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Physical and optical properties of Dy^{3+} bismuth barium borate glasses

Rungsan Ruamnikhom[1,*], Patarawagee Yasaka[2] and Jakrapong Kaewkhao[2]

[1]Faculty of Liberal Arts, Rajamangala University of Technology Rattanakosin,
Nakhon Pathom 73170, Thailand
[2]Center of Excellence in Glass Technology and Materials Science (CEGM),
Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand

Abstract

Trivalent dysprosium (Dy^{3+}) doped bismuth barium borate glasses with composition (40-x) B_2O_3:40Bi_2O_3:20BaO:xDy_2O_3 (where x = 0, 0.50, 1.00, 1.50, 2.00 and 2.50 mol.%) were prepared by melt quench technique at 1,100 ^oC. The density of the prepared samples was measured using Archimedes' principle. The results show the increasing in the glass density with respect to increasing in the doping concentrations of Dy_2O_3. The molar volume of the bismuth barium borate glasses doped with Dy^{3+} were calculated and found to be in the range 30.63-30.95 cm^3/mol. The analysis of FTIR spectrum of the sample depicts that the glass network is built up of mainly BiO_3, BO_3 and BO_4 units. The UV visible absorption spectra of the dysprosium doped bismuth barium borate glasses were found to be consists of five absorption peaks which correspond to transitions from ground state $^6H_{15/2}$ to various excited states.

Keywords: trivalent dysprosium, bismuth barium borate, optical

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1. Introduction

In recent years, a special attention is intensively focused on the rare earth (RE) ions doped glasses on the fabrication of new generation solid state devices like white LEDs, solid state lasers, flat panel displays, planar waveguide, optoelectronic devices and broadband amplifiers etc., due to their inhomogeneous line widths, flexibility in the selection of wide range of chemical composition and mass production [1, 2]. Among the various glasses, borate glasses are excellent host matrices because boron troxide (B_2O_3) acts as a good glass former and flux material [3]. Borate glasses are structurally more intricate compared to phosphate or silicate glasses due to two types of coordination of boron atoms with 3 and 4 oxygens and the structure of vitreous B_2O_3 consists of a random network of boroxyl rings and BO_3 triangles connected by B-O-B linkages. Moreover, the addition of a modifier oxide causes a progressive change of some BO_3 triangles to BO_4 tetrahedra and results in the formation of various cyclic units like diborate, triborate, tetraborate or pentaborate groups [4].

The heavy metal ions like Bi_2O_3, PbO, PbF_3, etc., containing in borate glasses, decreases the host phonon energy and thereby improves the effective fluorescence [5]. Moreover, the bismuth oxide contained host glass matrix improves chemical durability of the glass [6], Despite, the Bi_2O_3 is not a classical network former; it exhibits some superior physical properties like high density, high refractive index and exhibits high optical basicity, large polarizability and large nonlinear optical susceptibility [7]. The presence of two network forming oxides such as classical B_2O_3 and the conditional Bi_2O_3 glass former, the possible participation in the glass structure of both boron and bismuth ions with more than one stable coordination, the capability of the bismuth polyhedral and of the borate structural groups to form independent interconnected networks [8].

Over the last several years, bismuth barium borate glasses are also useful for variety of optical applications such as radiation shielding window, gamma-rays shielding materials and scintillation counters [9, 10]. Among the various rare earth ions, Dy^{3+} ions is one of the good luminescent ion which emits blue and yellow and moderate red emission. Despite, possible visible emission is exhibited from the Dy^{3+} ions, a special attention has also been focused on Dy^{3+} doped complexed materials due its capability of white light emission under the ultraviolet or blue excitation wavelengths [11]. Moreover, Dy^{3+} doped glasses are also used as promising materials for telecommunication technological applications due to their infrared emission at 1.32 μm apart from the display device applications [12].

The purpose of this study was therefore to develop bismuth barium borate glasses doped with Dy^{3+} ions. The study also focused on the fabrication process, material characterizations and analyses. The physical,

*Corresponding author; e-mail: rungsan.rua@rmutr.ac.th

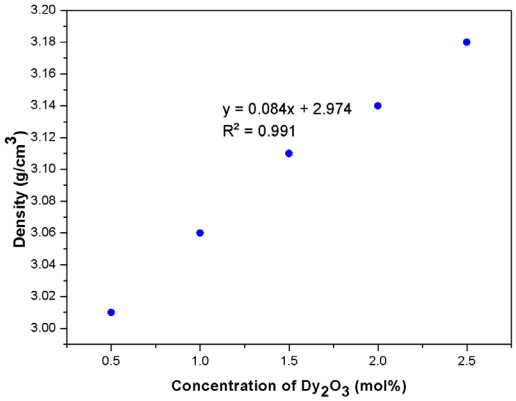

Figure 1 Densities of the Dy^{3+}-doped bismuth barium borate glasses with respect to the Dy_2O_3 content

