Pis'ma v ZhETF, vol. 99, iss. 10, pp. 647 – 650 © 2014 May 25

$KBaBP_2O_8:Tm^{3+}$: a novel blue-emitting phosphor with high color purity

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Submitted 2 April 2014

A series of novel blue emitting $K_{1+x}Ba_{1-2x}Tm_xBP_2O_8$ ($0.01 \le x \le 0.08$) phosphors were synthesized by a solid-state reaction at high-temperature for the first time. The phase purity and photoluminescence properties were investigated by X-ray diffraction (XRD) and fluorescence spectroscopy (FS) measurements, respectively. The influence of the doping concentration of Tm^{3+} on its relative emission intensity was investigated, and the critical distance was calculated. The as-prepared phosphor can be effectively excited with a 356 nm light, and exhibit blue emission at 457 nm with high color purity. The above work indicates this phosphor could be a potential candidate as blue emitting phosphor for application in white light-emitting diodes.

DOI: 10.7868/S0370274X14100014

1. Introduction. Tm^{3+}-doped inorganic compound as a blue emitting phosphor has potential application in light and display region such as white light-emitting diodes (w-LEDs), plasma display panels (PDPs), and field-emission display (FED) devices. For example, $LaAO_3:Tm^{3+}$ (A = Ga or Al) phosphors have comparable emission intensity to that of the commercial FED blue phosphor $Y_2SiO_5:Ce^{3+}$ under low-voltage electron beams excitation, and shows potential applications in FED [1, 2]; the mixed phosphor of the phosphor $Ca_3LaNa(PO_4)_3F:Tm^{3+}$ and the commercially available PDP blue phosphor $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) showed efficient luminescence and suitable antidegradation behavior [3]; the $Sr_2B_2O_5:Tm^{3+},Na^+$ phosphor [4] is a promising candidate as blue-emitting for the w-LEDs. So, the investigation on the luminescence properties of Tm^{3+} in different host lattices are important not only for enriching the spectroscopy content of Tm^{3+} ion in theory but also developing novel blue-emitting phosphor for possible industrial application.

Borophosphate phosphors, as an important family of luminescent materials, have attracted more and more attention in view of their low synthesis temperature, excellent chemical and thermal stability. In the past few years, many researchers have carried out a lot of works on the luminescence properties and potential applications of rare-earth ions in borophosphate phosphors, and obtained some significant conclusions [5–10]. A new kind of borophosphate compound $KBaBP_2O_8$ with three-dimensional diamond-like framework was reported firstly by Zhao et al. in 2009 [11]. It crystallizes in space group $I\bar{4}2d$ with the following lattice parameters: $a = 7.202(2)$, $c = 14.300(6)$ Å. Though some works on the luminescence properties of rare earth ions doped $KBaBP_2O_8$ have been published in recent years [7–10], there is no study on the luminescent properties of Tm^{3+} in $KBaBP_2O_8$ host. In this paper, we first synthesized novel blue-emitting phosphor $KBaBP_2O_8:Tm^{3+}$, and mainly investigated the luminescence properties of Tm^{3+} in $KBaBP_2O_8$ substrate in details.

2. Experimental. A series of polycrystalline powder samples with nominal chemical formula $K_{1+x}Ba_{1-2x}Tm_xBP_2O_8$ (x = 0.01, 0.02, 0.04, 0.06, 0.08) were prepared by a traditional high-temperature solid-state reaction. Since Tm^{3+} ions are expected to incorporate into the lattice sites of Ba^{2+} ions, K^+ ions with excess of x in formula $K_{1+x}Ba_{1-2x}Tm_xBP_2O_8$ were added as charge compensators. The reactants were K_2CO_3 (analytical reagent – A.R.), $BaCO_3$ (A.R.), H_3BO_3 (A.R.), $NH_4H_2PO_4$ (A.R.), and Tm_2O_3 (99.9 %), and used without further purification. The raw materials were carefully weighed stoichiometrically and ground in an agate mortar until the mixture appeared homogeneous. Then the mixture was preheated at 673 K for 2 h, reground, and finally fired at 1173 K for 8 h in a muffle furnace. The final products were cooled spontaneously to room temperature (RT) and crushed to fine particles. The phase purity as well as the structure of the final products was characterized by a powder X-ray diffraction (XRD) analysis with Cu K_α ($\lambda = 1.5405$ Å) radiation on a Bruker D8 Advance X-Ray Diffractometer. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured on a fluorescence spectrometer (HITACHI

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F-7000) equipped with a 150 W xenon lamp as the excitation source. All the measurements were performed at RT.

