

STUDIES OF DYSPROSIUM DOPED SILICATE GLASS

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Abstract

BaO-Al₂O₃-B₂O₃-SiO₂ glasses doped with oxide of dysprosium have been synthesized by normal melt quenching technique. The amorphous nature of the glasses has been confirmed using the X-ray diffraction patterns (XRD). The density of the glasses has been measured using Archimedes method. The obtained density values have used to calculate their molar volume. There is a decrease in the density by the addition of dysprosium oxide. Structural properties of these glass samples have been studied using Fourier Transform Infrared (FTIR) Fourier transform Raman (FT-Raman) spectroscopies. FTIR spectra revealed the existence of various structural groups in the glasses and determined and differentiated the various vibrational modes in the structural changes. The Raman spectra of glass samples exhibit different spectral bands and intensity of all bands changes with the doping of Dy₂O₃.

Keywords: - Silicate glass, X-ray Diffraction, Density, FT-IR, FT-Raman

1. INTRODUCTION

Glass is now acknowledged as the one of the best scientific material in the branch of material science due to its various applications. There are different kinds of glasses that have been studied by researchers, among them oxide glasses are most important. Glass has many privileges over crystalline materials. It can be cast in a variety of forms, sizes and shapes from small fibers to meter sized pipes. The scope to deep insight into the relationship between structure and properties can be utilized for the design of new materials like borosilicate based glasses [1].

Borosilicate glasses have wide range of applications in various sector of scientific technology and instrumentation due to their

admirable optical, thermal, electrical and mechanical properties. Borosilicate glasses also contribute a subject of extensive interest in many fields, from the Earth Science to the glass industry [2]. The introduction of Al₂O₃ to borosilicate matrix enhances the chemical durability, and moulds the glasses more thermal, electrical and radiation resistant and broaden the range of scope of applications of the materials [3-8].

2. EXPERIMENT

The glass system of 50AO-(5-x)Al₂O₃-30B₂O₃-15SiO₂-xA₂O₃ (x=5, A=Dy) was prepared by conventional melt quenching technique. High purity BaCO₃, Al₂O₃, B₂O₃, SiO₂ and Dy₂O₃ (99.9%, Sigma Aldrich

chemical) were used as the starting materials. Stoichiometric amount of powder chemical were mixed in an agate mortar with mixed distilled water as medium. The slurry was dried, then grounded well and melted in Platinum crucible at different temperatures in the range 1250-1265°C. The melts were poured into a pre-heated brass mould and then immediately transferred into a preheated muffle furnace for annealing at 350°C for 2hrs to eliminating the residual stresses due to temperature gradient, which is produced by rapid cooling. After annealing the glass samples were cooled to room temperature. Finally the transparent glasses were sliced, ground and polished to study the density and structural properties.

The amorphous nature of the glass samples were analysed using XRD (Bruker AXS D8 Advance). The densities of glass samples were measured by Archimede's principle using water as buoyancy liquid on electronic balance. The FT-IR spectra of the samples were recorded in the range 400 – 4000 cm⁻¹ at room temperature using Shimadzu FT-IR spectrometer, Japan. Raman spectra of the powdered samples were recorded in the wavenumber range 500- 4200 cm⁻¹ using Raman spectrometer (Alpha 3000RA AFM & RAMAN, WITec GmbH, Ulm, Germany).

3. RESULT AND DISCUSSIONS

3.1 XRD

The XRD patterns of the glasses were as shown in Fig. 1. No phase peaks were found in

the pure and lanthanum doped glasses indicating that it is a typically amorphous phase. The fig.1 exhibits a broad diffuse scattering at different angles instead of crystalline peaks, confirming a long range structural disorder characteristic of amorphous network [9].

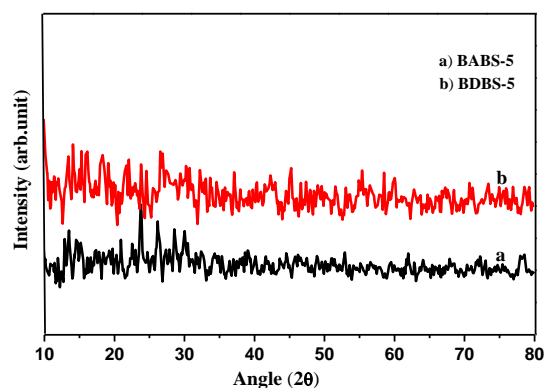


Figure 1. XRD patterns of BABS and BBDS

3.2 Density

The variation of density and molar volume is as shown in Table 1. The density of the glass was decreased with the addition of the Dy₂O₃.

The molar volume of the glass samples can be calculated from following expression:

$$V_m = M/\rho$$

Here, V_m is molar volume, ρ is the density of the sample and M is the molecular weight of the sample [10].

