

Preparation and luminescent properties of a rare earth borate red light-emitting material

B. YING, W.G. SHENG*

Shenyang University of Chemical Technology, Shenyang 110142, P.R. China

A new hydrated rare earth borate $K_2O \cdot CaO \cdot 4B_2O_3 \cdot 12H_2O:Eu$ was prepared by water solution method. The crystal structure, morphology, luminescence properties were investigated via XRD, IR, TG-DSC and SEM, respectively, and it was shown that one single crystal was obtained via spontaneous crystallization. The luminescent properties were also investigated by F-4600 spectrophotometer.

Keywords: *borate; solution method; rare earth doping; luminescence*

1. Introduction

Luminescent materials with borates as the host are considered as very useful in practice and preferred materials for the high definition and projective television, due to their low synthesizing temperature, simple preparation conditions and high luminescent brightness [1–6]. Borate doped Eu^{3+} shows intense red emission lines at 616 nm corresponding to the forced ED transition ($^5D_0 \rightarrow ^7F_2$) of Eu^{3+} . Now, the borate phosphors doped Eu^{3+} , such as $(Y,Gd)BO_3:Eu$, $YAl_3(BO_3)_4:Eu$ and $BaZr(BO_3)_2:Eu$ attract attention as red emitting phosphors for plasma display panels [7–11].

As water molecules or OH^- contained in a product have a quenching effect on the material luminescence, the present study mainly concentrates on anhydrous borate luminescent materials. The reports about hydrated borates are rare. In fact, as early as in 1965, Xie et al. [12] put forward that most of hydrated borates show luminous performance. In 2008, Liu et al. [13] prepared nanometer materials of $MgBO_2(OH):Eu(Y)$ by hydrothermal method. Under UV excitation, $MgBO_2(OH):Eu$ nanobelts showed strong red emission and the emission spectrum intensity increased greatly with

the Eu^{3+}, Y^{3+} co-doping. $MgBO_2(OH):Eu$ can be applied in fluorescent transparent panels. Huang et al. [14] synthesized $SrB_2O_4 \cdot 4H_2O:Eu$ by liquid co-precipitation method. The material had stronger luminescence in the UV region and could be used as a new hydrated borate matrix for light-emitting material. The researches showed that borate compounds formed by alkali (Li, Na, K, Rb, Cs) or alkaline earth metals (Mg, Ca, Sr, Ba) and rare earth elements are beneficial to reduce the concentration quenching effect and are expected to solve partially the problems such as color cast and luminous efficiency [15–20].

In the present work, a new rare earth hydrous borate $K_2O \cdot CaO \cdot 4B_2O_3 \cdot 12H_2O:Eu(KCB:Eu)$ has been realized by water solution method. We describe the structure of KCB:Eu and report its synthesis, crystal growth, IR, TG-DSC and the luminescence properties.

2. Experimental

2.1. Synthesis

KOH, H_3BO_3 , $CaCl_2 \cdot 2H_2O$ and Eu_2O_3 were mixed at 35 °C at a mass ratio of 25:50:7.43 with a stirring speed of 400 rpm, in a 500 mL three-neck flask. At the rate of temperature drop of 2 °C per day from 35 °C, single crystals of KCB:Eu began to generate after 3 days.

*E-mail: bywx@163.com

Characteristic crystallization began in a few days at room temperature. The resulting white crystals of KCB:Eu were recovered by filtration, washed by deionized water, and dried in a vacuum dryer to a solid mass, at room temperature.

2.2. Characterization

The compound was characterized by X-ray powder diffraction (D8 Advance, CuK α 1, 40 kV, 40 mA), FT-IR spectroscopy recorded on KBr pellets in the 400 cm⁻¹ to 4000 cm⁻¹ region on a Nicolet 470 spectrometer at room temperature. The emission and excitation spectra were measured by F-4600 spectrophotometer at room temperature.

