$Ca_2BO_3Cl:Ce^{3+}$, Tb^{3+}: A novel tunable emitting phosphor for white light-emitting diode*

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$Ca_2BO_3Cl:Ce^{3+}$, $Ca_2BO_3Cl:Tb^{3+}$, and $Ca_2BO_3Cl:Ce^{3+}$, Tb^{3+} phosphors are synthesized by a high temperature solid-state reaction. The emission intensity of Ce^{3+} or Tb^{3+} in Ca_2BO_3Cl is influenced by the Ce^{3+} or Tb^{3+} doping content, and the optimum concentrations of Ce^{3+} and Tb^{3+} are 0.03 mol and 0.05 mol, respectively. The concentration quenching effect of Ce^{3+} or Tb^{3+} in Ca_2BO_3Cl occurs, and the concentration quenching mechanism is d–d interaction for either Ce^{3+} or Tb^{3+}. The $Ca_2BO_3Cl:Ce^{3+}$, Tb^{3+} can produce colour emission from blue to green by properly tuning the relative ratio between Ce^{3+} and Tb^{3+}, and the emission intensity of Tb^{3+} in Ca_2BO_3Cl can be enhanced by the energy transfer from Ce^{3+} to Tb^{3+}. The results indicate that $Ca_2BO_3Cl:Ce^{3+}$, Tb^{3+} may be a promising double emission phosphor for UV-based white light emitting diodes.

Keywords: luminescence, phosphor, $Ca_2BO_3Cl:Ce^{3+}$, Tb^{3+}, energy transfer

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1. Introduction

White light-emitting diodes (LEDs) offer many advantages such as long service lifetime, thermal resistance, and high efficiency. Therefore, white LEDs are expected to be a new light source in the illumination field.[1−3] Currently, the most common and simple method is to combine a blue LED chip with a yellow light emitting phosphor YAG:Ce, however, YAG:Ce emits a greenish–yellow light and is deficient in a red spectral region, which leads to the fact that the white LED has a poor colour rendering property.[4] In order to solve this problem, the compensating red phosphors were introduced.[5] Moreover, the other methods to achieve white LEDs are suggested, for example, they can be obtained by combining a tri-colour (red, green, and blue) phosphor or a single-phase white emitting phosphor with an ultraviolet or near-ultraviolet (UV) LED, and the method yields white light with better spectral characteristics and colour rendering property. Therefore, more and more attention has been paid to the development of the new tri-colour or white emitting phosphor that can be excited in the range of UV or n-UV light due to the necessity of increasing the efficiency of white LED.[6−8] Among the phosphors, Ce^{3+}, Eu^{2+}, Tb^{3+} or Mn^{2+} doped phosphors have been studied widely.[9−12] Broad band emitters are usually used to sensitize the luminescence of rare earth and transition metal ions. Particularly, the Ce^{3+} ion shows an efficient broad band emission due to its 5d–4f electric dipole allowed transitions. Ce^{3+} ions act as a good sensitizer in co-doped materials, and trans-

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fer a part of their energy to activator ions such as Eu^{2+}, Tb^{3+} or Mn^{2+}.[13−16] In most cases, this kind of energy transfer belongs to resonance type. In recent years, the resonance energy transfer between impurity ions in a solid material has been the subject of intense research, mainly because of its importance in the development of efficient phosphor materials for solid state lighting.

As an important family of luminescent materials, chloroborates have attracted much attention. Recently, Eu^{2+}, Ce^{3+}, or Ce^{3+}/Eu^{2+} doped chloroborates were reported.[17−27] However, to the best of our knowledge, little attention has been paid to the luminescent properties of rare-earth co-doped Ca_2BO_3Cl. Among the rare-earth ions, Ce^{3+} and Tb^{3+} ions are two of the most important luminescent centres. Therefore, in the present paper, the luminescent characteristics and the energy transfer from Ce^{3+} to Tb^{3+} in Ca_2BO_3Cl are investigated. The phosphors can create the colour emission from blue to green. They can be effectively excited by UV and near-UV, and are suitable for serving as white LEDs.

