

## STRUCTURAL AND LUMINESCENCE CHARACTERIZATION OF YTTRIUM-BASED RED POWDER PHOSPHORS

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### Abstract

An investigation of Eu and Dy doped yttrium aluminates/borates samples prepared by solid-state reaction in reduction/air atmosphere is presented. The structure of the synthesized samples was studied by powder X-ray diffraction. The XRD patterns show formulation of several crystalline phases - predominately non-reacted Al<sub>2</sub>O<sub>3</sub>, polymorph modifications of yttrium borate and yttrium orthoaluminates, which were identified and discussed. A photoluminescence analysis was used for observation of optical properties. The spectrum was characterized by 2D and 3D excitation emission graphs. The correlations between synthesis conditions, doping elements, the structure and optical properties of the studied samples are commented. Yttrium-based red powder phosphors have a potential for practical application in lightning industry and other optoelectronic devices.

**Keywords:** Yttrium aluminates, yttrium borates, rare earth, x-ray powder diffraction, luminescence

### 1. INTRODUCTION

Yttrium compounds such as aluminates and borates are studied from the medium of the last century due to possibilities of their structure for designed excellent laser and optical materials which make them applicably in the many fields such as medicine, optic, military, automotive etc.[1].

Rare earth (RE) doped orthoborates with general formula ABO<sub>3</sub> (A=Ln, Y) widely studies because of their chemical stability, ultraviolet transparency [2] and magnetic properties [3]. RE borates possess the same crystal structure as the three polymorphs of calcium carbonate (aragonite, vaterite and calcite), depends on the ionic radius of RE cation [4]. YBO<sub>3</sub> compound crystallizes in different structures with different space groups and symmetries [5]. In the monoclinic YBO<sub>3</sub> host lattice, two kinds of Y<sup>3+</sup> ions with C1 and Ci crystal symmetries have been reported [6]. Furthermore, YBO<sub>3</sub> may have a hexagonal crystal structure with a P63/m space group(176) and Eu<sup>3+</sup> ions which are substituted into Y<sup>3+</sup> sites, have been surrounded by BO<sub>3</sub> groups. So, they provide a symmetry center resulting in a strong <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>1</sub> transition [7]. Also, the addition of boric acid leads to changes in the crystal structure from cubic to hexagonal (belonging to YBO<sub>3</sub>) [8].

The present investigations are directed to the synthesis and characterization of the structure and optical properties of Eu and Dy doped yttrium aluminates and borates.

### 2. EXPERIMENTAL

#### 2.1. Sample preparation

The synthesis was performed by mixing an equimolar ratio (0.5:1) Y<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>, boric acid (10 wt%), 2 mol% Eu<sub>2</sub>O<sub>3</sub> and 1 mol% Dy<sub>2</sub>O<sub>3</sub>, all purchased from Alfa Aesar (**Table 1**). The mixtures were placed into crucibles

and preheated at 1200 °C for 4 hours with a weak reduction/air atmosphere. After that, the samples were cooling at room temperature and analyzed.

**Table 1** Doping rare earth oxide and synthesis conditions for the samples

Sample	Doping RE oxide (mol%)	Synthesis conditions
# 83	Eu <sub>2</sub> O <sub>3</sub> , 2 mol%	Reduction atm.
# 85	Eu <sub>2</sub> O <sub>3</sub> , 2mol%	Air atm.
# 87	Eu <sub>2</sub> O <sub>3</sub> , 2 mol%; Dy <sub>2</sub> O <sub>3</sub> , 1 mol%	Reduction atm.

