

# Structural Investigation of Na<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> Glasses Doped with NdF<sub>3</sub>

M. S. Gaafar, S. Y. Marzouk

**Abstract**—Sodium borosilicate glasses doped with different content of NdF<sub>3</sub> mol % have been prepared by rapid quenching method. Ultrasonic velocities (both longitudinal and shear) measurements have been carried out at room temperature and at ultrasonic frequency of 4 MHz. Elastic moduli, Debye temperature, softening temperature and Poisson's ratio have been obtained as a function of NdF<sub>3</sub> modifier content. Results showed that the elastic moduli, Debye temperature, softening temperature and Poisson's ratio have very slight change with the change of NdF<sub>3</sub> mol % content. Based on FTIR spectroscopy and theoretical (Bond compression) model, quantitative analysis has been carried out in order to obtain more information about the structure of these glasses. The study indicated that the structure of these glasses is mainly composed of SiO<sub>4</sub> units with four bridging oxygens (Q<sub>4</sub>), and with three bridging and one nonbridging oxygens (Q<sub>3</sub>).

**Keywords**—Borosilicate glasses, ultrasonic velocity, elastic moduli, FTIR spectroscopy, bond compression model.

## I. INTRODUCTION

**M**ECHANICAL properties and structure of borosilicate glasses have been studied by many authors [1]–[3] since they are of technical and scientific interest due to their low thermal expansion coefficient and high resistance to chemical attack. Beside these specific properties, they have many applications in laboratory glassware, household cooking utensils and automobile headlamps. Moreover, glasses doped with rare earth ions have been the subject of many various investigations due to their potential as optical fiber lasers, amplifiers, and scintillating glasses [4]–[6]. In silicate glass systems, the doped rare earth ions dissolve in these glasses creating some non-bridging oxygens [7], [8].

Since the strength of materials changes with their elastic moduli, it is therefore possible to assess strength indirectly from their elastic property [9]. Studies of the elastic constants of the glassy materials gave considerable information about the structure of non-crystalline solids since they are directly related to the inter-atomic forces and potentials [9]–[15].

Sampaio et al. [16] measured the elastic properties of calcium aluminosilicate glasses with low silicate content containing small amounts of Er<sub>2</sub>O<sub>3</sub> or Yb<sub>2</sub>O<sub>3</sub>. They reported that the addition of small amounts of rare earth elements

induces a decrease in the elastic moduli. They attributed this decrease to the hypothesis that the rare earth ions act as network modifiers and therefore disrupting the glass network structure.

Bernard et al. [17] studied the effects of glass composition on the local structure around erbium atoms in TiO<sub>2</sub>–SiO<sub>2</sub> glasses doped with Er<sup>3+</sup>. The authors determined the effect of titanium onto the erbium local structure and the effect of the rare earth doping on the mixed titania–silica network. They interpreted these effects in terms of crystal field strength as a function of the average coordination number, which is found to be lower in high-coordination sites.

Saddeek [18] applied the bond compression model proposed by Bridge et al. [19] on calcium aluminosilicate glasses doped with Er<sub>2</sub>O<sub>3</sub> as well as with Yb<sub>2</sub>O<sub>3</sub>. He reported that, doping with rare earth oxide will change slightly the values of the bond compression bulk modulus ( $K_{bc}$ ), the average atomic ring diameter, and the average cross-link density. The ratio of the bond compression bulk modulus to the experimental bulk modulus ( $K_{bc} / K_{exp}$ ) was found to increase indicating that the network structure becomes weaker and the rigidity is decreased.

In the light of these observations, the present study was undertaken with a view to investigate the influence of adding NdF<sub>3</sub> to the mechanical properties and the network structure of Na<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glasses, using ultrasonic velocity and FTIR spectroscopy.

## II. EXPERIMENTAL

### A. Preparation of Glasses

SiO<sub>2</sub>–Na<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub> glasses doped with different NdF<sub>3</sub> contents have been prepared by rapid quenching method. Batches of each glass composition are listed in Table I. The analytical grade materials of purity more than 99.9% of SiO<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, H<sub>3</sub>BO<sub>3</sub>, and NdF<sub>3</sub> chemicals were used to prepare the glass samples.

Required amounts in wt % of chemicals in powder form were weighed using a digital balance (HR–200) having an accuracy of ±0.0001 gm. The homogeneity of the chemicals mixture was achieved by repeated grinding using an agate mortar. The mixture was preheated at 673 K for 60 min (in platinum crucible) to remove H<sub>2</sub>O and CO<sub>2</sub>. The preheated mixture was then melted in a muffle furnace whose temperature was controlled at 1873 K for 60 min, and bubble free liquid was obtained. The mixture was stirred intermediately in order to obtain homogeneous mixture. The molten mixture was then poured in a cuboidal-shaped split mold made of mild steel which had been preheated at about

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675 K. Annealing was carried out for a period of 60 min at 723 K. Bulk glass samples of about  $1 \times 1 \times 1 \text{ cm}^3$  were therefore obtained.