The molar volume of glass increases with the addition of the Dy₂O₃. Molar volume increases from 34.097 cm³/mole to 66.129 cm³/mole for

BDBS-5 and BABS-15 respectively. The molar volume depends on the ionic radius of the modifier [11]. The molar volume of the glasses increases due to increase in bond length or inter atomic spacing. It is due to the higher ionic radius of Dy^{3+} (0.912 \AA) than that of other glass former ions. The ionic radius of the modifier ion (Dy^{3+} is 0.912 \AA) is larger than that of the interstices of the network (ionic radius of Si^{4+} , Al^{3+} and B^{3+} are 0.40 , 0.53 and 0.27 \AA respectively). The volume of structural unit with its surrounding space will increase by insertion of dysprosium oxide [12].

Table 1. Variation of density and molar volume

Sample Code	Density, ρ (g/cm^3)	Molar Volume, V_o ($cm^3/mole$)
BABS-15	3.9201	34.0972
BDBS-5	2.2182	66.1298

3.3 FT-IR Spectra

FT-IR spectroscopy is a powerful tool for structural studies because it yields a means to determine local structure of building units which composes the glassy network [9]. In the borate glass structure, a random network of BO_3 triangles linked through B-O-B are consist [13] and in silicate glasses, SiO_4 tetrahedra is the main structural unit [14].

Figure 2 shows the FT-IR spectra of barium alumina borosilicate glass (BABS) and dysprosium doped BABS. In glasses,

absorption bands occur due to the vibrational mode of the borate networks [15]. The bands in the wave number range $600-700 \text{ cm}^{-1}$ confirms the bending of Si-O-B linkages in the glass network [16]. The band appeared around 781 cm^{-1} is due to the presence of the vibrational modes of AlO_4 structural units [17-18].

The bands observed in the range of $1000-1120 \text{ cm}^{-1}$ are due to the overlapping contributions in stretching vibration modes of Si-O-Si and B-O-B of SiO_4 and BO_4 structural units [19-20]. The bands that appear around 1260 and 1530 cm^{-1} are due to asymmetric stretching relation of non-bridging oxygen atoms (NBOs) of trigonal BO_3 units in metaborate chains [21]. A shift in the bands occur in doped glass system which is due to the addition of Dy_2O_3 .

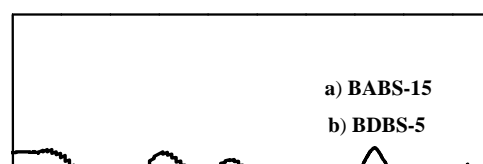


Figure 2. FT-IR spectra of BABS and BDBS

3.4 FT- Raman Spectra

FT-Raman spectra gives structural information about the local co-ordinating environments within glasses, especially the network forming silicate, borate and

aluminate species [22]. Figure 3 shows the FT-Raman spectra of barium aluminoborosilicate glass and dysprosium doped system.

Raman band assignments to glass structure have been reported for various relevant glass systems. The bands between 300 and 600 cm^{-1} are corresponds to the overall connectivity of the network or the degree of the borosilicate network polymerization. Here only one band around 490 cm^{-1} in this region. The bands between 900 and 1200 cm^{-1} are due to various silicate vibration modes or different types of bridging and/or non-bridging units [23]. In this region two bands occurs at 923 and 1151 cm^{-1} . The band between 1300 and 1500 cm^{-1} is characteristic of trigonal borate units, $\text{BO}_3/2$ [24, 25]. Single band $\approx 1435 \text{ cm}^{-1}$ is present in

4. CONCLUSIONS

Barium aluminoborosilicate glasses modified with Dy_2O_3 are synthesized successfully using normal melt quenching technique. The density of glass samples is measured and its variation depends on the composition of glass network. Molar volume of each glass system is calculated using corresponding densities. Structural characterizations are done using XRD, FT-IR and FT-Raman spectroscopies. The absorption peaks occur in FT-IR spectra is due to different stretching vibration modes and asymmetric stretching in different structural units like SiO_4 and of the borate network BO_3 and BO_4 units. Raman band assignments in the glass structure have been observed using FT-Raman spectroscopy. The bands in Raman

this range. There is a Raman shift occurs means bands show shifting in the band position towards higher side, due to the addition of Dy_2O_3 to the glass network.

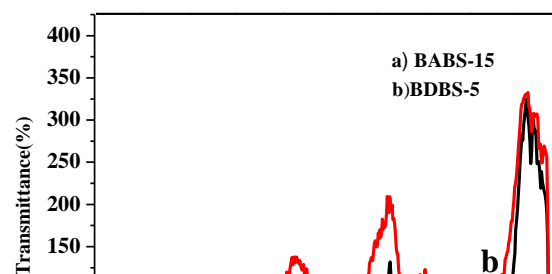


Figure 2. FT-Raman spectra of BABS and BDBS

spectra show shifting in the band position towards higher side due to the presence of Dy_2O_3 .

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