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Short communication

Multiwavelength excited white-emitting Dy^{3+} doped $Sr_3Bi(PO_4)_3$ phosphor

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Abstract

Multiwavelength excited white emitting phosphor Dy^{3+} doped $Sr_3Bi(PO_4)_3$ was synthesized by solid state reaction method. The phase of the as-prepared powders was measured by X-ray diffraction pattern (XRD) and the luminescent properties of $Sr_3Bi(PO_4)_3{:}Dy^{3+}$ were systematically investigated by excitation spectra, emission spectra and concentration quenching. The excitation spectra included bands located at 348 nm, 362 nm, 385 nm and 451 nm were due to the *f–f* transitions of Dy^{3+} within its $4f^9$ configuration. This excitation is useful for solid state lighting and light-emitting diodes. Under 348 nm excitation, the emissions of Dy^{3+} ions are observed at 481 nm (blue) due to the $^4F_{9/2}$–$^6H_{15/2}$ transitions, 575 nm (yellow) due to $^4F_{9/2}$–$^6H_{13/2}$ transitions and a weak 664 nm (red) due to $^4F_{9/2}$–$^6H_{11/2}$ transitions. The optimal emission intensity of the $Sr_3Bi_{1-x}(PO_4)_3{:}xDy^{3+}$ phosphors is found to be $x=0.07$. The chromaticity coordinates of the samples were in the near white region. All results demonstrated that $Sr_3Bi(PO_4)_3{:}Dy^{3+}$ might be a potential phosphor for NUV-based white light-emitting diodes.

Keywords: A. Powders: solid-state reaction; C. Optical properties; Luminescence; Phosphors

1. Introduction

Recently, trivalent dysprosium ions (Dy^{3+}) doped phosphors have been extensively studied due to its intense blue (484 nm, $^4F_{9/2}$–$^6H_{15/2}$) and yellow (575 nm, $^4F_{9/2}$–$^6H_{13/2}$) emissions and the potential applications in white light emission [1]. However, the ratio of the two dominant Dy^{3+} emission bands arising from the transitions $^4F_{9/2}$–$^6H_{15/2}$ (blue) and $^4F_{9/2}$–$^6H_{13/2}$ (yellow) changes in different hosts, because the yellow emission is strongly influenced by the chemical environment surrounding Dy^{3+} due to $\Delta J=2$ ($^4F_{9/2}$–$^6H_{13/2}$), while the blue emission ($^4F_{9/2}$–$^6H_{15/2}$) is relatively invariable. Therefore, the color tone of Dy^{3+}-doped phosphors can be modified by changing the relative intensity of the yellow light through the crystal field. At present, there are many hosts that can be activated by Dy^{3+}, such as borates [2–4], phosphates [5–8], aluminates [9,10], silicates [11–13], vanadates [14–16], molybdates [1], etc. Among these hosts, phosphates are good candidates due to their low synthetic temperatures, stabilities, and low costs. As a member of metal phosphate, $Sr_3Bi(PO_4)_3$ has an cubic structure with a space group of I-43d. However, to the best of our knowledge, the photoluminescence properties of $Sr_3Bi(PO_4)_3{:}Dy^{3+}$ phosphors have not been reported yet. In this paper, we synthesized the phosphor Dy^{3+} doped $Sr_3Bi(PO_4)_3$, in which luminescence properties were studied in detail by means of excitation and emission spectra.

2. Experimental

$Sr_3Bi(PO_4)_3{:}Dy^{3+}$ powders were prepared by solid-state reaction. The starting materials included $SrCO_3$ [analytical reagent (A.R.)], Bi_2O_3 (A.R.), $NH_4H_2PO_4$ (A.R.), and Dy_2O_3 (99.99%). Stoichiometric amounts of the starting reagents were thoroughly mixed and ground by an agate mortar. An excess (2%) of $NH_4H_2PO_4$ was used to compensate for the evaporation of $NH_4H_2PO_4$ at a high

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temperature. The mixtures were conducted at 1250 °C for 3 h in an electric furnace. After cooling down to the room temperature, the samples were ground into powder for characterizations.

The powder sample was characterized by X-ray diffraction (XRD) in a Bruker AXS D8 advanced automatic diffractometer (Bruker Co., German) with Ni-filtered Cu Kα radiation ($\lambda=1.54178$ Å). A scan rate of 0.02°/s was applied to record the patterns in the 2θ range 10–90°. Photoluminescence excitation and emissions spectra were collected in a fluorescence spectrophotometer (Hitachi F-4600). The chromaticity data were taken by the PMS-80 spectra analysis system. All the measurements were conducted at room temperature.