2. Experiment

The samples were synthesized by a high temperature solid-state reaction technique. According to the molecular formula $Ca_{2-x-y}BO_3Cl{:}xCe^{3+}$, yTb^{3+}, the raw materials $CaCO_3$, $CaCl_2$, H_3BO_3, CeO_2, and Tb_4O_7 (all materials are of analytical grade) were measured, then blended and milled thoroughly in an agate mortar. The mixed powders were calcined in corundum crucibles, which were introduced into a muffle furnace preheated to 900 °C and stayed in the furnace for 2.5 h in an atmosphere. Finally they were cooled down to room temperature and ground thoroughly again into powders. Moreover, all the samples were sieved under the same condition to ensure a similar particle size distribution.

The final phase was checked with a conventional X-ray diffraction (XRD) (D/max-rA, CuK.α, 40 kV, 100 mA, $\lambda = 0.15406$ nm). The spectral characteristics of the phosphors were performed by using a Hitachi F-4600 fluorescence spectrophotometer equipped with a 450-W Xe lamp. The commission International de l'Eclairage (CIE) chromaticity coordinate values were measured by a PMS-80 UV-VIS-NEAR IR Spectrophotocolorimeter. All the measurements were performed at room temperature.

3. Results and discussion

3.1. Crystal structure

The XRD patterns of $Ca_{2-x-y}BO_3Cl{:}xCe^{3+}$, yTb^{3+} were measured, and similar diffraction patterns were observed for each sample, which indicates that doping a little Ce^{3+}, Tb^{3+} or Ce^{3+}/Tb^{3+} does not affect the crystal structure of Ca_2BO_3Cl. As a representative, figure 1 shows the X-ray diffraction (XRD) patterns of $Ca_{1.97}BO_3Cl{:}0.03Ce^{3+}$, $Ca_{1.95}BO_3Cl{:}0.05Tb^{3+}$, and $Ca_{1.92}BO_3Cl{:}0.03Ce^{3+}$, $0.05Tb^{3+}$, indicating that there is no obvious difference between the experimental data and the standard JCPDS (Joint Committee of Powder Diffraction Standard) card (No. 29-0302) of Ca_2BO_3Cl, which means that the crystalline structure of Ca_2BO_3Cl cannot be influenced by a small amount of impurity. Ca_2BO_3Cl has a monoclinic crystal structure with a space group of $P2_{1/c}$ (14), and there are two types of seven-fold coordination Ca polyhedra: $CaCl_3O_4$ and $CaCl_2O_4$, where each O atom is surrounded by three Ca atoms, one B atom in the form of a distorted tetrahedron and the Cl atoms are always situated at the corners of the trigonal base,[28] and its lattice parameters are $a = 0.3948$ nm, $b = 0.8692$ nm, $c = 1.2402$ nm.

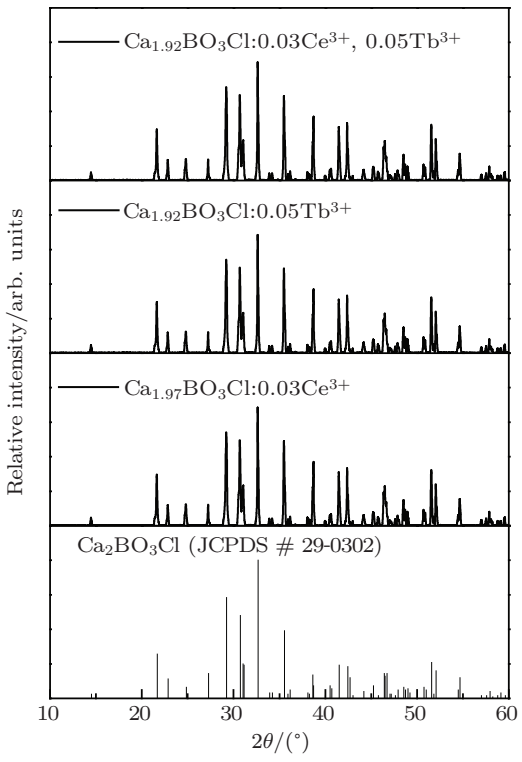


Fig. 1. The XRD patterns of $Ca_{1.97}BO_3Cl{:}0.03Ce^{3+}$, $Ca_{1.95}BO_3Cl{:}0.05Tb^{3+}$, $Ca_{1.92}BO_3Cl{:}0.03Ce^{3+}$, $0.05Tb^{3+}$ with the standard data of Ca_2BO_3Cl (JCPDS No. 29-0302).

