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Enhanced red-emitting by charge compensation in Eu^{3+}-activated Ca_2BO_3Cl phosphors

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Abstract

Eu^{3+}-activated Ca_2BO_3Cl with different charge compensation approaches were synthesized by the solid state reaction method, and systematically characterized by photoluminescence excitation and emission spectra, concentration quenching and CIE 1931 chromaticity coordinates at room temperature. All the samples show the characteristic red emission of Eu^{3+} ions with good CIE chromaticity coordinates. The relative emission intensities of Eu^{3+} ($^5D_0 \rightarrow {}^7F_2$) in $Ca_2BO_3Cl:Eu^{3+}$ phosphors with Li, Na, K introduced as charge compensators are enhanced about 2.1, 1.6 and 1.5 times than that of direct charge balanced. Such difference is considered to be due to the different ion radii effect on the spin–orbit couplings and crystal field of Eu^{3+} ions. These results show that $Ca_{2-1.5x}BO_3Cl:Eu_x^{3+}$ and $Ca_{2-2x}BO_3Cl$, Eu_x^{3+}, M_x^+ ($x=0.04$, $M=$Li, Na, K) phosphors exhibit potential applications in the field of solid state illumination.

Keywords: Photoluminescence; Charge compensation; Europium ions; Ca_2BO_3Cl

1. Introduction

The red luminescence of Eu^{3+} ions has been extensively studied as an activator ion because of its distinct 4f–4f transitions. The f-electrons of Eu^{3+} ions are well shielded from the chemical environment and own almost retained atomic character [1,2]. In consequence, Eu^{3+} ions have been used in most commercial red phosphors. Currently, the mainly commercial red phosphor is $Y_2O_2S:Eu^{3+}$ which shows chemical instability and low absorption efficiency in the near ultraviolet region [3,4]. So the search for new red phosphors with chemical stability and high photoluminescence efficiency is an attractive and challenging task.

Borates have been extensively investigated due to their high thermal, chemical stability and strong absorption in the near ultraviolet region. Rare earth doped borate phosphors have considerable practical applications in various devices such as solid-state lasers, optical communication, plasma display panel (PDP) and light-emitting diode (LED) [5–8]. The crystal structure of Ca_2BO_3Cl was first reported by Zak and Hanic [9] in 1976. Until recently, photoluminescence properties of rare earth doped Ca_2BO_3Cl phosphors such as $Ca_2BO_3Cl:Eu^{2+}$ [10], $Ca_2BO_3Cl:Ce^{3+}$ [11] and $Ca_2BO_3Cl:Eu^{2+}$, Ce^{3+} [12,13] have been investigated by many researchers. However, to the best of our knowledge, there is no report devoted to the photoluminescence properties of Eu^{3+}-activated Ca_2BO_3Cl phosphors until now. Generally, when a metal ion is substituted for an element with a different valency in the matrix, the charge compensator is needed by using ions such as Li^+, Na^+ or K^+ [14]. In 2007, J. Liu et al. [15] investigated photoluminescence by charge compensation in the phosphor system $CaMoO_4:Eu^{3+}$ and found that the efficient charge compensator can enhance the luminescence intensity. Subsequently, S.K. Shi et al. [16] have studied the effects of charge compensation on the luminescence behavior of Eu^{3+}-activated $CaWO_4$ phosphors. Additionally, S. Choi et al. [17] discussed the luminescence properties by the addition of charge compensators in red-emitting Eu^{3+}-activated $Ca_3Sr_3(VO_4)_4$.

In this work, $Ca_2BO_3Cl:Eu^{3+}$ phosphors were firstly prepared by our group. In order to enhance the luminescence

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intensity of the phosphors, different charge compensation approaches were applied in $Ca_2BO_3Cl:Eu^{3+}$. The effects of charge compensation on the luminescence properties have also been systematically discussed. Furthermore, the performance of the phosphors has also been compared with the commercial red phosphor $Y_2O_2S:Eu^{3+}$. The results indicate that Eu^{3+}-activated Ca_2BO_3Cl is a promising red phosphor for solid state illumination.