3. Results and discussion

3.1. X-ray diffraction analysis

The obtained phosphors are white powder. Fig. 1 shows the X-ray powder diffraction patterns of typical phosphors $Sr_3Bi_{0.93}(PO_4)_3$:$0.07Dy^{3+}$ and the standard data of $Sr_3Bi(PO_4)_3$. In Fig. 1, the diffraction patterns of the sample $Sr_3Bi_{0.93}(PO_4)_3$:$0.07Dy^{3+}$ phase was found to be in agreement with that of the host material $Sr_3Bi(PO_4)_3$ from the reported data JCPDS card no. 33-1319. $Sr_3Bi(PO_4)_3$ has the structural type of eulytine, and Bi^{3+} occupies distorted octahedron of oxygen ions due to three short and three long Bi–O distances, according to Ref. [17]. Therefore, it can be predicted that Bi^{3+} occupy noninversion centrosymmetric sites and some Bi^{3+} are replaced by Dy^{3+} in $Sr_3Bi(PO_4)_3$:Dy^{3+} because they have the same valence and ionic radii [18]. The lattice parameters values of $Sr_3Bi(PO_4)_3$ are $a=b=c=10.1990$ Å, $Z=4$ and $V=1060.90$ Å^3. There exists no impact of Dy^{3+} on the host structure even at the optimized dopant concentration of 7 mol%. These results indicated that Dy^{3+} were undoubtedly doped into the $Sr_3Bi(PO_4)_3$ crystal lattice.

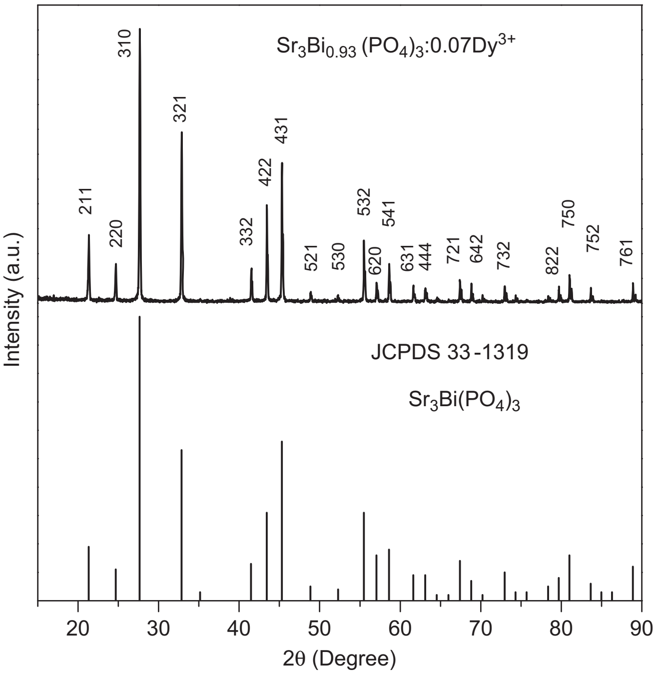

Fig. 1. The XRD patterns of typical phosphors $Sr_3Bi_{0.93}(PO_4)_3$:$0.07Dy^{3+}$ and the standard data JCPDS card no. 33-1319 of $Sr_3Bi(PO_4)_3$.

3.2. Excitation and emission spectra

Fig. 2 shows the excitation spectra of typical phosphors $Sr_3Bi_{0.93}(PO_4)_3$:$0.07Dy^{3+}$ monitoring at 575 nm. When the x value changed from 0.005 to 0.15 in $Sr_3Bi_{1-x}(PO_4)_3$:xDy^{3+}, the shapes of excitation spectra are similar except the intensity (not shown). The excitation spectra consist of a series of peaks from 300 nm to 500 nm with the stronger peaks located at 348 nm, 362 nm, 385 nm and 451 nm and some weak peaks located at 322.6 nm, 336 nm, 424 nm and 471.6 nm. Owing to the dense and overlapped nature of the excitation states in the $4f^9$ configuration of Dy^{3+} in the UV spectral range, these excitation peaks can only be tentatively ascribed to the transition from the $^6H_{15/2}$ ground state to the excitation states of $^4L_{19/2}$, $^4K_{15/2}$, $^6P_{7/2}$, $^6P_{5/2}$, $^4I_{13/2}$, $^4G_{11/2}$, $^4I_{15/2}$ and $^4F_{9/2}$ [1].

