The luminescence properties of yttria based phosphors and study of YBO$_3$ formation via H$_3$BO$_3$ addition

Seyed Mahdi Rafiaei$^*$

Department of Materials Science and Engineering, Golpayegan University of Technology, Golpayegan, Isfahan, Iran

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Abstract

In this paper, Y$_2$O$_3$:Eu$^{3+}$ nano-phosphor was synthesized through the facile solid-state method and influence of H$_3$BO$_3$ addition to the prepared Y$_2$O$_3$:Eu$^{3+}$ powder was investigated. The consumption of boric acid resulted in the formation of YBO$_3$ by changing the crystal structure from cubic to hexagonal. Noteworthy, through the use of specific quantities of H$_3$BO$_3$ (medium amount), YBO$_6$ impurity with the monoclinic crystal structure and the space group C2/m was formed. FESEM observations showed that the addition of H$_3$BO$_3$ leads to the coarsening of the synthesized particles; changing from approximately 80 nm to 1 µm. Also, it was concluded that the transformation of the crystal structure causes a dramatic change of phosphor emission colours from reddish to orange.

Keywords: Y$_2$O$_3$:Eu$^{3+}$, YBO$_3$ formation, structure, luminescence properties

I. Introduction

Eu$^{3+}$ doped Y$_2$O$_3$ and YBO$_3$ phosphors with brilliant emission characteristics and significant chemical stability have received much attention of researchers and engineers for their potential applications in optics-related fields [1,2]. Yttria is widely used in various interesting applications, such as white light emitting diodes [3], photovoltaic cells, up-conversion phosphors [4], lighting, sensors, and optical amplifiers [5]. Meanwhile, the main applications of YBO$_3$ are display panels, the next generation of flexible display instruments and LEDs [6,7]. Surprisingly, YBO$_3$ phosphor can be synthesized easily through the addition of boric acid to Y(CH$_3$COO)$_3$·xH$_2$O, but the crystal structure and luminescence characteristics of these two oxides are absolutely different. Y$_2$O$_3$ phosphors possess cubic crystal structure and Ia3 space group (No. 206). It is already known that in the crystal structure of Y$_2$O$_3$ host lattice, two types of trivalent yttrium ions can be found. Three-quarters of these locations are non-centrosymmetric with C2 symmetry and the rest one quarter is centrosymmetric with S6 symmetry. It should be noted that YBO$_3$ compound crystallizes in different structures with different space groups and symmetries [8,9]. In the monoclinic YBO$_3$ host lattice, two kinds of Y$^{3+}$ ions with C1 and C2 crystal symmetries have been reported [7]. Furthermore, YBO$_3$ may have a hexagonal crystal structure with a P6$_3$/m space group (No. 176) and Eu$^{3+}$ ions which are substituted into Y$^{3+}$ sites, have been surrounded by BO$_3$ groups. So, they provide a symmetry centre resulting in a strong 5D$_{0}$→7F$_{j}$ transition [10].

The extensive studies about Y$_2$O$_3$ reveal that different methods have been used to synthesize it, e.g. hydrothermal [11,12], sol-gel [13], spray pyrolysis [14], combustion [15,16], co-precipitation [17], micro-emulsion microwave [18] and electrospinning [19]. In addition, YBO$_3$ has been extensively synthesized through the employment of the wide range of techniques, such as combustion [20], solvothermal [21], solid-state [10], sol-gel [22], spray pyrolysis [23] and hydrothermal [24]. From the described approaches, plenty of research works have been devoted to the investigation of the facile, economic and effective solid-state procedure. However, the critical problem in the synthesis of the YBO$_3$ phosphor is that H$_3$BO$_3$ with a relatively low boiling temperature is not stable during application of high temperatures. So, large amounts of H$_3$BO$_3$ are subjected to evaporation and estimating the required quantities of boric acid to

$^*$Corresponding authors: tel: +98 91 3139 0739, e-mail: rafiaei@gut.ac.ir
produce YBO₃ is complicated in a way. Also, the addition of boric acid may give rise to the formation of impurities. Unfortunately, the literature is scarce on these issues and this work can provide important information about the optimum values of H₃BO₃ quantities for the synthesis of YBO₃.

