Synthesis and photoluminescence properties of novel yellowish-green-emitting phosphor $Sr_3P_4O_{13}$:Tb^{3+}

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A series of novel yellowish-green-emitting phosphors $Sr_3P_4O_{13}$:Tb^{3+} have been synthesized successfully via a conventional high-temperature solid-state reaction, and characterized by X-ray diffraction, photoluminescence excitation/emission spectra and decay curve for the first time. The concentration quenching phenomenon of Tb^{3+} was observed, and the optimal doping concentration of Tb^{3+} in $Sr_3P_4O_{13}$ was about 0.1. The critical distance of Tb^{3+} ion was calculated to be about 17.3 Å, indicating the multipole–multipole interaction could play an important role on the concentration quenching phenomenon of Tb^{3+} in $Sr_3P_4O_{13}$ host. The average decay time and CIE chromaticity coordinates were also determined for $Sr_3P_4O_{13}$:0.1Tb^{3+} phosphor with optimal photoluminescence intensity. The as-prepared $Sr_3P_4O_{13}$:Tb^{3+} phosphor could be excited by ultraviolet, and exhibit yellowish-green emission with short decay time of milliseconds, indicating the potential application in display and lighting region.

1. Introduction

Tb^{3+} ion, an important activator of yellowish-green-emitting materials, has attracted considerable attention over the past years due to its potential application in display and lighting region [1−7]. Currently, the investigation on the photoluminescence properties of Tb^{3+} in a novel host has been a research hotspot in order to develop the novel yellowish-green-emitting phosphors. Generally speaking, the phosphate is a proper host material for the activator due to the excellent properties including high thermal and chemical stability, large band gap, low material cost, and easy synthesis [8,9]. A famous example, $LaPO_4$:Ce^{3+},Tb^{3+}, has been applied in the lamp industry for many years as a commercial green-emitting phosphor.

$Sr_3P_4O_{13}$, a type of alkaline earth tetraphosphate, crystallizes in triclinic system and builds up from SrO_7 polyhedra and $P_4O_{13}^{6-}$ anions [8], which has attracted intense interest because it shows the potential as a proper host material. Cao et al. [11,12] developed two kinds of novel red phosphors $Sr_3P_4O_{13}$:Eu^{3+}, Bi^{3+} and $Sr_3P_4O_{13}$:Bi^{2+}, and investigated their photoluminescence properties in detail. Moreover, Zhang et al. [13] and Liu et al. [14] investigated the temperature-dependent luminescence properties of $Sr_3P_4O_{13}$:Eu^{2+} polycrystalline ceramics and the self-reduction process of Eu^{3+} to Eu^{2+} in $Sr_3P_4O_{13}$ host, respectively. These as-obtained phosphors above showed the potential application in white light emitting diodes (w-LEDs) based on the near UV and/or blue chips.

However, as per our knowledge, there has been no report found so far on the photoluminescence properties of Tb^{3+} ions activated $Sr_3P_4O_{13}$. So, in this work, Tb^{3+} doped $Sr_3P_4O_{13}$ phosphors were synthesized by a solid-state reaction at high-temperature for the first time and their photoluminescence properties were investigated in detail.

2. Experimental

The polycrystalline powder samples $Sr_{3(1-x)}Tb_{3x}P_4O_{13}$ (x = 0.02, 0.04, 0.06, 0.08, 0.1, 0.12 and 0.15) were prepared by a conventional solid-state reaction method at high temperature. In a typical procedure, the starting materials including $SrCO_3$ (A.R.), $NH_4H_2PO_4$ (A.R.) and Tb_4O_7 (99.99% purity) were firstly thoroughly mixed in an agate mortar via a grinding process in term of the stoichiometric amount. Then the mixture was transferred into a corundum crucible and sintered at 850 °C for 6 h in thermal carbon reducing atmosphere. Finally, the final product was naturally cooled to room temperature, and crushed into white powders, indicating all Tb^{4+} ions were reduced into Tb^{3+} ions.

The phase purity of the as-prepared samples was characterized by a powder X-ray diffraction (XRD) analysis over the 2θ angle range of 10–70° with Cu Kα (λ = 1.5405 Å) radiation on a Bruker D8 Advance X-Ray Diffractometer operating at 40 kV and 30 mA. The steady-state (excitation and emission) spectra and decay curve were measured by using an FLS980-Combined

Fluorescence Lifetime & Steady State Fluorescence Spectrometer (EDINBURGH INSTRUMENTS), in which a 450 w xenon lamp and a 100 w μF2 microsecond flash lamp were used as the excitation source, respectively. All the above measurements were carried out at room temperature.