Fig. 3 shows the emission spectra of typical phosphors $Sr_3Bi_{0.93}(PO_4)_3$:$0.07Dy^{3+}$. It is well known that Dy^{3+} emission located at 481 nm ($^4F_{9/2}$–$^6H_{15/2}$) is magnetic dipole origin and the 575 nm ($^4F_{9/2}$–$^6H_{13/2}$) is electric dipole origin. $^4F_{9/2}$–$^6H_{13/2}$ transition is predominant only when Dy^{3+} ions are located at low-symmetry sites with no inversion centers. From Fig. 3, it can be seen that the emissions of Dy^{3+} ions under different excitation wavelengths are observed at 481 nm (blue) due to the $^4F_{9/2}$–$^6H_{15/2}$ transitions, 575 nm (yellow) due to $^4F_{9/2}$–$^6H_{13/2}$ transitions and a weak 664 nm (red) due to $^4F_{9/2}$–$^6H_{11/2}$ transitions. The combination of the 481 nm blue emission and the 575 nm yellow emission yielded white light

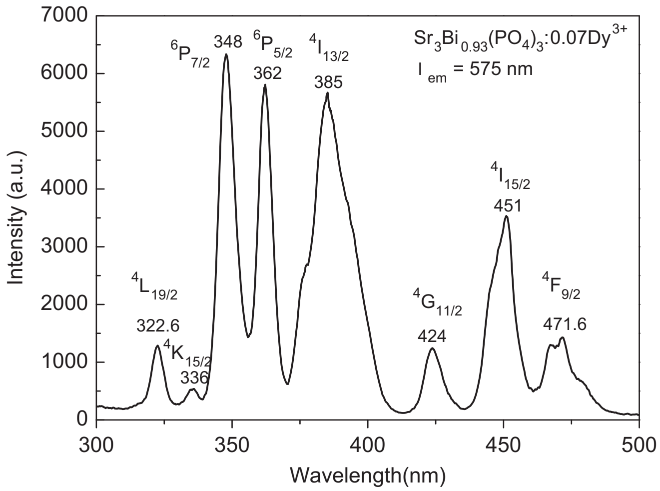

Fig. 2. The excitation spectra of typical phosphors $Sr_3Bi_{0.93}(PO_4)_3$:$0.07Dy^{3+}$ ($\lambda_{em}=575$ nm).

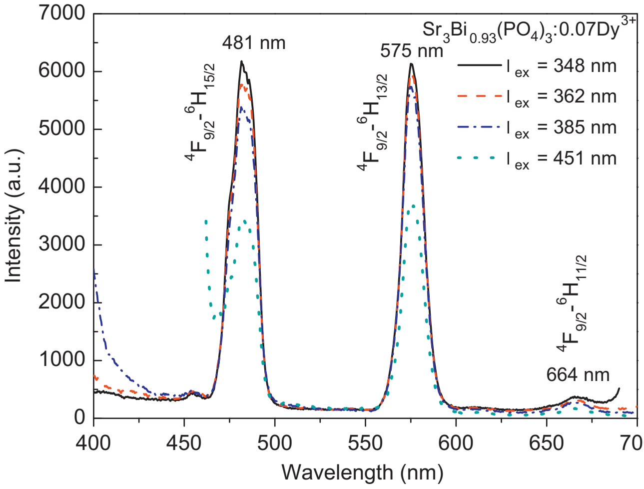

Fig. 3. The emission spectra of typical phosphors $Sr_3Bi_{0.93}(PO_4)_3$:0.07Dy^{3+} under various excitation wavelength (λ_{ex}=348 nm, 362 nm, 385 nm and 451 nm).

emissions, which could be used for the development of white LEDs.

3.3. The influence of Dy^{3+} on the luminescent intensity

In order to obtain the best doping concentration of Dy^{3+}, a series of $Sr_3Bi_{1-x}(PO_4)_3$:xDy^{3+} ($0.005 \leq x \leq 0.15$) phosphors were prepared. The emission spectra of $Sr_3Bi_{1-x}(PO_4)_3$:xDy^{3+} (x=0.005, 0.01, 0.03, 0.05, 0.07, 0.10, 0.15) excited under 348 nm are shown in Fig. 4. It can be seen that all the spectra of different contents of Dy^{3+} doped $Sr_3Bi(PO_4)_3$ are similar. The integrated emission intensity ratios of $^4F_{9/2}$–$^6H_{13/2}$ to $^4F_{9/2}$–$^6H_{15/2}$ for all the samples were calculated to be about a constant value 1.06, which demonstrates that the Dy^{3+} introduction does not result in an obvious change of the crystal structure even at such a high doping level of 15 mol%.

