

# Preparation and Luminescence Properties of $\text{Ba}_3\text{Y}(\text{PO}_4)_3:\text{RE}^{3+}$ (RE=Eu, Dy) Phosphors

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**Abstract:** In order to investigate the luminescence properties of  $\text{Ba}_3\text{Y}(\text{PO}_4)_3$  doped with rare earth ions, a series of  $\text{Eu}^{3+}$  and  $\text{Dy}^{3+}$  single doped  $\text{Ba}_3\text{Y}(\text{PO}_4)_3$  phosphor powders were prepared by high temperature solid phase method. The relevant performance of samples were characterized by X ray diffraction (XRD) and fluorescence spectra. The results showed that the prepared phosphor was a cubic phase of bismuth ore and the space group is I-43d. Under the excitation of near violet light, the narrow band emission of  $\text{Ba}_3\text{Y}(\text{PO}_4)_3:0.08\text{Eu}^{3+}$  was nearly located at 594nm, 613nm and 702nm, which showed orange red light emission. The  $\text{Ba}_3\text{Y}(\text{PO}_4)_3:0.08\text{Dy}^{3+}$  narrow band emission was located at 485nm and 575nm respectively, which showed white light emission. The matrix material was doped with a single active ion, and the white light emission was achieved through its coordination in different light regions. The characteristic emission peak of  $\text{Eu}^{3+}$  in the red light region (580~650nm,  $^5\text{D}_0\text{-}^7\text{F}_j$ ) could compensate for the lack of red components in the  $\text{Dy}^{3+}$  white light emission spectrum, thus the quality of white light of the single doped  $\text{Dy}^{3+}$  phosphor could be improved, and it was expected to be applied to light-emitting diode (LED) field.

## 1.Introduction

YAG:Ce blue plus yellow LED has been widely applied in many parts of the world, but its color saturation is relatively poor due to the lack of red light. In recent years, the research of fluorescent materials has been progressing rapidly[1-3]. Three main aspects are summarized: the first LED based on "blue and yellow" is based on the improvement of the color saturation of the phosphor by improving the red phosphor excited with the blue chip. Second, the excitation light source is ultraviolet and near ultraviolet chip, which is suitable for the white light produced by the excitation of RGB tricolor phosphor. The third way is to combine white light with UV and near ultraviolet chips to achieve white light. Therefore, the research of high efficiency single substrate white phosphor has great significance to further promote the industrialization of white LED. The study showed that different yellow and blue light intensity (Y/B) could be obtained by changing the type and doping amount of alkali metal ions. If Y/B was appropriate, the color coordinates were located in the white light area and warm white light, which was key to obtaining the single matrix and high quality phosphor. However, in many substrates, the Y/B values usually deviated from the ideal value so that it can not get warm white light. because the different doping concentration of the inorganic matrix  $\text{Dy}^{3+}$  will affect the Y/B value, the chromaticity stability of the phosphor prepared by doping  $\text{Dy}^{3+}$  is poor [4-5]. It had been studied that many  $\text{Dy}^{3+}$  activated luminescent materials (based on rare earth



phosphate) had attracted much attention because of their low synthetic temperature, high brightness, good physical and chemical stability [6]. In addition,  $\text{Eu}^{3+}$  usually sends red light, and its characteristic emission peak (580~650nm,  $^5\text{D}_0\text{-}^7\text{F}_1$ ) in the red light region can compensate for the lack of red components in the  $\text{Dy}^{3+}$  white light emission spectrum, thus improving the white light quality of the single doped  $\text{Dy}^{3+}$  phosphor. A single active ion is doped in the matrix, and white light emission is achieved through its coordination in different light regions. In this experiment, some different light emitting phosphors were compounded by doping rare earth  $\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}$ , and they can be applied to the field of LED by blending and realizing white light.

