Enhancement of green emission by the codoping A^+ (A = Li, Na, K) in $Ca_2BO_3Cl:Tb^{3+}$ phosphor*

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Tb^{3+}-doped Ca_2BO_3Cl compounds with different charge compensation approaches are synthesized by a high-temperature solid-state reaction method, and the luminescent properties and Commission Internationale de l'Eclairage (CIE) chromaticity coordinates are systematically characterized. $Ca_2BO_3Cl:Tb^{3+}$ can produce green emission under 376 nm radiation excitation. With codoped A^+ (A = Li, Na, K) as charge compensators, the relative emission intensities of $Ca_2BO_3Cl:Tb^{3+}$ are enhanced by about 1.61, 1.97, and 1.81 times compared with those of the direct charge balance, which is considered to be due to the effect of the difference in ion radius on the crystal field. The CIE chromaticity coordinates of $Ca_2BO_3Cl:Tb^{3+}$, A^+ (A = Li, Na, K) are (0.335, 0.584), (0.335, 0.585), and (0.335, 0.585), corresponding to the hues of green. Therefore, A^+ (A = Li, Na, K) may be the optimal charge compensator for $Ca_2BO_3Cl:Tb^{3+}$.

Keywords: luminescence, $Ca_2BO_3Cl:Tb^{3+}$, A^+ (A = Li, Na, K)

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1. Introduction

White light-emitting diodes (w-LEDs) are considered as a new generation of green and energy saving light source, owing to their small solid volume and strong ability to endure serious shock with high reliability. For this reason, many efforts have been made to replace incandescent and fluorescent lamps with w-LEDs.[1–3] However, commercial w-LEDs made by combining a blue LED chip with a yellow-emitting phosphor, YAG:Ce, have less satisfactory color rendering in the red region, and a red compensating phosphor must therefore be introduced.[4] Moreover, w-LEDs can be achieved by combining an ultraviolet or near-ultraviolet (n-UV) (350 nm–420 nm) LED chip with tri-color phosphors or a single-phase white light-emitting phosphor.[5–9] The strategy of using w-LEDs has the following advantages: the white color is generated by phosphors, so there is a high tolerance to UV chip color variation and an excellent color rendering index. Consequently, there is an urgent need to develop some new tri-color phosphors or white light-emitting phosphors that can be coupled well with UV or n-UV chips. To find the novel green-emitting phosphors, terbium is mostly used as an activator because of its strong green emission that originates from the $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+}.[10] In general, the phosphor consists of an activator and a host. In order to obtain efficient green emission, the host is another key factor, and therefore must have excellent physical and chemical stability.

Recently, chloroborate compounds have been widely utilized as excellent host materials for the rare earth-ion-doped phosphors. Much increasing attention has been focused on the development of luminescent materials based on chloroborate compounds.[11,22] Moreover, the luminescent properties of some phosphors can be improved by co-doped alkali metals.[23–25] Therefore, in the present paper, green-emitting phosphor $Ca_2BO_3Cl:Tb^{3+}$ compounds are synthesized by the solid-state reaction in air with codoping alkali metals A^+ (A = Li, Na, K), and their luminescent properties are investigated. The results may be beneficial to the study of green-emitting phosphors for white LEDs.

2. Experiment

A series of $Ca_2BO_3Cl:Tb^{3+}$ and $Ca_2BO_3Cl:Tb^{3+}$, A^+ (A = Li, Na, K) phosphors are synthesized by a high-temperature solid-state method. The starting materials, Tb_4O_7 (99.99%), $CaCO_3$, $CaCl_2$, H_3BO_3, Li_2CO_3, Na_2CO_3, and K_2CO_3 (all materials are of analytical grade), are weighed, and then blended and milled thoroughly in an agate mortar. The mixed powders are put into an alumina crucible and calcined in a muffle furnace at 900 °C for 2.5 h. Finally, the samples are cooled down to room temperature and ground thoroughly

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again into powder. The samples are sieved under the same conditions to ensure a similar particle size distribution.