From Fig. 4, it is quite clear that the emission intensity increases with the Dy^{3+} concentration increasing up to 7 mol%, then decreases for concentration quenching. The reason is that the odds of complex of non-radiative transition are increasing with the increasing of Dy^{3+}, so the fluorescent intensity of the phosphors becomes lower [19].

It is necessary to obtain the critical distance (R_c) that is the critical separation between the donor (activator) and acceptor (quenching site). According to the report of Blasse [20], if the activator is introduced solely on Z ion sites, the critical transfer distance (R_c) is approximately equal to twice the radius of a sphere:

$$R_c \approx 2\left[\frac{3V}{4\pi x_c N}\right]^{1/3} \tag{1}$$

where x_c is the critical concentration of the activator ion, N is the number of Z ions in the unit cell, and V is the volume of the unit cell, then there is on the average one activator ion per V/x_cN. For the $Sr_3Bi(PO_4)_3$ host, when $N = Z \times 1$ (Z=4), x_c=0.07, and V=1060.90 Å^3, the obtained R_c value is 19.3 Å. According to Ref. [21], nonradiative energy transfer in the luminescence of oxidic phosphors is based on resonance transfer by electric multipole–multipole interaction or exchange interaction. The situation in Dy^{3+} compounds can be characterized as follows [22]: If the Dy^{3+}–Dy^{3+} distance is larger than 5 Å, the exchange interaction becomes ineffective, and only a multipolar interaction is important; if the Dy^{3+}–Dy^{3+} distance is shorter than 5 Å, the exchange interaction becomes effective. As the R_c of Dy^{3+}–Dy^{3+} for $Sr_3Bi(PO_4)_3$:Dy^{3+} phosphor is calculated to be 19.3 Å, the multipolar interaction is the major mechanism of concentration quenching of Dy^{3+} in the $Sr_3Bi(PO_4)_3$:Dy^{3+} phosphor. Considering the energy match rule [1], three possible cross-relaxation channels (CRC) among Dy^{3+} are shown in Fig. 5, denoted as CRC1, CRC2 and CRC3. The Dy^{3+} at $^4F_{9/2}$ level can be de-excited to ($^6H_{9/2}$/$^6F_{11/2}$), ($^6F_{9/2}$/$^6H_{7/2}$) or $^6F_{1/2}$ level via these three cross-relaxation processes, in the mean while, the ground state Dy^{3+}

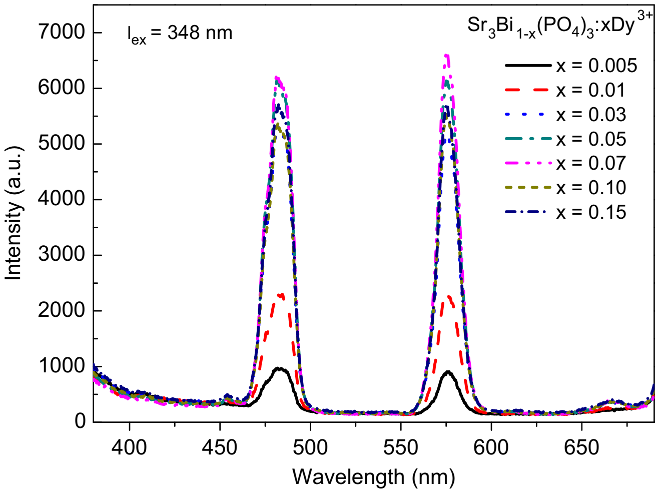

Fig. 4. The emission spectra of $Sr_3Bi_{1-x}(PO_4)_3$:xDy^{3+} (x=0.005, 0.01, 0.03, 0.05, 0.07, 0.10, 0.15) (λ_{ex}=348 nm).