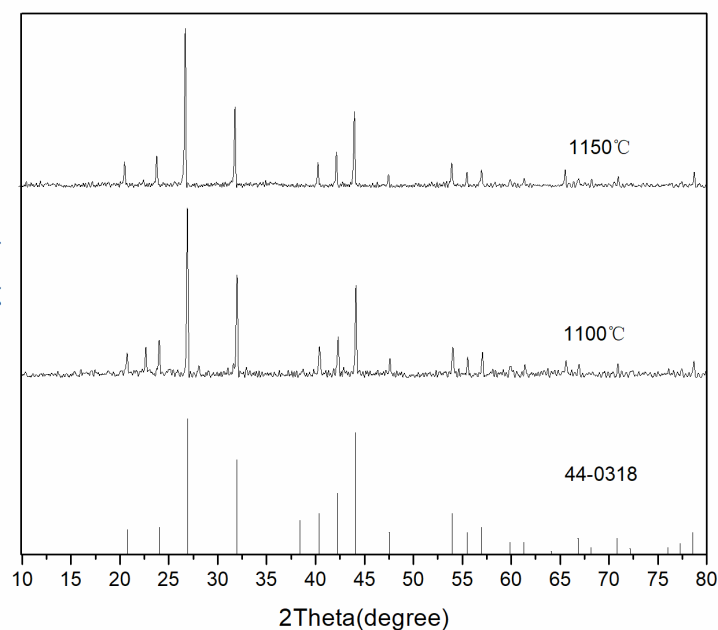
## 2. Experiment

$\text{BaCO}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{Dy}_2\text{O}_3$  and  $\text{Eu}_2\text{O}_3$  according to the stoichiometric ratio of  $\text{Ba}_3\text{Y}(\text{PO}_4)_3$  ( $x=0, 0.01, 0.02, 0.04, 0.06, 0.08, 0.10$ ) were accurately measured and placed in ceramic mortar. First, the medicine was ground with a proper amount of anhydrous ethanol, until the powder was mixed evenly. The samples were dried about 15min in the drying oven. The dry samples were precooked to  $600^\circ\text{C}$  in the crucible furnace with heat preservation for 1h. The grinding again samples with 10min was burned to  $1150^\circ\text{C}$  in the high temperature furnace and kept for 4h, and the samples were naturally cooled to room temperature.

X-ray (D8 Advance, Germany) diffractometer was used to measure the crystal phases of phosphors. Emission spectra of samples were measured by a fluorescence spectrophotometer (F-7000, Japan) with a 150W Xe lamp.

## 3. Results and Discussion

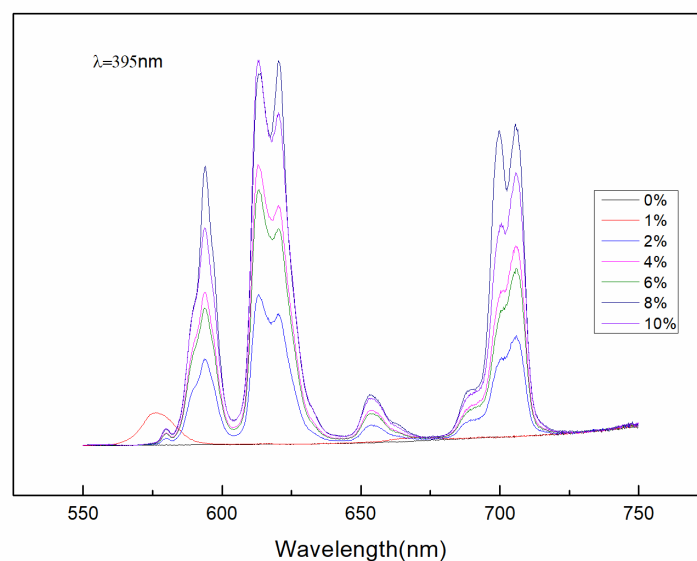
X ray diffraction pattern of sample  $\text{Ba}_3\text{Y}(\text{PO}_4)_3$  are shown in Fig.1. As seen in Fig.1, the XRD patterns of phosphors after heating at 1100 and  $1150^\circ\text{C}$  were well agreed the standard card 44-0318, but the crystal phase formed at  $1150^\circ\text{C}$  was better.  $\text{Ba}_3\text{Y}(\text{PO}_4)_3$  are in cubic lattice constant of  $a=b=c=10.46\text{\AA}$ ,  $V=1146.25\text{\AA}^3$  space group I-43d. In the matrix of  $\text{Ba}_3\text{Y}(\text{PO}_4)_3$ , the radius of  $r=0.89$  is  $r=0.89$ , while the radius of  $r=1.12$  doped  $\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}$  radius and  $r=1.17$  radius are similar to those of  $\text{Y}^{3+}$ . Therefore,  $\text{Eu}^{3+}$  and  $\text{Dy}^{3+}$  are more inclined to replace  $\text{Y}^{3+}$ , which is beneficial for the reduction of system energy and stability.



