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Facile synthesis and luminescence properties of Eu^{3+} doped $BiPO_4$ powders by polyvinyl-alcohol mediated solid state reaction

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Monoclinic phase $Bi_{0.95}Eu_{0.05}PO_4$ was synthesized by polymer–mediated solid-state reaction employing polyvinyl alcohol (PVA). The powder X-ray diffraction revealed the phase purity and isostructural nature of both Eu^{3+}-doped and undoped $BiPO_4$. The role of PVA molecules in assisting the particle growth during the phase formation and enhancing the degree of crystallinity significantly by its combustion. The synthesized materials were characterized using different spectroscopic techniques such as FT-IR, Raman and Photoluminescence (PL). The methodology discussed here is fundamentally important, which may provide an excellent platform for the phase-controlled synthesis and further optimized materials performance.

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Keyword: $BiPO_4$, Solid state reaction, Eu^{3+} doping, Luminescence

1. Introduction

Many synthetic procedures have been developed in recent years for the preparation of phosphate compounds, because they can provide many crystal field environments imposed on emission centre. Moreover, phosphate phosphors doped with rare earth ions have excellent thermal and charge stabilization [1,2] and also phosphate compounds are considered to be multifunctional materials. Owing to the ability of the tetrahedral PO_4^{3-} group to bond with other structural units, the family of phosphate has been documented possibly as one of the most promising kinds of novel inorganic material [3]. Bismuth phosphate ($BiPO_4$) is a kind of important phosphate salts, and it has three different modifications such as hexagonal phase (HP), low temperature monoclinic phase (LTMP), and high-temperature monoclinic phase (HTMP) [4,5], and they have recently been intensively studied because of their unique functionalities such as catalyst [6], microwave dielectric [7], orthophosphate ion sensor [8], and in separation of radioactive elements [9]. Meanwhile, $BiPO_4$ is also a type of metal phosphate which show luminescence property around 437 nm upon UV-excitation and this had been attributed to the $^3P_1 \rightarrow {}^1S_0$ transition of the Bi^{3+} ion in the lattice [10,11], and rare-earth ions (Eu^{3+}, Tb^{3+}, Dy^{3+}) doped phosphates have been proved to be entering appropriate host lattices for luminescence, and have been found widespread applications in various kinds of display devices [12]. Among the rare-earth ions, trivalent europium (Eu^{3+}) was the most important luminescence centers, due to its similar atomic radius with Bi^{3+} and fundamental level $^7F_0$ and four main emitting levels $^5D_0$, $^5D_1$,$^5D_2$, and $^5D_3$, which give an red emission. Until now, many methods such as hydrothermal, microwave heating, and conventional solid state reactions were used to synthesize $BiPO_4$, but above methods must be assisted with calcination high temperatures [13]. Therefore, low-temperature synthesis, facile solid state reaction especially for one pot reaction, provides several attractive advantages in $BiPO_4$ synthesis.

In this work, Eu^{3+}-doped $BiPO_4$ with monoclinic phase were prepared through PVA-mediated solid state reaction. The PVA-mediated synthesis is a facile and versatile technique, and PVA is nontoxic polymer, has a melting point of 230 °C and 180–190°C for the fully hydrolysed and partially hydrolysed grades, respectively. It decomposes rapidly above 200 °C as it can undergo thorough pyrolysis at relative low temperature, and the intermediate products was volatile molecules such as acetic acid, ethanal and water [14]. It could play vital role in preventing the metal ions hydrolyzation and optimization of $BiPO_4$ crystallization. The phases, surface structure, functional groups and luminescence properties were investigated carefully.

2. Experimental

All the chemical reagents were of analytical grade and used as received without further purification. The Eu^{3+}-doped $BiPO_4$ phosphate phosphors were synthesized by the PVA–mediated solid state reaction. Experimental details are as follows. Firstly, 1.6009 g (2.375 mmoles) of $Bi(NO_3)_3{\cdot}5H_2O$, 1.50 g PVA (PVA-124, MW:2400-2500), 0.661 g $(NH_4)_2HPO_4$, 1.2 mL 0.1 mol·L^{-1} $Eu(NO_3)_3$ solution and 5.0 mL absolute ethyl alcohol were mixted together in an agate mortar, followed by grinding carefully for 20 min, and the mixture was dried at 90°C in a silica crucible for 2 h, the dark yellow precursors were calcinated at 600 °C, followed by grinding, thus the white phosphor powder were obtained. $BiPO_4$ of different doping ion were prepared by similar method with changing the volume 0.1mol·L^{-1} $Eu(NO_3)_3$, $(Tb(NO_3)_3$ or $Dy(NO_3)_3$ solution.