3.2. Spectrum properties of Ca_2BO_3Cl: Ce^{3+} and Ca_2BO_3Cl:Tb^{3+} phosphors

Figure 2 shows the excitation and emission spectra of Ca_2BO_3Cl:0.03Ce^{3+} and Ca_2BO_3Cl:0.05Tb^{3+} phosphors. In Fig. 2(a), the excitation spectrum of Ca_2BO_3Cl:0.03Ce^{3+} monitored at 425 nm shows a broad band extending from 220 nm to 400 nm due to the 4f–5d transition of Ce^{3+} ions, and the excitation peaks located at 258 nm, 321 nm, and 350 nm, respectively. Ca_2BO_3Cl:0.03Ce^{3+} shows an asymmetric band extending from 380 nm to 600 nm with a maximum at about 425 nm under the 365-nm excitation. The characteristic double emission of Ce^{3+} ions is not clearly observed in the emission spectrum, but it can be resolved by a Gaussian fitting into two emission bands with the peaks at 418 nm (23923 cm^{-1}) and 448 nm (22321 cm^{-1}), respectively. However, the energy difference between the two fitted emission peaks is about 1602 cm^{-1}, which is smaller than that of the theoretically calculated value between $^2F_{5/2}$ and $^2F_{5/2}$ levels (2000 cm^{-1}). It means that there are two types of Ce^{3+} emitting centres in the phosphor due to different occupancies in the host Ca_2BO_3Cl, and the result is consistent with that in Ref. [23].

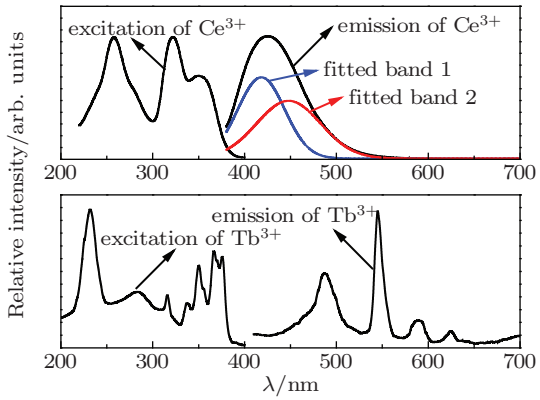


Fig. 2. (colour online) Emission and excitation spectra of $Ca_{1.97}BO_3Cl$:0.03Ce^{3+} (a) and $Ca_{1.95}BO_3Cl$:0.05Tb^{3+} (b).

Figure 2(b) depicts the excitation and emission spectra of Ca_2BO_3Cl:0.05Tb^{3+}. The excitation spectrum exhibits a series of sharp peaks between 200 nm and 400 nm. The sharp bands between 300 nm and 400 nm are assigned to the intra $4f^8$ transitions between the $^7F_6$ and $^5F_{5,4}$, $^5H_{7-4}$, $^5D_{1,0}$, $^5L_{10-6}$, $^5G_{6-2}$, and $^5D_{2-4}$ levels.[29] For more details of Tb^{3+} excitation refer to Ref. [30]. The emission spectrum of Ca_2BO_3Cl:Tb^{3+} phosphor excited by 365 nm presents four peaks at around 487 nm, 545 nm, 589 nm, and 625 nm which originate from the transitions between the excited $^5D_4$ level and $^7F_{J(J=6,5,4,3)}$ level of Tb^{3+} ion, respectively. The strongest emission peak is located at 545 nm, corresponding to the typical transition $^5D_4$–$^7F_5$ of Tb^{3+} ion.