Motivated by this brief background and the lack of the related database, the Y₂O₃ phosphor was synthesized via the simple solid-state technique. Transformation from Y₂O₃ to YBO₃ host lattice by addition of H₃BO₃ was investigated by XRD and FESEM. The luminescence studies on Eu³⁺ doped Y₂O₃ and YBO₃ phosphor materials were also carried out.

II. Experimental

2.1. Preparation

In this work, (Y₉₆Eu₀₄)₂O₃ phosphor was synthesized through the use of yttrium acetate (Y(CH₃COO)₃·xH₂O) and europium oxide (Eu₂O₃). The precursor powders with the highest purity (99.99%) were purchased from Aldrich Company and consumed without any purification. Accordingly, stoichiometric amounts of Y(CH₃COO)₃·xH₂O and Eu₂O₃ were ground in a crucible. Then, this mixture was transferred to a tube furnace to conduct calcination at 1100 °C for 2 h. The phosphors nominated as P₀, P₀.₀₂, P₀.₀₅, P₀.₁₅, P₀.₂₅, P₀.₅, P₁, P₂, and P₄ (see Table 1) were synthesized through consuming specific amounts of H₃BO₃, i.e. required amounts of boric acid were added to the calcined initial materials, followed by grinding.

Table 1. Sample notation and corresponding ratio of consumed H₃BO₃ to its stoichiometric quantity (R)

<table>
<thead>
<tr>
<th>Sample notation</th>
<th>R</th>
</tr>
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<tbody>
<tr>
<td>P₀</td>
<td>0</td>
</tr>
<tr>
<td>P₀.₀₂</td>
<td>0.02</td>
</tr>
<tr>
<td>P₀.₀₅</td>
<td>0.0₅</td>
</tr>
<tr>
<td>P₀.₁₅</td>
<td>0.₁₅</td>
</tr>
<tr>
<td>P₀.₂₅</td>
<td>0.₂₅</td>
</tr>
<tr>
<td>P₀.₅</td>
<td>0.₅</td>
</tr>
<tr>
<td>P₁</td>
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</tr>
<tr>
<td>P₂</td>
<td>2</td>
</tr>
<tr>
<td>P₄</td>
<td>4</td>
</tr>
</tbody>
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2.2. Characterization

To identify the crystal structure of the synthesized phosphors, X-ray diffraction (XRD, Rigaku, Japan) with CuKα radiation (λ = 1.54 Å) was employed. The Scherrer formula, \( D = \frac{0.9l}{\beta \cos \theta} \), was used to estimate the crystallite size of the prepared samples (where \( D \) is the average grain size, \( \lambda \) is the wavelength of X-ray, \( \beta \) and \( \theta \) are the full-width at half maximum and diffraction angle of the considered peaks, respectively). In addition, the morphology of produced phosphors was studied via the use of field emission scanning electron microscope (FE-SEM, Hitachi SU70, Japan). Finally, the optical properties of Y₂O₃/YBO₃ phosphors were characterized by a photoluminescence analyser (PL, Horiba Jobin Yvon Fluorolog-3, Japan).

III. Results and discussion

3.1. XRD analysis

Figure 1 shows the XRD spectra of P₀-P₄ compounds. The spectra of P₀-P₀.₁₅ compounds imply that the prominent peaks of diffraction are attributed to (211), (222), (400), (440) and (622) planes of a cubic crystal structure, suggesting that the obtained phosphor matches well with JCPDS No. 41-1105. Also, regarding the Scherrer formula, the crystallite size of Y₂O₃ (P₀) phosphor was simply calculated to be 45.6 nm. Accordingly, it is clear that for \( R \) values from 0 to 0.25, the structure of the synthesized phosphors is very similar to that of Y₂O₃. Obviously, the peak at 29.2° of (222) plane has the strongest intensity of diffraction, while the addition of small quantities of boric acid gives rise to its slight increase. Conversely, the use of higher quantities of the additive significantly decreases the diffraction intensity, thus suppresses the crystallization of Y₂O₃.

