Physica B xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Physica B

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

Physical and optical properties of lithium borosilicate glasses doped with Dy^{3+} ions

D.D. Ramteke[a,*], R.S. Gedam[b], H.C. Swart[a]

[a] Department of Physics, University of the Free State, P.O. Box 339, Bloemfontein 9300, South Africa
[b] Department of Applied Physics, Visvesvaraya National Institute of Technology, Nagpur 440010, India

ARTICLE INFO

Keywords:
Glasses
Rare earth ions
Luminescence
WLED

ABSTRACT

The borosilicate glasses with Dy^{3+} ions were prepared by the melt quench technique with varying concentration of Dy_2O_3. The glasses were characterized by the density calculation, absorbance and photoluminescence (PL) spectroscopy measurements. Density and molar volume of the glasses increases with increase in Dy^{3+} ions in the glass matrix. This behavior is correlated with the higher molecular weight and larger ionic radius of Dy^{3+} ion compared to the other constituents of glass matrix. Emission of Dy^{3+} doped glasses showed three bands at 482, 573 and at 665 nm which correspond to $^6H_{15/2}$ (blue), $^6H_{13/2}$ (yellow) and $^6H_{11/2}$ (red) transitions. The emission spectra of glasses with different concentration of Dy^{3+} ions shows that, glasses with 0.5 mol% of Dy_2O_3 shows highest emission and decreases with further doping. CIE 1931 chromaticity diagram showed that the emission of these glasses was in the white region. Photographs of these glasses under 349 nm Light emitting diode excitation also confirmed the white light emission from these glasses.

1. Introduction

Glasses are considered as fascinating material in the condensed matter. By appearance it shows the properties of crystals but it does not show the sharp melting point like crystals. They behave isotopically under the absence of applied forces and internal stresses [1]. The glasses can be synthesized over the wide range of composition and properties of the material can be tuned by varying the composition [2]. With insertion of rare earth ions in the glass matrix, glasses are the promising candidate for solid state light applications. Borosilicate glasses are interesting to study as they offer the wide range of composition, high chemical stability and good rare earth solubility [3].

On comparison with the other rare earth ions Dy^{3+} ions are interesting to study. Dy^{3+} ions offer laser emission around 1.3 µm laser emission due to the $^6F_{11/2}(^6H_{9/2}) \rightarrow {}^6H_{15/2}$ transition. Strong emission in the visible region around 485 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) and 575 nm ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) makes Dy^{3+} ions doped material promising candidates for white light applications [2–6]. The yellow component of Dy^{3+} ions related to the $^6H_{13/2}$ transition is hypersensitive in nature and has a strong dependence on the symmetry of the host. On the other hand the $^6H_{15/2}$ transition does not get affected by the surrounding of the host material because of its magnetic dipole nature, while the $^6H_{11/2}$ transition is electric dipole in nature. As the emission from Dy^{3+} ions fulfill the basic criteria of white light emission, they are interesting to study. By selecting the proper host it is possible to tune the yellow to blue ratio for the white light emission [4–11].

The present work is an extension of our previous work [3]. The previous work is related to the effect of codoping of Sm^{3+} and Dy^{3+} ions on the emission properties of the glasses. Also there was attempt made in the previous work to study any possible energy transfer mechanism between Sm^{3+} and Dy^{3+} ions. As Dy^{3+} ions are well known for W-LED application without any co-dopant rare earth ions, it is interesting to study the effect of Dy^{3+} ions on the properties of the glasses. In the present study we study the effect of different concentration of Dy^{3+} ions on the physical and optical properties of the borosilicate glasses. We reported the variation of density (ρ), molar volume (V_M), concentration of ions (N), internuclear distance (r_i), polaron radius (r_p) and field strength (F). We also report the variation of luminescence intensity as a function of mol% of Dy_2O_3.