3.3. Concentration quenching mechanism of Ce^{3+} or Tb^{3+} in Ca_2BO_3Cl

For Ca_2BO_3Cl:Tb^{3+}, the values of Tb^{3+} optimum doping content are discussed and the results are shown in Fig. 3. The emission intensity first increases with the increasing of Tb^{3+} doping content, and reaches a maximum at 0.05-mol Tb^{3+}, then decreases. For Ca_2BO_3Cl:Ce^{3+}, the results are similar to those of Ca_2BO_3Cl:Tb^{3+}, and are shown in the inset of Fig. 4, and the maximal emission intensity is observed when Ce^{3+} doping content increases up to 0.03-mol Ce^{3+}. The phenomenon of decrease in emission intensity after a certain concentration is called concentration quenching and is attributed to energy migration among rare earth ions.[31]

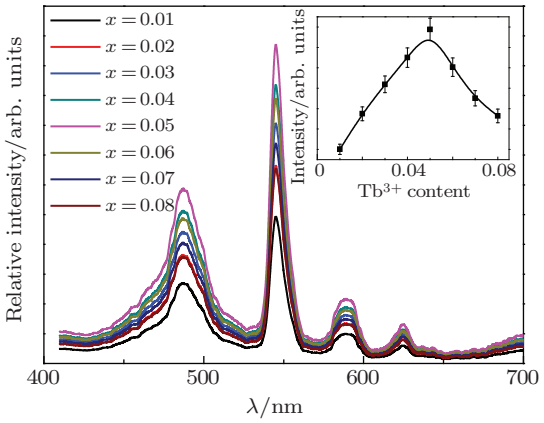


Fig. 3. (colour online) Emission spectra of $Ca_{2-x}BO_3Cl$:xTb^{3+} phosphor with several different values of Tb^{3+} content (x = 0.01–0.08). The inset shows the emission intensity of $Ca_{2-x}BO_3Cl$:xTb^{3+} phosphor versus Tb^{3+} content.

While considering the mechanism of energy transfer in oxide phosphor, Blasse[32] has pointed out that if the activator is introduced solely on Z ion sits, then there is on the average one activator ion per (V/x_cN), where x_c is the critical concentration. N is the number of Z ions in the unit cell and V is the volume of the unit cell. The critical transfer distance (R_c) is approximately equal to twice the radius of a sphere with volume V, and expressed as

$$R_c \approx 2[3V/(4\pi x_c N)]^{1/3}. \quad (1)$$

Therefore, for Ca_2BO_3Cl, the critical energy transfer distances between RE^{3+} ions for Ce^{3+} or

Tb^{3+} in the two phosphors can be calculated by using the equation, where x_c is the critical concentration of Ce^{3+} or Tb^{3+}, N is the number of Z ions in the unit cell ($N = 4$ for Ca_2BO_3Cl), and V is the volume of the unit cell ($V = 0.4256$ nm^3). In this case, the values of critical doping content of Ce^{3+} and Tb^{3+} in Ca_2BO_3Cl host are 0.03 mol and 0.05 mol, respectively. Therefore, the R_c values of Ce^{3+} and Tb^{3+} are 1.892 nm and 1.596 nm, respectively.

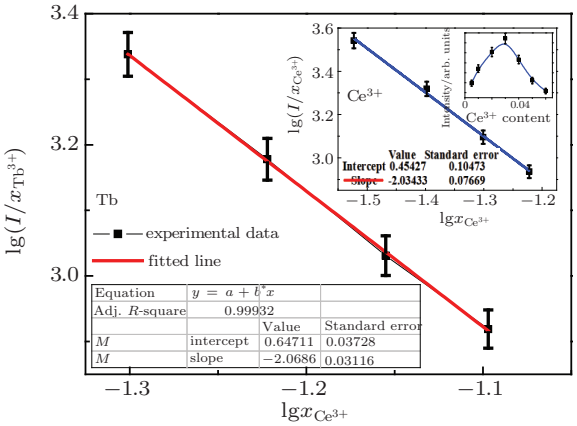


Fig. 4. (colour online) Plot of $\lg(I/x_{Tb^{3+}})$ versus $\lg x_{Tb^{3+}}$ in Ca_2BO_3Cl:Tb^{3+} phosphors. The inset shows the plot of $\lg(I/x_{Ce^{3+}})$ versus $\lg x_{Ce^{3+}}$ in Ca_2BO_3Cl:Ce^{3+} phosphors, and the emission intensity of $Ca_{2-x}BO_3Cl$:xCe^{3+} phosphor as a function of Ce^{3+} content.