3. Results and discussion. Fig. 1 shows XRD patterns of the as-prepared phosphor $K_{1+x}Ba_{1-2x}Tm_xBP_2O_8$ ($x = 0.06$) and the cal-

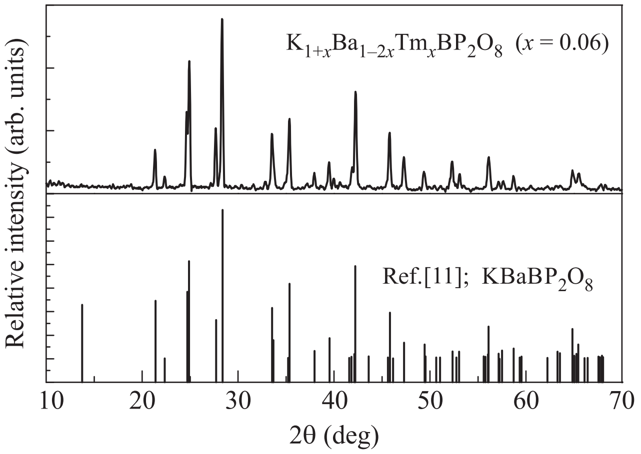

Fig. 1. XRD pattern of $K_{1+x}Ba_{1-2x}Tm_xBP_2O_8$ ($x = 0.06$)

culated data from the single-crystal structure of $KBaBP_2O_8$ [11]. The phase constitution of $KBaBP_2O_8$ is almost not changed when the doped Tm^{3+} and K^+ ions enter into the host lattice. As expected, these ions occupy normal Ba^{2+} sites due to the similar ionic radii. The diffractions for all samples are similar and agree well with the calculated XRD pattern, meaning that all samples are of single pure phase. Furthermore, this synthetic temperature is much mild compared with commercial phosphors synthesized at above 1273 K by the conventional solid state reaction technique [12].

Fig. 2 curve *1* presents the excitation spectrum of $KBaBP_2O_8$:$0.06Tm^{3+}$ phosphor by monitoring the emission wavelength at 457 nm. The spectrum shows a narrow excitation peak at 356 nm, which is assigned to the typical $^3H_6 \rightarrow {}^1D_2$ transition of Tm^{3+} ion. Fig. 2 curve *2* shows the emission spectrum of $KBaBP_2O_8$:$0.06Tm^{3+}$ phosphor upon the excitation with a 356 nm light, in which the major emission at 457 nm corresponding to the transition of $^1D_2 \rightarrow {}^3F_4$ of Tm^{3+} can be observed. Compared with other Tm^{3+}-doped phosphors [4, 13], the transitions from $^1G_4$ to $^3H_6$ ($\sim$ 475 nm) manifold are very weak, which indicates that multi-phonon-relaxation process from $^1D_2$ to $^1G_4$ is not dominant in view of the large energy gap ($\sim 7000\,\mathrm{cm}^{-1}$) resulting in the very weak intensity lines of the emission from the $^1G_4$ level [14, 15]. A simplified energy level diagram of Tm^{3+} ion and related transitions are plotted in Fig. 3. When the higher $4f$ energy

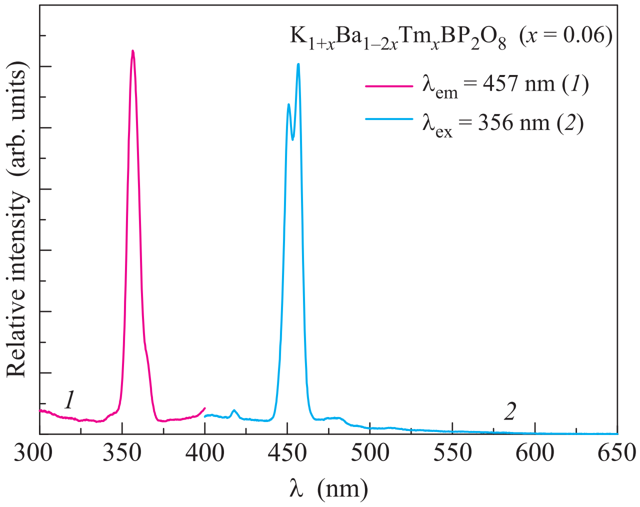

Fig. 2. UV excitation spectrum (*1*) and emission spectrum (*2*) of $K_{1+x}Ba_{1-2x}Tm_xBP_2O_8$ ($x = 0.06$)

