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A new green-yellowish emitting fluoro-apatite compound phosphor $Ba_3TbK(PO_4)_3F:Sm^{3+}$ with high thermal stability

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Abstract: A novel fluoro-apatite-type compound, $Ba_3TbK(PO_4)_3F$ was developed via a high-temperature solid-state reaction route for the first time. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and high-resolution TEM (HRTEM) were used to investigate the component element and microstructure of the phosphor was systematically investigated. The luminescence properties of $Ba_3TbK(PO_4)_3F:Sm^{3+}$ were investigated systemically. The results revealed that the $Ba_3TbK(PO_4)_3F:Sm^{3+}$ phosphor could be efficiently excited in a broad wavelength region ranging from 200 to 400 nm, which matched perfectly with the ultraviolet (UV) light-emitting diode (LED) chips. Based on the energy transfer (ET) between Tb^{3+} and Sm^{3+}, the color hue of $Ba_3Tb_{1-n}K(PO_4)_3F:nSm^{3+}$ (n=0–0.03) was modulated from green (0.305, 0.591) to yellow (0.486, 0.437) area by controlling the Sm^{3+} doping concentration. The critical distance between Tb^{3+} and Sm^{3+} ions in $Ba_3TbK(PO_4)_3F:Sm^{3+}$ was calculated and the corresponding energy quenching mechanism was identified. Fascinatingly, both the $Ba_3TbK(PO_4)_3F$ and $Ba_3Tb_{0.995}K(PO_4)_3F$: $0.005Sm^{3+}$ phosphors exhibited very high thermal stability from room temperature (25 ºC) to 300 ºC, which is extremely important for practical application. In addition, the activation energy for thermal quenching of the $Ba_3Tb_{0.995}K(PO_4)_3F:0.005Sm^{3+}$ sample was estimated to be as high as 0.312 eV. These findings demonstrated that as-prepared phosphor may serve as a high-performance candidate for the application in w-LEDs.

Keywords: phosphors; optical properties; $Ba_3TbK(PO_4)_3F$; thermodynamic properties; rare earths

White light emitting diode (White-LED) has attracted greatly increasing attention due to its unique advantages, such as energy saving, high luminescence efficiency, long lifetime and safety[1,2]. To the best of our knowledge, the most commercially available white LEDs are fabricated by combining InGaN chip with a yellow-emitting phosphor ($Y_3Al_5O_{12}:Ce^{3+}$). But this w-LED system faces the limitations of poor color rendering index (CRI) and high correlated color temperature (CCT) owing to the lack of sufficient red emission, which seriously restricts the white color quality[3–4]. Aiming at obtaining warm-white LED, much increasing attention has been paid to improve the properties of YAG. More Ce^{3+} contents can increase the red components, but this yellow light emission is not efficient and concentration quenching appears. Combining Ce^{3+} with rare-earth ions such as Gd, Lu, Pr, surely causes the redshift of emission but decrease of intensity. In addition, ion substitution in YAG has also been reported[5]. After Y^{3+} is replaced with Tb^{3+}, the emission peak of $Tb_3Al_5O_{12}:Ce^{3+}$ shifts to 575 nm but the intensity becomes lower than before[6,7]. Considering the slow progress in the improvement of YAG, it is sensible to explore new yellow-emitting phosphor upon n-UV light in the field of optical materials.

As it is well known, the rare earth ion Sm^{3+} is a renowned red emission emitting sensitizer because of the $^4G_{5/2}$ to $^6H_{7/2}$ transition. Nevertheless, the absorption efficiency of Sm^{3+} in the near-UV (n-UV) region is weak due to the low oscillator strength and narrow line width of Sm^{3+} 4f–4f absorption transitions[8]. It was reported that using energy transfer from sensitizers to activators by rare earth ions in a proper host is an effective way to solve the above problem[9]. From the above-mentioned consideration, it is necessary to enhance the emission intensity of Sm^{3+}-doped phosphors by utilizing the efficient sensitizer. As we know, the absorption of Tb^{3+} ions is weak in near-UV and visible region, which restricts the phosphors containing Tb^{3+} ions to be applied to w-LEDs. However, high concentration of Tb^{3+} ions in a host lattice can settle this tough problem, without inducing serious concentration quenching. So we selected $Ba_3TbK(PO_4)_3F$ as the mother structure, from which make high ratio of

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Tb^{3+} to Sm^{3+} ions. In addition, many papers reported that an efficient energy transfer takes place between Tb^{3+} and Sm^{3+} ions in some hosts. For example, $K_2YF_5:Tb^{3+}$, Sm^{3+} [10], $CaYAlO_4:Tb^{3+}$/ Sm^{3+} [11], $Y_2O_2S:Tb^{3+}/Sm^{3+}$ [12]. On the other hand, apatite-type phosphors have drawn considerable attention owing to their efficient luminescence, superior chemical and thermal stabilities.

Herein, we demonstrated the fabrication of a new series of high-purity fluoro-apatite-type phosphors $Ba_3TbK(PO_4)_3F$ and Sm^{3+} doped $Ba_3TbK(PO_4)_3F$ via a conventional high-temperature solid-state reaction route. By adjusting Sm^{3+} doping content, the emitting color of $Ba_3TbK(PO_4)_3F:Sm^{3+}$ varies from green to yellow. The temperature-dependent photoluminescence emission (PL) spectra were investigated to evaluate its practical application characteristics. The results revealed that the $Ba_3TbK(PO_4)_3F$ and $Ba_3TbK(PO_4)_3F:Sm^{3+}$ phosphors display exceedingly high thermal stability. Moreover, the energy transfer mechanism between the Tb^{3+} and Sm^{3+} ions was studied systematically.

