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A novel orange emissive phosphor $LaPO_4$:Bi, Sm with sharp and splitting emission peaks of Sm^{3+}

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ABSTRACT

Bi^{3+}, Sm^{3+} co-doped $La_{0.99-x}Bi_xSm_{0.01}PO_4$ polycrystalline samples were synthesized by calcining precursors at 800 °C in air. The precursors were obtained via low-heating temperature solid-state reactions. Crystal structures of the phosphor were examined with XRD and a pure phase was confirmed. The excitation spectra show that the phosphor can be efficiently excited by near-ultraviolet light, and the optimized concentration of Bi^{3+} is 0.9 mol%. Three sharp, strong, and splitting emission peaks are located at 562, 596, and 642 nm, corresponding to CIE (Commission International de l'Eclairage) chromaticity coordinates $x=0.42$ and $y=0.39$, which indicate the orange light emitting property. So, the phosphor is promising in UV-LED chip-based white light-emitting diodes.

1. Introduction

White light-emitting diodes (W-LEDs) are the most probable solid-state lighting sources to replace conventional incandescent and fluorescent lamps [1,2] due to their high efficiency, long lifetimes, good reliability, and fast response as well as their energy-saving, environment-friendly merits. A conventional W-LED, which is composed of a blue LED and a yellow-emitting phosphor, has a low color-rendering index (680), because it lacks a red component (above 600 nm) [3]. Therefore, it is urgent to explore novel reddish emission phosphors doped with Pr^{3+}, Eu^{3+} or Sm^{3+} ions, which are suitable for near-UV (370–410 nm) or blue (about 460 nm) excitation [4,5]. Among many synthetic methods, the low heating temperature solid-state reaction process [6–8] has many advantages such as relatively low reaction temperature, simplicity, high purity, good homogeneity, etc. Due to their high melting temperature, chemical stability, and high light yields of the doped materials, lanthanum phosphate ($LaPO_4$) and its solid solutions have been proven to be appropriate hosts as highly efficient emitters of fluorescent light [9]. Although there are some reports on the $LaPO_4$ host lattice relating to phosphors [10–13], to the best of our knowledge, Bi^{3+} and Sm^{3+} co-doped $LaPO_4$ phosphor for white emission has not been reported yet. It is interesting that, in some works, doped $LaPO_4$ has been prepared by the thermal decomposition of doped lanthanum phosphate hydrates [14,15]. It suggests that Bi^{3+} and Sm^{3+} co-doped $LaPO_4$ can be obtained from the thermal decomposition of its hydrate precursor. Thus, the thermal treatment of doped lanthanum phosphate hydrates is a promising synthetic method to convert simple compounds into advanced fluorescent materials. Nonetheless, novel synthesis methods for Bi^{3+} and Sm^{3+} co-doped $LaPO_4$ from corresponding phosphate hydrates still need further study and innovation.

In the present work, Bi^{3+}, Sm^{3+}-co-doped $LaPO_4$ was synthesized via a simple chemical route. The luminescent properties of Bi^{3+}, Sm^{3+}-co-doped $LaPO_4$ were studied, and the influences of the concentration of Bi^{3+} on the luminescence intensity were investigated. The chromaticity coordinates of $x=0.42$ and $y=0.39$ have been calculated from the emission spectra obtained by the CIE (Commission International del'Eclairage) system, which indicates that the phosphor has the orange light emitting property. So the phosphor is a potential orange component for W-LEDs based on UV-LEDs.

2. Experimental

All chemicals were of reagent grade purity, and purchased from the Sinopharm Chemical Reagent Co. Ltd., China. X-ray powder diffraction (XRD) was performed at a scanning rate of 5°/min from 5° to 70° for 2θ at room temperature using a Rigaku D/max 2500V diffractometer equipped with a graphite monochromator utilizing monochromatic CuKα radiation ($\lambda=0.154178$ nm). TG/DTG measurements were made with a NETZSCH STA 409 PC/PG thermogravimetric analyzer in an air atmosphere with a flow rate of 20 mL min^{-1}. Powder samples of

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6.0 ± 0.1 mg were used in the experiments with heating rates of 11 °C min^{-1}. Excitation and emission spectra were recorded at room temperature on a FL3-P-TCSPC spectrophotometer equipped with a xenon lamp as the excitation source. The contents of La, Sm, Bi and P were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Perkin-Elmer Optima 3100 RL).

