Research Article

Preparation of ZnO-SrO-B_2O_3 Glass Systems Doped with Dy_2O_3 for the White Light Emission Material Application

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ABSTRACT

ZnO-SrO-B_2O_3 glasses doped with Dy^{3+} ions were prepared by a conventional melt quenching technique. The molar volume density and refractive index tends to increase with increasing of Dy_2O_3 concentration. The absorption bands show energy levels transition from $^6H_{15/2}$ ground state to excited states such as 781 nm ($^6F_{3/2}$), 801 nm ($^6F_{5/2}$), 895 nm ($^6F_{7/2}$), 1083 nm ($^6F_{9/2}$), 1254 nm ($^6F_{11/2}$) and 1661 nm ($^6H_{11/2}$), and the intensity of the peak at 1254 nm is the highest. The excitation spectra of the 7 peaks glass sample were found in the wavelength range of 320-470 nm with the highest intensity peak at 386 nm. The emission spectra represent four emission bands, and all emission bands are over the visible range. The peak at 575 nm is the highest intensity peak. The CIE chromaticity (x,y) coordinates fall in the white light region of the CIE chromaticity diagram. The experimental decay time (τ_{exp}) of $^6H_{13/2}$ transition of Dy^{3+} ions obtained from the measurement tends to increase with increasing of Dy_2O_3 concentration. These results show the potential for use in white LED applications.

Keywords: Dysprosium, Borate glasses, Photoluminescence

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Introduction

Presently, glass materials doped with rare earth ions (RE^{3+}) have received attention for use as laser, optical fiber and white light emitting diodes (W-LEDs) [1]. The dysprosium ion (Dy^{3+}) is one of the most popular rare-earths used in light emitting applications because the obtained light is in the visible range, and if there is a suitable emitting ratio between blue and yellow, it can provide white light [2]. The glasses of desired properties can be synthesized by choosing suitable composition of the host matrix. Glass host having alkali and alkaline-earth metals has advantages over other composition because this does not only reduce melting temperature but also acts as modifiers [1-6]. Furthermore, among the glass former, borate is the most attractive to researchers because of its low melting temperature, high mechanical and chemical stability and high transparency [4-7]. Borate glass is attractive in creating high-quality light sources due to its high solubility of RE-ions. Due to this uniqueness, RE ion-doped borate glass can be prepared with a wide range of concentrations. To apply for the suitable applications, including the application of a high-power laser, medium can be effective because it can be used without damage in the medium. Another highlight is the good dispersion of RE ions in the borate host, resulting in the extraction of effective luminescence [8]. Another important component of the glass structure is the intermedia, where ZnO is one of the most popular one in addition to its low cost and direct wide band gap, intrinsic emitting property, large excitation binding energy, nontoxic and hygroscopic nature [9, 10]. In this context, Dy^{3+} doped B_2O_3:ZnO:SrO glass was chosen to examine the physical and optical properties.

Experimental techniques

Synthesis

ZnO-SrO-B_2O_3 glass doped with dysprosium were prepared using the composition of (65-x)B_2O_3: 10ZnO: 25SrO: xDy_2O_3 (where x = 0.00, 0.50, 1.00, 1.50, 2.00 and 2.50 mol %). The chemicals are high purity boric acid (H_3BO_3), zinc oxide (ZnO), strontium oxide (SrO), and dysprosium oxide (Dy_2O_3). The chemical powders were mixed and put into the alumina crucible at 6 different concentrations. The crucibles were kept in an electrical furnace with a 5 °C/min heat rate from room temperature to 1200 °C in an air atmosphere. After soaking the crucible for 3 hrs at 1200 °C, the melted chemicals were poured into the preheated graphite mold. The forming glasses were kept at 500 °C for 3 hrs in the oven for annealing. The glass samples were cut to the cuboid shape 10x15x3 mm^3 and polished for measurements.