**Figure 1.** XRD patterns of different temperatures

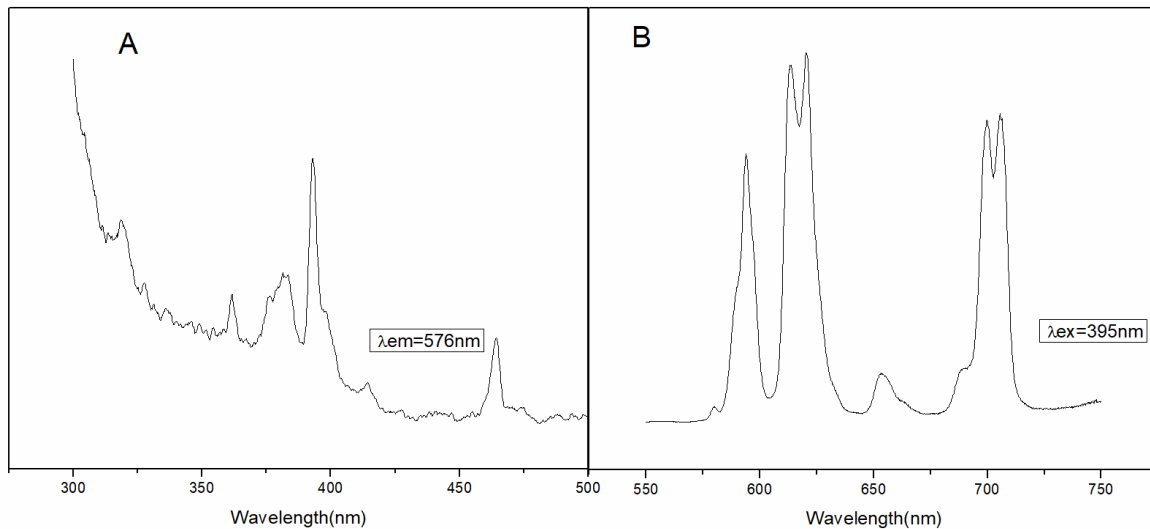
As shown in Fig.2, the emission spectra of  $\text{Ba}_3\text{Y}(\text{PO}_4)_3$  with different  $\text{Eu}^{3+}$  doping concentrations

will be directly affected by the doping concentration of  $\text{Eu}^{3+}$ , and the luminous intensity [7] of  $\text{Ba}_3\text{Y}(\text{PO}_4)_3$  will directly affect the emission spectrum. It can be seen from the diagram that the overall trend of luminescence intensity is increased with the increase of  $\text{Eu}^{3+}$  doping concentration, and the intensity decreases when the concentration increases to a certain extent. When the  $\text{Eu}^{3+}$  concentration is less than 2%, the luminescence intensity is weak because of the sample in less active ion. When the  $\text{Eu}^{3+}$  concentration is less than 8%, the emission intensity increased gradually with the increase of  $\text{Eu}^{3+}$  concentration. The light of 607nm and 691nm are rapid increased due to the  $^5\text{D}_0$  to  $^7\text{F}_2$  transition, and the light of 595nm also was increased by  $^5\text{D}_0$  to  $^7\text{F}_1$  transition. But the change is relatively small compared with the former. When the concentration of  $\text{Eu}^{3+}$  is more than 8%, the emission strength decreases with the increase of the concentration of  $\text{Eu}^{3+}$ , which indicates that the high concentration of rare earth ions has a concentration quenching effect on the phosphor, thus reducing the relative intensity of the luminescence.



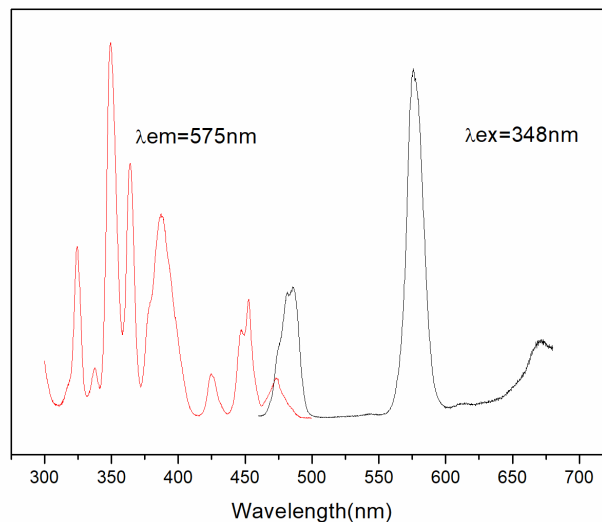
**Figure 2.** Emission spectra of  $\text{Ba}_3\text{Y}(\text{PO}_4)_3$  with different  $\text{Eu}^{3+}$  doped contents.