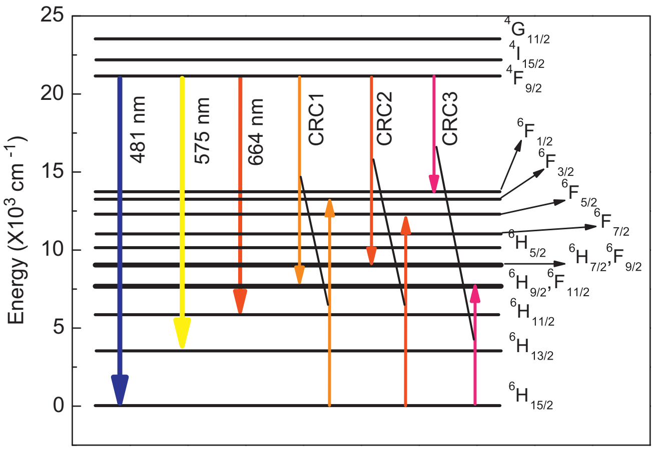

Fig. 5. Energy level scheme of Dy^{3+} represents the mechanisms for different observed emissions and possible cross-relaxation processes.

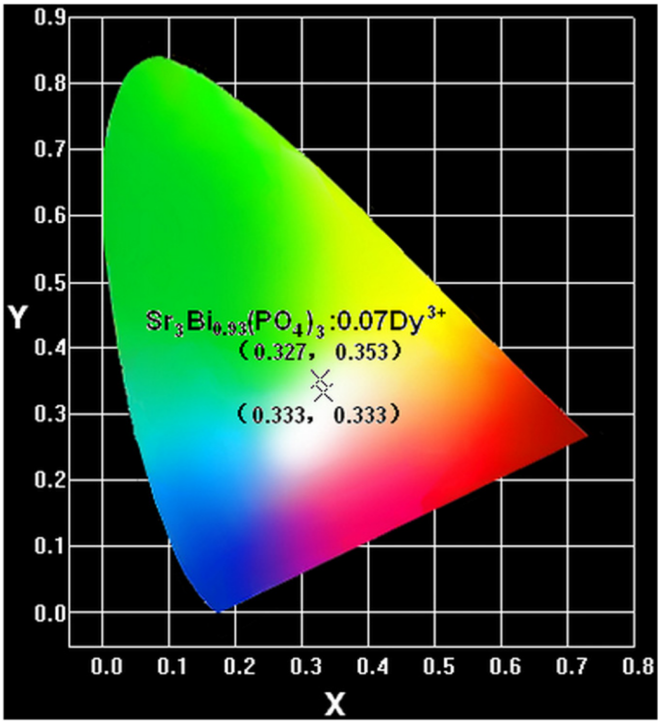

Fig. 6. The CIE chromaticity coordinate for the prepared typical $Sr_3Bi_{0.93}(PO_4)_3$:$0.07Dy^{3+}$ under the excitation wavelength of 348 nm.

accepting the energies from the Dy^{3+} at $^4F_{9/2}$ level will arrive at $^6F_{3/2}$, $^6F_{5/2}$ and ($^6H_{9/2}$/$^6F_{11/2}$) level. Finally, all the Dy^{3+} ions involved in CRC1, CRC2 and CRC3 processes will get in their ground states, thus the luminescence related to $^4F_{9/2}$ level are quenched.

3.4. Color parameters of samples

Color coordinates are one of the important factors for evaluating phosphors' performance. It is a well known fact that the color coordinates are same if the spectra profiles are identical. In such case, the color coordinates for the sample doped with 7 mol% Dy^{3+} were calculated using the intensity-calibrated emission spectra data and the chromatic standard issued by the Commission Internationale de I'Eclairage in 1931 (CIE 1931). The CIE chromaticity diagram of $Sr_3Bi_{0.93}(PO_4)_3$:$0.07Dy^{3+}$ under 348 nm excitation is shown in Fig. 6 with the cross symbols × ($x=0.327$, $y=0.353$). It indicates that the color coordinates of present phosphors are close to the "ideal white" ($x=0.333$, $y=0.333$) in chromaticity diagram.

4. Conclusions

The novel white emitting phosphors $Sr_3Bi_{1-x}(PO_4)_3$:xDy^{3+} with various Dy^{3+} concentrations have been synthesized by the conventional solid-state reaction. The structure of the compound was confirmed by the XRD technique. The peaks of the emissions of Dy^{3+} ions are located at 481 nm (blue), 575 nm (yellow) and 664 nm (red) under the excitation of 348 nm, 362 nm, 385 nm and 451 nm. Concentration quenching occurs when the Dy^{3+} concentration is beyond 7 mol%. The CIE color coordinates indicates that the phosphors are suitable for white light-emitting. The photoluminescence results show that the excitation peaks are useful for solid state lighting in lamp industry.

Acknowledgments

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