As a representative, the concentration quenching mechanism of Tb^{3+} in Ca_2BO_3Cl:Tb^{3+} is studied. The inset of Fig. 3 shows that with doping content 0.05-mol Tb^{3+}, the concentration quenching of Tb^{3+} in Ca_2BO_3Cl:Tb^{3+} occurs. Non-radiative energy transfer from one Tb^{3+} to another Tb^{3+} ion may occur by exchange interaction, radiation reabsorption or multiple–multiple interaction: Tb^{3+} is an isolated emission centre in Ca_2BO_3Cl:Tb^{3+}. The transition of Tb^{3+} is allowed while exchange interaction is responsible for the energy for forbidden transitions and typical critical distance is about 0.5 nm.[33] It means that the mechanism of exchange interaction plays no role in the energy transfer between Tb^{3+} ions in Ca_2BO_3Cl:Tb^{3+}. The mechanism of radiation reabsorption comes into effect only when a broad overlap of the fluorescent spectra of the sensitizer and activator appears, and in the view of spectrum properties of Ca_2BO_3Cl:Tb^{3+} the overlap is unlikely to happen. So the concentration quenching mechanism of Tb^{3+} in Ca_2BO_3Cl:Tb^{3+} ought to be the electric multiple–multiple interaction according to the Dexter's theory. If the energy transfer occurs between the same sorts of activators, the multipolar interaction can be determined from the change of the emission intensity. The emission intensity per activator ion obeys the equation[34,35]

$$(I/x) = K[1 + \beta(x)^{Q/3}]^{-1}, \tag{2}$$

where x is the activator concentration; $Q = 6$, 8, 10 for dipole–dipole (d–d), dipole–quadrupole (d–p), quadrupole–quadrupole (q–q) interactions, respectively; K and β are constants for the same excitation conditions for a given host crystal.

The critical concentration of Tb^{3+} is determined to be 0.05 mol. For Ca_2BO_3Cl:Tb^{3+}, the plot of $\lg I/x_{Tb^{3+}}$ versus $\lg x_{Tb^{3+}}$ is shown in Fig. 4. It shows that the dependence of $\lg I/x_{Tb^{3+}}$ on $\lg x_{Tb^{3+}}$ is linear and the slope is -2.07. Therefore, the value of Q can be calculated to be 6.21, which is close to 6. It indicates that the d–d interaction is the concentration quenching mechanism of Tb^{3+} in Ca_2BO_3Cl:Tb^{3+}. Similarly, the inset of Fig. 4 shows the dependence of $\lg I/x_{Ce^{3+}}$ on $\lg x_{Ce^{3+}}$ is also linear and the slope is -2.03, and the value of Q is about 6. It means that the concentration quenching mechanism of Ce^{3+} in Ca_2BO_3Cl:Ce^{3+} is the d–d interaction, too.

3.4. Spectral properties of Ca_2BO_3Cl:Ce^{3+}, Tb^{3+} phosphors

Figure 5 depicts the emission spectra of $Ca_{2-x-y}BO_3Cl$:xCe^{3+}, yTb^{3+} ($x = 0.03$, $y = 0$–0.08). With the increase of Tb^{3+} concentration, the phosphors can create colour emission from blue to yellowish-green; moreover, the emission intensity of Ce^{3+} decreases dramatically and monotonically, and the emission intensity of Tb^{3+} increases and has a maximum intensity at $y = 0.05$. The same results can also be seen from Fig. 6, which further supports the occurrence of the energy transfer from Ce^{3+} to Tb^{3+}. In the present blue and yellowish-green double emitting phosphor Ca_2BO_3Cl:Ce^{3+}, Tb^{3+}, the energy transfer plays an important role. The 5d–4f transition of Ce^{3+} is electric–dipole allowed and is several orders of magnitude stronger than the forbidden 4f–4f electronic transitions within the $4f^n$ configuration of Tb^{3+}. Therefore, Ce^{3+} can strongly absorb UV or near-UV radiation and efficiently transfer its energy to Tb^{3+} to enhance the emission of Tb^{3+}.[36] The Ce^{3+} ions act as sensitizers and the Tb^{3+} ions as activators in this work. The energy levels of Tb^{3+} are suitable for energy transfer to take place from the allowed Ce^{3+} emission of 4f–5d upon excitation with 365-nm UV light. In the present system Ca_2BO_3Cl:Ce^{3+}, Tb^{3+},

first Ce^{3+} ions are excited by UV light, then energy transfer takes place from Ce^{3+} to Tb^{3+}.