2. Experimental

The Dy^{3+} containing lithium borosilicates were prepared by a simple melt quench technique with high purity chemicals as defined in the Ref. [3]. The general formula of the prepared glasses is as follow:

$$30Li_2O\colon (70 - xDy_2O_3)\left\{\frac{1}{7}SiO_2\colon \frac{6}{7}B_2O_3\right\} \text{ where } x = 0.5, 1, 1.5, 2.$$

* Corresponding author.
E-mail address: durgaprasadr@ufs.ac.za (D.D. Ramteke).

http://dx.doi.org/10.1016/j.physb.2017.07.035
Received 11 April 2017; Received in revised form 8 July 2017; Accepted 17 July 2017

Fig. 1. Glasses with different mol% of Dy_2O_3.

X-ray diffraction pattern (XRD) were measured using a Bruker D8 advanced instrument with Cu target radiation (λ = 0.154056 nm). The density of the glasses was measured by the Archimedes principle using a Mettler Toledo (AB54-S) weighing balance with toluene (0.86455 g/cm^3) as an immersion liquid. The optical absorption spectra of the prepared glasses were recorded on the LAMBDA 950 UV/Vis/NIR spectrophotometer (PerkinElmer) by using as prepared glasses. The glasses were crushed in the powder form for photoluminescence study. The excitation and emission spectra of prepared glasses were recorded by an Edinburgh Instruments FS5 spectrophotometer. The obtained glasses were also excited with a 349 nm Light emitting diode (LED) to obtain white light emission.

3. Results and discussion

Fig. 1 shows the photograph of the as prepared glasses. The glasses were colorless and transparent. Fig. 2 shows X-ray diffraction spectra of the as prepared glasses. Spectra contains the broad humps and there is absence of any sharp peaks related to any of the constituent materials. This confirms the amorphous nature of the glasses. Also it confirms that the starting materials are well dissolve during the glass making process. The measured values of density (ρ) and calculated values of molar volume (V_M), concentration of ions (N), internuclear distance (r_i), polaron radius (r_p) and field strength (F) were calculated by using the equations in Ref. [3] and are tabulated in Table 1. From this table it is observed that the density and molar volume of the glasses increased with an increase in Dy_2O_3 concentration in the glass matrix. The increase in the values of density is related to the higher molecular weight of Dy_2O_3 compared to the other oxides, as replacement of fewer ions by Dy^{3+} and oxygen has a noticeable change. The increase in the molar volume is related to the expansion of the glass network. When any impurity is added to the glass network it occupies the position of the interstitial space (voids). Since Dy^{3+} ions has a larger ionic radius, it expands the glass network when it goes to an interstitial position. There is also another possibility that, there is a change in boron to oxygen and silicon to oxygen ratio due to addition of Dy_2O_3 which promotes the de-polymerization of the glass network and increases the cross linking ability of various borate and silicates group which expands the glass network and there is an increase in the molar volume [12].

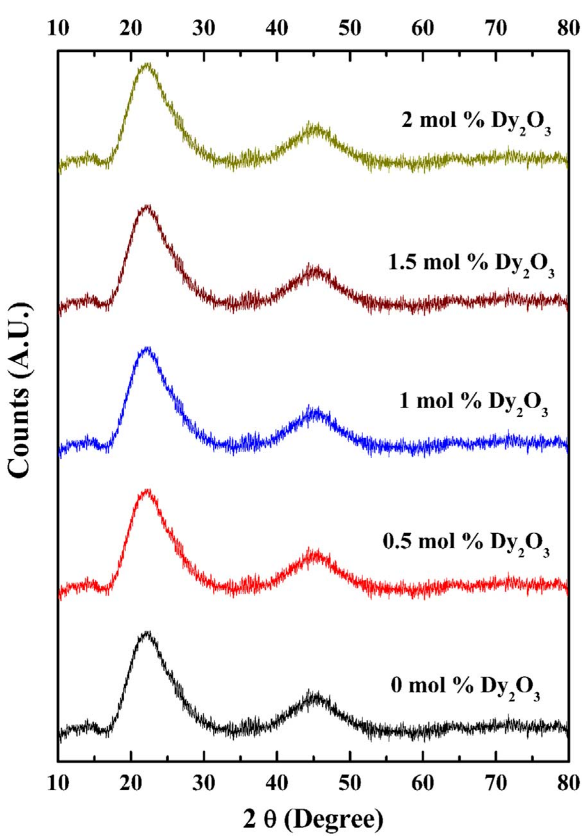

Fig. 2. XRD spectra of lithium borosilicate glasses with different mol% of Dy_2O_3.