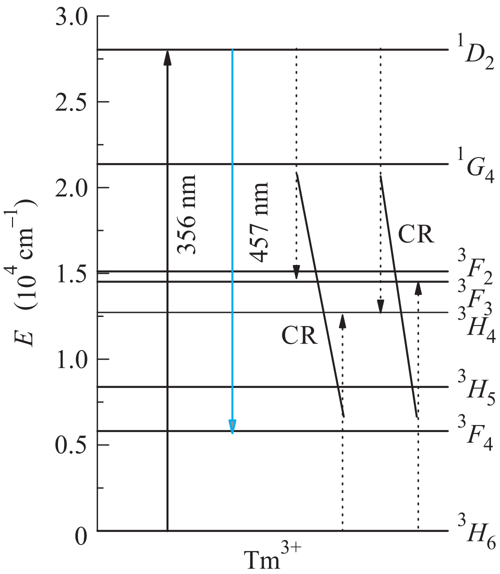

Fig. 3. Schematic energy level diagram of Tm^{3+} ion

level $^1D_2$ of Tm^{3+} ions is excited by 356 nm light, it gives rise to the blue emission through the $^1D_2 \rightarrow {}^3F_4$ radiative transition process. It can be seen that the blue $^1D_2 \rightarrow {}^3F_4$ emission is quite sharp, revealing the high color purity and excellent chromaticity coordinate characteristics of $KBaBP_2O_8$:$0.06Tm^{3+}$ phosphor.

Fig. 4 shows the emission spectra of a series of $K_{1+x}Ba_{1-2x}Tm_xBP_2O_8$ phosphors with the dopant concentration of Tm^{3+} ranging from 1 to 8 mol %. The most efficient emission intensities occurred at $x = 0.06$ in the $K_{1+x}Ba_{1-2x}Tm_xBP_2O_8$ system (see the inset of Fig. 4), which is comparable with that in other Tm^{3+} doped phosphors [1, 2, 4, 15–18]. The drop in intensity

CIE chromaticity coordinate (x, y) of some Tm^{3+}-doped phosphors

Serial number	Phosphor	Chromaticity coordinate (xy)	Reference
1	$KBaBP_2O_8$:Tm^{3+}	0.155, 0.046	This work
2	$LaGaO_3$:Tm^{3+}	0.155, 0.063	[1]
3	$Ba_2B_5O_9Cl$: Tm^{3+}	0.172, 0.088	[20]
4	$Sr_2B_5O_9Cl$: Tm^{3+}	0.166, 0.115	[21]
5	Y_2O_3: Tm^{3+}	0.158, 0.150	[22]
6	$Sr_2B_2O_5$:Tm^{3+}	0.173, 0.165	[4]

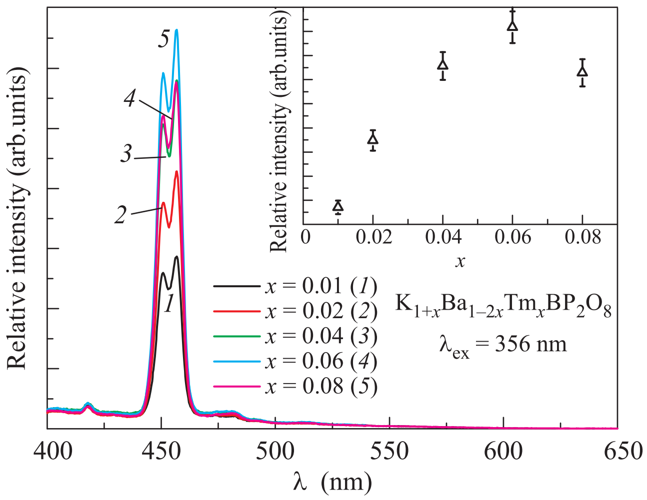

Fig. 4. Emission spectra of $K_{1+x}Ba_{1-2x}Tm_xBP_2O_8$ at different Tm^{3+} concentrations. The inset shows the concentration dependent emission intensity of $K_{1+x}Ba_{1-2x}Tm_xBP_2O_8$ phosphors

as the Tm^{3+} content increased (concentration quenching effect) was caused by the rise of nonradiative decay channels, which was promoted by the interaction with quenching centers during the cross relaxation (CR) processes among Tm^{3+} ions [14], such as $(^1D_2 \rightarrow {}^3F_3) + (^3H_6 \rightarrow {}^3H_4)$ or $(^1D_2 \rightarrow {}^3H_4) + (^3H_6 \rightarrow {}^3F_3)$, as shown in Fig. 3.

