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White luminescence of Tm–Dy ions co-doped aluminoborosilicate glasses under UV light excitation

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ABSTRACT

Tm^{3+} and Dy^{3+} ions co-doped aluminoborosilicate glasses were prepared in this study. The luminescence properties of the glasses were analyzed. A combination of blue, green, yellow, and red emission bands was shown for these glasses, and white light emission could be observed under UV light excitation. White light luminescence color could be changed by varying the excitation wavelength. Concentration quenching effect was investigated in this paper. Furthermore, the dependence of luminescence properties on glass compositions was studied. Results showed that the luminescence intensity changed with different network modifier oxides, while the white color luminescence was not affected significantly.

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1. Introduction

Rare earth doped glasses are useful materials for bulk lasers, optical fibers, waveguide lasers, and optical amplifiers [1–3]. Recently, researches of rare earth doped glasses not only focus on infrared optical devices, but also show growing interest in visible optical devices, especially for white light emitting diode (white LED) application [4–11].

White LEDs receive lots of attention in solid state lighting area for replacement of conventional incandescent and fluorescent lamps, due to advantages in energy use and related environmental benefits. Compared to conventional phosphors used for white LEDs, e.g. Li-α-SiAlON:Eu^{2+} [12], Ca-α-SiAlON:Eu^{2+} [13], $Ba_3MgSi_2O_8$:Eu^{2+}, Mn^{2+} phosphors [14], etc., rare earth doped white color luminescence glass has some potential advantages, such as homogeneous light emitting, simpler manufacture procedure, lower production cost, and better thermal stability. White light emitting glass was first developed by Zhang et al. [4] in 1991, and it receives increasing interest in recent years [5–11,15]. A few studies were concerned on borosilicate glass matrix [4,7,11]. The borosilicate glass matrix has good mechanical, thermal, and chemical stability, and can broaden application areas of rare earth doped glass materials. On the other hand, aluminoborosilicate glass has been receiving increasing interest as rare earth doped matrix [16,17]. The aluminoborosilicate glass matrix can maintain the good physical and chemical properties of borosilicate glass. Moreover, in addition to SiO_2 and B_2O_3, Al_2O_3 has been receiving significant consideration as a glass network forming oxide due to its high solubility of rare earth ions in silicate glass matrix [18]. This is because co-doping Al and rare earth ions in silicate glass matrix can dissolve clustering rare earth ions and disperse them homogeneously in glass network. Therefore, the present work chooses aluminoborosilicate glass as glass matrix in which rare earth ions are doped.

Recently, we have reported a zinc-aluminoborosilicate glass, which emitted white light under UV light excitation by co-doping Eu_2O_3 and Dy_2O_3 [19]. The white light emission was combined with multi-color emission bands of Eu^{2+}, Eu^{3+}, and Dy^{3+} ions. However, the luminescence color of the Eu–Dy ions co-doped glasses was strongly dependent on $Eu^{3+} \rightarrow Eu^{2+}$ reduction in air, and the reduction reaction affects relative concentration of Eu^{2+} and Eu^{3+} ions significantly. Since many factors affect the $Eu^{3+} \rightarrow Eu^{2+}$ reduction process in glass materials prepared in air, e.g. glass optical basicity, rigidity of glass network, valence of glass network modifier oxides, etc., the reaction was sensitive to glass compositions [20–22]. This leads to a restriction of glass application area. In order to solve this problem, the Tm–Dy ions co-doped aluminoborosilicate glass material is developed in this study, which has potential application for white LEDs.

The present work prepares a series of Tm_2O_3 and Dy_2O_3 co-doped aluminoborosilicate glasses emitting white light under UV light excitation. Besides, the concentration quenching effect and the dependence of luminescence properties on glass compositions are investigated in this study.