## 2.2. Analytical procedures

### *Powder X-ray diffraction analysis*

The XRD analysis was performed by Bruker D8 Advance powder diffractometer operating with a Cu –K $\alpha$  radiation source ( $\lambda = 1.5406$  nm) and Lynx Eye PSD detector, in steps of 0.02° over the range of 10° – 80° 2 $\theta$ , with a time per step of 2.8 sec (32 kW, 15 mA). The crystalline phases were identified using the powder diffraction files PDF 01-070-5679 (corundum Al<sub>2</sub>O<sub>3</sub>), 00-013-0531 (yttrium borate YBO<sub>3</sub>), 01-088-0356(yttrium borate YBO<sub>3</sub>), 01-089-3501 (yttrium borate YBO<sub>3</sub>), 00-034-0291 (yttrium borate Y<sub>3</sub>BO<sub>6</sub>), 00-050-1745 (yttrium borate Y<sub>17.33</sub>(BO<sub>3</sub>)<sub>4</sub>(B<sub>2</sub>O<sub>5</sub>)<sub>2</sub>O<sub>16</sub>), 00-055-1088 (aluminum yttrium oxide Y<sub>4</sub>Al<sub>2</sub>O<sub>9</sub>) and 01-074-4232 (yttrium aluminate Y(AlO<sub>3</sub>)) from ISDD PDF-2 database using the DiffractPlus EVA v.12 program (2009) [9].

### *Photoluminescent analysis*

The measurement was performed by fiberized laser driven white light source (LDLS-Energetic) and a monochromator (Ocean Optics MonoScan 2000) which were used to scan the excitation wavelength  $\lambda_c$  from 220 nm to 550 nm with a spectral width  $\delta\lambda \approx 15$  nm. An Ocean optics QE65000 spectrometer measuring spectra in the range from 200 nm to 900 nm was used to take the luminescence spectra for each excitation wavelength from 220 nm to 550 nm each 10 nm.

## 3. RESULTS AND DISCUSSION

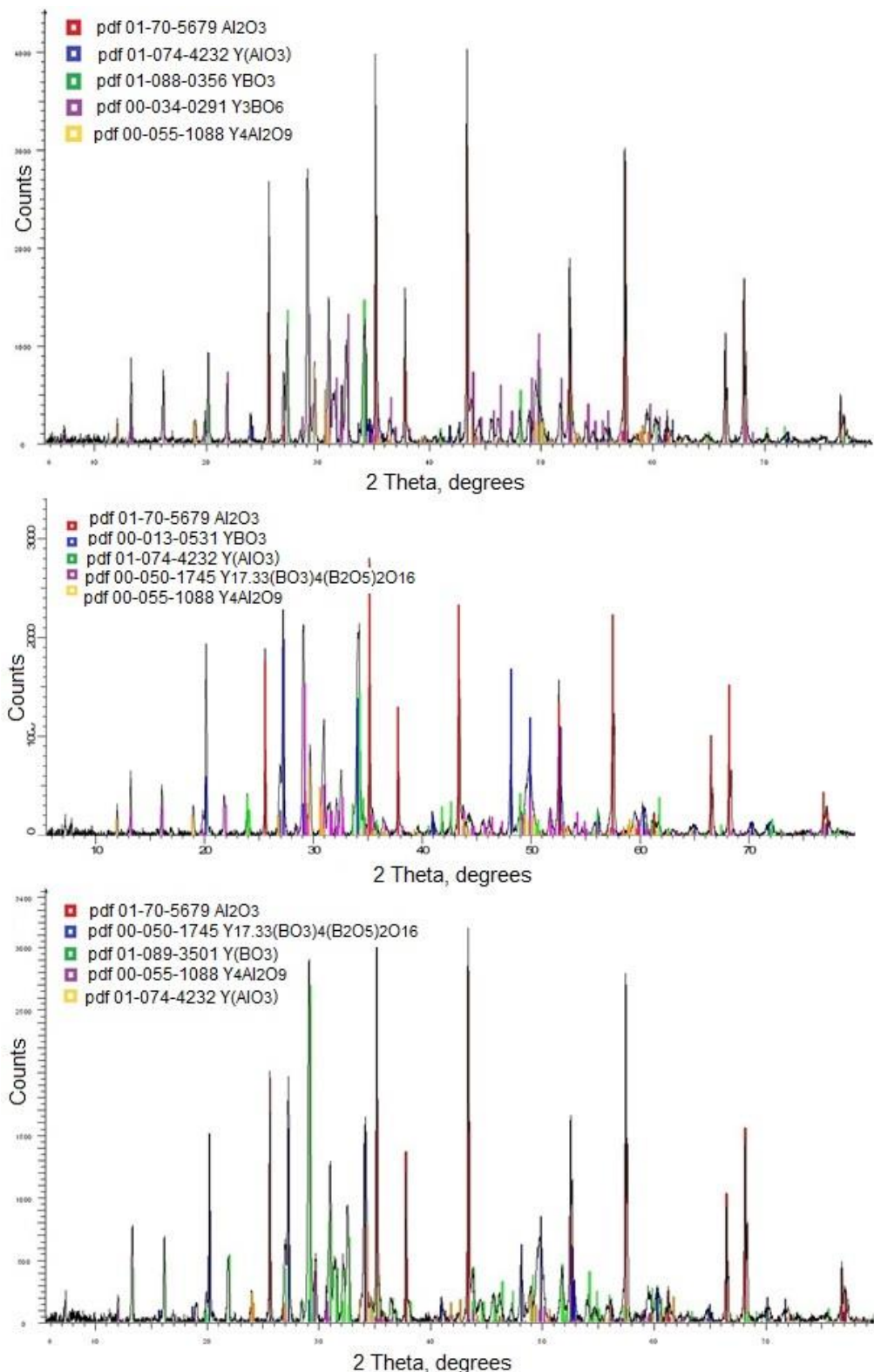
The prepared samples were fine white powders and they were structurally characterized. Several crystalline phases, such as predominately non-reacted Al<sub>2</sub>O<sub>3</sub> and follow formed phases: polymorph modifications of Yttrium borate, and Yttrium orthoaluminates (YAM and YAP) were observed in the X-ray diffractograms of samples (**Figure 1**).