Measurements

In this study, glass density was determined using Archimedes' principle by using water as a liquid immersed according to the following equation.

$$\rho = \left[\frac{W_{air}}{W_{air} - W_{water}} \right] \times \rho_{water}$$

Where, ρ is the density of present glasses, W_{air} is obtained by weighing the glass in the air and W_{water} is obtained by weighing the glass in the water, while ρ_{water} is the mass per unit volume of water that is mostly given as 1 g/cm^3. The molar volume (V_M) was calculated using the following relation.

$$V_M = \frac{M_T}{\rho}\ (\mathrm{cm^3/mol})$$

Where, M_T is the total molecular weight of the present glasses. The refractive index can be determined with an Abbe refractometer using 589.3 nm light source and monobromonaphthalene is used as a contact liquid.

Absorption spectra were recorded in the wavelength region 250-2000 nm using UV-Vis-NIR spectrophotometer (Shimadzu 3600). Photoluminescence (excitation and emission) spectra were recorded using cary eclipse fluorescence spectrophotometer (Agilent technologies Inc.) under the excitation wavelength of 386 nm in the spectral region of 400-800 nm. The luminescence spectra and decay curves of $^4F_{9/2}$ level of Dy^{3+} ions of these glasses were carried out by cary-eclipse fluorescence spectrophotometer (Agilent technologies Inc.) under the excitation wavelength of 386 nm. For the luminescence, color of the present glasses excited under 386 nm has been characterized by the CIE 1931 chromaticity diagram.

Results and discussion

Physical properties

The glass samples were prepared using the composition of (65-x)B_2O_3: 10ZnO: 25SrO: xDy_2O_3 (where x = 0.00, 0.50, 1.00, 1.50, 2.00 and 2.50 mol%) as shown in Figure 1. The ZnO-SrO-B_2O_3 glasses with different Dy_2O_3 concentration are transparent and have good optical characteristics.

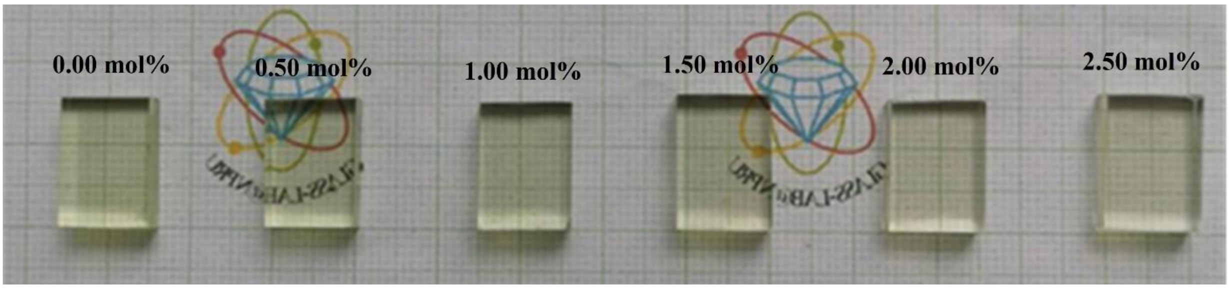


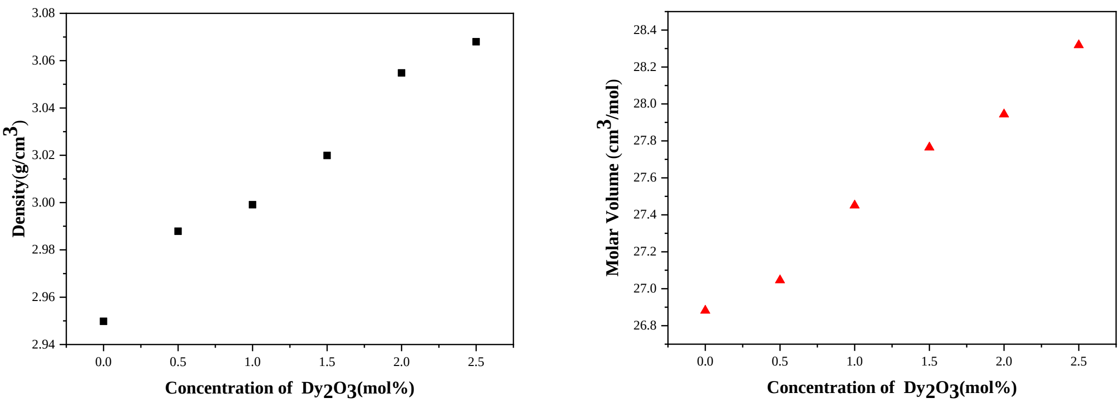
Figure 1 ZnO-SrO-B_2O_3 glasses with different Dy_2O_3 concentration.