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2. Experimental

Four series of Tm/Dy ions doped aluminoborosilicate glasses were prepared in this study. The nominal general composition of the glass samples was (in mol%): (I) xTm$_2$O$_3$–(0.25$-x$)Dy$_2$O$_3$–99.75ABS, (II) y(0.3Tm$_2$O$_3$–0.7Dy$_2$O$_3$)–(100$-y$)ABS, (III) 0.075Tm$_2$O$_3$–0.175Dy$_2$O$_3$–Li$_2$O–mCaO–(7.0$-m$)BaO–ZnO–Al$_2$O$_3$–B$_2$O$_3$–SiO$_2$, and (IV) 0.075Tm$_2$O$_3$–0.175Dy$_2$O$_3$–RO–Al$_2$O$_3$–B$_2$O$_3$–SiO$_2$. Here, $x = 0$–0.25 mol%, $y = 0.5$–1.5 mol%, $m = 0$–7.0 mol%, ABS represents host glass SiO$_2$–Al$_2$O$_3$–B$_2$O$_3$–ZnO–Li$_2$O–BaO, and RO represents different network modifier oxides Li$_2$O, MgO, CaO, and BaO. Details of compositions are presented in Table 1. Analytical reagent SiO$_2$, Al$_2$O$_3$, H$_3$BO$_3$, ZnO, Li$_2$CO$_3$, MgO, CaCO$_3$, BaCO$_3$, and high-purity Tm$_2$O$_3$ (99.95%) and Dy$_2$O$_3$ (99.99%) were used as the raw materials. The raw materials were mixed well and melted at 1500 °C for 2 h. Then, the melts were poured into a carbon mold, cooled in air, and subsequently annealed at 530 °C for 2 h. The samples were cut into 2 cm × 2 cm for luminescence measurement.

Luminescence spectra were obtained at room temperature using Hitachi F-4500 fluorescence spectrophotometer under excitation of Xe lamp. Optical transmission and absorption spectra of the polished samples in UV–vis range were recorded at room temperature using Hitachi UV-4100 UV–vis spectrophotometer. The glass transition temperature (T_g) of the host glass was obtained using DTA CRY-2, with a heating rate of 10 °C/min.

3. Results

According to DTA result, the G2 sample possesses a high glass transition temperature (T_g) of 588 °C. The vitreous host also exhibits high transmission, around 90.5% in visible range.

3.1. Optical spectra of aluminoborosilicate glasses with different rare earth ions content

Fig. 1 presents the UV–vis absorption spectra of Series I. In single Dy$_2$O$_3$ doped glass, two strong absorption bands centered at 386 and 452 nm are induced by $^6H_{15/2} \rightarrow {}^4I_{13/2}$, $^4F_{7/2}$ and $^6H_{15/2} \rightarrow {}^4I_{15/2}$ transitions of Dy^{3+} ions, respectively. In single Tm$_2$O$_3$ doped glass, a broad absorption band from 450 to 480 nm is due to the overlap of $^3H_6 \rightarrow {}^1G_4$ and $^3F_4 \rightarrow {}^1D_2$ transitions of Tm^{3+} ions. In Tm–Dy co-doped case, all of the absorption bands referred to above are presented, and a broader absorption band from 430 to 480 nm is shown in Fig. 1 due to the three transitions of Dy^{3+} and Tm^{3+} ions referred to above.

Table 1
Nominal general composition of Tm/Dy ions doped aluminoborosilicate glass samples (in mol%)

Series	No.	RE_2O_3			Li$_2$O	MgO	CaO	BaO	ZnO	Al$_2$O$_3$	B$_2$O$_3$	SiO$_2$
		Total	Tm$_2$O$_3$	Dy$_2$O$_3$								
I	G1	0.25	0.000	0.250	7			7	10	13	13	50
	G2	0.25	0.075	0.175	7			7	10	13	13	50
	G3	0.25	0.250	0.000	7			7	10	13	13	50
II	G4	0.50	0.150	0.350	7			7	10	13	13	50
	G5	0.75	0.225	0.525	7			7	10	13	13	50
	G6	1.00	0.300	0.700	7			7	10	13	13	50
	G7	1.50	0.450	1.050	7			7	10	13	13	50
III	G8	0.25	0.075	0.175	7		0.0	7.0	10	13	13	50
	G9	0.25	0.075	0.175	7		3.5	3.5	10	13	13	50
	G10	0.25	0.075	0.175	7		7.0	0.0	10	13	13	50
IV	G11	0.25	0.075	0.175	24					13	13	50
	G12	0.25	0.075	0.175		24				13	13	50
	G13	0.25	0.075	0.175			24			13	13	50
	G14	0.25	0.075	0.175				24		13	13	50