2.3. Determination of crystal structure

A white crystal of KCB:Eu with approximate dimension 3 mm \times 1 mm \times 1 mm was selected for single crystal X-ray diffraction. Diffraction data were collected at 293 K on an automated Bruker Smart-1000 CCD four-circle diffractometer with graphite monochromatized MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). All calculations were performed with programs from the SHELXTL crystallographic software package. Final least-squares refinement was performed on F_o^2 with the data having $F_o^2 \geq 2\sigma(F_o^2)$.

3. Results and discussion

3.1. Crystal structure

Fig. 1 shows the XRD patterns of KCB (JCPDS Card No. 76-1013) and KCB:Eu crystals. The diffraction peaks in the patterns correspond well with the expected positions. Adding Eu³⁺ has not changed the crystal morphology obviously. Both crystals are found to belong to orthorhombic system, with a space group of P2₁2₁2₁, Z = 4. Their unit cell parameters are shown in Table 1. It can be seen that the two crystal lattices exhibit slight different distortions and the cell parameters a, b and c become smaller due to Eu addition. It may be caused by Eu³⁺ ($r_{\text{Eu}^{3+}} = 0.0950 \text{ nm}$) which could replace Ca²⁺ ion ($r_{\text{Ca}^{2+}} = 0.099 \text{ nm}$) in the structure. The SEM photographs of the sample crystals are shown in Fig. 2, which clearly reveals

the orthorhombic structure of single crystal. The crystal surface becomes coarser with the rare earth ion adding.

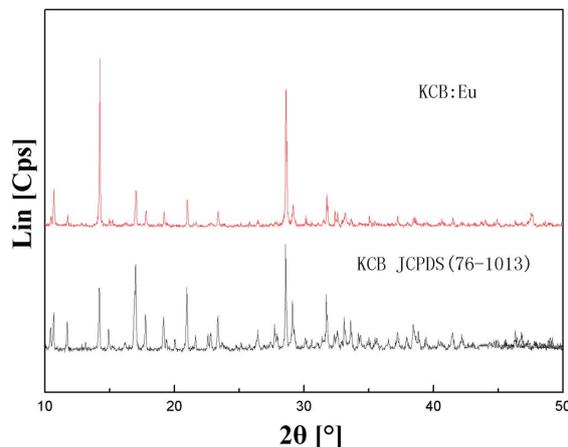


Fig. 1. XRD patterns of KCB and KCB:Eu.

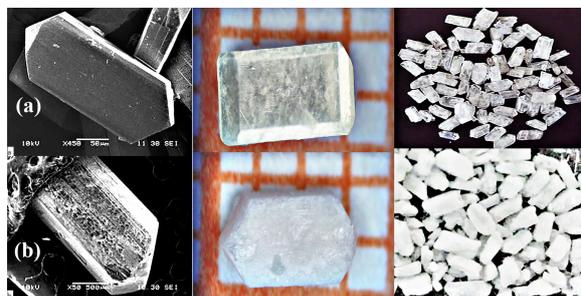


Fig. 2. The SEM and photographs of KCB (a), and KCB:Eu (b) at different magnifications.

3.2. FT-IR spectroscopy

The FT-IR spectra scanned between 500 cm⁻¹ to 4000 cm⁻¹ in the transmittance mode are shown in Fig. 3.

The bands at 3204 cm⁻¹ to 3612 cm⁻¹ are the stretching vibrations of the O–H group. The bands at 1635 cm⁻¹ and 1684 cm⁻¹ are assigned to the H–O–H bending modes, which shows that this compound contains crystalline water. The bands at 1345 cm⁻¹, 1402 cm⁻¹ and 1455 cm⁻¹ belong to B–O asymmetric stretching in BO₃. The bands at 1294 cm⁻¹ and 1164 cm⁻¹ can be assigned to B–O–H. The bands at 1002 cm⁻¹, 1040 cm⁻¹

Table 1. The lattice parameters of KCB:Eu

Compound	a [nm]	b [nm]	c [nm]	α [°]	β [°]	γ [°]	V [nm ³]
K ₂ Ca[B ₄ O ₅ (OH) ₄] ₂ · 8H ₂ O	1.65597	1.24030	1.15801	90	90	90	2.36471
K ₂ Ca[B ₄ O ₅ (OH) ₄] ₂ · 8H ₂ O:Eu	1.64990	1.23480	1.15090	90.2054	90.1923	90	2.34472