The precursors of $La_{0.99-x}Bi_xSm_{0.01}PO_4 \cdot XH_2O$ were synthesized by solid-state reaction at low-heating temperature. In a typical synthesis, $La(NO_3)_3 \cdot 6H_2O$ (8504.1 mg, 19.64 mmol), $Sm(NO_3)_3 \cdot 6H_2O$ (88.9 mg, 0.20 mmol), and $BiCl_3$ (50.5 mg, 0.16 mmol) powders as well as 1.5 mL surfactant polyethylene glycol-400 (PEG-400) were added into a mortar with grinding for 15 min. Then, $(NH_4)_3PO_4 \cdot 3H_2O$ (4265.7 mg, 21 mmol) powder was added into the above mixture with grinding three times, and the resulting mixture was fully ground for another 30 min. The reaction mixture gradually became damp, and then a paste formed quickly. The paste was sealed with preservative film and kept at 60 °C for 10 h, then washed with deionized water to remove soluble inorganic salts. The resulting solid was washed with a small amount of anhydrous ethanol and dried at 90 °C for 5 h to give the precursor $La_{0.982}Bi_{0.008}Sm_{0.01}PO_4 \cdot XH_2O$. The phosphor $La_{0.982}Bi_{0.008}Sm_{0.01}PO_4$ was obtained by calcining the precursor at 800 °C for 4 h.

3. Results and discussion

Fig. 1 shows the XRD patterns of the precursor dried at 90 °C for 5 h and the product resulting from calcining the precursor at 800 °C for 4 h. Fig. 1a shows that all diffraction peaks in the pattern of the precursor ($La_{0.982}Bi_{0.008}Sm_{0.01}PO_4 \cdot XH_2O$) could be indexed to obtain lattice parameters: $a=b=0.710258$ (7) nm, $c=0.64944$ (5) nm, $\alpha=\beta=90°$, $\gamma=120°$, which are in agreement with those of hexagonal $LaPO_4 \cdot 0.5H_2O$ with space group P and cell parameters: $a=b=0.71$ nm, $c=0.6494$ nm; $\alpha=\beta=90°$, $\gamma=120°$ (PDF card 46-1439), indicating that the structure of $La_{0.982}Bi_{0.008}Sm_{0.01}PO_4 \cdot XH_2O$ is the same as that of $LaPO_4 \cdot 0.5H_2O$.

Fig. 1c shows that all diffraction peaks in the pattern of the sample whose precursor is $La_{0.982}Bi_{0.008}Sm_{0.01}PO_4 \cdot XH_2O$ calcined at 800 °C could be indexed to obtain lattice parameters: $a=0.682016$ (7) nm, $b=0.707155$ (6) nm, $c=0.647993$ (4) nm; $\alpha=90°$, $\beta=103.2513(7)°$, $\gamma=90°$, which are in agreement with those of monoclinic $LaPO_4$ (PDF card 83-0651) with space group

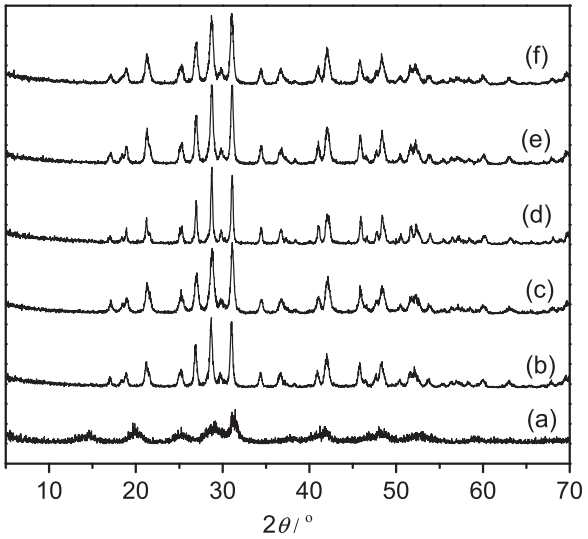

Fig. 1. XRD patterns of precursor and calcined samples ($La_{0.99-x}Bi_xSm_{0.01}PO_4$) calcined at 800 °C for 4 h: (a) precursor, $La_{0.982}Bi_{0.008}Sm_{0.01}PO_4 \cdot 4.5H_2O$; (b) $x=0.006$; (c) $x=0.008$; (d) $x=0.009$; (e) $x=0.010$; and (f) $x=0.012$.

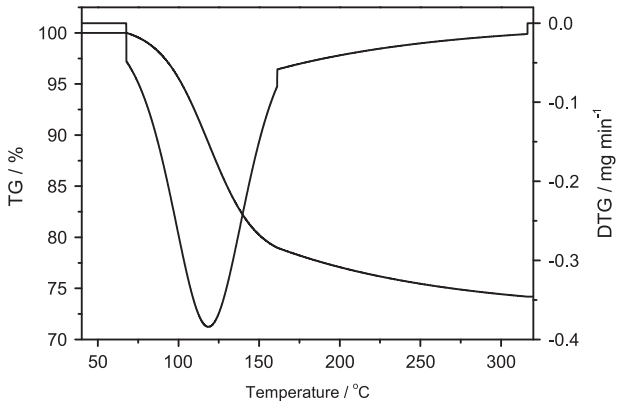

Fig. 2. TG/DTG curves of $La_{0.982}Bi_{0.008}Sm_{0.01}PO_4 \cdot 4.5H_2O$.

