

Luminescence Properties of Eu^{3+} ion doped Strontium Borate Phosphate Phosphors

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Abstract. The Eu^{3+} -activated strontium borate phosphate phosphors of $2\text{SrO}-n\text{B}_2\text{O}_3-(1-n)\text{P}_2\text{O}_5:1\%\text{Eu}^{3+}$ ($0.01 \leq n \leq 0.90$) were synthesized by solid state method. The results indicate the ratio of B to P is below 1, the magnetic dipole $^5\text{D}_0-^7\text{F}_1$ emissions of Eu^{3+} is stronger, the fluorescent lifetime of $^5\text{D}_0$ levels gradually increase with the ratio values; however, when the ratio is beyond 1, the electric dipole $^5\text{D}_0-^7\text{F}_2$ emission of Eu^{3+} is stronger, the lifetime of $^5\text{D}_0$ level gradually decrease because of the increasing radiative transition rate of $^5\text{D}_0-^7\text{F}_1$.

Introduction

Recently, the considerable variety in crystal structure of the borophosphate compounds provides a great deal of objects for the study aiming at exploring new functional materials. As far as luminescence is concerned, attention has been brought to alkaline earth borophosphate lattices doped with rare earth ions, because it has high luminescence, moderately synthetical temperature, great X color coordinate and low thermal degradation. Generally, the borophosphates doped with rare earth ions, such as $\text{MBPO}_5: \text{Ln}$ (M = alkaline earth, Ln = rare earth ions) are reported to be isostructural with mineral stillwellite, which are built up with BO_4 and PO_4 tetrahedra^[1,2]. The ions are coordinated with nine oxygen ions with C_2 symmetry. The basic anionic constituents of these compounds are recommended to be interpreted in terms of BPO_4 groups, i.e. $\text{PO}_4^{+4}-\text{BO}_4^-$, where B and P are four-coordinated. The alkaline earth borophosphates are built up with BO_4 and PO_4 tetrahedra, which formed three-dimensional netlike structures. The structures of these borophosphates can keep rare earth ions from oxidation because of their stable structures. In 1965, Blasse^[3] first reported the emission of Eu^{2+} in $\text{MBPO}_5: \text{Eu}^{2+}$ ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$). Ding shijin et al. reported Ce, Tb, and Gd ions codoped green phosphor $\text{La}(\text{BO}_3, \text{PO}_4)$ ^[4]. Rare earth ions doped materials are of great importance because of their practical application in lighting and display^[5,6]. Eu^{3+} is important RE ion, which has been applied in red phosphors. Until now, only little attention has been paid to the studies on photoluminescence and luminescence dynamics in Eu^{3+} -doped alkaline earth borophosphate systems. In the present paper, we systemically synthesize the red emitting phosphors $2\text{SrO}-n\text{B}_2\text{O}_3-(1-n)\text{P}_2\text{O}_5:1\%\text{Eu}^{3+}$ by the solid-state reaction and study on their photoluminescence properties and fluorescent lifetime of Eu^{3+} .

Experiment

$2\text{SrO}-n\text{B}_2\text{O}_3-(1-n)\text{P}_2\text{O}_5:1\%\text{Eu}^{3+}$ phosphors were prepared by the solid-state reaction at high temperature. The changes of photoluminescence properties with composition were studied by adjusting the ratio of H_3BO_3 to $(\text{NH}_4)_2\text{HPO}_4$.

Results and discussion

Figure 1 shows that the XRD patterns in samples become broader to different degree in contrast to the standard cards. There is considerable line broadening, indicating lattice strain in the diffraction patterns of the mixed borate and phosphate compounds^[7]. It may be attributed to the different structure between BO_4^- and PO_4^- .

