Journal of Solid State Chemistry 181 (2008) 2725–2730

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

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

Shimin Liu [a], Gaoling Zhao [a], Xiaohua Lin [a], Hao Ying [b], Junbo Liu [b], Jianxun Wang [a], Gaorong Han [a,*]

[a] State Key Lab of Silicon Material, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China
[b] Hangzhou Bluestar New Material Technical Co. Ltd., Hangzhou 310012, China

ARTICLE INFO

*Article history:*
Received 28 March 2008
Received in revised form
5 June 2008
Accepted 8 June 2008
Available online 18 June 2008

*Keywords:*
White light
Luminescence
Rare earth
Aluminoborosilicate glass

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.



## 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.

* Corresponding author. Fax: +86 571 87952341.
*E-mail address:* hgr@zju.edu.cn (G. Han).

0022-4596/$ - see front matter © 2008 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2008.06.027

## 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) $x$$Tm_2O_3$–(0.25−$x$)$Dy_2O_3$–99.75ABS, (II) $y$(0.3$Tm_2O_3$–0.7$Dy_2O_3$)–(100−$y$)ABS, (III) 0.075$Tm_2O_3$–0.175$Dy_2O_3$–$Li_2O$–$m$CaO–(7.0−$m$)BaO–ZnO–$Al_2O_3$–$B_2O_3$–$SiO_2$, and (IV) 0.075$Tm_2O_3$–0.175$Dy_2O_3$–$R$O–$Al_2O_3$–$B_2O_3$–$SiO_2$. Here, $x$ = 0–0.25 mol%, $y$ = 0.5–1.5 mol%, $m$ = 0–7.0 mol%, ABS represents host glass $SiO_2$–$Al_2O_3$–$B_2O_3$–ZnO–$Li_2O$–BaO, and $R$O represents different network modifier oxides $Li_2O$, MgO, CaO, and BaO. Details of compositions are presented in Table 1. Analytical reagent $SiO_2$, $Al_2O_3$, $H_3BO_3$, ZnO, $Li_2CO_3$, MgO, $CaCO_3$, $BaCO_3$, and high-purity $Tm_2O_3$ (99.95%) and $Dy_2O_3$ (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 $Dy_2O_3$ 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 $Tm_2O_3$ 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.

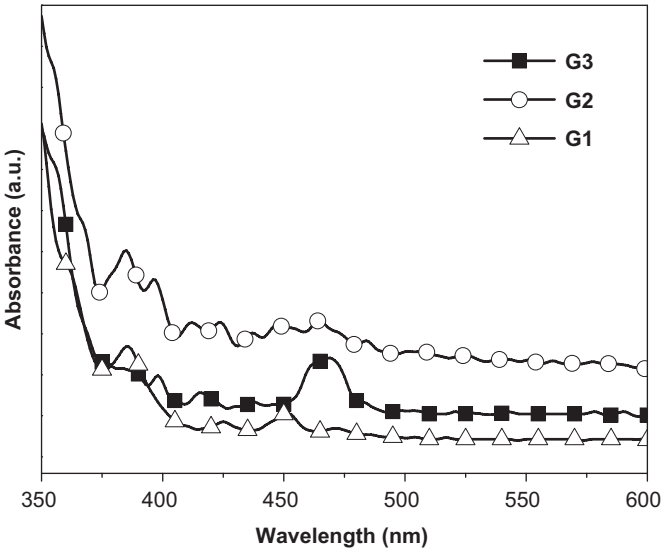


**Fig. 1.** UV–vis absorption spectra of $x$$Tm_2O_3$–(0.25−$x$)$Dy_2O_3$–99.75ABS samples. G1, G2, and G3 correspond to $x$ = 0, 0.075, and 0.25 mol%, respectively.

The luminescence spectra of Series I are shown in Fig. 2. Fig. 2(a) presents the emission spectra of $x$$Tm_2O_3$–(0.25−$x$)$Dy_2O_3$–99.75ABS ($x$ = 0–0.25, in mol%) glasses under 355 nm excitation at room temperature. It shows that in single $Dy_2O_3$ 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 $Tm_2O_3$ 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 0.075$Tm_2O_3$–0.175 $Dy_2O_3$–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 $Tm_2O_3$ and $Dy_2O_3$ 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 $Tm_2O_3$ and $Dy_2O_3$ 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 $Tm_2O_3$ and $Dy_2O_3$ 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

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

| Series | No. | $RE_2O_3$ | | | $Li_2O$ | MgO | CaO | BaO | ZnO | $Al_2O_3$ | $B_2O_3$ | $SiO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Total | $Tm_2O_3$ | $Dy_2O_3$ | | | | | | | | |
| 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 |