The density and refractive index of the polished glass sample was measured. The resulting density was used to calculate the molar volume. Table 1 shows the physical properties of ZnO-SrO-B_2O_3. The molar volume, density and refractive index of Dy^{3+}-doped ZnO-SrO-B_2O_3 glass tended to increase with the Dy_2O_3 concentration. It was found that the density increased with increasing of Dy_2O_3 concentration (Figure 2a). The values of density are in the range of 2.9498±0.0017 to 3.0680±0.0009 g/cm^3. The molar volume of glasses present increase in the contents from 0.00 to 2.50 mol%, between

26.8817±0.0084 to 28.3181±0.0365 cm^3/mol (Figure 2b). This could be due to the fact that Dy_2O_3 was connected to the non-bridging oxygen (NBOs) in the glass structure [11, 12]. The refractive index of ZnO-SrO-B_2O_3 glasses at different Dy_2O_3 contents showed an increase in the concentration of Dy_2O_3 with values between 1.5785±0.0002 to 1.5859±0.0001.

Table 1 Physical properties of the ZnO-SrO-B_2O_3 glass at different Dy_2O_3 contents.

Concentration of Dy_2O_3 (mol%)	Density (g/cm^3)	Molar volume (cm^3/mol)	Refractive index
0.00	2.9498 ± 0.0012	26.8817 ± 0.0122	1.5785 ± 0.0002
0.50	2.9879 ± 0.0007	27.0461 ± 0.0076	1.5802 ± 0.0002
1.00	2.9991 ± 0.0012	27.4509 ± 0.0201	1.5839 ± 0.0003
1.50	3.0199 ± 0.0011	27.7646 ± 0.0154	1.5859 ± 0.0001
2.00	3.0548 ± 0.0014	27.9437 ± 0.0098	1.5844 ± 0.0003
2.50	3.0680 ± 0.0036	28.3181 ± 0.0365	1.5850 ± 0.0001



(a) (b)

Figure 2 (a) Variation of density (ρ) and (b) molar volume (V_M) for the Dy^{3+} doped ZnO-SrO-B_2O_3 glass.

Absorption spectra

The absorption spectra of ZnO-SrO-B_2O_3 glass were examined in the wavelength range 250-2000 nm as shown in Figure 3. The absorption bands showed the energy levels transition from the $^6H_{15/2}$ ground state to the excited states such as 781 nm ($^6F_{3/2}$), 801 nm ($^6F_{5/2}$), 895 nm ($^6F_{7/2}$), 1083 nm ($^6F_{9/2}$), 1254 nm ($^6F_{11/2}$), and 1661 nm ($^6H_{11/2}$) [13, 14]. From the image, the peak at 1254 nm is the peak with the highest intensity. Corresponding to the transition $^6H_{15/2} \longrightarrow {}^6F_{11/2}$ in the NIR region, this is the hypersensitive transition (the 4f transition which is very sensitive to the environment) that obeys the alternative rule, $||\Delta S| = 0$, $|\Delta L| \leq 2$ and $|\Delta J| \leq 2$. This transition is sensitive to the local environment of rare-earth ions [15].