2. Experimental

A series of Eu^{3+}-activated Ca_2BO_3Cl powder samples were synthesized by the conventional solid state reaction. $CaCO_3$ (99.9%), $CaCl_2$ (99.9%), Eu_2O_3 (99.99%) and H_3BO_3 (A.R) were used as raw materials. The stoichiometric amounts of starting materials were weighted and thoroughly mixed in an agate mortar; the mixtures were then put in an alumina crucible and calcined at 900 °C for 4 h in air. In some cases, appropriate amount of Li_2CO_3 (99.9%), Na_2CO_3 (99.9%) or K_2CO_3 (99.9%) was added as the charge compensator. Stoichiometric amounts of Y_2O_3 (99.99%), elemental sulfur (S) (99.9%), Eu_2O_3 (99.99%) and the flux Na_2CO_3 (99.9%) were intimately ground and heated at 1100 °C in a reduced atmosphere for 2 h according to Ref. [18].

The crystal structure of the phosphors were characterized by X-ray powder diffractometer (XRD) (Bruker D8 Focus) with Cu-kα ($\lambda = 1.540598$ Å) radiation at 40 kV and 40 mA. The lattice parameters of the phosphors are calculated by the MDI Jade 5.0 software which is based on least-square method. Excitation and emission spectra were measured by the fluorescence spectrometer (FLUOROMAX-4) with a xenon lamp. All the measurements were carried out at room temperature.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of $Ca_{2-1.5x}BO_3Cl:Eu_x^{3+}$ and $Ca_{2-2x}BO_3Cl:Eu_x^{3+}$, M_x^+ ($x=0.04$, $M=$Li, Na, K). Obviously, all the samples exhibit similar diffraction peaks and match well with the single phase Ca_2BO_3Cl (JCPDS no. 29-0302), which belongs to monoclinic structure with space group $P2_1/c$. The minor difference is only the relative intensity of characteristic diffraction peaks due to the doped Eu^{3+} ions and the charge compensators, which does not affect phase identification.

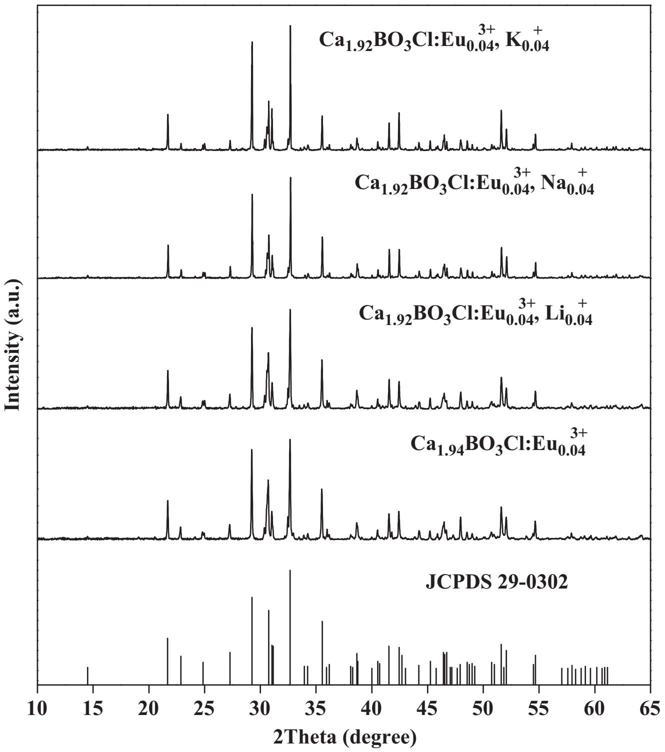

Fig. 1. The XRD patterns of $Ca_{2-1.5x}BO_3Cl:Eu_x^{3+}$ $Ca_{2-2x}BO_3Cl:Eu_x^{3+}$, M_x^+ ($x=0.04$, $M=$Li, Na, K) and standard card of Ca_2BO_3Cl (JCPDS 29-0302).