Fig. 3 (A) is the excitation spectrum of  $\text{Ba}_3\text{Y}(\text{PO}_4)_3:0.08\text{Eu}^{3+}$  emitted by 576nm, which are located at four different peaks of 350-475nm. The excitation peak of 395nm is the largest, and the most intense reason is the  $^7\text{F}_0$  to  $^5\text{L}_6$  transition of  $\text{Eu}^{3+}$ . The peak of 370nm is the  $^7\text{F}_0$  to  $^5\text{H}_3$  transition of  $\text{Eu}^{3+}$ , the peak of 383nm is the  $^7\text{F}_0$  to  $^5\text{F}_8$  transition of  $\text{Eu}^{3+}$ , and the peak of 463nm is the  $^7\text{F}_0$  to  $^5\text{D}_2$  transition of  $\text{Eu}^{3+}$ . The located at 389nm may be a f to f high-energy level transition absorption, and the  $^7\text{F}_0$  to  $^5\text{L}_6$  of  $\text{Eu}^{3+}$  the transition occurs. As shown in Fig.3 (B), there are 6 emission peaks due to the transition emission of  $\text{Eu}^{3+}$  under 395nm excitation, and the emission peak at 672nm is the strongest. The peak of 590nm, 615nm and 621nm, 702nm, 712nm are respectively the  $^5\text{D}_0$  to  $^7\text{F}_1$ ,  $^5\text{D}_0$  to  $^7\text{F}_2$ ,  $^5\text{D}_0$  to  $^7\text{F}_3$ ,  $^5\text{D}_0$  to  $^7\text{F}_4$  transition. The  $\text{Eu}^{3+}$  doped  $\text{Ba}_3\text{Y}(\text{PO}_4)_3$  material is red because of the emission range of 620-760nm is the red light region, which show the intensity of the emission peaks of 672nm, 702nm and 712nm is higher. The wavelengths of  $^5\text{D}_0$  transition to  $^7\text{F}_1$  ( $J=0-5$ ) and  $^5\text{D}_1$  transition to  $^7\text{F}_1$  ( $J=0-5$ ) are different with the addition of  $\text{Eu}^{3+}$  rare earth ions. The transition mechanism is the f-f transition[2], which is almost unaffected by the crystal field. The emission spectrum of  $\text{Ba}_3\text{Y}(\text{PO}_4)_3:0.08\text{Eu}^{3+}$  is linear, and  $\text{Eu}^{3+}$  in the matrix lattice determines its emission wavelength. On the one hand,  $\text{Eu}^{3+}$  occupy the non inversion symmetry in the lattice. The red light is produced because of the 5d configuration mixed into the  $^4\text{F}_6$  configuration, thus the uneven crystal field causes the F-F transition not to be maintained. On the other hand, the location of the  $\text{Eu}^{3+}$  is the center of the lattice inversion symmetry, and its emission spectrum is almost all in the  $^5\text{D}_0$  to  $^7\text{F}_1$  orange emission area.



**Figure 3.** (A)The excitation spectra and the emission spectra(B) of Ba<sub>3</sub>Y(PO<sub>4</sub>)<sub>3</sub>:0.08Eu<sup>3+</sup>

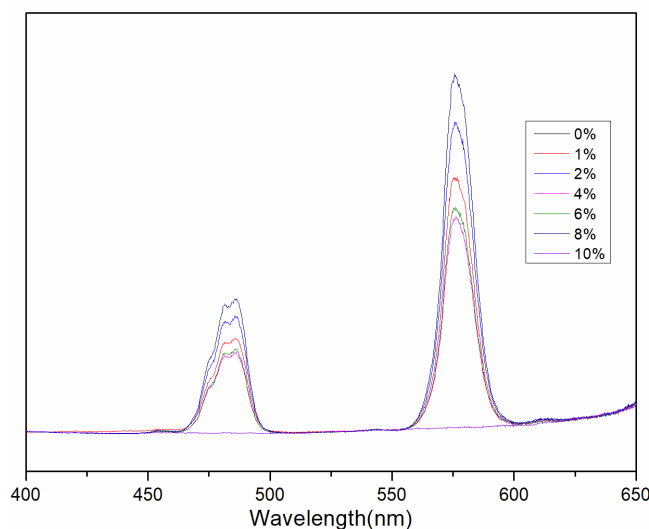
Fig. 4 is the emission spectrum of Ba<sub>3</sub>Y(PO<sub>4</sub>)<sub>3</sub>:0.08Dy<sup>3+</sup>. There are three peaks with different emission intensities. The emission peak of 484nm corresponds to the blue light emission. It may be the <sup>4</sup>F<sub>9/2</sub> to <sup>6</sup>H<sub>15/2</sub> transition of Dy<sup>3+</sup>. The emission peak of 575nm is yellow light emission, which may be produced by the <sup>4</sup>F<sub>9/2</sub> to <sup>6</sup>H<sub>13/2</sub> transition of Dy<sup>3+</sup>. The emission peak of 671nm is corresponding to the weaker red emission relative to the former. The transition is produced because of the three emission peaks are located in the blue, yellow and red regions, thus they can be combined to get better white light.