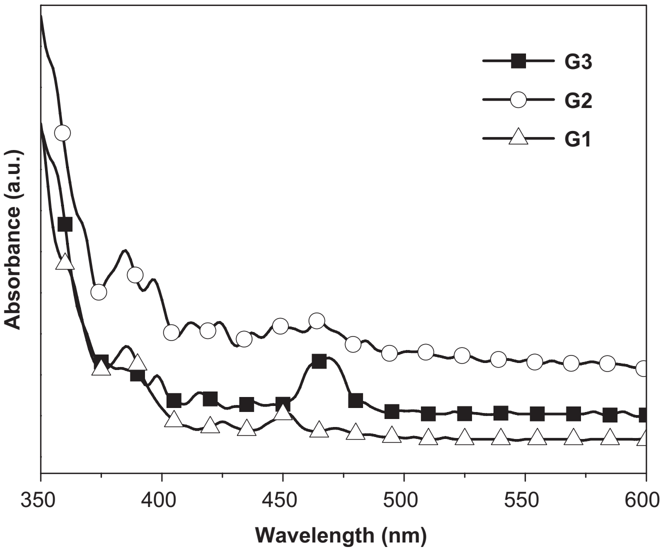

Fig. 1. UV–vis absorption spectra of xTm$_2$O$_3$–(0.25$-x$)Dy$_2$O$_3$–99.75ABS samples. G1, G2, and G3 correspond to $x = 0$, 0.075, and 0.25 mol%, respectively.

The luminescence spectra of Series I are shown in Fig. 2. Fig. 2(a) presents the emission spectra of xTm$_2$O$_3$–(0.25$-x$)Dy$_2$O$_3$–99.75ABS ($x = 0$–0.25, in mol%) glasses under 355 nm excitation at room temperature. It shows that in single Dy$_2$O$_3$ doped glass, there are two strong emission bands attributed to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ for Dy^{3+} at 485 nm (greenish blue) and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ for Dy^{3+} at 576 nm (yellow), and two small emission bands attributed to $^4F_{9/2} \rightarrow {}^6H_{11/2}$ for Dy^{3+} at 665 nm and $^4F_{9/2} \rightarrow {}^6H_{9/2}$ for Dy^{3+} at 751 nm. In single Tm$_2$O$_3$ doped glass, there is a strong emission band attributed to $^1D_2 \rightarrow {}^3F_4$ for Tm^{3+} at 458 nm (blue) with a shoulder of $^1G_4 \rightarrow {}^3H_6$ for Tm^{3+} at 478 nm. In Tm–Dy co-doped case, most of the emission bands referred to above still exist. But the existence of small band of $^1G_4 \rightarrow {}^3H_6$ for Tm^{3+} at 478 nm is uncertain, because it may be overlapped by the strong emission band of $^4F_{9/2} \rightarrow {}^6H_{15/2}$ of Dy^{3+} ions at 485 nm. In addition, the emission intensity of Tm–Dy co-doped glass is lower than that in single doped glasses, because the concentration of Tm^{3+} or Dy^{3+} ions in co-doped case is smaller than that in single doped case.

Fig. 2(b) presents the excitation spectra of 0.075Tm$_2$O$_3$–0.175Dy$_2$O$_3$–99.75ABS sample monitored at different emission wavelengths. It indicates that the emission intensity of Tm^{3+} and Dy^{3+} ions can be adjusted by changing excitation light, and the luminescence color could be adjusted. Interestingly, it should be noted that all of the excitation spectra monitored at different emission wavelengths show an overlap excitation band from 345 to 375 nm. It indicates that the blue, green, and yellow emission bands referred to above can be excited by UV light simultaneously in the Tm$_2$O$_3$ and Dy$_2$O$_3$ co-doped glasses.

Luminescence colors of the samples excited at 355 nm are characterized by CIE chromaticity diagram and are shown in Fig. 2(c). It shows that blue and yellowish white light can be observed in single Tm$_2$O$_3$ and Dy$_2$O$_3$ doped samples, respectively. Since white light can be synthesized by an appropriate combination of blue and yellow light, typical white light emission can be achieved in Tm$_2$O$_3$ and Dy$_2$O$_3$ co-doped aluminoborosilicate glass, as shown in Fig. 2(c). The co-doped concentration proportion of Tm^{3+} and Dy^{3+} ions is equal to 3:7. The chromaticity coordinates of