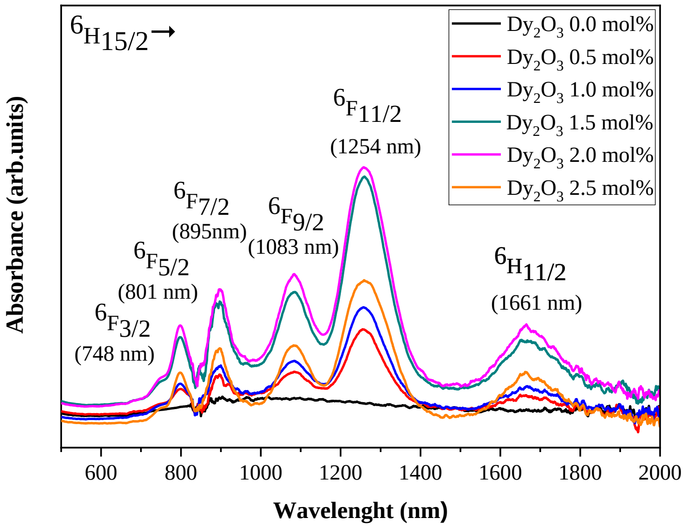


Figure 3 The absorption spectra of the ZnO-SrO-B_2O_3 glass at different Dy_2O_3 contents.

Luminescence and radiative properties

The emission wavelength at 575 nm was fixed to determine the excitation spectra of the glass sample. The excitation spectrum of the seven-peaks glass sample was found in the wavelength range 320-470 nm consisting of 324 nm ($^6P_{3/2}$), 350 nm ($^6P_{7/2}$), 363 nm ($^6P_{5/2}$), 386 nm ($^4F_{7/2}$), 425 nm ($^4G_{11/2}$), 452 nm ($^4I1_{5/2}$) and 470 nm ($^4F_{9/2}$) from $^6H_{15/2}$ state, respectively, with the highest intensity peak at 386 nm (Figure 4). The highest intensity peak was used to excite the sample glass to determine the emission spectra as shown in Figure 5. The emission spectra depicted four emission bands, and all emission bands were over the visible range, comprising of 481 nm ($^6H_{15/2}$), 575 nm ($^6H_{13/2}$) 664 nm ($^6H_{11/2}$) and 751 ($^6H_{9/2}$) [16-19]. The $^6H_{15/2}$ was electric dipole (ED) transition, corresponding to $^6H_{13/2}$ which was magnetic-dipole (MD) transition. Whereas the ED transition has highest intensity as compared to MD transition in emission spectra. The ED transition followed selection rule of $\Delta L = 2$, $\Delta J = 2$ and was sensitive to the local environment of the host matrix around Dy^{3+}-ions. The highest intensity of ED as compared to MD transition depicted the asymmetric nature of the host matrix. The quenching of intensity in emission spectra was observed at 1.0 mol% of Dy^{3+}-ions, which was due to the energy transfer through non radiative energy and cross relaxation channels [3-6].

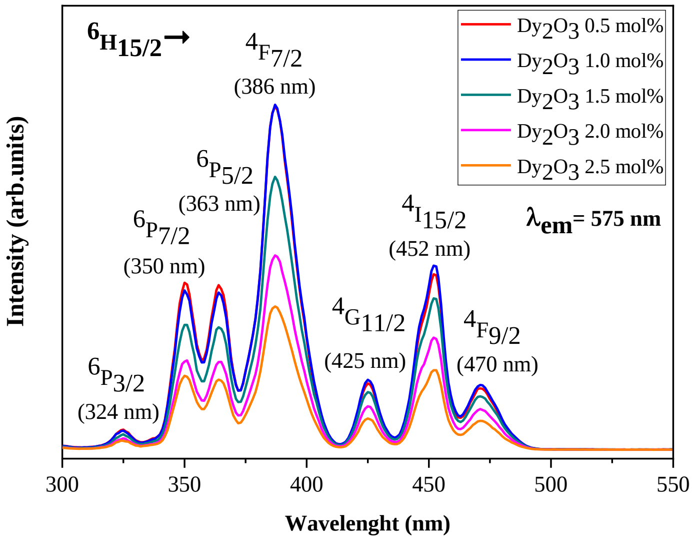


Figure 4 The excitation spectra of the ZnO-SrO-B_2O_3 glass at different Dy_2O_3 concentrations.