Several complementary methods were used to characterize the doping $BiPO_4$. The crystallinity and phase purity of the samples were accomplished by powder X-ray diffraction (XRD) with a X-ray diffractometer (D8 ADVANCE, Bruker, USA) using graphite monochromatized Cu Ka irradiation (k = 0.15406 nm). FT-IR spectral was measured with an infrared spectrophotometer (Perkin-Elmer 580B, USA), using a KBr pellet technique. Characteristic vibration energy changing of chemical bond and group were recorded on a Laser Raman microscope equipment (Xplora, Horiba, France). PL (Photoluminescence) spectra were recorded with a Hitachi F-7000 spectrophotometer.

The emission spectra of the sample were measured by an Edinburgh Analytical Instruments FLS920 fluorescence-life time.

3. Results and discussions

3.1. Phase Tailoring of $BiPO_4$:Eu^{3+} via PVA mediated solid-state reaction.

Phase purity and structure of all samples were confirmed by XRD patterns, Fig. 1 shows the XRD patterns of the Eu^{3+}-doped $BiPO_4$ samples prepared with and without PVA additive.

The diffraction peaks of the two samples are well indexed to the high temperature monoclinic-type $BiPO_4$ (JCPDS No. 43-0637, space group:P21/m (11)) and Monoclinic-type $BiPO_4$ (JCPDS No. 15-0767, space group: P21/n(14)) peaks can be detected, indicating the formation of mix phase of monoclinic $BiPO_4$, and PVA could bond with $BiPO_4$ crystals closely and optimize of crystallization obviously, because PVA molecules can provide enough –OH groups bonding with metal ions and heat during combustion process.

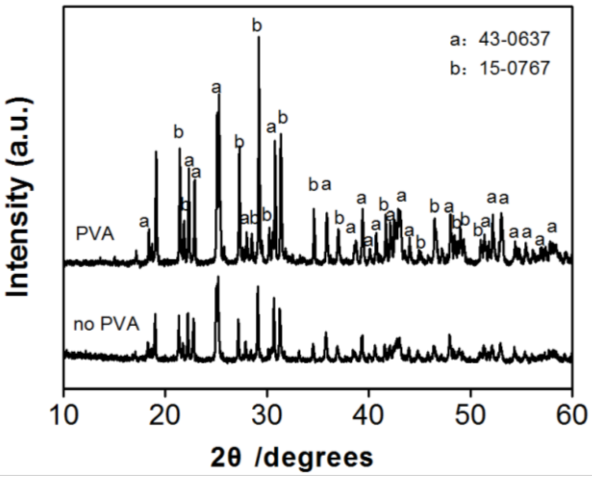

Fig. 1. XRD patterns of the the Eu^{3+}-doped $BiPO_4$ samples prepared with and without PVA additive

Calcination temperature plays another important role in formation of crystal structure of samples, in Fig. 2, it can be seen that monoclinic-type $BiPO_4$ with space group of P21/m (11) below 500 °C, and mix-phase of monoclinic $BiPO_4$ is formed at 600 °C. And it is known that the chains of monoclinic $BiPO_4$ are less symmetrically arranged and hence the structure consists of a compact space-filling network, and the monoclinic phase since can be synthesized above relative high temperature [15], and hexagonal phase not appears, because the use of acidic $Bi(NO_3)_3{\cdot}5H_2O$ precursor as the nearly neutral environment [16].