3. Results and discussion

The XRD patterns of samples $Sr_{3(1-x)}Tb_{3x}P_4O_{13}$ (x = 0.02, 0.06, 0.1, 0.12 and 0.15) are shown in Fig. 1 in order to determine the pure-phase formation. At low Tb^{3+} concentration range (x ≤ 0.1), all the diffraction peaks are in agreement with the reported standard diffraction lines from the Joint Committee on Powder Diffraction Standards (JCPDS) data 20-1207 [$Sr_3P_4O_{13}$] except for a minor peak (marked with #) at 2θ = 33.78°, which in fact can also be attributed to the $Sr_3P_4O_{13}$ host [13,14]. The above-obtained results indicates that the doping of Tb^{3+} ions does not cause significant changes of $Sr_3P_4O_{13}$ structure, which leads to pure-phase formation of $Sr_3P_4O_{13}$:Tb^{3+} when the doping level of Tb^{3+} is low (x ≤0.1). Meanwhile, we find that two minor peaks (marked with *) not belonging to $Sr_3P_4O_{13}$ at 25.78 and 34.84 exist in the XRD pattern of sample $Sr_3P_4O_{13}$ doped with higher Tb^{3+} contents (x = 0.12 and 0.15), indicating that there is a solid solubility limit when Tb^{3+} ions substitute for Sr^{2+} ions owing to the charge imbalance. The effect of impurity on the luminescence of Tb^{3+} in $Sr_3P_4O_{13}$ could be neglected due to the weak diffraction intensity.

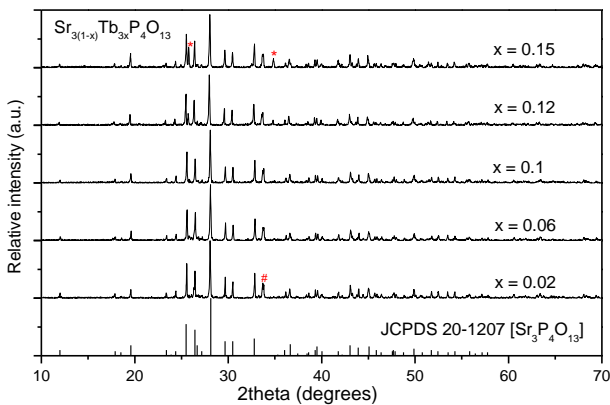*Fig. 1. XRD patterns of samples*
$Sr_{3(1-x)}Tb_{3x}P_4O_{13}$ (x = 0.02, 0.06, 0.1, 0.12 and 0.15)

The photoluminescence excitation and emission spectra of sample $Sr_{3(1-x)}Tb_{3x}P_4O_{13}$ (x = 0.1) are shown in Fig. 2, in which the monitoring wavelength are 541 nm and 251 nm, respectively. The excitation spectrum (curve a) consists of a strong and broad excitation band peaking at 251 nm due to the $4f^8{\rightarrow}4f^75d^1$(f-d) transition of Tb^{3+} ion and some weak excitation peaks in the range of 270–400 nm corresponding to the f-f transitions of Tb^{3+} ion [2].

Obviously, the excitation band peaking at 251 nm has the maximum intensity among all the excitation bands because the f-d transition is electric parity-allowed transition and f-f transition is electric parity-forbidden transition [15,16]. The emission spectrum (curve b) is composed of four groups of emission peaks located at ~487, ~541, ~580, and ~620 nm due to the $^5D_4{\rightarrow}^7F_J$ (J = 6, 5, 4, 3) transitions of Tb^{3+} ion, in which the $^5D_4{\rightarrow}^7F_5$ emission at 541 nm is dominant because this transition has largest probability for both electric-dipole and magnetic-dipole induced transitions [3,17].
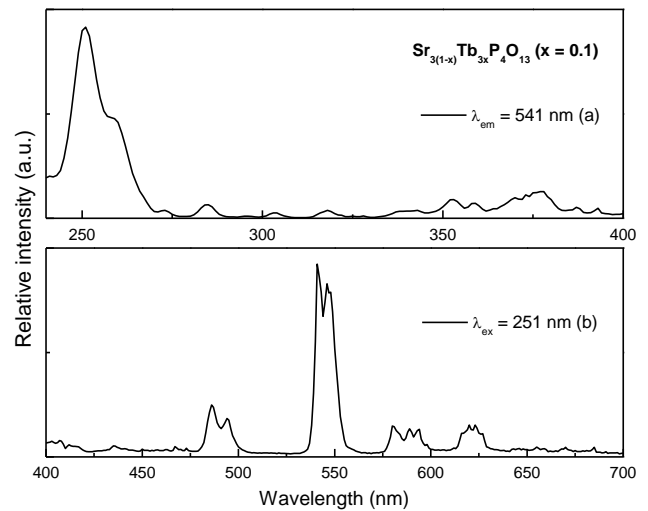