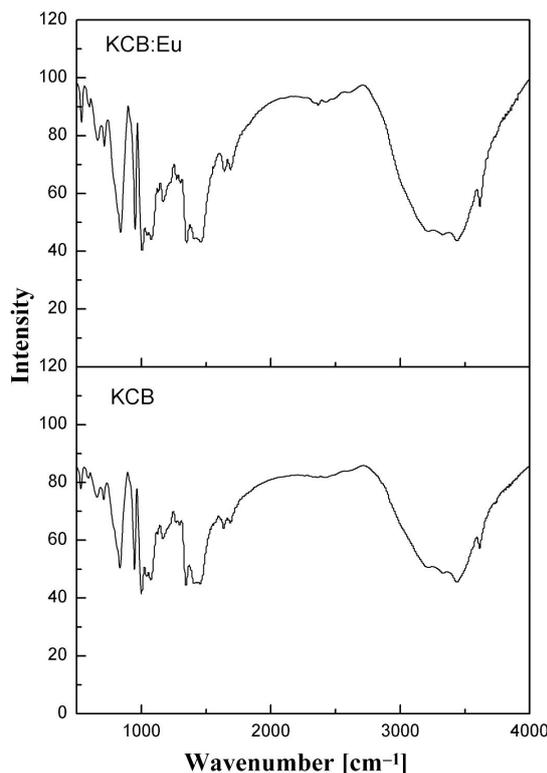


Fig. 3. FT-IR spectra of KCB and KCB:Eu.

and 1071 cm⁻¹ are the asymmetric and symmetric stretching modes of B–O in BO₄, respectively. The band at 591 cm⁻¹ is the characteristic peak of the tetraborate anion of (B₄O₅(OH)₄) [21]. The band at 460 cm⁻¹ is the bending mode of B–O in BO₄. Such results confirm the existence of (B₄O₅(OH)₄) groups in the structure, which is consistent with the above structural determination. Eu–O vibration frequency has not caused any microstructural changes in the sample.

3.3. Thermal behavior

The thermal gravity-differential scanning calorimetric (TG-DSC) analysis of KCB:Eu has

been performed using NETZSCH STA 449C simultaneous thermal analyzer (Fig. 4). There is a sharp endothermic peak at about 100.9 °C in the DSC curve, which corresponds to the melting point of KCB:Eu. There is also another sharp exothermic peak at 683.1 °C, which corresponds to the recrystallization phase.

Two step weight losses appeared in the TG curve (equation 1). One step lost 8 H₂O at 80 °C to 120 °C with a mass loss up to 21.8 % (The loss rate of 8 H₂O is 22.3 % in theory) and another step lost 4 H₂O at 120 °C to 600 °C with a mass loss up to 10.2 %:

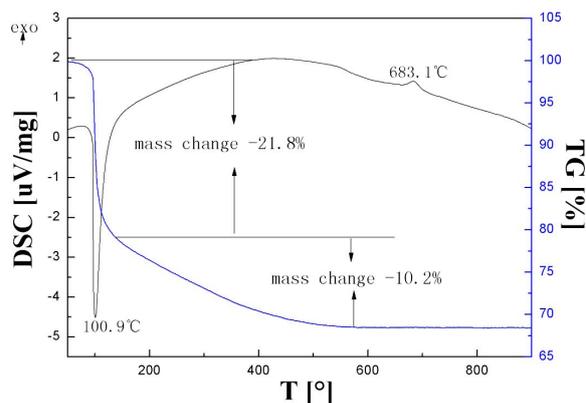
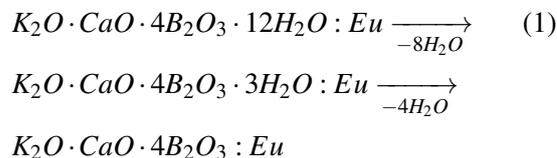


Fig. 4. TG DSC curves of KCB:Eu.