In Ca_2BO_3Cl crystal lattice, the structure consists of Ca^{2+}, Cl^- and BO_3^{3-} ions arranged in distinct. Ca atoms occupy the sites with two types of seven-fold coordination ($CaCl_3O_4$ and $CaCl_2O_5$), each O atom is surrounded by three Ca atoms, one B atom in the form of a distorted tetrahedral and the Cl atoms are always situated at the corners of the trigonal base [9]. As we all know, both the ionic radii of Eu^{3+} ($r=0.0947$ nm) and M^+ ($M^+=Li^+$, Na^+, K^+; the ionic radii are 0.092 nm, 0.118 nm and 0.138 nm, respectively.) are close to that of Ca^{2+} ($r=0.112$ nm). The three coordinated B^{3+} ($r=0.027$ nm) sites are too small for Eu^{3+} or M^+ to occupy [19]. Based on the effective ionic radius of cations with different coordination numbers, it is assumed that Eu^{3+} and M^+ ions are preferably to replace Ca^{2+} ions. Generally, when a metal cation substitutes for an ion with different valence in host lattice, charge compensator such as Li^+, Na^+ or K^+ is employed to keep the charge balance. The charge compensation in above mentioned structure can most probably be described by two possible mechanisms: (a) two Ca^{2+} ions are replaced by one Eu^{3+} ions and one alkaline cation, $2Ca^{2+} \rightarrow Eu^{3+} + M^+$, where M^+ is an alkaline cation like Li^+, Na^+ or K^+; (b) the charge compensation is provided by a calcium vacancy, $3Ca^{2+} \rightarrow 2Eu^{3+} + V_{Ca}$. Therefore, Eu^{3+} and M^+ co-doped in Ca_2BO_3Cl matrix may induce a lattice distortion.

The corresponding cell constants and unit cell volume of the samples are summarized in Table 1. The increases of cell constants and unit cell volume are possibly assigned to the fact that the ionic radii of Na^+ ($r=0.118$ nm) and K^+ ($r=0.138$ nm) are larger than that of Ca^{2+} ($r=0.112$ nm). On the contrary, the cell constants and unit cell volume of the samples have a little 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 Eu^{3+} and alkaline ions are randomly distributed in the cation (Ca^{2+}) sites of the host. The cations with different radius in the host compound can result in some distortions of the sub-lattice structure around the luminescent center ions, hence different photoluminescence properties are produced [20].

Table 1
The calculated lattice parameters of the phosphors.

Phosphors	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)
$Ca_{1.94}BO_3Cl:Eu^{3+}_{0.04}$	3.9502	8.6814	12.4076	418.92
$Ca_{1.92}BO_3Cl:Eu^{3+}_{0.04}$, $Li^{+}_{0.04}$	3.9491	8.6810	12.4041	418.37
$Ca_{1.92}BO_3Cl:Eu^{3+}_{0.04}$, $Na^{+}_{0.04}$	3.9518	8.6830	12.4126	419.05
$Ca_{1.92}BO_3Cl:Eu^{3+}_{0.04}$, $K^{+}_{0.04}$	3.9519	8.6838	12.4139	419.42

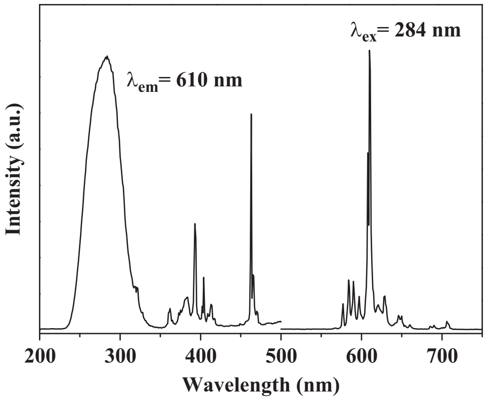

Fig. 2. Excitation (left) and emission (right) spectra of $Ca_{1.94}BO_3Cl:Eu^{3+}_{0.04}$ phosphor.

