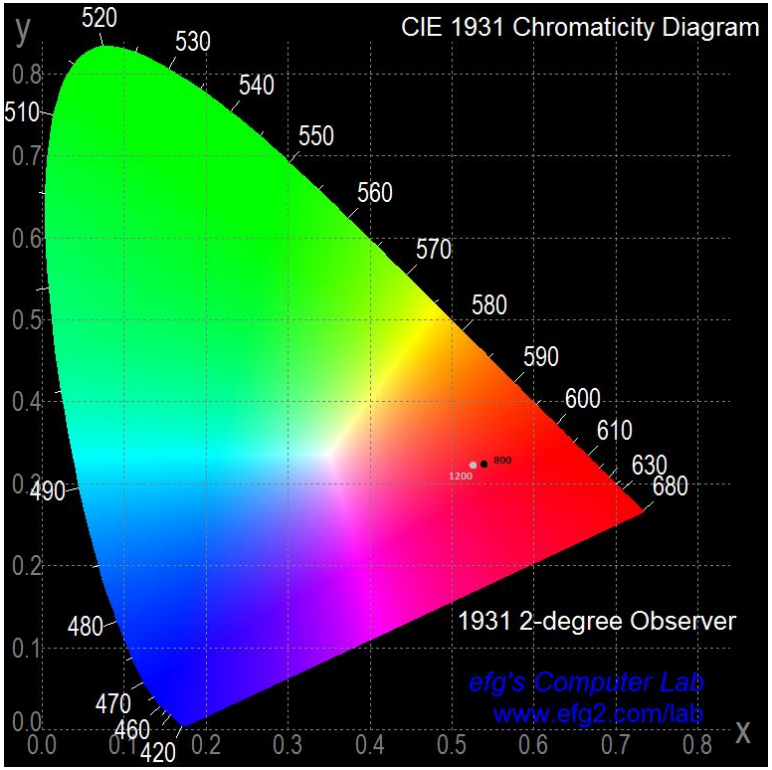


Photoluminescence Emission Spectra and fluorescence microscopy images of samples calcined at 800° C and 1200 °C

- **Colour of powder samples calcined at 800 °C and 1200 °C is nearly reddish as observed from fluorescence microscopy**
- **The R/O ratio was found to be 1.25 and 0.97 for 800 °C and 1200 °C calcined Eu^{3+}-doped YBO_3 phosphors, respectively and the higher R/O ratio is mainly due to surface disorder associated with smaller particle size**

S. Srivastava et al., *Dalton Trans.*,2015,44,7765-7769

Chromaticity Coordinates



- **The x and y chromaticity coordinates were found to be 0.53 and 0.32, respectively for Eu^{3+}-doped YBO_3 phosphor heat-treated at 800 °C.**
- **The chromaticity coordinates for higher temperature calcined (1200 °C) Eu^{3+}-doped YBO_3 phosphor was found to be nearly same (x = 0.52, and y= 0.32)**
- **This provides for another evidence that the borohydride derived phosphor has got good thermal stability**

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Findings of the corresponding work

- **Size reduction plays a significant part in enhancement of R/O ratio**
- **Excitation wavelength dependent luminescent behavior was found**
- **Excitation wavelengths determine the emission color of the prepared phosphor**
- **Color purity can be improved based upon the fabrication procedure**
- **Chromaticity coordinates were better as compared to the boric acid employed solid state route**
- **Variations in excitation wavelengths lead to possibility of color tuning from pink to orange red**