As a matter of fact, boric acid has the role of flux material via the solid-state procedure. With the use of small amounts of the additive, the crystallinity of the synthesized phosphor is improved. This issue is related to the fact that the mentioned material, with a relatively lower melting point, facilitates the melting of components and enhances the growth of yttria crystals [10]. In other words, according to our calculations, it was found that the addition of small amounts of H₃BO₃ has enlarged the distance of (222) plane from 3.035 Å to 3.059 Å, implying the expansion of yttria unit cell. However, higher amounts of H₃BO₃, not only decreases the peak intensity but also shrinks the inter-planar distance from 3.059 Å to 3.053 Å and 3.052 Å. This observation clarifies that relatively larger amounts of the used additive suppress the growth of Y₂O₃ material. It seems that the flux material provides efficient obstacles among
the produced oxide nano-particles. The study of XRD spectra of P0.25P2 compounds shows that the synthesized phosphors belong to YBO3 phase, possess hexagonal crystal structure and are consistent with JCPDS No. 16-0277. The prominent diffraction peaks are attributed to (002), (010), (102), (110), (104), (112), (200), (202), and (114) planes. Interestingly, by the addition of boric acid the prominent peak of the considered compounds shifts from approximately 29.2° to 27.26° (shown by the dashed lines). The XRD spectra of P0.5, P1, and P2 phosphors reveal that further increase of H3BO3 leads to the significant formation of YBO3. Consequently, exploring the probable reactions within the solid-state procedure remains an interesting issue in this study. The possible reactions between Y2O3 and H3BO3 can be considered as follows:

\[
\begin{align*}
Y_2O_3 + 2 H_3BO_3 & \rightarrow 2 YBO_3 + 3 H_2O \quad (1) \\
2 Y_2O_3 + 2 H_3BO_3 & \rightarrow YBO_3 + Y_3BO_6 + 3 H_2O \quad (2)
\end{align*}
\]

It can be easily found that with the addition of H3BO3 during the explained solid-state procedure, YBO3 or YBO3/Y3BO6 can be produced. Therefore, the formation of Y3BO6 was monitored by the employment of XRD spectra. As a matter of fact, in the case of using large amounts of boric acid, especially for synthesis of P2 phosphor, some impurity peaks can be seen. Referring to the mentioned reactions and also JCPDS No. 34-0291, 41-1105 and 16-0277, it can be easily concluded that the impurity peaks include Y2O3 and Y3BO6 phases.

Figure 2 shows the existence of Y3BO6 impurities in P0.15 and P0.25 phosphors marked with the red circles. It is seen that the attributed main diffraction planes can be seen at the 2θ of 13.34°, 22.06°, 31.11°, 32.75°, 49.95° and 59.73°. It is obviously observed that the increase of boric acid addresses the increase of considered diffraction intensities. Y3BO6 crystallizes in the monoclinic space group C2/m, with the lattice constants: \( a = 18.162 \, \text{Å}, b = 3.651 \, \text{Å} \) and \( c = 14.006 \, \text{Å} \), while \( \alpha, \beta \) and \( \gamma \) are 90°, 119.69° and 90°, respectively (JCPDS No. 34-0291). It is clear that the formation of Y3BO6 is achieved for the specific amounts of H3BO3 which is in agreement with the introduced solid-state reactions. It can be seen that the strongest diffraction intensities belong to P0.15 and P0.25 materials.

3.2. FESEM observations

According to Figure 3, it is seen that the particle size of P0 sample is about 80 nm, while through the addition of boric acid, the particle size grows gradually to approximately 1 μm in P2 phosphor. Interestingly with the increase of H3BO3, the particle size changed dramatically from nanoscale to microscale. This result is consistent with the crystallite sizes of P0 and P2 phosphors, which were estimated to 45.6 nm and 52.4 nm, respectively. In other words, it is observed that with the use of boric acid via solid-state approach, the transformation of materials from Y2O3 to YBO3 with a huge growth of particles would happen.