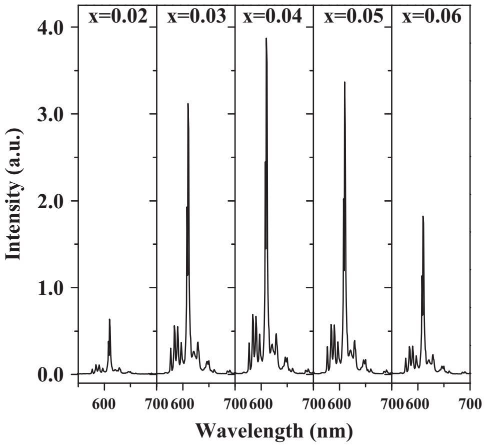

Fig. 3. Emission spectra of $Ca_{2-1.5x}BO_3Cl:Eu^{3+}_x$ phosphors with various Eu^{3+} concentrations ($\lambda_{ex}=284$ nm).

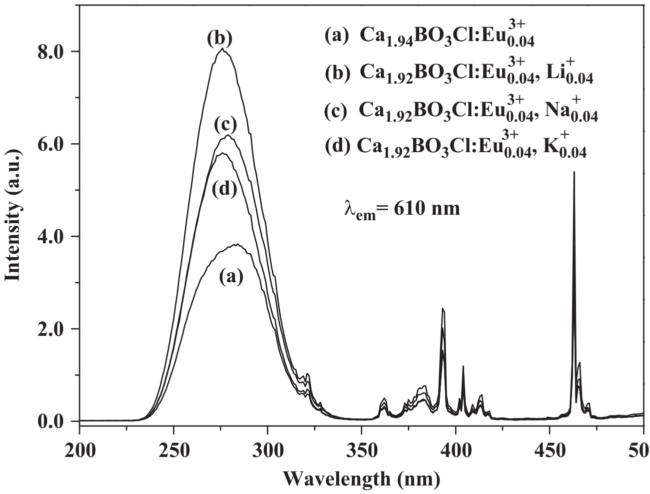

Fig. 4. Excitation spectra of $Ca_{2-1.5x}BO_3Cl:Eu^{3+}_x$ and $Ca_{2-2x}BO_3Cl:Eu^{3+}_x$, M^{+}_x ($x=0.04$, M=Li, Na, K).

The excitation and emission spectra of $Ca_{1.94}BO_3Cl:Eu^{3+}_{0.04}$ phosphor are presented in Fig. 2. The excitation spectrum monitored at 610 nm exhibits one broad band centered at 284 nm corresponded to the O–Eu charge transfer band (CTB) transition and the other sharp lines around at 396 nm and 466 nm attributed to the f–f transitions of Eu^{3+} ion. Upon excitation of 284 nm, the emission spectrum consists of five clusters of typical linear emission peaks in the range of 570–710 nm, which result from $^5D_0\rightarrow{}^7F_J$ ($J=0$, 1, 2, 3 and 4) transitions of Eu^{3+} ions, respectively. The main peak is the $^5D_0\rightarrow{}^7F_2$ transition of Eu^{3+} at 610 nm, other emission transitions from the $^5D_0$ excited levels to ^7F_J ($J=0$, 1, 3 and 4) ground states are relatively weak. It is known that the $^5D_0\rightarrow{}^7F_2$ transition assigned to the forced electron dipole transition of Eu^{3+} is hypersensitive to its local environment, which is permitted only as Eu^{3+} occupied in a low symmetry site. While the cluster of peak near 590 nm corresponds to the allowed magnetic dipole $^5D_0\rightarrow{}^7F_1$ transition of Eu^{3+}, which is located in a high symmetry site [21,22]. In $Ca_{2-1.5x}BO_3Cl:Eu^{3+}_x$ and $Ca_{2-2x}BO_3Cl:Eu^{3+}_x$, M^{3+}_X ($x=0.04$, M=Li, Na, K) host lattices, the $^5D_0\rightarrow{}^7F_2$ electric dipole transition becomes the strongest among all these $^5D_0\rightarrow{}^7F_J$ transitions due to the lack of inversion symmetry and the break of parity selection rules [21,23,24], which is advantageous for obtaining a pure red phosphor with good CIE chromaticity coordinates. The emission spectra of $Ca_{2-1.5x}BO_3Cl:Eu^{3+}_x$ phosphors with various Eu^{3+} concentrations under excitation of 284 nm are illustrated in Fig. 3. With the increase of Eu^{3+} concentration, the emission intensity has gradually enhanced and reached to the maximum at $x=0.04$, and then the emission intensity gradually decreased. This is usually due to the fact that the internal concentration quenching occurs when the Eu^{3+} concentration is higher than $x=0.04$.