The XRD patterns show most intensive peaks belong to non-reacted Al<sub>2</sub>O<sub>3</sub> (corundum) with the following crystallographic parameters: rhombohedral crystal structure, space group R-3c; cell parameters:  $a = 0.47597$  nm,  $b = 0.4760$  nm,  $c = 1.29935$  nm; cell vol. = 0.25493 nm<sup>3</sup>, density 3.985 g.cm<sup>-3</sup>(PDF 01-070-5679).

The formulation of five polymorph modifications of yttrium borate was observed with intensive peaks. As is known, compounds equimolar in RE oxides and boric oxide having the general formula ABO<sub>3</sub>. RE borates possess the same crystal structure as the three polymorphs of calcium carbonate. The structure type of a particular borate depends on the ionic radius of the RE cation involved. The large cations (La, Nd) formed aragonite (orthorhombic crystal system, bipyramid crystal lattice) the intermediate cations (Eu - Yb) formed vaterite (hexagonal crystal system, dihexagonal bipyramid crystal lattice) and smallest (Lu) forms calcite (hexagonal scalenohedral) at low temperature and vaterite like structure at above 1310 °C [4].

The phase of Y<sub>17.33</sub>(BO<sub>3</sub>)<sub>4</sub>(B<sub>2</sub>O<sub>5</sub>)<sub>2</sub>O<sub>16</sub>, known as Y<sub>3</sub>BO<sub>6</sub> [11] is with following lattice parameters: monoclinic crystal structure, non-symmetric, optical activity, space group Cm; cell parameters:  $a = 1.81662$  nm,  $b = 0.36516$  nm,  $c = 1.39775$  nm; cell vol. = 0.805 nm<sup>3</sup>, density 4.611 g.cm<sup>3</sup> (samples 85 and 87).