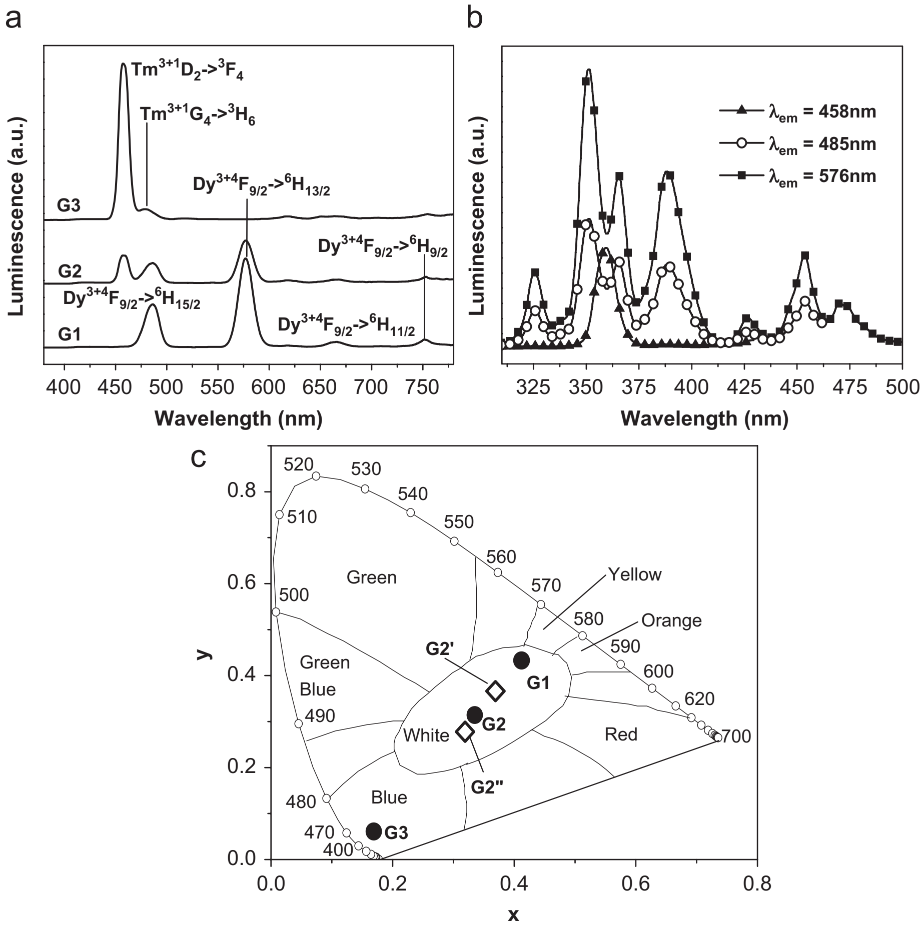

Fig. 2. Luminescence spectra of xTm$_2$O$_3$–(0.25−x)Dy$_2$O$_3$–99.75ABS samples: (a) emission spectra under 355 nm excitation, (b) excitation spectra of G2 sample monitored at different emission wavelengths, and (c) chromaticity diagram corresponding to emission light under 355 nm excitation. G1, G2, and G3 correspond to $x = 0$, 0.075, and 0.25 mol%, respectively. The marks of G2′ and G2″ in chromaticity diagram represent the chromaticity coordinates of the emission for the G2 sample under 353 and 358 nm excitation, respectively.

the emission for the 0.075Tm$_2$O$_3$–0.175Dy$_2$O$_3$–99.75ABS sample under 353 and 358 nm excitation are also shown in Fig. 2(c). It shows that the luminescence color can be changed from warm white to cold white by changing excitation light. This tunability can broaden application areas. For example, warm white light is preferred for reading, while cold white light is preferred for public lighting.

Moreover, the concentration quenching effect is investigated in Fig. 3. The total rare earth oxides concentration was varied form 0.5 to 1.5 mol%, and the proportion of Tm^{3+} and Dy^{3+} ions was kept at 3:7. It shows that the intensity of luminescence bands increases from $y = 0.5$ mol% to $y = 0.75$ mol%, and quenches at $y = 1.0$ mol%.