TABLE I  
GLASS COMPOSITION

Glass	Composition (mol %)			
	SiO <sub>2</sub>	Na <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>	Er <sub>2</sub> O <sub>3</sub>
A	72.20	10.00	17.80	0.00
B	71.76	9.94	17.69	0.61
C	71.32	9.88	17.6	1.20
D	70.89	9.82	17.48	1.81
E	70.46	9.76	17.38	2.40
F	70.05	9.70	17.27	2.98

In order to measure the ultrasonic velocity accurately, each glass sample was first ground on a glass plate using SiC abrasives by setting it in a holder to maintain the two opposite faces parallel. It was then polished with fine alumina abrasive and machine oil on a glass plate. The variation in the sample thickness was found to be  $\pm 20 \mu\text{m}$ .

#### B. Density Measurements

Density ( $\rho$ ) of all glass samples was calculated employing Archimedes principle using toluene and applying the relation;

$$\rho = \rho_b \left( \frac{W_a}{W_a - W_b} \right) \quad (1)$$

where  $\rho_b$  is the density of the buoyant,  $W_a$  and  $W_b$  are the sample weights in air and the buoyant respectively. The experiment was repeated three times, and the error in density measurement in all glass samples is  $\pm 5 \text{ kg/m}^3$ .

#### C. Ultrasonic Velocity Measurements

The ultrasonic velocities were obtained applying pulse – echo technique by measuring the elapsed time between the initiation and the receipt of the pulse appearing on the screen of a flaw detector (USM3 – Kraütkramer) by standard electronic circuit (Hewlett Packard 54615 B). The velocity was therefore, calculated by dividing the round trip distance by the elapsed time according to the relation;

$$U = \frac{2X}{\Delta t} \quad (2)$$

where  $X$  is the sample thickness and  $\Delta t$  is the time interval.

All velocity measurements in this study were carried out at 4 MHz frequency, and at room temperature 298 K. The estimated error in velocity measurements was  $\pm 21 \text{ m/s}$  for longitudinal velocity and  $\pm 11 \text{ m/s}$  for shear velocity.

#### D. Fourier Transform Infrared (FTIR) Studies

The infrared spectra of the glasses were recorded at room temperature using KBr disc technique. The spectra in the wave number range between 200 and 2000  $\text{cm}^{-1}$  with a resolution of 2  $\text{cm}^{-1}$  were obtained using JASCO, FT/IR-430 spectrometer (Japan). Infrared spectra were corrected for the dark current

noises and background using the two point's baseline correction. The spectra were normalized by making the absorption of any spectrum varies from zero to one arbitrary unit. Such normalization is necessary to eliminate the concentration effect of the powder sample in the KBr disc.

Deconvolution of the FTIR absorption spectra enables us to throw more light on the structural changes of SiO<sub>4</sub> tetrahedron as they are the most abundant units in the glass compositions. By knowing the fractions of SiO<sub>4</sub> tetrahedron, (Q<sub>4</sub>) and (Q<sub>3</sub>), using the method described by Shelby [20], we were able to obtain the average number of bridging oxygens per tetrahedron (BO), fraction of nonbridging oxygens (NBO) and the average number of oxygens per tetrahedron.

Furthermore, the change in Si—O and B—O bonds in the glass compositions was obtained applying the equation reported by [21] and [22] as,

$$F_{M-O} = 4\pi^2 c^2 \mu v_{eff}^2 \quad (3)$$

where  $c$  is the speed of light,  $\mu$  is the reduced mass of cation site, and  $v_{eff}$  is the effective cation site vibration frequency

### III. DETERMINATION OF ELASTIC MODULI

Elastic moduli (longitudinal (L), shear (G), bulk (K), and Young's (E)) as well as Debye temperature ( $\theta_D$ ), softening temperature ( $T_s$ ), and Poisson's ratio ( $\sigma$ ) of SiO<sub>2</sub>–Na<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub> glasses doped with different Er<sub>2</sub>O<sub>3</sub> contents have been determined from the measured ultrasonic velocities and density using the relations [23];

$$\begin{aligned} L &= \rho U_l^2 \\ G &= \rho U_s^2 \\ K &= L - \left( \frac{4G}{3} \right) \\ E &= (1 + \sigma)2G \\ \sigma &= \left( \frac{L - 2G}{2(L - G)} \right) \end{aligned} \quad (4)$$