1 Experimental

1.1 Materials and synthesis

All the powder samples $Ba_3TbK(PO_4)_3F$ and $Ba_3TbK(PO_4)_3F:Sm^{3+}$ were synthesized by traditional solid-state reaction. The starting materials $BaCO_3$, K_2CO_3, $(NH_4)H_2PO_4$, NH_4HF_2, Tb_4O_7 and Sm_2O_3 were weighed in a given stoichiometric ratio. After fixed end grinding thoroughly, the mixture was calcined at 1080 ºC for 3 h. The final products were obtained when the furnace was cooled to room temperature.

1.2 Characterization

The phase formation of the final products were examined by powder X-ray diffraction (XRD, XD-3, PGENERAL, China) in the 2θ range from 10º to 70º, with graphite monochromatized Cu Kα radiation (λ=0.15406 nm) operating at 40 kV and 30 mA. The step scanning rate (2θ ranging from 5º to 100º) used as Rietveld analysis was 3 s/step with a step size of 0.04. Powder diffraction data were obtained by the Rietveld method using the computer software General Structure Analysis System (GSAS) program. The photoluminescence emission (PL) and photoluminescence excitation (PLE) spectra of the as-prepared powders were indentified on a fluorescence spectrophotometer (F-4600, HITACHI, Japan) with a photomultiplier tube operating at 400 V, and a 150 W Xe lamp used as the excitation lamp, and a 400 nm cutoff filter was used to eliminate the second-order emission of source radiation in the measurement. Diffuse reflection spectra were measured on a Shimadzu UV-3600 UV-vis-NIR spectrophotometer attached with an integral sphere. The luminescence decay curve was recorded on a spectrofluorometer (HORIBA, JOBIN YVON FL3-21) with a 370 nm pulse laser radiation (nano-LED) as the excitation source, and the pulse width of the laser is 12 ns. All the above-mentioned measurements were performed at room temperature. The temperature-dependence luminescence properties were identified on the same spectrophotometer, combined with a self-made heating attachment and a computer-controlled electric furnace.

2 Results and discussion

The crystal structure of $Ba_3TbK(PO_4)_3F$ sample was refined using the computer software General Structure Analysis System (GSAS) program[13]. Fig. 1 shows the powder XRD pattern for Rietveld structure analysis of the $Ba_3TbK(PO_4)_3F$ based on the $Ba_6La_2Na_2(PO_4)_6F_2$ phase model[14], and no impurity phase is detected. Fractional atomic coordinates, occupancies and isotropic thermal parameters of this sample are presented in Table 1, K^+ and Tb^{3+} are designed to occupy in the sites of Na^+ and La^{3+}, respectively, because of the similar ion radius and the equal charge number[15]. Table 1 also lists the reflection conditions R_{wp}(%)=9.12, R^p(%)=5.95 and χ^2= 2.616, and all the parameters suggest that the pure $Ba_3TbK(PO_4)_3F$ compound is synthesized successfully. $Ba_3TbK(PO_4)_3F$ sample is indexed with hexagonal crystal system and space group *P*-6, *a*=0.9839(72) nm, *c*= 0.7478(38) nm, *V*=0.627053 nm^3, which differ from $Ba_6La_2Na_2(PO_4)_6F_2$ compound *a*=0.9939(24) nm, *c*= 0.7441(95) nm, *V*=0.636670 nm^3 resulting from the substitute of Na^+ by K^+ and La^{3+} by Tb^{3+} according to Vegard's rule. Schematic illustration of the crystal structure of $Ba_3TbK(PO_4)_3F$ viewed from the *b* axis, and the coordination environment around Ba/Tb, Ba/K and Tb/K are given in Fig. 2. There are two cations sites in $Ba_3TbK(PO_4)_3F$ host coordinated，which are seven (M1) and nine (M2) O^{2-}/F^- ions. Ba/Tb ions site in M1 coordinated by 5O and 2F, meanwhile, Ba/K and Tb/K ions

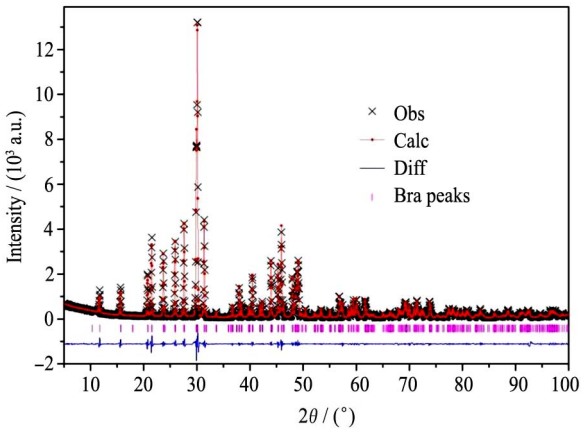

Fig. 1 Powder XRD patterns for Rietveld structure analysis of the selected $Ba_3TbK(PO_4)_3F$ phosphor based on the $Ba_6La_2Na_2(PO_4)_6F_2$-ICSD-10030 phase model