The crystalline phases of the samples are characterized by powder X-ray diffraction spectroscopy (XRD6000 Shimadzu) with CuK.α ($\lambda = 0.15406$ nm) radiation operating at 40 kV and 40 mA, and the XRD patterns are recorded in a range of $10^\circ \leq 2\theta \leq 60^\circ$. The excitation and excitation spectra are measured by a Hitachi F-4600 fluorescence spectrophotometer equipped with a 450 W Xe lamp. The Commission International de l'Eclairage (CIE) chromaticity coordinate values are measured by the PMS-80 UV-VIS-NEAR IR Spectrorphotocolorimeter. All the measurements are performed at room temperature.

3. Results and discussion

3.1. The crystal structure of $Ca_2BO_3Cl:Tb^{3+}$, A^+ (A = Li, Na, K)

The X-ray diffraction patterns for $Ca_2BO_3Cl:Tb^{3+}$ and $Ca_2BO_3Cl:Tb^{3+}$, A^+ (A = Li, Na, K) are measured, and a similar diffraction pattern is observed for each sample. As a representative, figure 1 shows the XRD patterns of $CaBO_3Cl:5\%Tb^{3+}$, $5\%A^+$. Comparing the measured data with the standard Joint Committee of Powder Diffraction Standard (JCPDS) card (No. 29-0302) of Ca_2BO_3Cl, the unchanged diffraction pattern indicates that a small amount of impurity has almost no influence on the crystalline structure of Ca_2BO_3Cl. Ca_2BO_3Cl has a monoclinic crystal structure with a space group of $P2_{1/}c$ (14), and the lattice parameters are $a = 0.3948$ nm, $b = 0.8692$ nm, and $c = 1.2402$ nm.

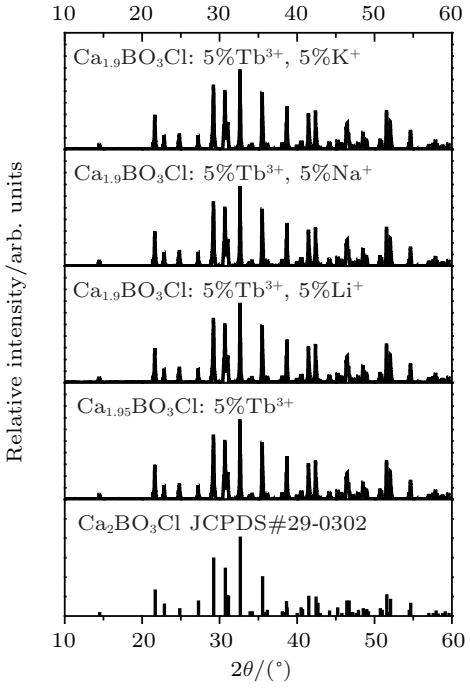


Fig. 1. The X-ray diffraction patterns of $Ca_2BO_3Cl:5\%Tb^{3+}$ and $Ca_2BO_3Cl:5\%Tb^{3+}$, $5\%A^+$ (A = Li, Na, K) with the standard data of Ca_2BO_3Cl (JCPDS No. 29-0302).