Fig. 4 illustrates the excitation spectra of $Ca_{2-1.5x}BO_3Cl:Eu^{3+}_x$ and $Ca_{2-2x}BO_3Cl:Eu^{3+}_x$, M^{+}_x ($x=0.04$, M=Li, Na, K) monitored at 610 nm. It is easy to notice that all the phosphors exhibit the similar peaks. However, there are two changes between $Ca_{2-1.5x}BO_3Cl:Eu^{3+}_x$ and $Ca_{2-2x}BO_3Cl:Eu^{3+}_x$ ($x=0.04$, M=Li, Na, K) by carefully analyzing the excitation spectra of all samples. One evident change is the relative intensities of the as-prepared phosphors with different charge compensator. The relative intensities of the excitation spectra decrease with the increase of ionic radius of the alkali metal ions ($Li^+ < Na^+ < K^+$). The other minor change is the position of the CTB. It is noted that the peaks have a slightly blue shift of 2–4 nm when the charge compensators are introduced into the phosphors. Both of the phenomena are assumed to be caused by the different ion radii of M^+ (one Eu^{3+} and one M^+ 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 sample shown in Table 1. Indeed, the difference of ionic radii would modify the sub-lattice structure around the luminescent center ions, which influences the spin–orbit couplings and crystal field of Eu^{3+} ions. In $Ca_2BO_3Cl:Eu^{3+}$ phosphors, the doped Eu^{3+} and alkaline ions are randomly distributed in the cation (Ca^{2+}) sites of the host. The CTB of O–Eu is attributed to the electron transitions from an oxygen 2p orbit to an empty Eu 4f orbit. They are closely related to the couplings between the luminescent center and crystal lattice, and the couplings mainly depend on the distance from the metal ion to the ligand [25]. When alkali metal ions are co-doped in $Ca_2BO_3Cl:Eu^{3+}$, the coordination conditions for Eu^{3+} will be influenced. As a result, the distances of O–Eu could have a slight change. Furthermore, the relative intensities of excitation and emission for $Ca_2BO_3Cl:Eu^{3+}$ would vary with different alkali metal ions as charge compensator.

Fig. 5 shows the emission spectra of $Y_2O_2S:Eu^{3+}$, $Ca_{2-1.5x}BO_3Cl:Eu_x^{3+}$ and $Ca_{2-2x}BO_3Cl:Eu_x^{3+}$, M_x^+ ($x=0.04$, $M=$Li, Na, K) under excitation wavelength of 284 nm, respectively. It is obvious that the four emission spectra of Eu^{3+}-activated Ca_2BO_3Cl phosphors exhibit the similar peaks. When the M^+ ($M=$Li, Na, K) are employed as charge compensators in $Ca_{2-1.5x}BO_3Cl:Eu_x^{3+}$ phosphors, the emission intensities of $^5D_0\rightarrow{}^7F_2$ transition have remarkably increased. The relative emission intensities of the phosphors with Li, Na or K introduced as the charge compensators are enhanced about 2.1, 1.6 and 1.5 times than those direct charge balanced, respectively. Among them, the emission intensity of as-prepared phosphor with Li^+ as the charge compensator is higher than that of phosphors co-doped by Na^+, Eu^{3+} and K^+, Eu^{3+}. The reason is that Li^+ ions are easy to enter into Ca_2BO_3Cl: Eu^{3+} crystal lattice than the others, because the ionic radius of Li^+ (0.092 nm) is smaller and the ionic radius of Na^+ ($r=0.118$ nm) and K^+ ($r=0.138$ nm) are larger than that of Ca^{2+} ($r=0.112$ nm). Currently, $Y_2O_2S:Eu^{3+}$ is reported to be the main commercial red phosphor. For future comparison of photoluminescence spectra of Eu^{3+}-activated Ca_2BO_3Cl with $Y_2O_2S:Eu^{3+}$, we prepare $Y_2O_2S:Eu^{3+}$ phosphor according to the results reported by K.R. Reddy et al. [18]. The emission spectrum of $Y_2O_2S:Eu^{3+}$ under excitation wavelength of 284 nm is also shown in Fig. 5. The emission intensity of $Y_2O_2S:Eu^{3+}$ is higher than that of $Ca_{2-1.5x}BO_3Cl:Eu_x^{3+}$, but lower than that of $Ca_{2-2x}BO_3Cl:Eu_x^{3+}$, M_x^+ ($x=0.04$, $M=$Li, Na, K). The emission intensities of $Ca_{2-2x}BO_3Cl:Eu_x^{3+}$, M_x^+ ($x=0.04$, $M=$Li, Na, K) are about 1.8, 1.4 and 1.3 times than that of the commercial $Y_2O_2S:Eu^{3+}$ phosphor, respectively.