Fig. 2. Photoluminescence excitation (a) and emission
(b) spectra of sample $Sr_{3(1-x)}Tb_{3x}P_4O_{13}$ (x = 0.1)

The emission spectra of $Sr_{3(1-x)}Tb_{3x}P_4O_{13}$ (x = 0.02, 0.04, 0.06, 0.08, 0.1, 0.12 and 0.15) upon excitation with 251 nm are shown in Fig. 3 to confirm the optimal doping concentration of Tb^{3+} in $Sr_3P_4O_{13}$. It can be observed that all the emission spectra are similar with each other in shape with various photoluminescence intensities. The optimal doping concentration (x value) of Tb^{3+} is about 0.1. After that (x > 0.1), the concentration quenching phenomenon is obvious, which is associated with the non-radiative energy transfer process among the different Tb^{3+} ions. The obtained value (x = 0.1) for the optimal doping concentration of Tb^{3+} in $Sr_3P_4O_{13}$ is closed to that in other hosts (e.g. β-$Ca_2P_2O_7$, 0.1 [2], $Ba_2CaZn_2Si_6O_{17}$, 0.1 [3]; $GdSrAl_3O_7$, 0.1 [4]; $NaSrPO_4$, 0.04 [5]; $Sr_2B_2O_5$, 0.07 [18]; Sr_2ZnMoO_6, 0.1 [19]), indicating the inherent characteristic of Tb^{3+} independent on crystal structure. As is well known to us, the critical energy transfer distance (R_c) is an important parameter for luminescence properties of phosphors to understand the concentration quenching phenomenon, which is approximately equal to twice the radius [$2(3V/4\pi x_c N)^{1/3}$] of a sphere with the volume of the unit cell [20], where x_c is the critical concentration (optimal concentration), N is the number of cations in the unit cell and V is the volume of the unit cell. In this work,

$V = 537.757$ Å^3, $N = 2$ [10] and $x_c = 0.1$. So, R_c is calculated to be ~17.3 Å and much larger than the typical distance for exchange interaction (< 5 Å) [3,5], which indicates multipole–multipole interaction can play an important role on the concentration quenching phenomenon of Tb^{3+} in $Sr_3P_4O_{13}$ host because the typical distance for multipole–multipole interaction is about 20 Å [21].
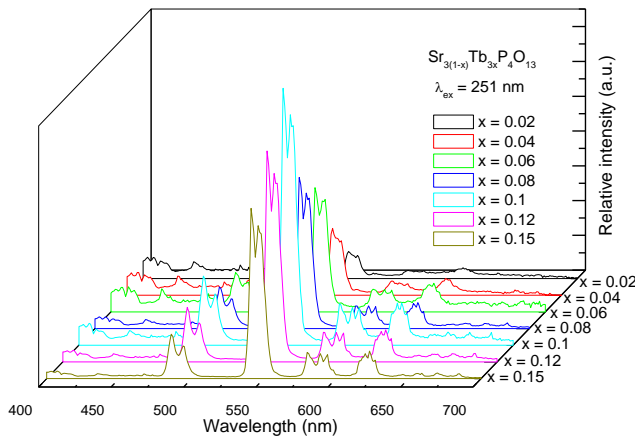

Fig. 3. Emission spectra of $Sr_{3(1-x)}Tb_{3x}P_4O_{13}$ (x = 0.02, 0.04, 0.06, 0.08, 0.1, 0.12 and 0.15) upon excitation with 251 nm