For the Ca_2BO_3Cl crystal lattice, the structure consists of Ca^{2+}, Cl^-, and BO_3^{3-} ions. The Ca atoms occupy the sites with two types of seven-fold coordinations ($CaCl_3O_4$ and $CaCl_2O_5$). Each O atom is surrounded by three Ca atoms, one B atom is surrounded by three Ca atoms, one B atom is in the form of a distorted tetrahedral, and the Cl atoms are always situated at the corners of the trigonal base.[26] As is well known, the ionic radii of Tb^{3+} ($r_{Tb} = 0.092$ nm) and A^+ (A = Li, Na, K; $r_{Li} = 0.059$ nm, $r_{Na} = 0.124$ nm, $r_K = 0.138$ nm) are close to that of Ca^{2+} ($r_{Ca} = 0.100$ nm). The three coordinated B^{3+} ($r_B = 0.027$ nm) sites are too small for Tb^{3+} or A^+ to be occupied. Based on the effective ionic radii of cations with different coordination numbers, it is assumed that Tb^{3+} and A^+ ions are preferable to replace the Ca^{2+} ions. Generally, when a metal cation is substituted for an ion with a different valence in the host lattice, the charge compensator, such as Li^+, Na^+ or K^+, is employed to keep the charge balance. The charge compensation in the above mentioned structure is most likely to be described by two possible mechanisms: (i) two Ca^{2+} ions are replaced by one Tb^{3+} ion and one alkaline cation, $2Ca^{2+} \rightarrow Tb^{3+} + A^+$, where A^+ is an alkaline cation like Li^+, Na^+, and K^+; (ii) the charge compensation is proved by a calcium vacancy, $3Ca^{2+} \rightarrow 2Tb^{3+} + V_{Ca}$. Therefore, Tb^{3+} and A^+-codoped Ca_2BO_3Cl may induce a lattice distortion.[23]

The crystal unit cell parameters can be calculated by using the XRD data with Jade 5.0 software, and the corresponding cell constants and unit cell volumes of the samples are summarized in Table 1. The increases in the cell constants and unit cell volumes are possibly ascribed to the fact that the ionic radii of Na^+ and K^+ are larger than that of Ca^{2+}. On the contrary, the cell constants and unit cell volumes of the samples each have a slight decline when the Li^+ ions are added as the charge compensator, because the ionic radius of Li^+ is smaller than that of Ca^{2+}. In general, the doped Tb^{3+} and alkaline ions are randomly distributed in the cation (Ca^{2+}) sites of the host. The cations with different radii in the host compound can lead to some distortions of the sub-lattice structure around the luminescent center ions, thereby producing different luminescent properties.[27]

Table 1. The calculated unit cell parameters of the samples.

Samples	a/nm	b/nm	c/nm	V/nm^3
Ca_2BO_3Cl	0.3948	0.8692	1.2402	0.4188
$Ca_2BO_3Cl:5\%Tb^{3+}$	0.3946	0.8687	1.2401	0.4183
$Ca_2BO_3Cl:5\%Tb^{3+}$, $5\%Li^+$	0.3942	0.8681	1.2397	0.4175
$Ca_2BO_3Cl:5\%Tb^{3+}$, $5\%Na^+$	0.3951	0.8689	1.2411	0.4193
$Ca_2BO_3Cl:5\%Tb^{3+}$, $5\%K^+$	0.3954	0.8691	1.2414	0.4198

3.2. The luminescent properties of $Ca_2BO_3Cl:Tb^{3+}$, A^+ (A = Li, Na, K)

Our previous results show that with the increase in Tb^{3+} doping content, the emission intensity of $Ca_2BO_3Cl:Tb^{3+}$ is gradually enhanced and reaches a maximal value at $x =$ 5 mol% Tb^{3+}, and then gradually decreases. This is usually due to the fact that internal concentration quenching occurs when the Tb^{3+} concentration is higher than $x = 5$ mol%. Therefore, the Tb^{3+}-doped content is fixed at $x = 5$ mol%.[22]

Figure 2 shows the emission spectra of $Ca_2BO_3Cl:Tb^{3+}$ and $Ca_2BO_3Cl:Tb^{3+}$, A^+ (A = Li, Na, K) under 376 nm radiation excitation. As shown in Fig. 2, for all the samples, no difference can be observed in the sharp emission band and position under the same radiation excitation, except for the emission intensity. As a representative, figure 2 shows that the emission spectrum of $Ca_2BO_3Cl:5\%Tb^{3+}$ has emission peaks at 487, 545, 589, and 625 nm, which are assigned to the $^5D_4$-to-$^7F_{J(J=6,5,4,3)}$ transitions of Tb^{3+}, respectively, and the strongest emission peak located at 545 nm corresponds to the $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+}.[10] The inset of Fig. 2 shows the luminescence photograph under 365 nm ultraviolet light.