In 1969, Blasse [19] assumed that the average shortest distance between the nearest activator ions is equal to the critical distance (R_c) at which the probability of the nonradiative transfer is equal to the probability of the radiative emission. Therefore, the R_c for Tm^{3+} in the $KBaBP_2O_8$ host can be estimated by the following equation:

$$R_c = 2\left(\frac{3V}{4\pi x_c N}\right), \tag{1}$$

where V is the volume of the unit cell, x_c is the optimal concentration of activator ion, and N is the number of formula units per unit cell. By taking the appropriate values [11] of x_c, N, and V (0.01, 4, 741.7(4) Å^3, respectively), R_c is determined to be about 18.1 Å.

As the sample $KBaBP_2O_8$:$0.06Tm^{3+}$ shows the much stronger emission intensity and similar emission shape relative to that in other samples, as discussed above, which is chosen as a case to investigate the CIE chromaticity coordinates and color purity for the $KBaBP_2O_8$:Tm^{3+} phosphors. Fig. 5 shows

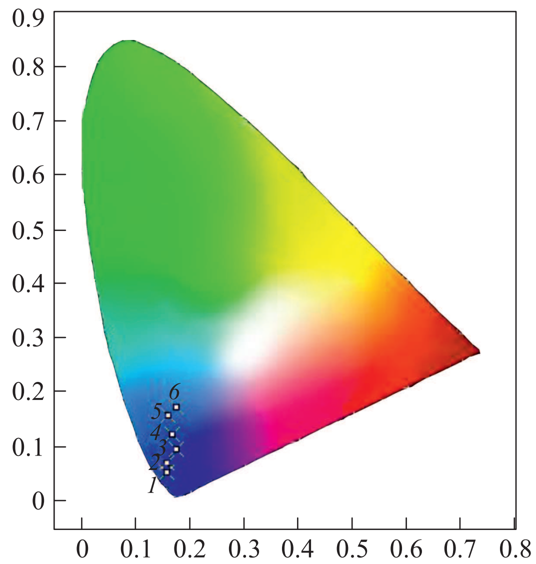

Fig. 5. Chromaticity coordinates of Tm^{3+} doped phosphors

the CIE chromaticity coordinate (x, y) of the sample $KBaBP_2O_8$:$0.06Tm^{3+}$ calculated in term of the emission spectrum under 356 nm excitation as well as that of other Tm^{3+} doped phosphors. The CIE coordinates are determined to be (0.155, 0.046), which is identical to the European Broadcasting Union (EBU) illuminant blue (0.15, 0.06) and National Television System Committee (NTSC) illuminant blue (0.14, 0.08) [16]. The obtained blue (x, y) coordinates are also comparable with that in other Tm^{3+} doped phosphors [1, 4, 20–22] (see Table).

Furthermore, the color purity of a dominant color is the weighted average of the (x, y) coordinate relative to the coordinate of the CIE white illuminants and the coordinate of the dominant wavelength [23, 24]. The dominant wavelength is defined as the single monochromatic wavelength that appears to be same color as the light source, which is about 455 nm in the current example in terms of the reported method [23]. Hence, the color purity can be described by the following equation:

$$\text{Color purity} = \frac{\sqrt{(x - x_i)^2 + (y - y_i)^2}}{\sqrt{(x_d - x_i)^2 + (y - y_i)^2}} \cdot 100\,\%, \quad (2)$$

where (x, y) and (x_i, y_i) are the color coordinates of the emission light and the CIE white illuminate $(0.3101, 0.3162)$, respectively, and (x_d, y_d) are the chromaticity coordinates $(0.151, 0.0227)$ of the dominant wavelength point (455 nm). The calculated color purity of the orange $KBaBP_2O_8$:$0.06Tm^{3+}$ is about 93.3 %. It is easy to understand that the $KBaBP_2O_8$:$0.06Tm^{3+}$ phosphor have good color purity, because the location of color coordinates of its blue-light emission is close to the spectral edge of the CIE chromatic diagram owing to the dominant $^1D_2 \to {}^3F_4$ transition of Tm^{3+}.