3.2. *Optical spectra of Tm– Dy co-doped aluminoborosilicate glasses with different network modifier oxides*

Firstly, the glass composition was changed slightly by substituting CaO for BaO. Fig. 4(a) shows the emission spectra of 0.075Tm$_2$O$_3$–0.175Dy$_2$O$_3$:mCaO–(7.0−m)BaO–Li$_2$O–ZnO–Al$_2$O$_3$–B$_2$O$_3$–SiO$_2$ (in mol%) glasses under 355 nm excitation. The emission intensity increases on substituting CaO for BaO. In addition, Table 2 summarizes the emission intensity ratio of Tm–Dy co-doped aluminoborosilicate glasses with different network modifier oxides. Here, $I_{576/458}$, $I_{485/458}$, and $I_{576/485}$ correspond to emission intensity ratio of transitions Dy^{3+}($^4F_{9/2}\rightarrow{}^6H_{13/2}$)/Tm^{3+}($^1D_2\rightarrow{}^3F_4$), Dy^{3+}($^4F_{9/2}\rightarrow{}^6H_{15/2}$)/Tm^{3+}($^1D_2\rightarrow{}^3F_4$), and Dy^{3+}($^4F_{9/2}\rightarrow{}^6H_{13/2}$)/Dy^{3+}($^4F_{9/2}\rightarrow{}^6H_{15/2}$), respectively. Table 2 also presents that $I_{576/458}$ and $I_{485/458}$ decrease on substituting CaO for BaO. Fig. 4(b) exhibits that the luminescence color is kept white though the CaO concentration in glass matrix is varied.

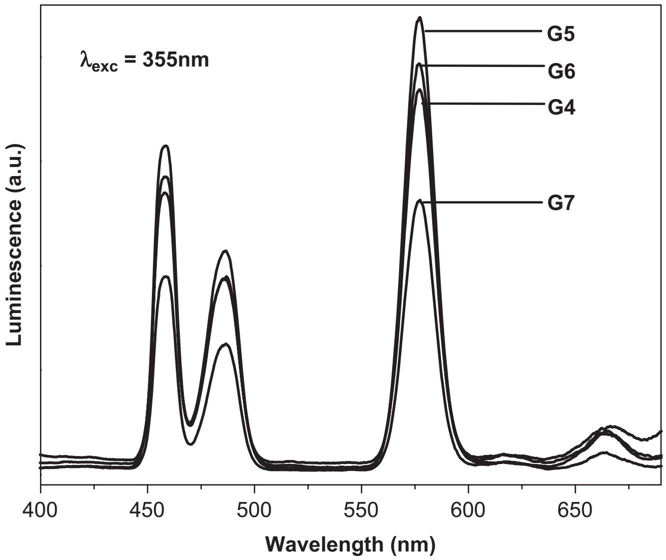

Fig. 3. Emission spectra of y(0.3Tm$_2$O$_3$–0.7Dy$_2$O$_3$)–(100−y)ABS (in mol%) glasses under 355 nm excitation at room temperature. G4, G5, G6, and G7 correspond to $y = 0.50$, 0.75, 1.00, and 1.50 mol%, respectively.