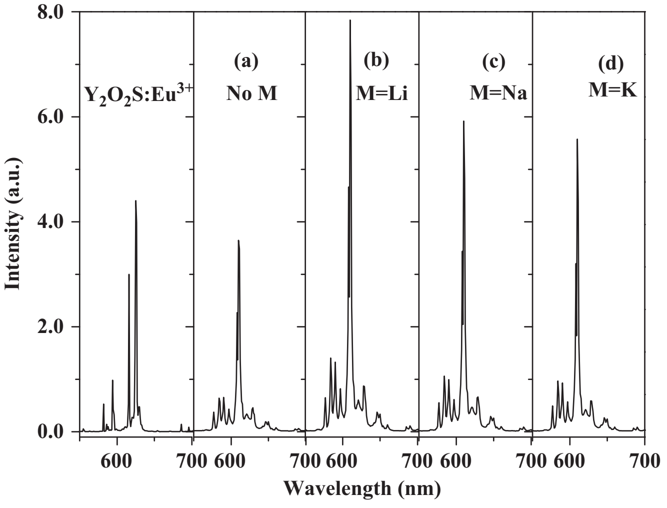

Fig. 5. Emission spectra of $Ca_{2-1.5x}BO_3Cl:Eu_x^{3+}$, $Ca_{2-2x}BO_3Cl:Eu_x^{3+}$, M_x^+ ($x=0.04$, $M=$Li, Na, K) and $Y_2O_2S:Eu^{3+}$ ($\lambda_{ex}=284$ nm).

In general, when a trivalent metallic ion, such as Eu^{3+}, is incorporated into a host lattice and substituted by a divalent metallic ion, the charge balancing is necessarily required by co-dopeding alkali metal ions [14]. In the charge compensated phosphors $Ca_{2-1.5x}BO_3Cl:Eu_x^{3+}$ and $Ca_{2-2x}BO_3Cl:Eu_x^{3+}$, M_x^+ ($x=0.04$, $M=$Li, Na, K), one Eu^{3+} ion is expected to replace one Ca^{2+} ion, the other sites are occupied by calcium vacancy (V_{Ca}) or alkali metal ions ($M=$Li, Na, K). As above mentioned, the energy absorbed from the charge-transfer state is more efficient than that of calcium vacancy (V_{Ca}) due to the positive change of coordination conditions of Eu^{3+} after alkali metal ions are added. In consequence, the phosphors with efficient charge compensation exhibit higher red-light emission. Some previous works have been reported the studies related to charge compensation in Eu^{3+} doped tungstate and molybdate phosphors [15,16], our results are in good agreement with them.