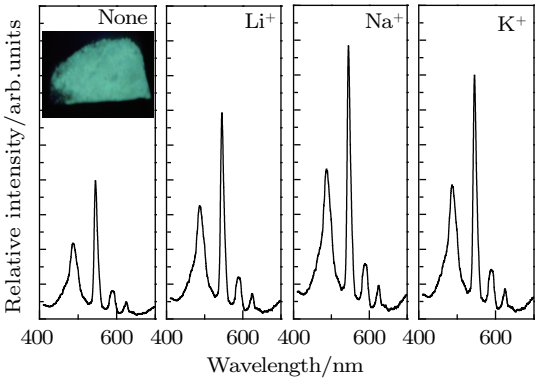


Fig. 2. (color online) The emission spectra of $Ca_2BO_3Cl:5\%Tb^{3+}$ and $Ca_2BO_3Cl:5\%Tb^{3+}$, $5\%A^+$ (A = Li, Na, K) (λ_{ex} = 376 nm). The inset shows the luminescence photograph of $Ca_2BO_3Cl:5\%Tb^{3+}$.

For the 545-nm emission of the samples, the excitation spectra are shown in Fig. 3. It is easy to notice that all the samples exhibit similar peaks, which consist of several narrow lines in a range of 300 nm–400 nm and a broad band at 280 nm. The broad band is attributed to the spin-allowed transition from the 4f to 5d state of Tb^{3+}, the sharp lines correspond to the absorption due to the forbidden f–f of Tb^{3+}, and the strongest peak is located at 376 nm. However, an obvious difference can be found between $Ca_2BO_3Cl:Tb^{3+}$ and $Ca_2BO_3Cl:Tb^{3+}$, A^+ by carefully analyzing the excitation spectra of all the samples. One evident difference is the relative intensities of the as-prepared phosphors with different charge compensators. The relative intensities of the excitation spectra first increase, and then decrease with the increasing ionic radii of the alkali metal ions ($Li^+ < Na^+ < K^+$). The result is assumed to be caused by the different ion radii of A^+ (one Tb^{3+} and A^+ ion replacing two Ca^{2+} ions), which may distort the sub-lattice structure around the luminescent center ions. This deduction is in good agreement with the cell constants and unit cell volume of the samples in Table 1. Indeed, the difference between ion radii would modify the sub-lattice structure around the luminescent center ions. For $Ca_2BO_3Cl:Tb^{3+}$, the doped Tb^{3+} and alkaline ions are randomly distributed at the cation (Ca^{2+}) sites of the host. When the alkali metal ions are co-doped in $Ca_2BO_3Cl:Tb^{3+}$, the coordination conditions for Tb^{3+} will be influenced. Hence the relative excitation and emission intensity of $Ca_2BO_3Cl:Tb^{3+}$ will vary, with the difference in the alkali metal ion serving as the charge compensator.

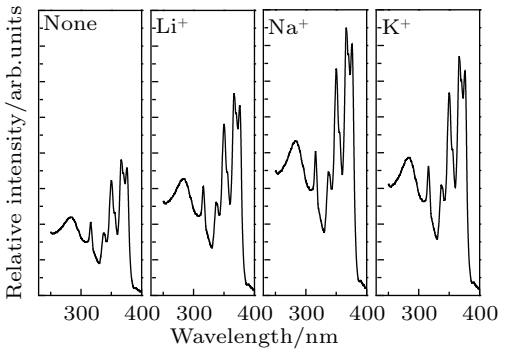


Fig. 3. The excitation spectra of $Ca_2BO_3Cl:5\%Tb^{3+}$ and $Ca_2BO_3Cl:5\%Tb^{3+}$, $5\%A^+$ (A = Li, Na, K) (λ_{em} = 545 nm).