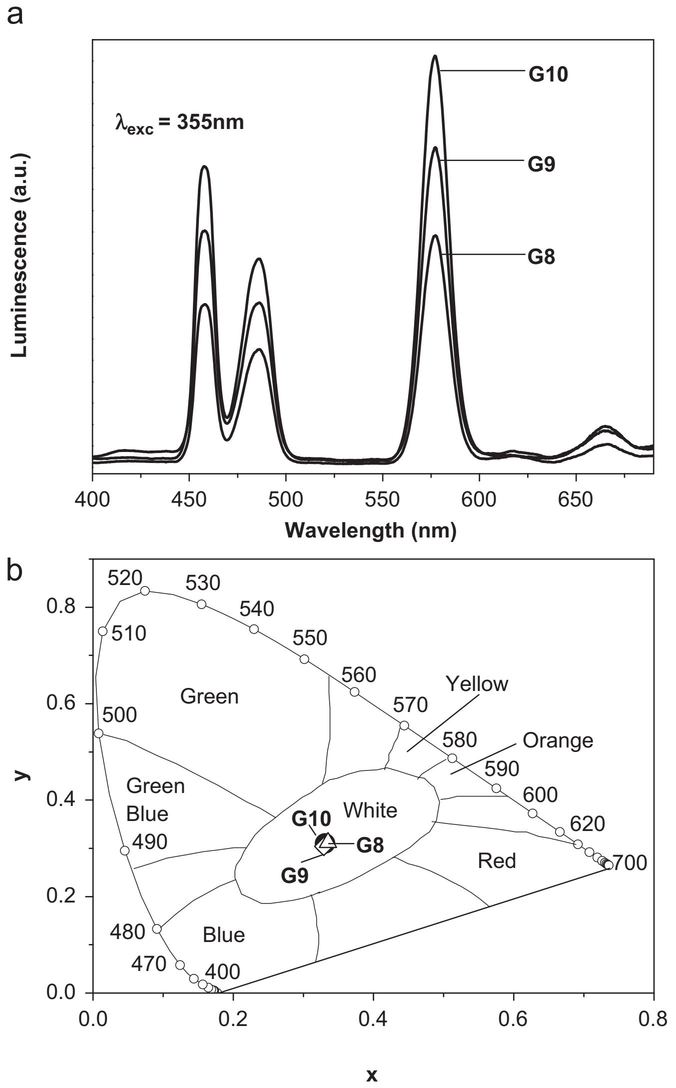

Fig. 4. (a) Emission spectra under 355 nm excitation and (b) corresponding chromaticity diagram of $0.075Tm_2O_3$–$0.175Dy_2O_3$:mCaO–(7.0−m)BaO–Li_2O–ZnO–Al_2O_3–B_2O_3–SiO_2 (in mol%) glasses. G8, G9, and G10 correspond to $m = 0$, 3.5, and 7.0 mol%, respectively.

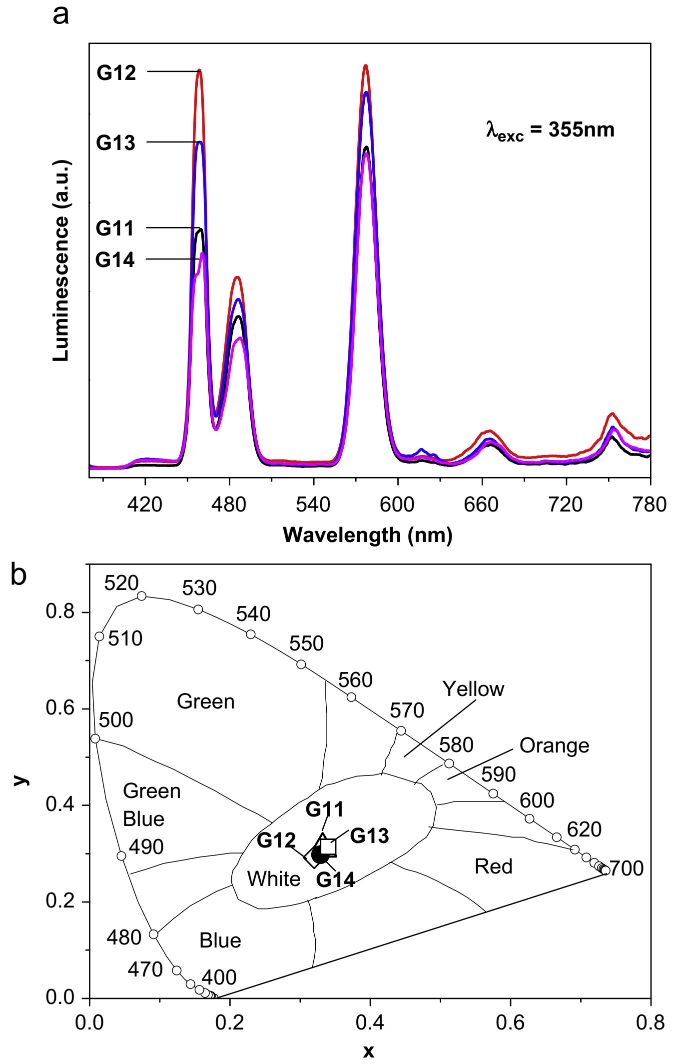

Fig. 5. (a) Emission spectra under 355 nm excitation and (b) corresponding chromaticity diagram of $0.075Tm_2O_3$–$0.175Dy_2O_3$:RO–Al_2O_3–B_2O_3–SiO_2 (in mol%) glasses, RO represents different network modifier oxides. G11, G12, G13, and G14 correspond to $R\text{O} = Li_2O$, MgO, CaO, and BaO, respectively.