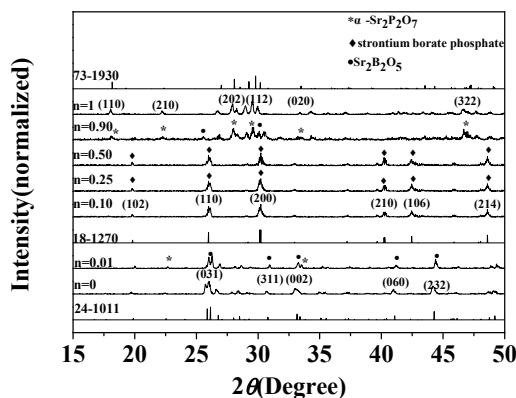


Fig.1 The X-ray diffraction patterns (XRD) in different n samples

Figure 2 indicates that the CT band is related closely to the covalence between O^{2-} and Eu^{3+} and coordination environment around Eu^{3+} [8]. The main peak location of the CT band hardly shift in different samples with $n=0, 0.01, 0.10, 0.25, 0.50, 0.90$ and 1 .

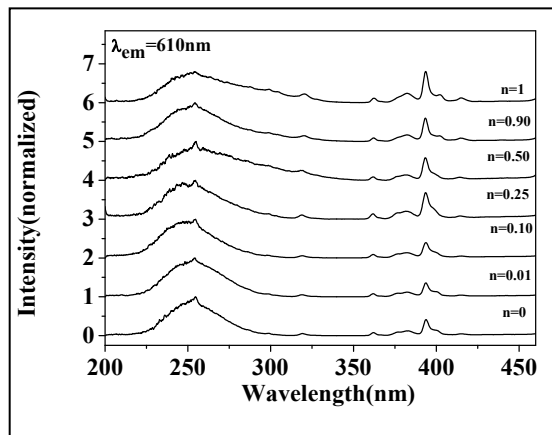


Fig.2 The excitation spectra for Eu^{3+} -activated $2SrO-nB_2O_3-(1-n) P_2O_5$ powders

Figure 3 shows the emission spectra contain the characteristic transition lines from the lowest excited $^5D_0-^7F_J$ ($J=0, 1, 2$) of the Eu^{3+} ion with the emissions for $J=0$ at 580 nm, $J=1$ at 591 nm and $J=2$ at the range from 610 to 620 nm. The intensity ratios of $^5D_0-^7F_2$ to $^5D_0-^7F_1$ varied with the ratio of H_3BO_3 to $(NH_4)_2HPO_4$.

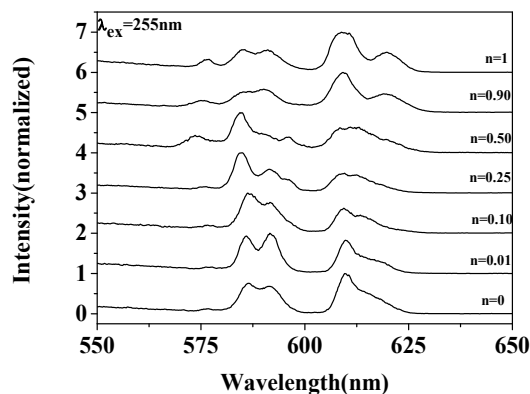


Fig.3 The emission spectra for $2SrO-nB_2O_3-(1-n) P_2O_5:1\%Eu^{3+}$ samples

Table 1 shows that in the samples of $n=0.01-0.50$, the value of the intensity ratios of $^5D_0-^7F_2$ to $^5D_0-^7F_1$ are less than 1 and gradually increase. While in the $n=0$ and $n=0.50-0.90$ samples, the ratios

are beyond 1, the electric dipole $^5D_0 \rightarrow ^7F_2$ transition is stronger. In terms of the Judd-Ofelt theory [9,10], the magnetic dipole transition is permitted. The electric dipole transition is allowed only on the condition that the europium ion occupies a site without an inversion center and is sensitive to local symmetry.