In order to investigate the influence of the charge compensation on the luminescent property of phosphor, and obtain the ideal results, the charge compensation A^+ (A = Li, Na, K) is introduced into the procedure of synthesizing the $Ca_2BO_3Cl:Tb^{3+}$ phosphor. With the charge compensation A^+, the $^5D_4 \rightarrow {}^7F_5$ (545 nm) relative emission intensities of $Ca_2BO_3Cl:Tb^{3+}$ are shown in Fig. 4. The results show that the emission intensity can be changed by adjusting the category and doping content of the alkali carbonate. With co-doping Li^+, Na^+, and K^+, the normalized intensities of $Ca_2BO_3Cl:Tb^{3+}$ are 1.61, 1.97, and 1.81, respectively.

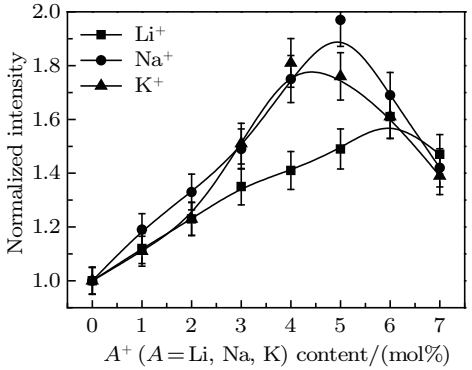


Fig. 4. The normalized intensities of $Ca_2BO_3Cl:Tb^{3+}$, with alkali carbonates (A) serving as the charge compensation (A^+) (λ_{ex} = 376 nm).

Generally, a trivalent metallic ion such as Tb^{3+} is incorporated into the host lattice, which may substituted by a divalent metallic ion. The charge balancing is a necessary requirement of co-doped alkali metal ions.[23–25] For $Ca_2BO_3Cl:Tb^{3+}$ and $Ca_2BO_3Cl:Tb^{3+}$, A^+ (A = Li, Na, K), one Tb^{3+} ion is expected to replace one Ca^{2+} ion, with the other sites occupied by a calcium vacancy (V_{Ca}) or alkali metal ions A^+ (A = Li, Na, K). As a result, the phosphor with efficient charge compensation exhibits higher green emission. Our results are in agreement with some of the previous results related to charge compensation in rare earth-ion-doped phosphors.[23–25]

The CIE 1931 chromaticity coordinates of the $Ca_2BO_3Cl:Tb^{3+}$ and $Ca_2BO_3Cl:Tb^{3+}$, A^+ (A = Li, Na, K) phosphors are measured and shown in Table 2. The CIE chromaticity coordinates of $Ca_2BO_3Cl:Tb^{3+}$ and $Ca_2BO_3Cl:Tb^{3+}$, A^+ (A = Li, Na, K) are (0.335, 0.584), (0.335, 0.584), (0.335, 0.585), and (0.335, 0.585), which correspond to the hues of green. The results indicate that $Ca_2BO_3Cl:Tb^{3+}$, A^+ may have promising application as the green-emitting phosphor in white LEDs.

Table 2. The CIE chromaticity coordinates of the samples.

Samples	Ca_2BO_3Cl:5%Tb^{3+}	Ca_2BO_3Cl:5%Tb^{3+}, 5%Li^+	Ca_2BO_3Cl:5%Tb^{3+}, 5%Na^+	Ca_2BO_3Cl:5%Tb^{3+}, 5%K^+
(x, y)	(0.335, 0.584)	(0.335, 0.584)	(0.335, 0.585)	(0.335, 0.585)

4. Conclusions

In this paper, we synthesized the green-emitting phosphor $Ca_2BO_3Cl:Tb^{3+}$ by using the solid-state method. Two approaches to achieving the charge compensation are attempted: (I) $2Ca^{2+} \rightarrow Tb^{3+} + A^+$ (A = Li, Na, and K); and (II) $3Ca^{2+} \rightarrow 2Tb^{3+} + V_{Ca}$. The luminescent intensity of the $Ca_2BO_3Cl:Tb^{3+}$ phosphor can be obviously enhanced by co-doping the charge compensator, and the samples show the characteristic green emissions of Tb^{3+} ions with good CIE chromaticity coordinates. By using the charge compensator Na^+, the phosphor has the strongest emission intensity, and is about 1.97 times stronger than that of the direct charge balance. Hence, Na^+ may be an optimal charge compensator for $Ca_2BO_3Cl:Tb^{3+}$.