Table 2
Emission intensity ratio of Tm–Dy co-doped aluminoborosilicate glasses with different network modifier oxides

No.	Series III			Series IV			
	G8	G9	G10	G11	G12	G13	G14
$I_{576/458}$	1.42	1.38	1.33	1.34	1.01	1.15	1.47
$I_{485/458}$	0.72	0.70	0.67	0.64	0.48	0.52	0.61
$I_{576/485}$	1.98	1.98	1.98	2.11	2.10	2.22	2.41

$I_{576/458}$, $I_{485/458}$, and $I_{576/485}$ correspond to emission intensity ratio of transitions $Dy^{3+}(^4F_{9/2}\rightarrow{}^6H_{13/2})/Tm^{3+}(^1D_2\rightarrow{}^3F_4)$, $Dy^{3+}(^4F_{9/2}\rightarrow{}^6H_{15/2})/Tm^{3+}(^1D_2\rightarrow{}^3F_4)$, and $Dy^{3+}(^4F_{9/2}\rightarrow{}^6H_{13/2})/Dy^{3+}(^4F_{9/2}\rightarrow{}^6H_{15/2})$, respectively.

Then the effects of four different network modifier oxides on the luminescence properties of Tm^{3+} and Dy^{3+} co-doped aluminoborosilicate glasses are investigated in Fig. 5. Fig. 5(a) presents the emission spectra of Tm^{3+} and Dy^{3+} ions co-doped samples with different network modifier oxides. No new transition band exhibits in the emission spectra. The emission intensity decreases in the order of MgO→CaO→BaO. Table 2 shows that relative emission intensity ratio $I_{576/458}$ and $I_{485/458}$ increase in the order of MgO→CaO→BaO. Moreover, the white luminescence color is not changed significantly with different network modifier oxides, as characterized in Fig. 5(b). This is probably due to the decrease of $I_{576/485}$, which is also indicated in Table 2. The emission band at 485 nm emits greenish blue light. The color is similar to that of emission band at 458 nm. This behavior indicates that the glass matrix can be adjusted to some extent in order to obtain some other desired thermal, mechanical, or optical properties, while the white luminescence color will not be affected. This adjustability can broaden application areas. For example, the white light emission glass with high softening temperature can be used in high-temperature environments, and the glass with low softening temperature is easy to be shaped into any form.

4. Discussion

According to the emission and excitation spectra, the energy transition process of the Tm^{3+} and Dy^{3+} ions co-doped aluminoborosilicate glass is described in the energy level diagram, as shown in Fig. 6. Two non-radiative transition processes of $^1D_2\rightarrow{}^1G_4$ for Tm^{3+} ion and $^6P_{5/2}\rightarrow{}^6F_{9/2}$ for Dy^{3+} ion are indicated

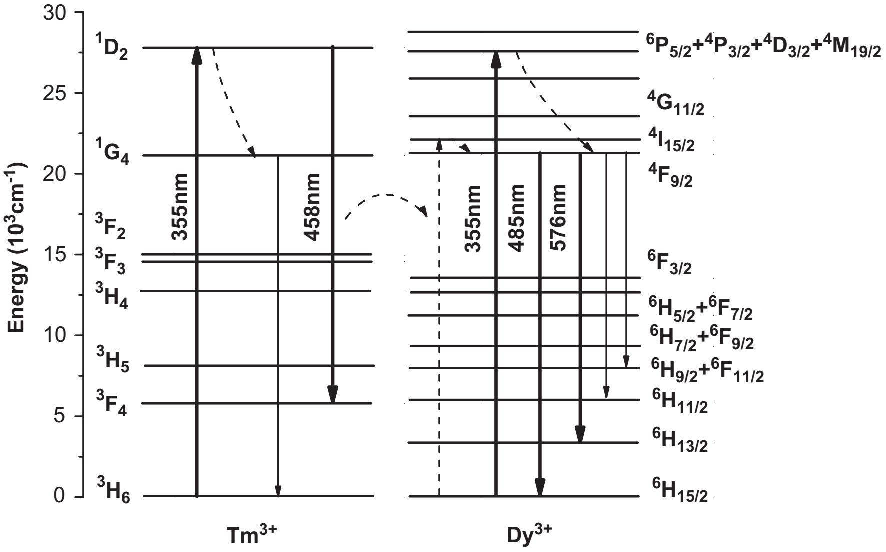

Fig. 6. Energy transition process of Tm^{3+} and Dy^{3+} ions in aluminoborosilicate glass.

in the energy diagram. In addition, it should be pointed out that a broad absorption band from 430 to 480 nm is shown in Fig. 1 due to the overlap of transitions of $^6H_{15/2} \rightarrow {}^4I_{15/2}$ for Dy^{3+}, and $^3H_6 \rightarrow {}^1G_4$ and $^3F_4 \rightarrow {}^1D_2$ for Tm^{3+} ions. Since the emission band of Tm^{3+} ions at 458 nm overlaps with the broad absorption band, the 458 nm emission light may be absorbed by the transition $^6H_{15/2} \rightarrow {}^4I_{15/2}$ for Dy^{3+} ions. Thus, a potential energy transfer process from Tm^{3+} to Dy^{3+} ions is indicated in Tm–Dy co-doped glass, as indicated in Fig. 6.