Table 1
Properties of lithium boro-silicate glasses containing Dy_2O_3.

X mol% Dy_2O_3	*0*	*0.5*	*1*	*1.5*	*2*
Density(g/cm^3)	2.30	2.34	2.39	2.44	22.43
Molar volume (cm^3)	24.66	24.92	25.02	25.11	25.88
$N \times 10^{20}$ (ions/cm^3)	0	1.21	2.41	3.60	4.65
r_i Å	0	20.23	16.08	14.06	12.90
r_p Å	0	8.15	6.48	5.67	5.20
$F \times 10^{14}$ (cm^{-2})	0	4.52	7.15	9.34	11.09

Fig. 3 shows the absorbance spectra for the all prepared glasses. Spectra show various absorption bands related to the Dy^{3+} ions. Bands observed are at wavelengths of 349, 363, 386, 424, 453, 471, 794, 894, 1082, 1264 and 1661 nm. These bands are related to the $^6H_{15/2}\to{}^6P_{7/2}$, $^6H_{15/2}\to{}^6P_{5/2}$, $^6H_{15/2}\to{}^4I_{13/2}$, $^6H_{15/2}\to{}^6G_{11/2}$, $^6H_{15/2}\to{}^4I_{15/2}$, $^6H_{15/2}\to{}^4F_{9/2}$, $^6H_{15/2}\to{}^6F_{5/2}$, $^6H_{15/2}\to{}^6F_{7/2}$, $^6H_{15/2}\to{}^6H_{7/2}$, $^6H_{15/2}\to{}^6F_{11/2}+{}^6H_{9/2}$ and $^6H_{15/2}\to{}^6H_{11/2}$ [13].

From the Fig. 3 it is observed that the $^6H_{15/2}\to{}^6P_{7/2}$ transition is the most prominent one and therefore it was selected to study the excitation and emission properties. Further for the confirmation of selected excitation wavelength mapping was performed and is shown in Fig. 4. From the mapping it is clear that maximum emission was observed in the 400–700 nm range for the 349 nm excitation. Fig. 5 shows the excitation and emission spectra for 1.5 mol% Dy_2O_3 as representative. The excitation spectra at 573 nm shows seven excitation bands identified as $^4M_{17/2}$, $^6P_{7/2}$, $^6P_{5/2}$, $^4I_{13/2}$, $^4G_{11/2}$, $^4I_{15/2}$ and $^4F_{9/2}$. $^6P_{7/2}$ Dy^{3+} transition at 349 nm is the most prominent one and by this excitation emission spectra were recorded. Emission spectra of 1.5 mol% Dy_2O_3 containing glasses shows three bands at 482 nm,

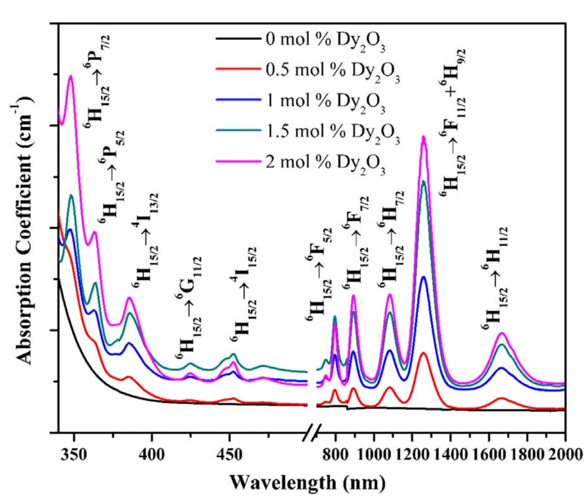

Fig. 3. Optical absorption spectra of the glasses containing different mol% of Dy_2O_3.