$P2_1/a(14)$ and cell parameters: $a=0.6831$ nm, $b=0.70705$ nm, and $c=0.65034$ nm ($\alpha=90°$, $\beta=103.27°$ and $\gamma=90°$), suggesting that $La_{0.982}Bi_{0.008}Sm_{0.01}PO_4$ has the same structure as that of $LaPO_4$. As shown in Fig. 1, it can be seen that all the samples of $La_{0.99-x}Bi_xSm_{0.01}PO_4$ have similar XRD patterns. Hence, the calcined samples are pure.

Fig. 2 shows the TG/DTG curves of $La_{0.982}Bi_{0.008}Sm_{0.01}PO_4 \cdot 4.5H_2O$ ($\beta = 11$ °C min^{-1}). Thermal decomposition of $La_{0.982}Bi_{0.008}Sm_{0.01}PO_4 \cdot 4.5H_2O$ below 800 °C occurs in one main stage. The mass loss starts at about 68 °C, and ends at about 317 °C, and the observed mass loss is 25.81%. Furthermore, the theoretic mass loss of water is only 3.69% for $La_{0.982}Bi_{0.008}Sm_{0.01}PO_4 \cdot 0.5H_2O$. As we can see in Fig. 2, $La_{0.982}Bi_{0.008}Sm_{0.01}PO_4 \cdot 4.5H_2O$ contains a lot of non-crystal water.

A sample of $La_{0.982}Bi_{0.008}Sm_{0.01}PO_4 \cdot 4.5H_2O$ (0.0300 g) was dissolved in 10 mL of 1:1 aqueous HCl solution which contains several drops of H_2O_2 ($\geq 30\%$) so; then the solution was diluted to 100.00 mL with distilled water. The contents of lanthanum (La), samarium (Sm), bismuth (Bi) and phosphorus (P) in the solution were determined by inductively coupled plasma atomic emission spectrometry. The data showed that the mass percentages of lanthanum, samarium, bismuth, and phosphorus were 43.44%, 0.49%, 0.54%, and 9.90%, respectively. In other words, the molar ratio of La:Sm:Bi:P in the sample is 0.983:0.010:0.008:1.004, which is close to that of $La_{0.982}Bi_{0.008}Sm_{0.01}PO_4 \cdot 4.5H_2O$ (0.982:0.008:0.01:1). The water content is 25.80%, which is in agreement with the result of TG. The composition and XRD analyses indicate that only 0.5 molecule water is crystal water and 4.00 molecule water is non-crystal water in $La_{0.982}Bi_{0.008}Sm_{0.01}PO_4 \cdot 4.5H_2O$, which is similar to that of $LaPO_4 \cdot nH_2O$ reported by Fuentes [16].

Fig. 3 shows the dependence of the Bi^{3+}-doping concentration (x) of the $La_{0.99-x}Bi_xSm_{0.01}PO_4$ ($x=0.006$, 0.008, 0.009, 0.010, 0.012) phosphors calcined at 800 °C for 4 h on the relative PLE (photoluminescence excitation) and PL (photoluminescence) intensities. All $La_{0.99-x}Bi_xSm_{0.01}PO_4$ samples show similar PLE and PL spectra except for their relative intensity. As we can see in Fig. 3a, the excitation spectra consist of a series of peaks in the range of 315–510 nm. The strongest one (401 nm) and some other peaks (316, 344, 360, 374, 414,437, 459, and 474 nm) are ascribed to the transitions from the ground state to the excited states of Sm^{3+} [17].

Fig. 3b shows the emission spectra of calcined samples ($La_{0.99-x}Bi_xSm_{0.01}PO_4$) excited at 401 nm at ambient temperature. The PL emission intensity enhances with the increase of the Bi^{3+} doping ratio and reaches a maximum value at $x=0.09$ and the luminescence intensity begins to decrease when the Bi^{3+} doping ratio is higher than 0.9 mol%, as shown in Fig. 3b. This quenching process is generally attributed to the energy migration between Bi^{3+} and Sm^{3+} ions. Therefore, the optimum molar concentration of Bi^{3+} in $La_{0.99-x}Bi_xSm_{0.01}PO_4$ phosphors in this work is 0.9 mol%.