3.3. PL analysis

The excitation characterization was conducted on P0.02 compound (see Fig. 4a), since according to the discussed XRD spectra, P0.02 phosphor possesses well-formed crystal structure. There is a broad band from 210 nm to 280 nm that is attributed to the charge transfer band (CTB) between O2− and Eu3+ ions with the orbitals of 2p and 4f, respectively [25]. Figure 4b belongs to the photoluminescence emission of P0 and P0.5 compounds under the excitation wavelength of 255 nm. The PL spectrum of P0 sample is composed of \( {^5}D_0 \rightarrow {^7}F_1 \) and \( {^5}D_0 \rightarrow {^7}F_2 \) peaks which are related to the magnetic dipole and forced electric dipole transitions. It can be easily found that \( {^5}D_0 \rightarrow {^7}F_2 \) is the dominant peak observed at 612 nm [26]. Usually in the cubic crystal structure of Y2O3, through the substitution of Y3+ by Eu3+ ions, no inversion centre is provided and the electric dipole transition is partially allowed. Furthermore, the \( {^5}D_0 \rightarrow {^7}F_1 \) and \( {^5}D_0 \rightarrow {^7}F_2 \) transitions are observed in the emission result of P0.5 sample too. By contrast, it is seen that the \( {^5}D_0 \rightarrow {^7}F_1 \) magnetic dipole transition at 592 nm

![Figure 2. XRD spectra of: a) P0.15 and b) P0.25 phosphors](image-url)
is the dominant peak [25]. YBO$_3$ host lattice possesses a hexagonal crystal structure in which Y$^{3+}$ ions are surrounded by BO$_3$ groups. Through the doping procedure, the ions of Eu$^{3+}$ are substituted at Y sites, making a symmetry centre and also a powerful $^5$D$^0$ − $^7$F$_{1}$ transition occurs. Noteworthy, with the increase of boric acid and the transformation of the crystal structure from cubic to hexagonal, the emission colour of produced phosphors changes slightly from reddish to orange (see the inset of Fig. 4b).

Figure 5a shows the emission behaviour of P$_{0}$-P$_{0.15}$ phosphors. It is concluded that the addition of small amounts of H$_3$BO$_3$ to yttrium acetate within the solid-state process, improves the photoluminescence properties, effectively. Interestingly, this result agrees well with the XRD spectra and clarifies that the addition of H$_3$BO$_3$ has enhanced the crystallinity of Y$_2$O$_3$ host lattice. However, similar to the results reported by other researchers, it is clear that higher quantities of the flux decrease the luminescence properties of phosphors [27,28]. Noteworthy, in this case, the additives give rise to the formation of impurities, suppress the crystallinity and therefore photoluminescence characteristics of the synthesized phosphors. According to Fig. 5b, it is observed that the highest and the lowest intensities of PL spectra of YBO$_3$ based phosphors are attributed to P$_{0.5}$ and P$_2$ compounds, respectively. It can be mentioned that based on the low boiling point of H$_3$BO$_3$, there is a remarkable evaporation of boric acid within the high temperature solid-state procedure. Therefore, P$_{0.5}$ sample has higher luminescence properties than P$_{0.25}$ phosphor. However, if the quantity of added boric acid is more than the required mass for the formation of YBO$_3$, some impurities will be made in the compound and thus the intensity of photoluminescence emission would be suppressed.

Interestingly, although Y$_3$BO$_6$ was detected in XRD spectra, no specific emission peak was observed related to the considered Y$_3$BO$_6$. The volumes of Y$_2$O$_3$ and Y$_3$BO$_6$ unit cells are 1192.4 Å$^3$ and 806.80 Å$^3$, respectively.
tively, which results in the larger distance of Y–O in Y$_2$O$_3$ than that in Y$_2$BO$_6$. Regarding the ionic sizes of Y$^{3+}$ and Eu$^{3+}$, which are 1.04 Å and 1.087 Å, respectively, it is easily found that Eu$^{3+}$ ions prefer to be doped more efficiently in the Y$_2$O$_3$ host. Moreover, as shown in the XRD spectra, Y$_3$BO$_3$ has been formed as an impurity and the quantity of this compound is very small. So, any specified peak cannot be observed in the PL spectra.

IV. Conclusions

In this work, Eu$^{3+}$ doped Y$_2$O$_3$ nano-phosphor and YBO$_3$ phosphor were synthesized via facile solid-state approach. It was found that the addition of H$_2$BO$_3$ not only increases the particle size from approximately 80 nm to 1 μm, but also changes the crystal structure from cubic to hexagonal (belonging to YBO$_3$). In addition, the XRD results showed that Y$_3$BO$_3$ (as an impurity phase) was formed with the addition of medium amount of boric acid. The luminescence analyses proved that P$_{0.03}$ and P$_{0.5}$ compounds show the highest emission intensity for the Y$_2$O$_3$ and YBO$_3$ based phosphors, respectively.

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