



Preparation, luminescence and electrons selected energy level transition of Dy^{3+} in $\text{Ba}_7\text{Hf}(\text{PO}_4)_6$ through temperature control

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ABSTRACT

A novel single-phase Eulytite-type orthophosphate $\text{Ba}_7\text{Hf}(\text{PO}_4)_6:\text{Dy}^{3+}$ was prepared via sintering method. X-ray powder diffraction analysis confirmed the obtained samples were good single phase and no impure phase was found. The optical properties of $\text{Ba}_7\text{Hf}(\text{PO}_4)_6:\text{Dy}^{3+}$ phosphors were characterized and the influence on the luminescent properties with various Dy^{3+} contents was studied clearly. Moreover, the photoluminescence spectra, decay times as well as the temperature quenching spectra of $\text{Ba}_7\text{Hf}(\text{PO}_4)_6:\text{Dy}^{3+}$ phosphors were studied minutely. The experiment results illustrated the prepared $\text{Ba}_7\text{Hf}(\text{PO}_4)_6:\text{Dy}^{3+}$ phosphor showed two photoluminescence bands centered at 485 nm and 578 nm which were attributed to ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ transitions of Dy^{3+} when pumped by UV. Meanwhile, an abnormal phenomenon was found that when the temperature increased, the emission intensity of $\text{Ba}_7\text{Hf}(\text{PO}_4)_6:\text{Dy}^{3+}$ at 485 nm and 578 nm gradually decreased but the emission spectra at 451 nm assigned to ${}^4\text{I}_{15/2} \rightarrow {}^6\text{H}_{15/2}$ increased sharply with increasing temperature. Hence, temperature dependent ${}^4\text{I}_{15/2} \rightarrow {}^6\text{H}_{15/2}$ transition was analyzed in detail by X-ray powder diffraction, emission spectra and decay curves at different temperature, which was rarely discussed before. We found that the electrons preferentially select energy level transition of Dy^{3+} in $\text{Ba}_7\text{Hf}(\text{PO}_4)_6$ through temperature control. All the results showed that $\text{Ba}_7\text{Hf}(\text{PO}_4)_6:\text{Dy}^{3+}$ is a high-performance single-component phosphor.

1. Introduction

The lanthanide ions doped luminescent applications: scintillator, persistent phosphors, dosimeter, white-LED, bio-imaging and anti-counterfeiting induced great interest to the scientists [1–13], because the lanthanide (*Ln*) ions doped compounds can exhibit excellent luminescence properties. Recently, among the ions (Yb^{3+} , Er^{3+} , Dy^{3+} , Eu^{3+} and Ce^{3+}), Dy^{3+} ions are attracting much attention from the scientists due to the unique optical properties. It is well known, Dy^{3+} can exhibit strong yellow and blue emission excited by UV light, which can be ascribed to the transitions of ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ [17]. Hence, a single-phase Dy^{3+} doped compounds which can emit white light can be widely used in the white-LED, temperature sensors, scintillator and dosimeter. Therefore, searching high efficient Dy^{3+} doped compounds which have intense absorption in UV range is an urgent need for luminescent applications.

Currently, eulytite-type orthophosphates with the general formula $\text{A}_7\text{B}(\text{PO}_4)_6$ ($\text{A} = \text{Sr}, \text{Ba}$ $\text{B} = \text{Hf}, \text{Zr}$) have attracted much attention as host materials for rare earth because of the excellent thermal and chemical-physical stability. Furthermore, the special optical properties of Dy^{3+} -doped eulytite-type orthophosphates phosphors have attracted more

notice because of the significant use to the solid-state light [14–16]. Ratnam et al. [18] discussed the photoluminescence of NaCaPO_4 with various doping concentration of Dy^{3+} . Zhang et al. [19] studied the relationship between the structure and emission properties of Dy^{3+} -doped $\text{Sr}_7\text{Zr}(\text{PO}_4)_6$ phosphor. However, most of the researches only pay attention to changing the two bands emission intensity ratio by control the host structure and then turn the color coordinate of white-LED. Until now, there is no study focusing on the structure and PL properties of $\text{Ba}_7\text{Hf}(\text{PO}_4)_6:\text{Dy}^{3+}$ phosphor. Meanwhile, besides the transitions of ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ there is no research caring about the transition between the other energy levels. Especially, the ${}^4\text{I}_{15/2} \rightarrow {}^6\text{H}_{15/2}$ transition is rarely discussed. The electrons transition of Dy^{3+} through temperature control in eulytite-type orthophosphates hosts is not clear yet.