This Tm^{3+} to Dy^{3+} energy transfer process helps understand the variation of $I_{576/458}$ and $I_{485/458}$ values of Tm–Dy co-doped glasses with different network modifier oxides. It is easy to understand that the $I_{576/458}$ and $I_{485/458}$ values will increase if the Tm^{3+} to Dy^{3+} energy transfer process is enhanced. An assumption is employed here that the Tm^{3+} to Dy^{3+} energy transfer process can be enhanced if the rare earth ions are not well separated in glass matrix. In other words, if Tm and Dy ions cluster together in glass matrix, the probability of energy transfer process from Tm^{3+} to Dy^{3+} ions will increase. Based on this assumption, different network modifiers will affect aluminoborosilicate glass network and the separation degree of rare earth ions in glass matrix. Thus, the $I_{576/458}$ and $I_{485/458}$ values will be changed with different network modifier oxides, as shown in Table 2. The details will be discussed below.

The good three-dimensional (3D) frameworks of silicate glass enable rare earth ions to be well separated [11]. It was reported by previous studies [23,24] that the mixing behavior of boron and aluminum groups in alkali aluminoborate or alkali aluminoborosilicate glasses is driven by a tetrahedral–tetrahedral (including $[BO_{4/2}]^-$ and $[AlO_{4/2}]^-$) avoidance rule. This is because the high charge concentration on oxygen linking two tetrahedral, trivalent network cations is apparently energetically unfavorable in glasses with large, monovalent modifier cations. However, in systems with higher field strength modifiers such as Ca^{2+} or Mg^{2+}, this 'avoidance' is less important as these cations can stabilize such linkages more easily. Thus, considering the 'field strength' factor, the 'avoidance' rule seemed to be enhanced in the order of MgO → CaO → BaO, viz. the amount of $[XO_{4/2}]^-$–$[XO_{4/2}]^-$ (X = Al or B) linkages will decrease in the order of MgO → CaO → BaO in aluminoborosilicate glasses. Since 3D framework is better developed by tetrahedral linkages rather than two-dimensional $[BO_3]$ triangles, the rare earth ions can be better separated in aluminoborosilicate glasses in the order of BaO → CaO → MgO. Thus, the energy transfer probability from Tm^{3+} to Dy^{3+} ions in aluminoborosilicate glasses will increase in the order of MgO → CaO → BaO. As a result, the $I_{576/458}$ and $I_{485/458}$ values decrease by substituting CaO for BaO in Series III, and increase in the order of MgO → CaO → BaO in Series IV.

Moreover, it was reported that group optical basicity of $[XO_{4/2}]^-$ (X = Al or B) is higher than that of $[BO_{3/2}]$ [25]. Thus, when Tm or Dy ions are well surrounded by $[XO_{4/2}]^-$ rather than $[BO_{3/2}]$ in aluminoborosilicate glass, the emission intensity will increase with increasing optical basicity. Since rare earth ions can be better separated by $[XO_{4/2}]^-$ groups in aluminoborosilicate glasses in the order of BaO → CaO → MgO, the emission intensity will increase in the same order in Series IV, and also increase on substituting CaO for BaO in Series III.

5. Conclusions

Tm^{3+} and Dy^{3+} ions co-doped aluminoborosilicate glasses were prepared in this study. A typical white luminescence was observed in the glass under 355 nm excitation when the doped concentration proportion of Tm^{3+} and Dy^{3+} ions was equal to 3:7. The luminescence intensity increased with increasing rare earth oxides concentration, quenched at 1.0 mol%. Moreover, the dependence of luminescence properties on glass compositions was also studied. The relative emission intensity ratio between different emission bands changed with different network modifier oxides, while the white color luminescence was not affected significantly.

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