**Figure 4** The excitation spectrogram and emission spectrogram of Ba<sub>3</sub>Y(PO<sub>4</sub>)<sub>3</sub>:0.08Dy<sup>3+</sup>

It can be seen from the excitation peak that the excitation peak located at 324nm may be caused by <sup>6</sup>H<sub>15/2</sub> to <sup>6</sup>P<sub>3/2</sub>. The excitation peak of 340nm, 354nm, 425nm, 454nm and 474nm is respectively the <sup>6</sup>H<sub>15/2</sub> to <sup>6</sup>P<sub>7/2</sub>, <sup>6</sup>H<sub>15/2</sub> to <sup>6</sup>P<sub>5/2</sub>, <sup>6</sup>H<sub>15/2</sub> to <sup>4</sup>M<sub>21/2</sub>, <sup>6</sup>H<sub>15/2</sub> to <sup>4</sup>G<sub>11/2</sub> and <sup>6</sup>H<sub>15/2</sub> to <sup>4</sup>I<sub>15/2</sub>. The strongest excitation peak is the excitation peak at 354nm. As shown in Fig.5, it can be seen that the intensity of luminescence first increases with the increase of doping concentration, and then decreases with the increase of doping concentration. When the doping concentration of Dy<sup>3+</sup> is less than or equal to 8%, the luminescence intensity of Ba<sub>3</sub>Y(PO<sub>4</sub>)<sub>3</sub>:xDy<sup>3+</sup> increases with the increase of Dy<sup>3+</sup> doping concentration. When the Dy<sup>3+</sup> concentration is equal to 8%, the luminescence intensity of the sample is the largest. When the doping concentration of Dy<sup>3+</sup> increases to 10%, the luminescence intensity of

the sample becomes weaker, which is both concentration quenching. The doping concentration of  $\text{Dy}^{3+}$  rises to a certain extent, and there will be no radiative energy transfer, resulting in the weakening of luminous intensity. The concentration quenching of inorganic nonconductive photoluminescent materials is caused by the electric multipole between ions -- Dexter theory [8].



**Figure 5.** The Emission spectra of  $\text{Ba}_3\text{Y}(\text{PO}_4)_3$  with different  $\text{Dy}^{3+}$  doped contents.

#### 4. Conclusions

A series of  $\text{Dy}^{3+}$  and  $\text{Eu}^{3+}$  single doped  $\text{Ba}_3\text{Y}(\text{PO}_4)_3$  phosphors were synthesized by the traditional high-temperature solid-state method. Under the excitation of near ultraviolet light, the phosphors of this series have great luminescence properties.  $\text{Ba}_3\text{Y}(\text{PO}_4)_3:\text{Dy}^{3+}$  phosphor white light emission and  $\text{Ba}_3\text{Y}(\text{PO}_4)_3:\text{Eu}^{3+}$  phosphor red light emission. Because doping  $\text{Eu}^{3+}$  ions compensate for the lack of red light components in  $\text{Dy}^{3+}$  cold white light in  $\text{Ba}_3\text{Y}(\text{PO}_4)_3:\text{Dy}^{3+}$  phosphor, the  $\text{Dy}^{3+}$  is changed by changing  $\text{Dy}^{3+}$ . The concentration and relative doping ratio of  $\text{Eu}^{3+}$  ions can achieve the luminescence color of phosphor, from cold white light to warm white light, and then to orange red light. When the concentration of doped ions is too high, the concentration quenching effect will happen.  $\text{Ba}_3\text{Y}(\text{PO}_4)_3:\text{Dy}^{3+}$  and  $\text{Ba}_3\text{Y}(\text{PO}_4)_3:\text{Eu}^{3+}$  have potential applications in near ultraviolet excited white light diode (NUV-WLED) devices.

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