Hence, we want to do some basic researches for Dy^{3+} -doped eulytite-type orthophosphates. In this study, the photoluminescence of $\text{Ba}_7\text{Hf}(\text{PO}_4)_6:\text{Dy}^{3+}$ phosphors was discussed clearly. In addition, the abnormal thermal quenching process as well as the increased possibilities of ${}^4\text{I}_{15/2} \rightarrow {}^6\text{H}_{15/2}$ transition are analyzed and discussed by temperature dependent X-ray powder diffraction, emission spectra and temperature dependent life time in detail. The results suggest the

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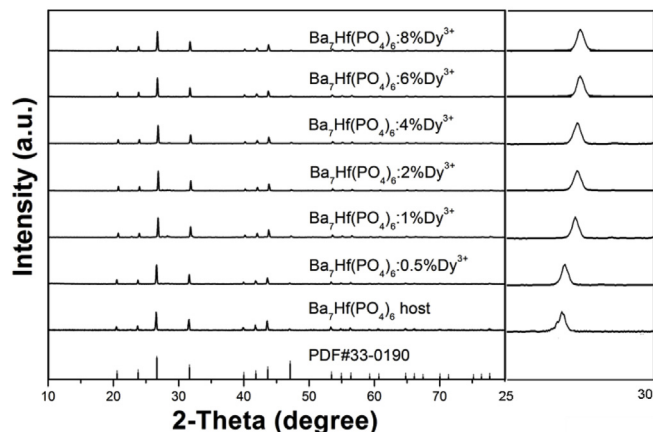


Fig. 1. The measured XRD patterns of $\text{Ba}_7\text{Hf}(\text{PO}_4)_6:\text{Dy}^{3+}$ with various concentrations of Dy^{3+} .

electrons preferentially selected $^4\text{I}_{15/2} \rightarrow ^6\text{H}_{15/2}$ energy level transition of Dy^{3+} with increasing temperature in eulytite-type orthophosphates hosts. And the $\text{Ba}_7\text{Hf}(\text{PO}_4)_6:\text{Dy}^{3+}$ phosphor is a high-performance single-component white-emission phosphor.

2. Experimental

$\text{Ba}_7\text{Hf}(\text{PO}_4)_6:\text{Dy}^{3+}$ was synthesized by $\text{BaCO}_3(\text{AR})$, $\text{HfO}_2(\text{AR})$, $(\text{NH}_4)_2\text{HPO}_4(\text{AR})$ and $\text{Dy}_2\text{O}_3(\text{AR})$. The raw materials were mixed with ethanol for 30 min. Afterwards, the prepared materials was dumped to an Al_2O_3 crucible and sintered to 1300°C for 5 h and then cooled down.

3. Results and discussion

As shown in Fig. 1, the crystal structural research and phase purity of $\text{Ba}_7\text{Hf}(\text{PO}_4)_6:\text{Dy}^{3+}$ with various concentrations of Dy^{3+} were studied by X-ray diffraction measured by Haoyuan 2700-BH equipped with Cu $\text{K}\alpha$ radiation. The XRD patterns of $\text{Ba}_7\text{Hf}(\text{PO}_4)_6:\text{Dy}^{3+}$ phosphors are the same with that of orthorhombic $\text{Sr}_7\text{Zr}(\text{PO}_4)_6$ (JCPDS card no. 33–0190 [17]) and there is no impurity line observed. Moreover, with increasing doping Dy^{3+} in $\text{Ba}_7\text{Hf}(\text{PO}_4)_6$, the diffraction peaks shift to large angle which indicate that Dy^{3+} substitute Ba^{2+} in the host lattice. The shift of the diffraction position is due to the changes in the lattice parameters as a result of the different ionic radii of Dy^{3+} and Ba^{2+} . As we know, the space group of $\text{Ba}_7\text{Hf}(\text{PO}_4)_6$ is $\text{I}43\text{d}$ ($Z = 2$) with an orthorhombic structure [20]. The three-dimensional network of $\text{Ba}_7\text{Hf}(\text{PO}_4)_6$ structure is constituted by oxygen octahedra which share edge and form corrugated chains. The corrugated chains connected with independent $[\text{PO}_4]$ tetrahedra groups by sharing corners. Two positions in the octahedral are occupied by Ba and Hf atoms randomly [21]. The flexible and plastic structure is benefit to act as an excellent host material for rare earth [22].

Fig. 2 shows the PLE spectra of $\text{Ba}_7\text{Hf}(\text{PO}_4)_6:\text{Dy}^{3+}$ monitored at 610 nm with various Dy^{3+} concentrations at room temperature measured by an FS5-MCS (Edinburgh) fluorescence spectrophotometer. The excitation spectra originated from 250 nm to 500 nm include seven different excitation peaks centered at 452, 425, 387, 365, 351, 325 and 297 nm which can be assigned to the $^6\text{H}_{15/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{G}_{11/2}$, $^4\text{M}_{21/2}$, $^4\text{P}_{3/2}$, $^4\text{M}_{15/2}$, $^4\text{K}_{15/2}$ and $^4\text{K}_{13/2}$ transitions, respectively. Among all the excitation bands, the peak with highest emission intensity is located at 351 nm which can be ascribed to $^6\text{H}_{15/2} \rightarrow ^4\text{M}_{15/2}$ transition. So, for determining the optimized doping concentration of Dy^{3+} ($x = 0.005\text{--}0.08$), the PL spectra of $\text{Ba}_7\text{Hf}(\text{PO}_4)_6:\text{Dy}^{3+}$ samples were excited at 351 nm.