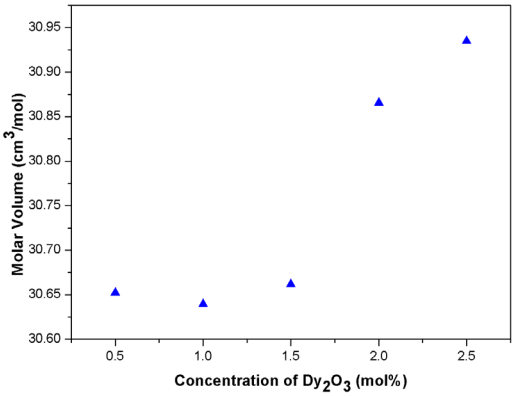

Figure 2 Molar volumes of the Dy^{3+}- doped bismuth barium borate glasses with respect to the Dy_2O_3 content

structural and optical properties were investigated with respect to the concentrations of the Dy^{3+} ions.

2. Materials and methods

Dy_2O_3 doped bismuth barium borate glasses with compositions (40-x) B_2O_3:40Bi_2O_3:20BaO:xDy_2O_3 (where x having values 0.5, 1.0, 1.5, 2.0 and 2.50 mol.% resp.) have been melted in alumina crucible by melt-quench technique at 1,100 °C for 3 hours. The melts were air quenched by pouring it onto a preheated stainless steel mould and annealed at 500 °C for 3 hours to decreased thermal strains. The cut glass samples were polished into dimension 1.00 cm × 1.50 cm × 0.30 cm for the study of physical and optical properties. The densities based on Archimedes' principle using water at the room temperature. The molar volume was calculated using the relation $V_M = M_T/\rho$, where M_T is the total molecular weight of the multicomponent glass system. The optical absorption spectra of the glass samples were recorded using a Shimadzu 3600 UV-VIS-NIR spectrophotometer in the range 200-2,500 nm. The FTIR vibration spectra of the present glasses were recorded at room temperature in the wavenumber range 650-3,000 cm^{-1} using an Agilent-Cary 630 FTIR which has a resolution of 1 cm^{-1}.

3. Results and discussion

The density of the prepared samples based on the Archimedes' principle, the determined density of the glass samples varied in a range of 3.01-3.18 g/cm^3 with respect to the Dy_2O_3 concentrations are shown in Figure 1. The results show the increase in the glass density with respect to increase in the doping concentrations of Dy_2O_3. The glass density was also increased because of relatively higher molecular mass of Dy_2O_3 in comparison to that of B_2O_3 within the glass matrix. In addition, the percentage of the Dy_2O_3 content also performed differently within the matrix. The molar volume is almost stable from 0.50 to 1.50 % mol concentrations, due to Dy^{3+} acting as a part of former, and increased when the concentrations are in range of 1.50%-2.50%, due to Dy^{3+} entering into the glass network as a modifier and non-bridging oxygen (NBOs), as shown in Figure 2.

The absorption spectra of the Dy^{3+} doped bismuth barium borate glasses recorded in the UV-Vis-NIR region are shown in Figure 3. It is observed from the figure that, the absorption spectra exhibit five absorption bands around 796, 902, 1096, 1276 and 1681 nm due to the $4f^9$ electronic transition of the Dy^{3+} ions from the $^6H_{15/2}$ ground level to the various excited states such as $^6F_{5/2}$, $^6F_{7/2}$, $^6F_{9/2}$,$^6H_{7/2}$, $^6F_{11/2}$, $^6H_{9/2}$ and $^6H_{11/2}$, respectively [13]. As the concentration increases, the intensity of the absorption bands is found to increase whereas the band center does not differ. The absorption transitions such as $^6H_{15/2} \rightarrow {}^6F_{11/2}$ and $^6H_{15/2} \rightarrow {}^6H_{11/2}$ are found to posses higher intensity which are highly sensitive to the host environment known as hypersensitive transitions [14].

Figure 4 shows the FTIR spectra of (40-x)B_2O_3 : 40Bi_2O_3 : 20BaO : xDy_2O_3 with x = 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 mol%, respectively. According to Krogh-Moe model, the structure of borate glass consists of BO_3 triangles with certain fraction of six membered (boroxol) rings [15]. In B_2O_3 glasses boron [B^{3+}] ions are triangularly coordinated by oxygen to form glasses easily. The BO_3 triangles are corner bonded in a random network [16]. The introduction of transition metal ions in these glasses helps the boron to form tetraborate groups and progressive substitution of boroxal rings by triborate and tetraborate groups [17]. The boroxal ring shows its characteristic frequency at 806 cm^{-1} and the presence or absence of this band decides the existence or absence of boroxal rings in the structure. In the present set of glasses no band was observed at or around 806 cm^{-1} indicating that no boroxol rings are present in these glasses. The peaks of the IR spectra of the glasses under study are listed