General, the  $\text{Ln}_3\text{BO}_6$  crystallize in three different space groups, i.e.,  $P21/c$  for  $\text{Ln} = \text{La}$  to  $\text{Nd}$  and  $C2/m$ ,  $C2$ , or  $Cm$  for  $\text{Ln} = \text{Pm}$  to  $\text{Yb}$  [10]. Orthorhombic yttrium borate ( $\text{YBO}_3$ ) is with crystal parameters: space group  $Cmcm$ ;  $a = 1.1335 \text{ nm}$ ,  $b = 0.6544 \text{ nm}$ ,  $c = 0.881 \text{ nm}$ ; cell vol. =  $0.653.49 \text{ nm}^3$ ; density  $4.504 \text{ g.cm}^3$ , was founded also (PDF 01-089-3501) (sample 87).



**Figure 1** Powder X-ray diffraction patterns for the synthesised samples

Interaction between  $Y_2O_3$  and  $Al_2O_3$  was observed by the formulation of yttrium aluminate compounds with low intensive peaks visible in the XRD patterns. The monoclinic  $Y_4Al_2O_9$  (known as YAM crystal structure) has cell parameters  $a = 1.11224$  nm,  $b = 1.04663$  nm,  $c = 0.73743$  nm; space group P21/a; Cell Vol. =  $0.81378$  nm<sup>3</sup>; centrosymmetric (PDF 00-055-1088). The yttrium orthoaluminate (YAM) has an orthorhombic structure (perovskite type ceramic structure), centrosymmetric, with space group Pbnm; cell parameters:  $a = 0.518027$  nm,  $b = 0.532951$  nm,  $c = 0.737059$  nm; cell vol. =  $0.20349$  nm<sup>3</sup>; density  $5.349$  g.cm<sup>3</sup> (PDF 01-074-4232).

In XRD patterns of samples 83 and 85 presences a structure of yttrium borate was different from presented in XRD pattern of sample 87. From ICSD PDF indexing refers to the hexagonal  $YBO_3$  phase. The interpreting of the crystal structure (monoclinic, hexagonal or orthorhombic) of  $YBO_3$  is important due to their magnetic properties. As known the  $YBO_3$  (Sm to Lu) has a unit cell similar to that of vaterite, which is hexagonal. But these borates can form so-called  $\pi$ -Ln $BO_3$  with both hexagonal or pseudo-vaterite and monoclinic structure [4]. Also, characteristic for lanthanides with ionic radius 0.09 to 0.104 nm until 1200 °C form metastable Ln $BO_3$  compounds. To identify the correct unit cell, it's compared both hexagonal and orthorhombic peaks position and it's found out that the band with highest intensity for these two phases are corresponding. Also, the density and the molar volume are fully identical according to PDF01-088-0356 and PDF 01-089-3501. Therefore, it's established that the peaks in x-ray roentgenograms of the samples possess orthorhombic structure. The possibility that the hexagonal cell of  $YBO_3$  is only a subcell of the rhombohedral structure is discussed in [11]. The presence of monoclinic  $Y_3BO_6$  phase indexed with PDF 00-034-0291 was compared with indexed phase  $Y_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$  from XRD patterns of samples 85 and 87, respectively. It was observed that both phases are very similar – with the same crystal structure and cell parameters, but different space group –  $Cm$  for  $Y_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$  and  $C_{2/m}$  for  $Y_3BO_6$  phase. There is a possibility these crystal structures are other RE, such as Eu or Dy due to that these space groups belong to Ln $_3BO_6$  (Ln = Pm to Yb) [10].

The aluminates phases observing in sample 83 are  $YAIO_3$  orthorhombic (perovskite like crystal structure) (PDF 074-4232) and monoclinic  $Y_4Al_2O_9$  (YAM) (PDF 00-0055-1088) [12]. Yttrium orthoaluminate,  $YAIO_3$ , is known to have a perovskite like crystal structure (I). It is therefore usually termed YAP (yttrium-aluminum-perovskite) in analogy to YAG (yttrium-aluminum-garnet). Its potential as an efficient laser host has been extensively studied in the past [2-7]. In order to facilitate the discussion on the defects responsible for the absorption, exact structural information was required. So it was decided to perform a complete crystal structure analysis of  $YAIO_3$  by X-ray methods.