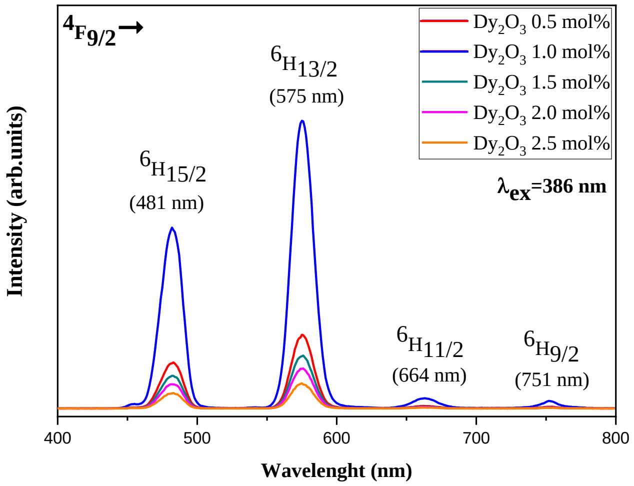


Figure 5 The emission spectra of the ZnO-SrO-B_2O_3 glass at different Dy_2O_3 contents.

Figure 6 shows an energy level diagram for the excitation and emission spectra of the glass sample corresponding to the findings of both the excitation and emission spectra [16-19].

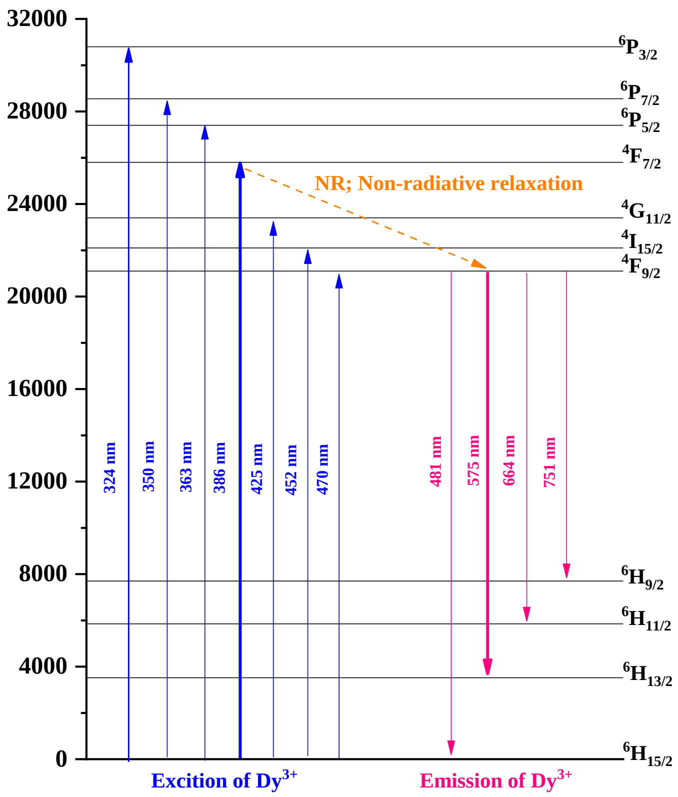


Figure 6 The Partial energy levels diagram of the Dy^{3+} ions in the ZnO-SrO-B_2O_3 glass.

Decay curve analysis

A wavelength of 386 nm was used to determine the decay profile of $^4F_{9/2}$ excited level in ZnO-SrO-B_2O_3 glass and to monitor the 575 nm emission, with 386 nm and 575 nm being the optimal value obtained by the emission process. The experimental lifetime (τ_{exp}) values obtained from the measurement were 0.538, 0.431, 0.351, 0.297 and 0.266 ms. The decrease of τ_{exp} values of $^4F_{9/2}$ emission level with the increase of Dy^{3+} ions increases is shown in Figure 7, possibly due to energy transfer through the non-radiative decay, non-radiative energy transfer and cross relaxation channels among Dy^{3+} ions at higher concentrations [20].