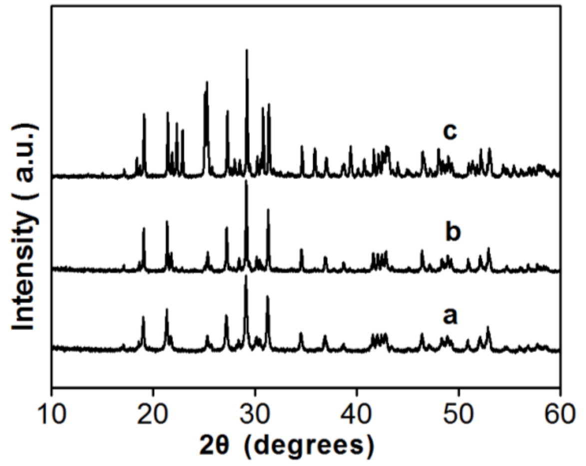

Fig. 2. XRD patterns of the the Eu^{3+}-doped $BiPO_4$ samples calcinated with different temperature (a, 400°C; b, 500 °C; c, 600 °C)

Fig. 3 shows the FTIR spectrum of the as-synthesized $BiPO_4$ samples prepared (a) with and (b) without Eu^{3+} dopant. FT-IR spectra are very comparable to reference data of $BiPO_4$ (Fig. 3:$\upsilon(PO_4)$: 1150–850 cm^{-1}, $\delta(PO_4)$: 630–520 cm^{-1}) [17]. The bands centered at 3423 and

1618cm^{-1} are probably due to υ(O–H) and δ(H–O–H), respectively, produced by the water solution of $Eu(NO_3)_3$.

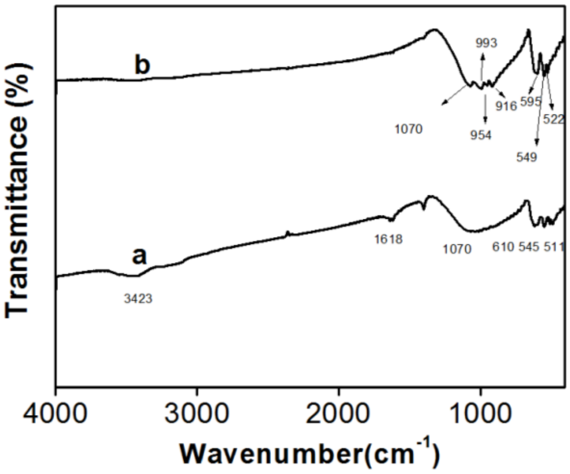

Fig. 3. FT-IR spectra of $BiPO_4$ samples prepared (a) with and (b) without Eu^{3+} dopant

The laser Raman spectra of $BiPO_4$ samples prepared (a) with and (b) without Eu^{3+} dopant are shown in Fig. 4. It can be observed that intense line at 175 cm^{-1} and a shoulder at 247 cm^{-1} are due to the stretching vibration modes of heavy metal ion, Bi^{3+} (Bi–O), in BiO_8 polyhedron. The Peaks at 1043 and 988 cm^{-1} are due to the symmetric (ν1) and asymmetric (ν3) stretching vibrations of the $–PO_4$ group, respectively. And the increasing peaks at 175, 247, 499, 550, 599, 988 and 1043cm^{-1}, are also observed for $BiPO_4$ doped with Eu^{3+} (5%) indicating that the monoclinic structure is largely retained in the samples. The increasing peak intensities can ascribe to that Eu^{3+} possesses smaller radius than Bi^{3+} and higher coordination number [18].

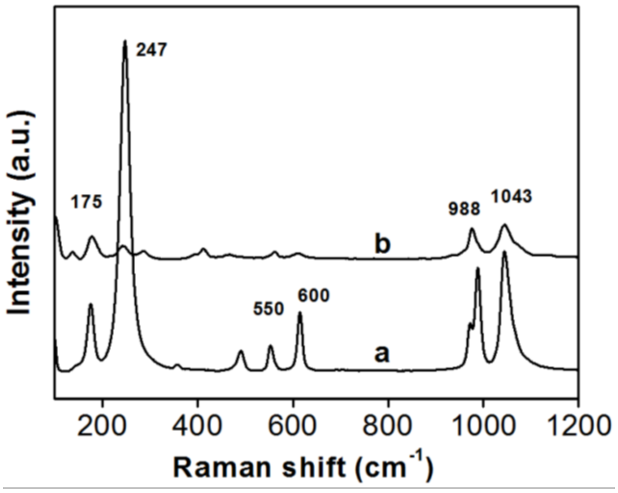

Fig. 4. Raman spectra of $BiPO_4$ samples prepared (a) with and (b) without Eu^{3+} dopant