3.4. Emission and excitation spectra

Fig. 5 shows the excitation spectra of KCB:Eu at a wavelength of 616 nm. One broad excitation band in the range of 220 nm to 350 nm is

attributed to the charge-transfer (CTB) transition of $\text{Eu}^{3+}-\text{O}^{2-}$ (CTB) and $\text{B}^{3+}-\text{O}^{2-}$ (CTB). The sharp peaks in the 350 nm to 500 nm ultraviolet-visible range are due to the 4f-4f transition of Eu^{3+} . There are two groups of the strongest sharp excitation spectrum lines located at 467 nm (${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$) and 395 nm (${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$) nearby. It shows that KCB:Eu luminescent materials can be effectively stimulated by 395 nm ultraviolet light and 467 nm visible light.

Emission spectrum under 395 nm excitation is shown in Fig. 6. There are two emission peaks of Eu^{3+} near 591 nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$) and 616 nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$). The main emission peak at 616 nm belongs to the typical ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ red emission energy level transition of Eu^{3+} . The excitation wavelength at 395 nm is matched with the output wavelength of the UV and blue light which is widely used now.

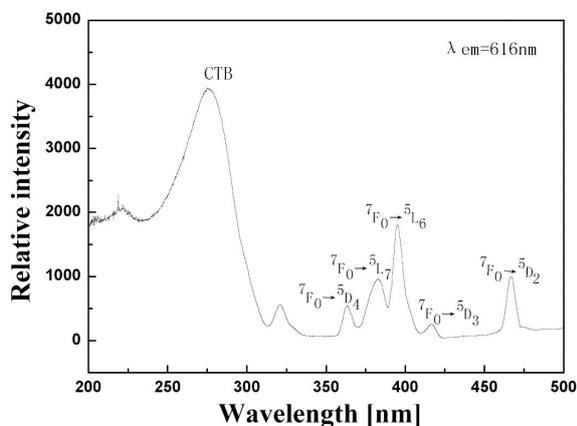


Fig. 5. The excitation spectrum of KCB:Eu monitored at 616 nm.

The emission spectra (at 616 nm) of KCB:xEu ($x = 0.012, 0.024, 0.036, 0.048$) under 395 nm excitation are shown in Fig. 7. The emission intensity of phosphors increases with an increase in Eu^{3+} concentration. When x is greater than 3.6 wt.%, the material luminous intensity decreases. When Eu^{3+} content is low, the average distance of adjacent Eu^{3+} in the lattice matrix is longer, the cross relaxation almost never happens. With the excessive amount of Eu^{3+} doping, the average distance between adjacent Eu^{3+} is short and the cross

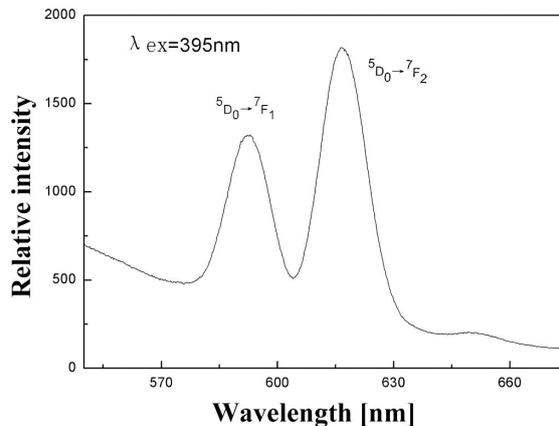


Fig. 6. The emission spectrum of KCB:Eu under 395 nm excitation.

relaxation becomes very easy. The energy of Eu^{3+} dissipates in the form of radiation in the lattice matrix, which makes the concentration quenching phenomenon happen.

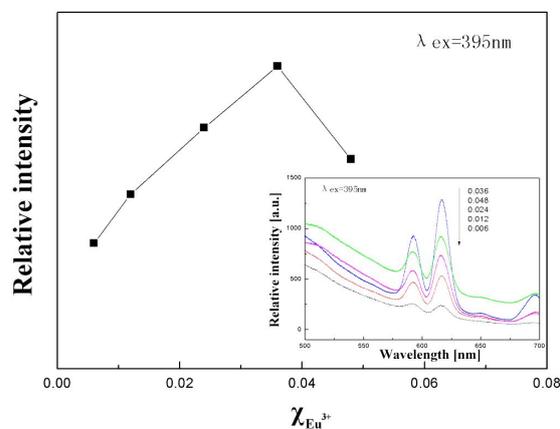


Fig. 7. The influence of Eu^{3+} concentration on luminescence intensity of KCB:Eu.