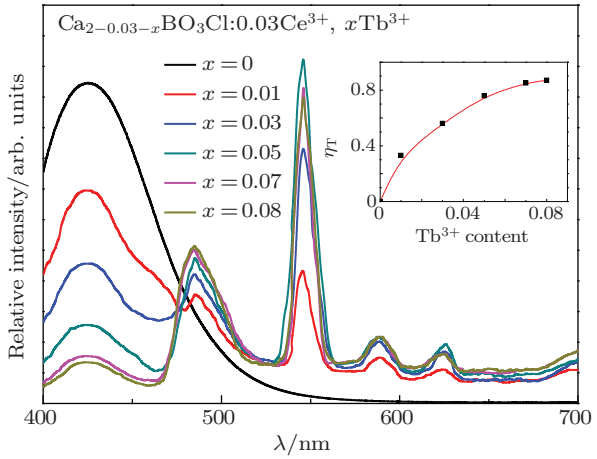


Fig. 5. (colour online) Emission spectra of $Ca_{2-0.03-x}BO_3Cl$:0.03Ce^{3+}, xTb^{3+} with several different values of Tb^{3+} content (λ_{ex} = 365 nm). The inset shows the energy transfer efficiency versus Tb^{3+} content.

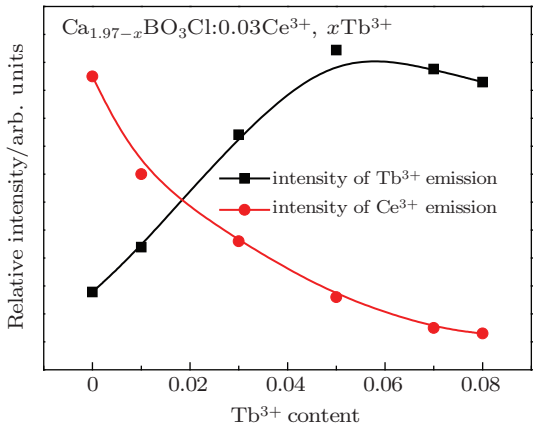


Fig. 6. (colour online) Dependences of emission intensity of Ce^{3+} and Tb^{3+} on Tb^{3+} content in $Ca_{1.97-x}BO_3Cl$:0.03Ce^{3+}, xTb^{3+}.

Figure 7 depicts the energy-level scheme with electronic transitions (Ce^{3+}, Tb^{3+}) and energy transfer process (Ce^{3+} →Tb^{3+}). The optical properties of Ca_2BO_3Cl:Ce^{3+}, Tb^{3+} are determined by the transitions between f-electron and d-electron states of cerium and between different f-electron states of terbium. Upon UV excitation, energy transfer takes place from 5d (Ce^{3+}) to the high excitation levels of Tb^{3+} ($4f^n$) followed by the cross relaxation to the $^5D_4$ level of Tb^{3+}, which decays radiactively to various lower levels of $^7F_{J(J=6,5,4,3)}$.

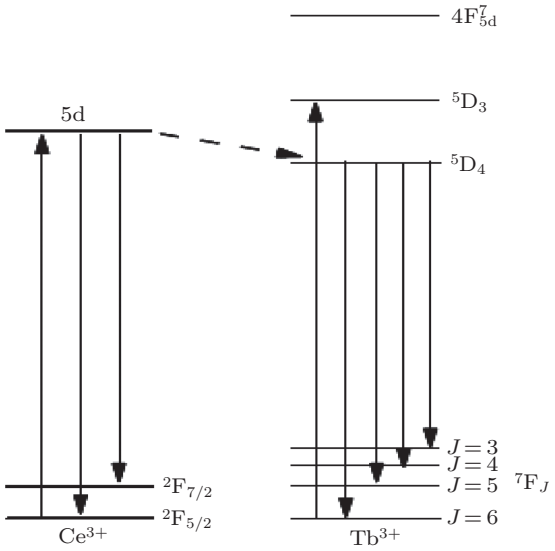


Fig. 7. Energy-level scheme of Ca_2BO_3Cl:Ce^{3+}, Tb^{3+} showing electronic transitions and energy transfer process.