Fig. 5 shows the excitation spectrum of $BiPO_4$: (5 % Eu^{3+}) sample at emission wavelength 593 nm. A broad excitation centred at 270 nm is attributed to the charge transfer band (CTB) of Eu–O in the $BiPO_4$ host. The narrow excitation lines appearing at longer wavelengths correspond to the characteristic f→f transitions of Eu^{3+}. These lines are assigned as follows: $^7F_0 \rightarrow {}^5H_6$ (315 nm), $^7F_0 \rightarrow {}^5D_4$ (360 nm), $^7F_0 \rightarrow {}^5L_7$ (380 nm), $^7F_0 \rightarrow {}^5D_3$ (412 nm) and the main excitation line $^7F_0 \rightarrow {}^5D_3$ (394 nm).

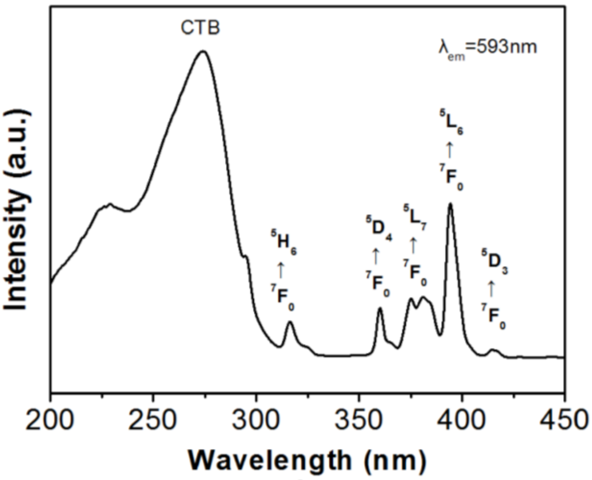

Fig. 5. Excitation spectra of $BiPO_4:Eu^{3+}$ samples

Fig. 6 shows the emission spectrum of $BiPO_4$: (5% Eu^{3+}) sample at excitation wavelength 394 nm. It could be clearly observed that enhancement in the intensity of reddish orange emission after PVA addition. P. Arunkumar et al found that DEG (polyethylene glycol) addition will reduces the PL (photoluminescence) emission intensity of $BiPO_4$ (5% Eu^{3+}), it ascribes to deteriorating effect of DEG molecules bound on $BiPO_4$: (5% Eu^{3+}) surface and absorbed water molecules, [15] however, the PVA molecules addition shows different performance, because of the less water amount involving. In other hands, the combustion of PVA molecules can further enhance the $BiPO_4$ crystal lattice during the calcination process. Calcination temperature will affects the PL emission also, Fig. 7 shows the emission spectra of Eu^{3+} doping $BiPO_4$ samples calcined at different temperature, it can be seen that PL emissions enhance with temperature increase obviously, it ascribes to less Eu^{3+} entering host lattice at low calcination temperature, and the amount of luminescence center increases alone with the increasing temperature, however, decreasing volume of material sharply, owning to sintering at excess temperature of calcination can be the cause of decrease of defect levels in the host of $BiPO_4$, then the PL emission declines slightly. Thus, the optimal temperature of calcination is 600 ^oC.

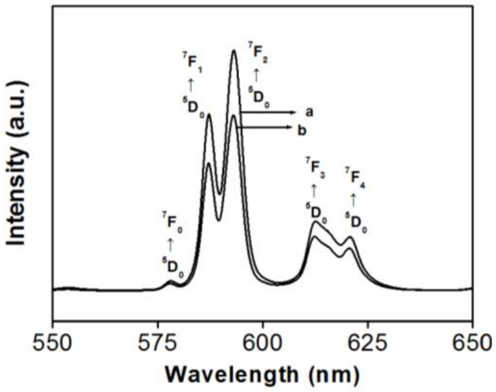

Fig. 6. Emission spectra of Eu^{3+} doping $BiPO_4$ samples prepared (a) with and (b) without PVA addition