Table 1. The intensity ratio of $^5D_0 \rightarrow ^7F_2$ to $^5D_0 \rightarrow ^7F_1$

| The intensity ratio of $^5D_0 \rightarrow ^7F_2$ to $^5D_0 \rightarrow ^7F_1$ | |
|---|-------|
| B/P | ratio |
| 0 | 1.07 |
| 0.01 | 0.69 |
| 0.10 | 0.60 |
| 0.25 | 0.61 |
| 0.50 | 0.94 |
| 0.90 | 1.54 |
| 1 | 1.57 |

Figure 4 gives the fluorescence decay dynamics for Eu^{3+} at 611 nm emission in the $n=0.01$, 0.25, 0.50 and 0.90 samples. The lifetime can be described as Eq. 1,

$$\tau = \frac{1}{W_R + W_{NR}} \quad (1)$$

where W_R is the radiative transition rate and W_{NR} the nonradiative relaxation rate, respectively. Generally, W_{NR} is sensitive to the temperature, it can increase with the elevating temperature; however, W_R mainly depends on the local environment and hardly changes with temperature. The 5D_0 level is the lowest excited one, the energy difference between 5D_0 level and 7F_6 is $\sim 12000 \text{ cm}^{-1}$. According to the theory of multi-phonon relaxation, the nonradiative relaxation rate hardly happens and can be neglected. Thus we have reason to consider that the total radiative transition rate of $^5D_0 \rightarrow ^7F_J$ is the reverse of the lifetime of Eu^{3+} . When the ratio of B to P is below 1, the electric dipole $^5D_0 \rightarrow ^7F_2$ transition is weaker and the action of $^5D_0 \rightarrow ^7F_J$ is not obvious. However, when the ratio is beyond 1, the electric dipole $^5D_0 \rightarrow ^7F_2$ transition is strengthened, the action of $^5D_0 \rightarrow ^7F_J$ increases, the lifetime of 5D_0 levels gradually decreases because of the increasing radiative transition rate of $^5D_0 \rightarrow ^7F_J$.

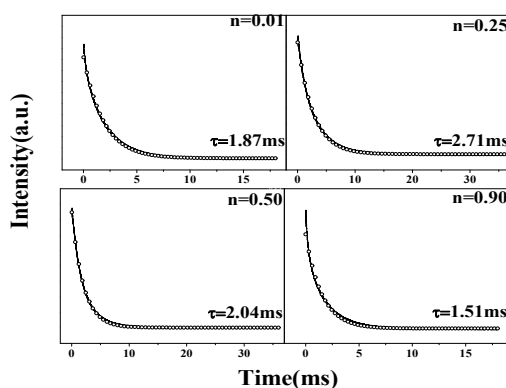


Fig.4 Fluorescent decay curves of different samples under the 266nm excitation at room temperature

Conclusions

The Eu^{3+} -activated strontium borate phosphate phosphors of $2\text{SrO}-n\text{B}_2\text{O}_3-(1-n) \text{P}_2\text{O}_5:1\% \text{Eu}^{3+}$ ($0.01 \leq n \leq 0.90$) were synthesized by high temperature solid state method. The structures, photoluminescent spectra and luminescent dynamics of Eu^{3+} were studied. The results demonstrate

that the structure of the samples with $n=0.10-0.50$ belongs to the hexagonal phase, while the structures of the $n=0.01$ and $n=0.90$ samples are the mixed phases of α - $\text{Sr}_2\text{P}_2\text{O}_7$ and $\text{Sr}_2\text{B}_2\text{O}_5$. Charge transfer (CT) transition from $2p$ orbital of O^{2-} ions to the $4f$ orbital of Eu^{3+} ions hardly changed with compositions. In the samples of $n=0.10-0.50$, the Eu^{3+} ion occupies a site with an inversion center, and the magnetic dipole $^5\text{D}_0$ - $^7\text{F}_1$ transition is stronger. While in the $n=0.01$ and $n=0.90$ samples, the Eu^{3+} ion occupies a site without the inversion center, the electric dipole $^5\text{D}_0$ - $^7\text{F}_2$ transition is stronger. When the ratio of B to P is below 1, the luminescent lifetime of $^5\text{D}_0$ levels at room temperature gradually increases with the ratio values; however, when the ratio is beyond 1, the lifetime of $^5\text{D}_0$ levels gradually decrease because of the increasing radiative transition rate of $^5\text{D}_0$ - $^7\text{F}_1$.

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