From measured the 3D excitation emission matrices (EEM) of the samples and present the topographic view of the normalized spectra in **Figure 2** it is compared the photoluminescent efficiency by different synthesis conditions of the samples.

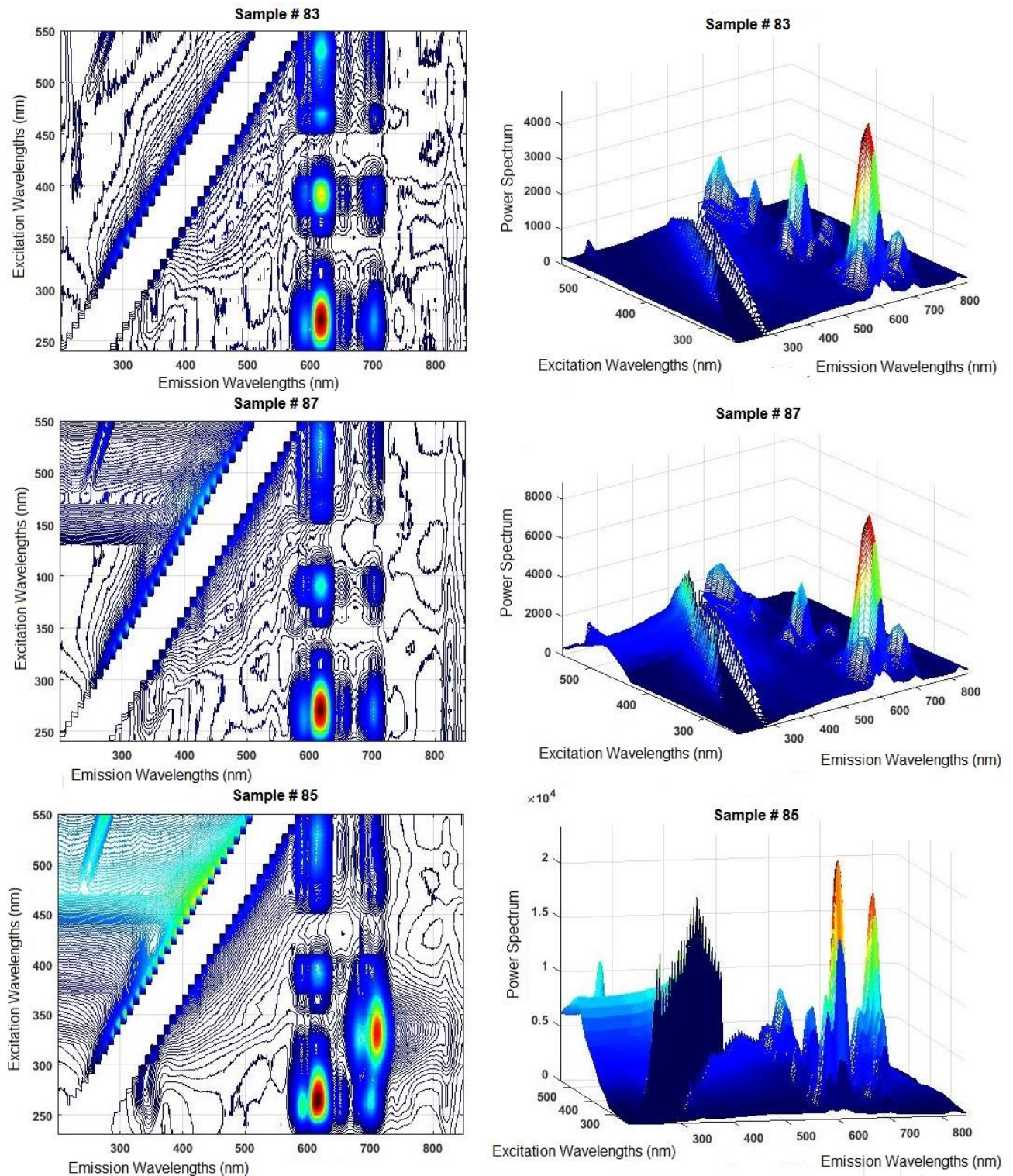
The orange-red emission (around 620 nm) from all samples is indication for an interpolation of europium ions into the crystal structure of yttrium aluminates due to their comparable valence and ionic radii,  $Eu^{2+}$  incorporates onto  $Y^{2+}$  site.