Finally, the sample $Sr_{3(1-x)}Tb_{3x}P_4O_{13}$ (x = 0.1) with optimal photoluminescence intensity is chosen to investigate the fluorescent decay behavior and the Commission International del'Eclairage (CIE) chromaticity coordinates. The decay curve ($\lambda_{ex} = 251$ nm, $\lambda_{em} = 541$ nm) is shown in Fig. 4, which is fitted by the double-exponential equation and the average decay time (τ^*) can be calculated in term of the following equations [22]

$$I = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \qquad (1)$$

$$\tau^* = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \qquad (2)$$

where I is the luminescence intensity; A_1 and A_2 are the constants; t is the time, and τ_1 and τ_2 are the decay times for the exponential components. The calculated values of τ_1, τ_2 and τ^* are about 0.74 ms, 2.89 ms and 2.80 ms. So, the millisecond-level of decay time could be obtained in $Sr_3P_4O_{13}$:0.1Tb^{3+} phosphor, which is short enough for potential applications in display and lighting. The nature of non-exponential decay behavior could be due to the extra energy transfer process between Tb^{3+} ions via non-radiative relaxation. The CIE chromaticity coordinates are calculated to be (0.331, 0.541) in term of the corresponding emission spectrum upon excitation with 251 nm, which is shown in the Fig. 5. Obviously, this phosphor has a yellowish-green emission.
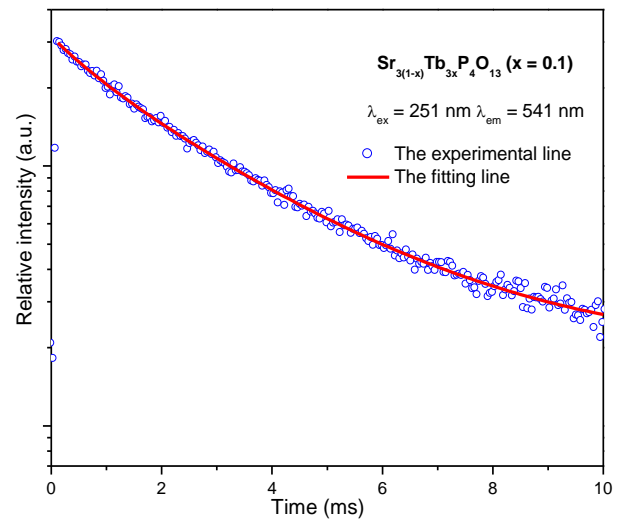

Fig. 4. Decay curve ($\lambda_{ex} = 251$ nm, $\lambda_{em} = 541$ nm) ofsample $Sr_{3(1-x)}Tb_{3x}P_4O_{13}$ (x = 0.1)
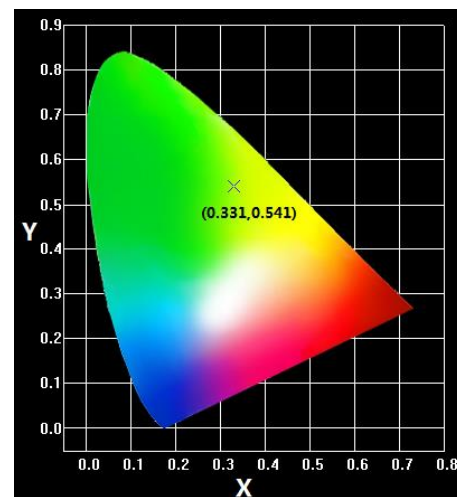
Fig. 5.CIE chromaticity coordinates of sample $Sr_{3(1-x)}Tb_{3x}P_4O_{13}$ (x = 0.1) ($\lambda_{ex} = 251$ nm)

4. Conclusions

This work reported the synthesis and photoluminescence properties of novel yellowish-green-emitting phosphor $Sr_3P_4O_{13}$:Tb^{3+} for the first time. The XRD results indicated the phosphors were synthesized successfully using conventional solid-state reaction method at 850 °C in thermal carbon reducing atmosphere. The optimal doping concentration of Tb^{3+}ions in $Sr_3P_4O_{13}$ host was about 0.1 and a critical distance of 17.3 Å was obtained for energy transfer between Tb^{3+} ions. The $Sr_3P_4O_{13}$:0.1Tb^{3+} phosphor could be excited efficiently by ultraviolet (~251 nm), and exhibit yellowish-green emission with the millisecond-level of decay time (2.8 ms) and CIE chromaticity coordinates (0.331, 0.541), respectively. The above results indicated

the as-obtained Sr$_3$P$_4$O$_{13}$:Tb^{3+} phosphor could be a potential yellowish-green-emitting phosphor candidate for both fundamental research and functional applications.

Acknowledgments

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