The CIE 1931 chromaticity coordinates of $Y_2O_2S:Eu^{3+}$, $Ca_{2-1.5x}BO_3Cl:Eu_x^{3+}$ and $Ca_{2-2x}BO_3Cl:Eu_x^{3+}$, M_x^+ ($x=0.04$, $M=$Li, Na, K) phosphors which were calculated based on the corresponding emission spectra are represented in Fig. 6, respectively. The CIE chromaticity coordinates of $Y_2O_2S:Eu^{3+}$, $Ca_{2-1.5x}BO_3Cl:Eu_x^{3+}$ and $Ca_{2-2x}BO_3Cl:Eu_x^{3+}$, M_x^+ ($x=0.04$, $M=$Li, Na, K) are (0.641, 0.335), (0.599, 0.352), (0.615, 0.355), (0.611, 0.347) and (0.619, 0.349) corresponding to hues of reddish orange. It can be observed that the CIE coordinates of the samples $Ca_{2-2x}BO_3Cl:Eu_x^{3+}$, M_X^+ ($x=0.04$, $M=$Li, Na, K) are quite close to the NTSC standard values ($x=0.67$, $y=0.33$). The results indicate that $Ca_{2-2x}BO_3Cl:Eu_x^{3+}$, M_x^+ ($x=0.04$, $M=$Li, Na, K) phosphors have promising applications as the red luminescent materials in solid-state illumination.

4. Conclusions

In summary, Eu^{3+}-activated Ca_2BO_3Cl with different charge compensator were synthesized by the solid state reaction method, and their photoluminescence properties were investigated. Two approaches to achieve the charge compensation are tried: (a) $2Ca^{2+}\rightarrow Eu^{3+}+M^+$, where M^+ is a alkaline cation like Li^+, Na^+ or K^+; (b)

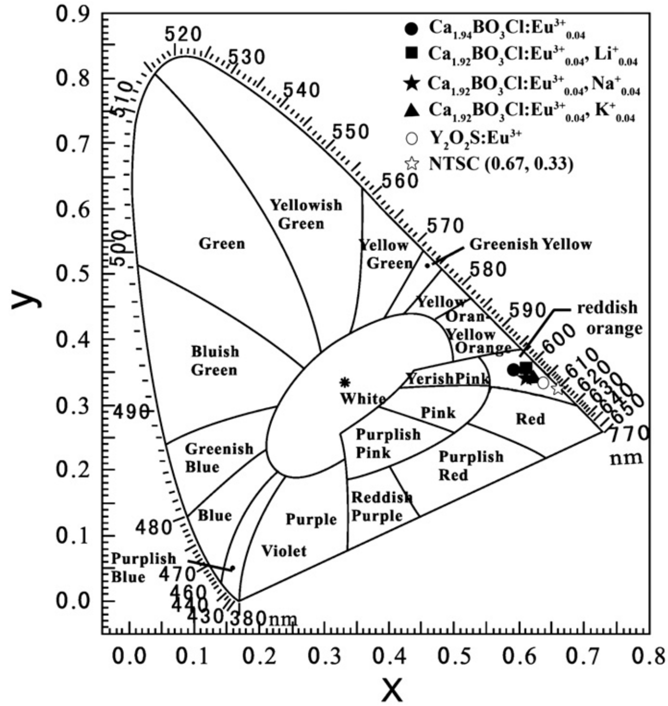

Fig. 6. The CIE 1931 chromaticity coordinates of $Ca_{2-1.5x}BO_3Cl:Eu_x^{3+}$ $Ca_{2-2x}BO_3Cl:Eu_x^{3+}$, M_x^+ (x=0.04, M=Li, Na, K) and $Y_2O_2S:Eu^{3+}$.

$3Ca^{2+} \rightarrow 2Eu^{3+} + V_{Ca}$. All the samples show the characteristic red emission of Eu^{3+} ions with good CIE chromaticity coordinates. The phosphors added alkaline cations as the charge compensator can significantly enhance luminescence intensity of Eu^{3+} ($^5D_0 \rightarrow {}^7F_2$) in $Ca_2BO_3Cl:Eu^{3+}$. The phosphor with Li^+ as the charge compensator exhibits the strongest emission intensity, about 2.1 times higher than that of direct charge balanced. In the meantime, The phosphor added Li^+ ions shows better emission than that of the current commercial red phosphor $Y_2O_2S:Eu^{3+}$ and about 1.8 times as high as $Y_2O_2S:Eu^{3+}$. Therefore, $Ca_2BO_3Cl:Eu^{3+}$ phosphors with charge compensation may become the substitutes of current commercially red emitting phosphors.

Acknowledgments

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