The spectra of sample 83 (doped with Eu) and sample 87 (doped with Eu and Dy), both synthesized at reduction atmosphere, exhibit same fluorescent peaks but for sample 87 are stronger. These fluorescent triplets at range 580 nm – 650 nm are typical for europium ions into crystal structures of yttrium compounds and as is known the dysprosium ions increase the emission of Eu ions due to energy trap mechanisms.

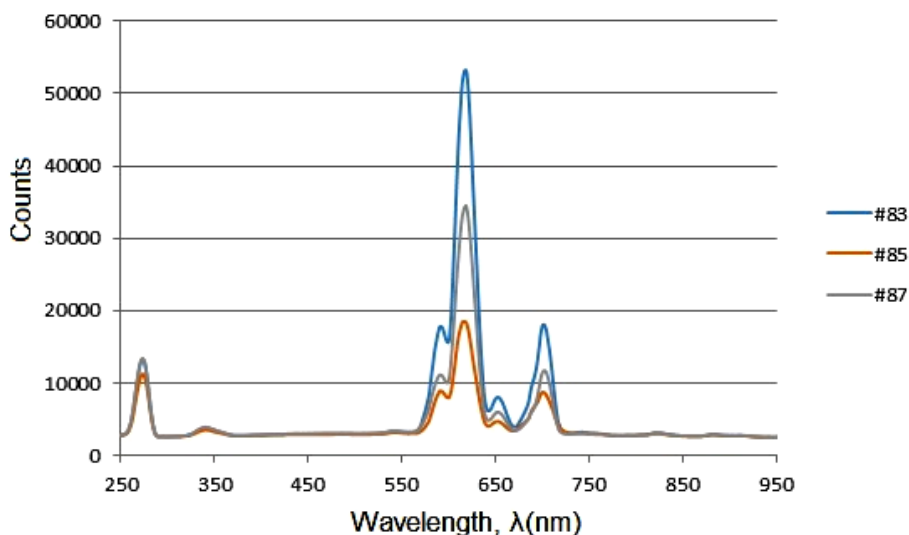
Of the Eu and Dy containing samples, sample 87 exhibited a weak fluorescent peak around 685 nm (**Figure 3**).

Sample 85 fabricated at air conditions was characterized with two strong emission peaks in the orange-red region. The peak at 620 nm is characterized with maximum excitation efficiency at 270 nm. The peak at 700 nm has been maximum excitation efficiency at 340 nm. This sample has the highest emission/excitation spectral distance  $\Delta\lambda = \lambda_{em,max} - \lambda_{exc,max}$  equaling 350 nm and 360 nm for both peaks.





**Figure 2** Excitation-emission spectra of the samples



**Figure 3** Photoluminescence spectra for the samples

#### 4. CONCLUSIONS

Yttrium aluminates and borates doped with europium and dysprosium have been synthesized and investigated by powder X-ray diffraction and photoluminescence analysis.

The obtained materials were fine white crystalline powders. The XRD patterns show formulation of several crystalline phases - predominately non-reacted aluminum oxide, polymorph modifications of yttrium borate and yttrium orthoaluminates.

Europium and dysprosium doped samples exhibit strong fluorescence.

Yttrium-based red powder phosphors have a potential for practical application in lightning industry and other optoelectronic devices.

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