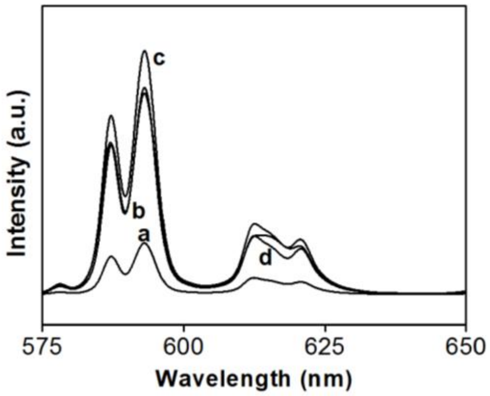

Fig. 7. Emission spectra of Eu^{3+} doping $BiPO_4$ samples calcined at (a) 400 °C, (b) 500 °C, (c) 600 °C, and (d) 700 °C

Fig. 8 shows emission spectra of $BiPO_4$ samples doping with (a) 5% Eu^{3+}, (b) 5% Tb^{3+}, and (c) 5% Dy^{3+} ions prepared by PVA-mediated solid state reaction. It can be observed that remarkable PL emission appears at 488, 548, 580 nm for 5% Tb^{3+} doping sample and 479, 575 nm for 5 % Dy^{3+} ions doping sample. And it can be foreseen that the facile method has great potential in preparation of good reddish orange and green light-emitting components.

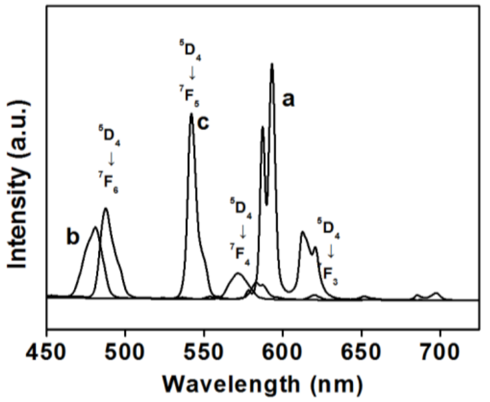

Fig. 8. Emission spectra of $BiPO_4$ samples doping with (a) Eu^{3+}, (b) Tb^{3+} , and (c) Dy^{3+} ions (5%)

Luminescence decay curves monitored by $^5D_0$–$^7F_1$ transition (λex = 394 nm) of Eu^{3+} for $Bi_{0.95}Eu_{0.05}PO_4$ is presented in Fig. 9. It can be observed that the curve exhibits a single- exponential feature that can be well reproduced by a mono- exponential function as in equation of $I = I_0 \exp(-t/\tau)$, where I is the intensity at time t, I_0 is the intensity at t = 0, and τ is the decay lifetime. The lifetime for $Bi_{0.95}Eu_{0.05}PO_4$ is 2.14 ms.

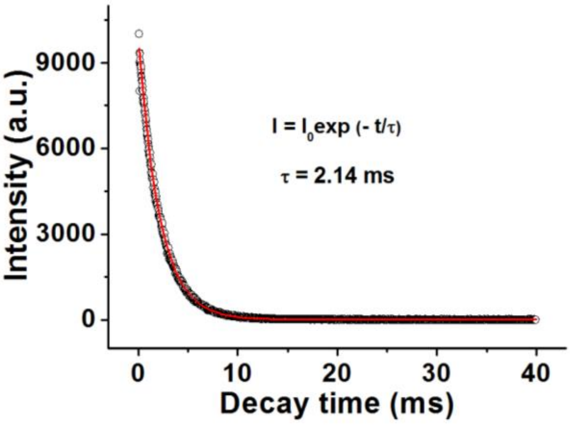

Fig. 9. Decay curves of $Bi_{0.95}Eu_{0.05}PO_4$ samples

4. Conclusion

In conclusion, a simple and facile PVA-mediated solid state reaction method has been employed to synthesize reddish orange mix phase of monoclinic $BiPO_4$:Eu^{3+} material. The crystal structure, IR, raman, and luminescence properties of the sample were discussed in detail. It is found that the PVA additive and calcination temperature play a crucial role in determining the final crystallography of the $BiPO_4$:Eu^{3+} product. By the similar methods, the $BiPO_4$:RE^{3+} (Dy^{3+}, and Tb^{3+}) phosphor exhibits strong multicolor emission, which may find potential applications in lighting.

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The authors declare that they have no conflict of interest.

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