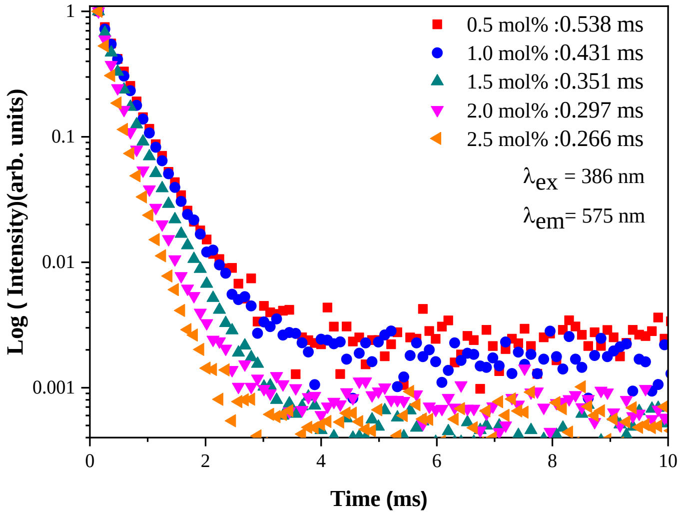
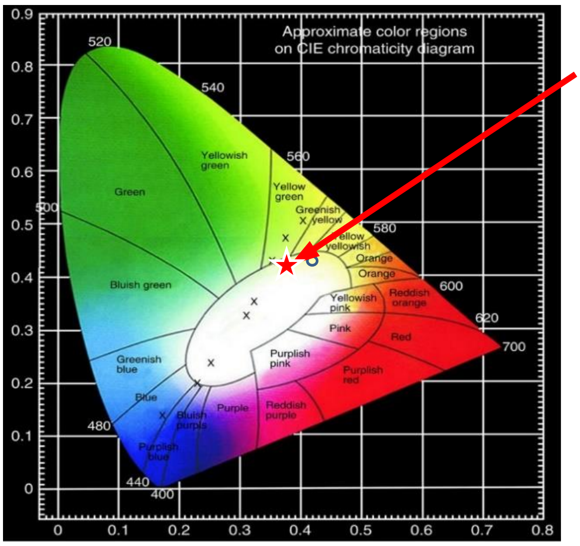


Figure 7 Luminescence decay profiles of the $^4F_{9/2}$ level of Dy^{3+} in ZnO-SrO-B_2O_3 glass at different Dy_2O_3 contents**.**

CIE chromaticity coordinates

As shown in Figure 5, at the excitation wavelength of 386 nm, the glass emits 4 peaks with 2 major peaks at wavelengths of 481 and 575nm which are yellow and blue light. With the proper ratio of yellow and blue, the white light can be displayed. As shown in Figure 8, the given (x, y) coordinates are shown in the white light range in the CIE chromaticity diagram. The CIE diagram confirms that these Dy^{3+} doped ZnO-SrO-B_2O_3 glass emits the white light region. This shows that the glass has the potential to be developed for use in white LED applications. [21].



λ_{ex} = 386 nm	
X	y
0.38	0.42

Figure 8 CIE chromaticity coordinates of ZnO-SrO-B_2O_3 glass at different Dy_2O_3 contents**.**

Conclusions

In the absorption spectra, the NIR region at the wavelength of 1265 nm ($^6H_{15/2}\rightarrow^6F_{11/2}$) is the hypersensitive transition for Dy^{3+} ions. Under the excitation of 386 nm, the emission spectra represent four emission bands, and all emission band are over the visible range at 481, 575, 664 and 751 nm, corresponding to the transitions $^4F_{9/2}\rightarrow^6H_{15/2}$, $^6H_{13/2}$, $^6H_{11/2}$ and $^6H_{9/2}$, respectively. The highest intensity photoluminescence in these glasses is 1.0 mol% of Dy_2O_3. The fluorescence lifetime for the $^4F_{9/2}$ level of Dy^{3+} ions is found to decrease from 0.538 to 0.266 ms when the concentration is increased, which indicated the presence of non-radiative process. The CIE diagram confirms that these Dy^{3+} doped glass emits white light. This shows that the glass has the potential to be use in white LED applications.

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