4. Conclusions

New rare earth borates KCB:Eu have been synthesized by water solution method and the crystals have been produced via spontaneous crystallization. They crystallized in orthorhombic space group $\text{P}2_12_12_1$ and had a fine shape. The sample melted at 100.9 °C and had two-step weight losses, one step lost 8 H_2O at 80 °C to 120 °C and the other lost 4 H_2O at 120 °C to 600 °C. Under

UV excitation, the Eu^{3+} doped KCB revealed a strong red-light emission peak located at about 616 nm. The results are significant to promoting research and development of hydration borate matrix in luminescent material applications.

References

- [1] HOU S., YU F.P., TANG Y.X., ZHANG S.J., ZHAO X., *IEEE T. Ultrason. Fer.*, 61 (2014), 561.
- [2] ZHANG Z.J., JIN T.T., XU M.M., HUANG Q.Z., LI M.R., ZHAO J.T., *Inorg. Chem.*, 54 (2015), 969.
- [3] YOU W.X., LAI F.Q., LIU X.L., JIANG H.H., LIAO J.S., WANG P., BIN Y., *Opt. Spectrosc.*, 116 (2014), 62.
- [4] YI X., CONG R., ZHOU Z., YANG T., *New J. Chem.*, 38 (2014), 122.
- [5] QIU X., SASAKI K., HIRAJIMA T., IGETA K., MIYAWAKI J., *Chem. Eng. J.*, 225 (2013), 664.
- [6] KURUMAJI T., OHGUSHI K., TOKURA Y., *Phys. Rev. B*, 89 (2014), 1719.
- [7] SZCZESZAK A., GRZYB T., BARSZCZ B., NAGIRNYI V., KOTLOV A., LIS S., *Inorg. Chem.*, 52 (2013), 4934.
- [8] SHUBHAM S., APARNA M., NIROJ K.S., SHANTANU K., BIBHUTI B., *RSC Adv.*, 15 (2015), 11009.
- [9] ÇELİK G., KURTULUS F., *Acta Phys. Pol. A*, 125 (2014), 325.
- [10] CHEN W.P., ZHOU A.H., *J. Phys. Chem. C*, 116 (2012), 24748.
- [11] SONG W., HUANG G., DAI R., WANG Z., ZHANG Z., *J. Chem. Mater. C*, 10 (2015), 2405.
- [12] XIE X.D., ZHENG J.P., LIU L.B., *Borate minerals*, Science Press, Beijing, 1965.
- [13] LIU J.P., LI Y.Y., HUANG X.T., LI Z.K., LI G.Y., ZENG H.B., *Chem. Mater.*, 20 (2008), 250.
- [14] HUANG H.S., LIU ZH., *Acta Chim. Sinica*, 70 (2012), 247.
- [15] WANG Z., JING Q., ZHANG M., PAN S., YANG Z., ZHANG H., *Inorg. Chem. Commun.*, 49 (2014), 63.
- [16] SAHARE P.D., SINGH M., KUMAR P., *J. Lumin.*, 160 (2015), 158.
- [17] BAI X.Y., ZHANG G.C., FU P.Z., *J. Solid State Chem.*, 180 (2007), 1792.
- [18] WANG Z.J., LIU H.Y., ZANG K., *Chinese J. Lumin.*, 31 (2010), 49.
- [19] SONG L.M., GAO J.H., YANG X.H., HUANG X.W., LIU G.Q., *Chinese J. Struct. Chem.*, 29 (2010), 1309.
- [20] YANG Z.P., SONG Z.F., MA X., WANG H.F., GUO Y.N., WEN J.W., *Chinese J. Lumin.*, 31 (2010), 724.
- [21] HUANG H.S., CHEN Z.S., LIU ZH., *Thermochim. Acta*, 459 (2007), 130.

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