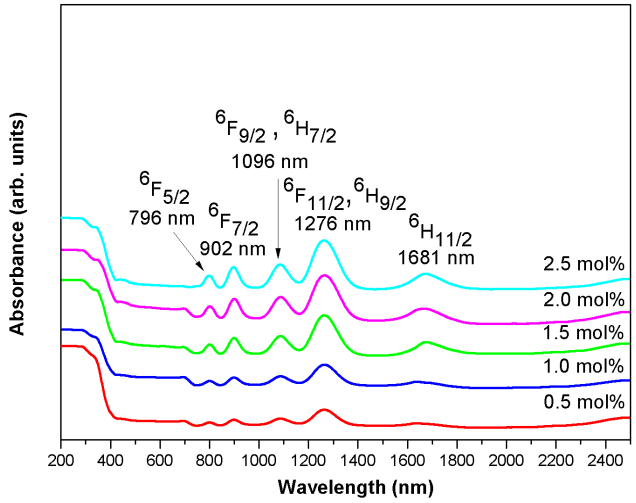

Figure 3 Absorption spectra of the Dy^{3+}-doped bismuth barium borate glasses with respect to the Dy_2O_3 content

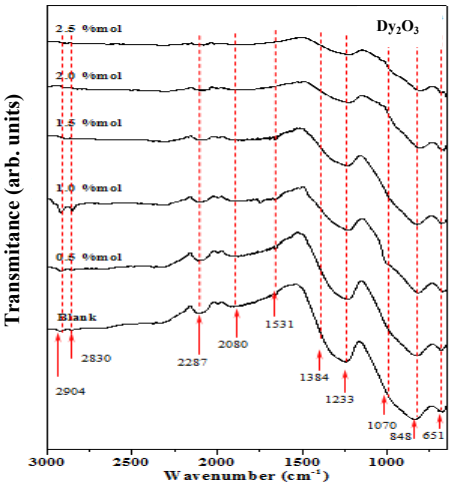

Figure 4 Infrared spectra of the Dy^{3+}-doped bismuth barium borate glasses with respect to the Dy_2O_3 content

Table 1 Peak table of FTIR analysis of Dy^{3+}-doped bismuth barium borate glasses with respect to the Dy_2O_3 content

Wavenumber (cm^{-1})	IR band assignments
651	The bending vibrations of B-O-B linkages of BO_3 units
848	Symmetrical stretching vibration of the Bi-O bonds in the BiO_3 groups
1070	Stretching vibrations of B-O bonds in BO_4 units from tri, tetra and penta borate groups
1233	B-O_{sym} stretch in BO_3 units from pyro and ortho borate groups
1384	B-O_{sym} stretch in BO_3 units from varied types of borate groups
1531	$B\text{-}O^-$ stretch in BO_2O^- units from varied types of borate groups
2080 - 2904	OH bending mode of vibration

in Table 1. The bands observed in the region 2080-2940 in all the glass samples are attributed to the hydroxyl or water group [18]. The present set of glasses show transmission bands in regions 2904, 2830, 2287, 2080, 1531, 1384, 1233, 1070, 848 and 651 cm^{-1}. It has been reported that the bands observed in the region 1233 cm^{-1} are due to the asymmetrical stretching relaxation of the B-O bond of trigonal BO_3 units [19]. The band around 1070 cm^{-1} originates from B-O bond stretching of the tetrahedral BO_4 units and is due to the vibration of some boron atoms attached to the non-bridging oxygen in the form of BO_4 vibrations [20]. The shoulder around 848 cm^{-1} is related to the symmetrical stretching vibration of Bi-O in [BiO_3] group [21]. The band observed around 651 cm^{-1} is the bond bending mode of B-O-B vibrations [22, 23].

4. Conclusions

Dy^{3+}-doped bismuth barium borate glasses with composition (40-x)B_2O_3:40Bi_2O_3:20BaO:xDy_2O_3 (where x = 0, 0.50, 1.00, 1.50, 2.00 and 2.50 mol.%) were prepared by melt quenching technique at 1,100 ^{0}C. The density of the prepared samples was measured using Archimedes' principle. The results show the increasing in the glass density with respect to increasing in the doping concentrations of Dy_2O_3. The molar volume of the bismuth barium borate glasses doped with Dy^{3+} were calculated and found to be in the range of 30.63-30.95 cm^3/mol. The analysis of FTIR spectrum of the sample depicts that the glass network is built up of mainly BiO_3, BO_3 and BO_4 units. The UV visible absorption spectra of the Dysprosium doped bismuth barium borate glasses were found to be consists of five absorption bands around 796, 902, 1096, 1276 and 1681 nm due to the $4f^9$ electronic transition of the Dy^{3+} ions from the $^6H_{15/2}$ ground level to the various excited states such as $^6F_{5/2}$, $^6F_{7/2}$, $^6F_{9/2}$, $^6H_{7/2}$, $^6F_{11/2}$, $^6H_{9/2}$ and $^6H_{11/2}$, respectively.

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