The energy transfer efficiency (η_T) can also be measured from the intensities of the sensitizer emission in the presence (I_S) and in the absence (I_{S0}) of the activator, through the following expression[37]

$$\eta_T = 1 - (I_S/I_{S0}), \tag{3}$$

where I_S and I_{S0} are the luminescence intensities of the sensitizer (Ce^{3+}) with and without activator (Tb^{3+}) being present. The determined values using Eq. (3) are depicted in the inset of Fig. 5. It can be seen that the energy transfer efficiency increases with Tb^{3+} concentration increasing.

3.5. CIE chromaticity coordinates of Ca_2BO_3Cl:Ce^{3+}, Tb^{3+} phosphor

Figure 8 shows the Commission Internationale de L'Eclairage (CIE) chromaticity coordinates of $Ca_{1.97-x}BO_3Cl$:0.03Ce^{3+}, xTb^{3+} (x = 0–0.08), showing that only the Ce^{3+}-doped Ca_2BO_3Cl sample presents blue emission under 365-nm light irradiation. With co-doped Tb^{3+}, the characteristic emission of the Tb^{3+} ions could be observed besides the Ce^{3+} emission. By changing the Tb^{3+} doping content, the tunable emission properties of $Ca_{1.97-x}BO_3Cl$:0.03Ce^{3+}, xTb^{3+} can be obtained. With Tb^{3+} content increasing, the chromaticity coordinates vary from (0.162, 0.078) to (0.193, 0.436), corresponding colour tones of the samples change gradually from blue to green by simply adjusting the relative doping Tb^{3+} content.

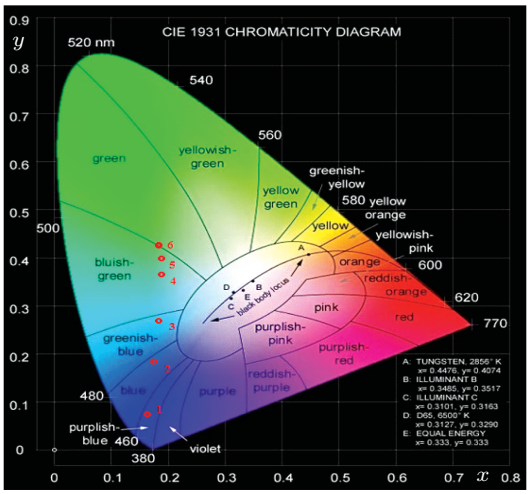


Fig. 8. (colour online) CIE chromaticity diagram for $Ca_{2-0.03-x}BO_3Cl$:$0.03Ce^{3+}$, xTb^{3+} phosphors excited at 365 nm, with $x = 0$ (1), 0.01 (2), 0.03 (3), 0.05 (4), 0.07 (5), and 0.08 (6).

4. Conclusions

$Ca_{2-x-y}BO_3Cl$:xCe^{3+}, yTb^{3+} phosphors were synthesized by a solid-state reaction. With the increase of Tb^{3+} or Ce^{3+} content, the emission intensity of Tb^{3+} or Ce^{3+} in Ca_2BO_3Cl first increases, and reaches a peak at 0.05 Tb^{3+} or 0.03 Ce^{3+}, then decreases because of the concentration quenching effect. The concentration quenching mechanisms for Tb^{3+} and Ce^{3+} are both d–d interaction. By the energy transfer from the Ce^{3+} to Tb^{3+} ions, the emission intensity of Tb^{3+} can be enhanced, and Ca_2BO_3Cl:Ce^{3+}, Tb^{3+} can create colour emission from blue to green by adjusting the relative ratio between Ce^{3+} and Tb^{3+}. The results indicate that the phosphor may have a potential application in white LED as double emitting phosphor.

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