The emission spectra of $\text{Ba}_7\text{Hf}(\text{PO}_4)_6:\text{Dy}^{3+}$ pumped by 351 nm are

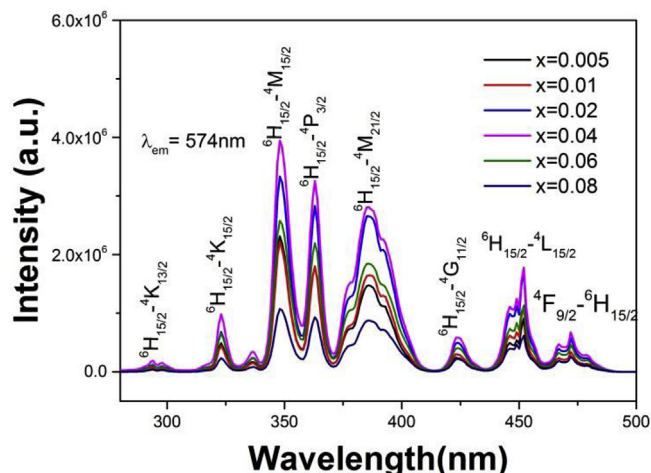


Fig. 2. The PLE spectra of various Dy^{3+} -doped $\text{Ba}_7\text{Hf}(\text{PO}_4)_6$ phosphor.

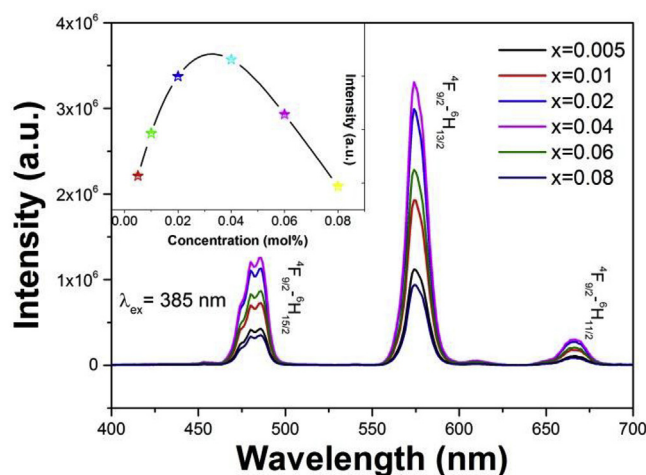


Fig. 3. The PL spectra of various Dy^{3+} -doped $\text{Ba}_7\text{Hf}(\text{PO}_4)_6$ phosphor.

presented at Fig. 3 which shows the emission spectra originate from 400 to 700 nm and the emission spectra conclude three different emission peaks. The peaks located at 485 nm, 578 nm and 670 nm can be assigned to $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$, $^6\text{H}_{13/2}$, $^6\text{H}_{11/2}$ transitions of Dy^{3+} , respectively [23–27]. Among all the emission bands, when the doping contents of Dy^{3+} increase, no obvious changes of the shape as well as the movement of peak position was observed besides of the emission intensity. The emission intensity comes up to the optimum doping concentration when x reaches 0.04 and then decreases gradually because of concentration quenching behavior. As we know $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ transition belongs to magnetically allowed transition which is scarcely influenced by the surrounding environment of Dy^{3+} ion. Conversely, the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ transition is a forced electric dipole transition and it is sensitive to the surroundings. Compared with the blue and yellow emission intensity, it is obvious Dy^{3+} located at a low-symmetry site with no inversion center in $\text{Ba}_7\text{Hf}(\text{PO}_4)_6$ [28].

The integrated emission intensity depends on Dy^{3+} concentration is presented in the inset picture. It is clear that the integrated emission intensities of $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ and $^6\text{H}_{13/2}$ transitions increase until Dy^{3+} comes up to $x = 0.04$, and then concentration quenching occurs when continue doping Dy^{3+} ions in $\text{Ba}_7\text{Hf}(\text{PO}_4)_6$. This demonstrates that the optimum doping contents of Dy^{3+} is around $x = 0.04$ for $\text{Ba}_7\text{Hf}(\text{PO}_4)_6$. The cross relaxation caused by the quenching transitions of $^4\text{F}_{9/2} + ^6\text{H}_{15/2} \rightarrow ^6\text{F}_{3/2} + ^6\text{H}_{9/2}$ where the ions decay non-radiatively can reasonably interpret the concentration quenching behavior. With increasing Dy^{3+} contents, the decreased distance between emitting

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