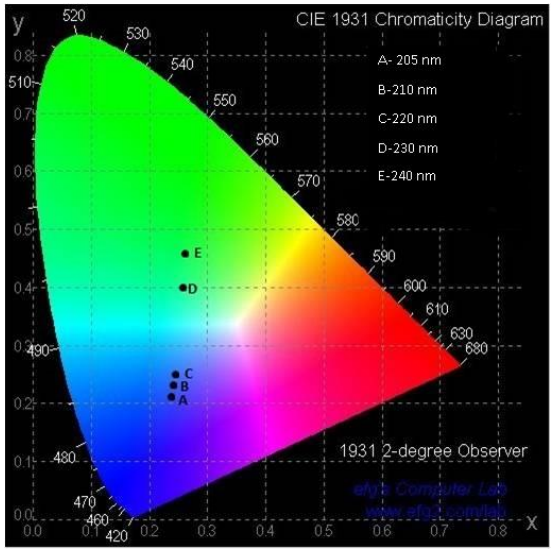
THE SAGA CONTINUES…

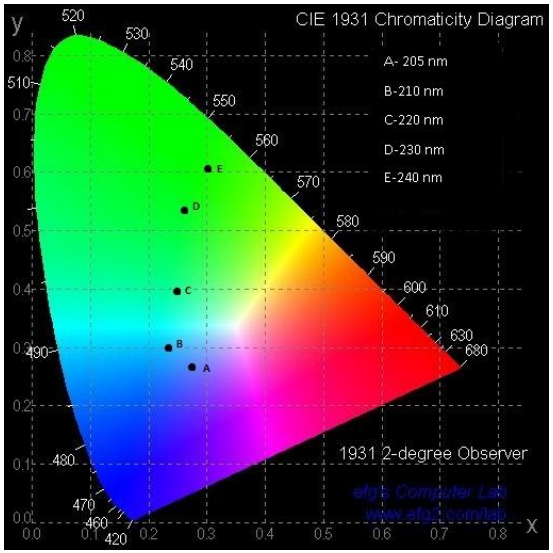
GREEN NANOPHOSPHOR ($YBO_3:Tb^{3+}$)

- **Tb^{3+} activated borate green phosphors may bestow advantages such as**
  - ✓ **better thermal stability**
  - ✓ **chemically inert to plasmas commonly used in plasma operated panels.**

- **$YBO_3:Tb^{3+}$ can be used as a green emitting phosphor in display technology.**
- **Probing for a new high-efficiency green phosphor with short decay time is needed.**

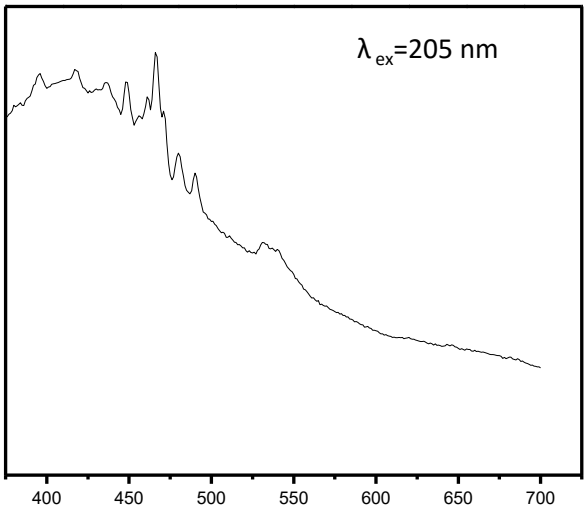
Variations in the Chromaticity Coordinates

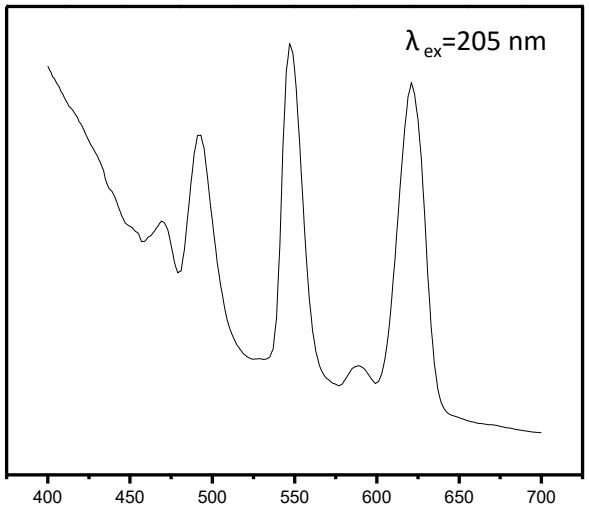




Solid state derived $YBO_3:Tb^{3+}$

Borohydride derived $YBO_3:Tb^{3+}$





FOLLOW THROUGH …

- **Literature gives a plethora of evidences for use of excess H_3BO_3 in addition to difficulties encountered in formation of high temperature stable YBO_3 .**

- **Different syntheses employed for YBO_3 fabrication aim towards improving colour purity and chromaticity. Our approach allows accomplishing this goal by means of a unique synthesis strategy for producing high temperature phase pure phosphors with better photoluminescence properties.**

- **The follow up of the properties unanimously depicts that the use of $NaBH_4$ is virtuous for synthesizing nanophosphors that could be put to use in light emitting diodes and flat display technology.**

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  My Co-supervisor
  Email: skbehera@gmail.com

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THANK YOU FOR YOUR ATTENTION!!!