References

[1] Schubert E F and Kim J K 2005 *Science* **308** 1274
[2] Lin C C and Liu R S 2011 *J. Phys. Chem. Lett.* **2** 1268
[3] Lin C C, Xiao Z R, Guo G Y, Chan T S and Liu R S 2010 *J. Am. Chem. Soc.* **132** 3020
[4] Brinkley S E, Pfaff N, Denault K A, Zhang Z, (Bert) Hintzen H T, Seshadri R, Nakamura S and DenBaars S P 2011 *Appl. Phys. Lett.* **99** 241106
[5] Sun J, Zhang X, Xia Z and Du H 2012 *J. Appl. Phys.* **111** 013101
[6] Li G, Zhang Y, Geng D, Shang M, Peng C, Cheng Z and Lin J 2012 *ACS Appl. Mater. & Interfaces* **4** 296
[7] Shang M, Li G, Geng D, Yang D, Kang X, Zhang Y, Lian H and Lin J 2012 *J. Phys. Chem. C* **116** 10222
[8] Huang C H and Chen T M 2011 *J. Phys. Chem. C* **115** 2349
[9] Yu J, Hao Z, Zhang X, Luo Y, Wang X and Zhang J 2012 *J. Electrochem. Soc.* **159** F56
[10] Yoo H S, Im W B, Kang J H and Jeon D Y 2008 *Opt. Mater.* **31** 131
[11] Zhang Q, Wang J, Zhang G and Su Q 2009 *J. Mater. Chem.* **19** 7088
[12] Han B, Zhang J, Cui Q and Liu Y 2012 *Physica B* **407** 3484
[13] Yang Z, Wang S, Yang G, Tian J, Li P and Li X 2007 *Mater. Lett.* **61** 5258
[14] Zhang X, Zhang J, Dong Z, Shi J and Gong M 2012 *J. Lumin.* **132** 914
[15] Xia Z, Liao L, Zhang Z and Wang Y 2012 *Mater. Res. Bull.* **47** 405
[16] Liu H, Xia Z, Zhuang J, Zhang Z and Liao L 2012 *J. Phys. Chem. Solids* **73** 104
[17] Guo C, Luan L, Shi L and Seo H J 2010 *Electrochem. Solid-State Lett.* **13** J28
[18] Li P, Xu Z, Zhao S, Zhang F and Wang Y 2012 *Mater. Res. Bull.* **47** 3825
[19] Guo C, Luan L, Shi F G and Ding X 2009 *J. Electrochem. Soc.* **156** J125
[20] Li P L, Xu Z, Zhao S L, Zhang F J and Wang Y S 2012 *Chin. Phys. B* **21** 047803
[21] Xiao F, Xue Y N and Zhang Q Y 2009 *Physica B* **404** 3743
[22] Li P L, Wang Y S, Zhao S L, Zhang F J and Xu Z 2012 *Chin. Phys. B* **21** 127804
[23] Yang F, Liang Y, Liu M, Li X, Wang N and Xia Z 2012 *Ceram. Int.* **38** 6197
[24] Mu Z, Hu Y, Chen L and Wang X 2011 *J. Electrochem. Soc.* **158** J287
[25] Yan X, Li W and Sun K 2010 *J. Alloys Compd.* **508** 475
[26] Zak Z and Hanic F 1976 *Acta Crystallographica Section B* **32** 1784
[27] Van Vliet J P M, Blasse G and Brixner L H 1988 *J. Solid State Chem.* **76** 160