4. Conclusions. In summary, a series of $KBaBP_2O_8$:Tm^{3+} phosphors were synthesized successfully by a solid-state reaction at 1173 K. These phosphors could be excited by a 356 nm light and exhibited blue emission originating from the intra-$4f$ orbital transitions from the $^1D_2$ level to the $^3F_4$ level of Tm^{3+}. The optimum concentration of Tm 3+ ions was around 6 mol %, and the critical distance of Tm^{3+} was calculated to be about 18.1 Å. The CIE coordinates are determined to be $(0.155, 0.046)$ with high color purity 93.3 %. The results manifested that $KBaBP_2O_8$:Tm^{3+} phosphor might be a potential blue emitting phosphor for w-LEDs.

The work is financially supported by the National Natural Science Foundation of China (# 21271111), the Science and Technology Project of Henan Province (# 142300410245), and the Science and Technology Research Key Project of Education Department of Henan Province (# 12A430021).

1. X. M. Liu and J. Lin, Appl. Phys. Lett. **90**, 184108 (2007).
2. X. M. Liu, L. S. Yan, and J. Lin, J. Phys. Chem. C **113**, 8478 (2009). 7.
3. M. Xiea, Y. Huangb, Y. Taob, H. Lianga, and Q. Su, J. Electrochem. Soc. **157**, 401 (2010).
4. L. H. Cai, L. L. Ying, J. H. Zheng et al., Ceram. Int. **40**, 6913 (2014).
5. T. W. Kuo, W. R. Liu, and T. M. Chen, Opt. Express **18**, 1888 (2010).
6. V. R. Kharabe, S. J. Dhoble, and S. V. Moharil, J. Phys. D: Appl. Phys. **41**, 205413 (2008).
7. J. Sun, G. Shen, X. Wang, and D. Shen, Mat. Lett. **93**, 169 (2013).
8. Sh. Su, W. Liu, R. Duan, L. Cao, G. Su, and Ch. Zhao, J. Alloys Comp. **575**, 309 (2013).
9. H. Fang, J. Sun, Ch. Geng, L. Zhang, Q. Yan, X. Wang, and D. Shen, Mat. Lett. **100**, 216 (2013).
10. B. Han, P. Li, J. Zhang, and H. Shi, Mater. Lett. **120**, 33 (2014).
11. D. Zhao, W.-D. Cheng, H. Zhang, Sh.-P. Huang, Z. Xie, W.-L. Zhang, and S.-L. Yang, Inorg. Chem. **48**, 6623 (2009).
12. R. Y. Yang and H. L. Lai, J. Lumin. **145**, 49 (2014).
13. H. Zhang, X. Fu, Sh. Niu, G. Sun, and Q. Xin, Sol. State Comm. **132**, 527 (2004).
14. L. Macalika, J. Hanuza, D. Jaque et al., Opt. Mater. **28**, 980 (2006).
15. G. S. R. Raju, J. Y. Park, H. Ch. Jung, E. Pavitra, B. K. Moon, J. H. Jeong, J. S. Yu, J. H. Kim, and H. Choi, J. Alloys Compd. **509**, 7537 (2011).
16. Y.-Ch. Li, Y.-H. Chang, Y.-F. Lin, Y.-J. Lin, and Y.-Sh. Chang, Appl. Phys. Lett. **89**, 081110 (2006).
17. H. Zhang, X. Fu, Sh. Niu, and Q. Xin, J. Non-Crystal. Solids **354**, 1559 (2008).
18. H. Zhang, X. Fu, Sh. Niu, and Q. Xin, J. Lumin. **128**, 1348 (2008).
19. G. Blasse, Philips Res. Rep. **24**, 131 (1969).
20. J. H. Hao, J. Gao, and M. Cocivera, Appl. Phys. Lett. **82**, 2224 (2003).
21. J. H. Hao and M. Cocivera, J. Phys.: Condens. Matter **14**, 925 (2002).
22. J. H. Hao, S. A. Studenikin, and M. Cocivera, J. Lumin. **93**, 313 (2001).
23. J. S. Kumar, K. Pavani, A. M. Babu et al., J. Lumin. **130**, 1916 (2010).
24. Z. D. Lou and J. H. Hao, Thin Solid Films **450**, 334 (2004).