Debye temperature of the glass samples was obtained from the relation given by [24] as,

$$\theta_D = \left( \frac{h}{K_B} \right) \left( \frac{3ZN_A}{4\pi V_a} \right)^{1/3} U_m \quad (5)$$

where  $h$  is Planck's constant,  $K_B$  is Boltzmann's constant,  $N_A$  is Avogadro's number,  $V_a$  is the molar atomic volume calculated from the effective molecular weight and density (i.e.  $M/\rho$ ),  $Z$  is the number of atoms in the chemical formula, and  $U_m$  is the mean ultrasonic velocity defined by,

$$U_m = \left( \frac{1}{3} \left( \frac{1}{U_l^3} + \frac{2}{U_s^3} \right) \right)^{-1/3} \quad (6)$$

Softening temperature ( $T_s$ ) is related to the ultrasonic velocity of shear waves ( $U_s$ ) by the equation [25],

$$T_s = \frac{U_s M}{C^2 Z} \quad (7)$$

where  $M$  is the effective molecular weight,  $Z$  is the number of atoms in the chemical formula, and  $C$  is the constant of proportionality and has the value  $507.4 \text{ (m.s}^{-1}.\text{K}^{1/2})$  for alumina–silicate glasses and is assumed to be the same for the glasses under investigation.

#### IV. RESULTS AND DISCUSSIONS

##### A. Density and Molar Volume

Experimental values of density and molar volume of the studied sodium borosilicate glass system with different  $\text{NdF}_3$  contents (0.0, 0.61, 1.2, 1.81, 2.4 and 2.98) mol % are given in Table II. Fig. 1 showed the variation of density and molar volume with  $\text{NdF}_3$  mol % content. The replacement of  $\text{NdF}_3$  (with higher molecular weight  $201.235 \text{ kgm/mol}$ ) on the

expense of all  $\text{SiO}_2$ ,  $\text{Na}_2\text{O}$ , and  $\text{B}_2\text{O}_3$  (with lower molecular weights 60.084, 61.979, and 69.62  $\text{kg/mol}$  respectively) leads to an increase in density from 2418 to 2573  $\text{kg/m}^3$  with the increase of  $\text{NdF}_3$  mol % content from 0.0 to 2.98 mol %. Such increase in density may be related also to the change in coordination number of  $\text{Nd}^{3+}$  ions as reported by [23], [26].

TABLE II  
DENSITY ( $\rho$ ), MOLAR VOLUME ( $V_s$ ), LONGITUDINAL VELOCITY ( $U_l$ ), AND SHEAR VELOCITY ( $U_s$ )

Glass	Density ( $\rho$ ) Kgm/ $\text{m}^3$ $\pm 5$	Molar volume ( $V_s$ ) $\text{m}^3/(\text{kg.mol})$ $\pm 0.00003$	( $U_l$ ) (m/s) $\pm 21$	( $U_s$ ) (m/s) $\pm 11$
A	2418	0.02563	6332	3790
B	2445	0.02569	5825	3537
C	2462	0.02585	5789	3518
D	2505	0.02575	5783	3500
E	2540	0.02571	5779	3490
F	2573	0.02570	5773	3477

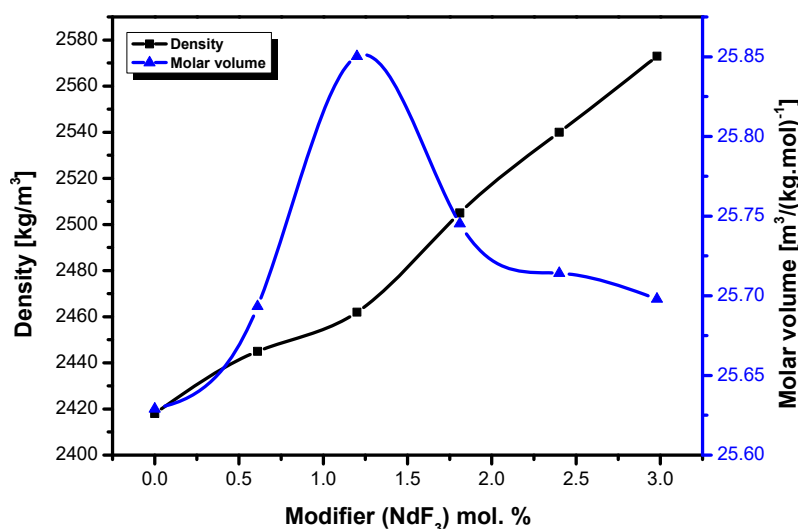


Fig. 1 Variation of density and molar volume with  $\text{NdF}_3$  mol % content

Molar volume, which is defined as the volume of one g mol of glass increases from 0.02563 to 0.02585  $\text{m}^3/(\text{kg.mol})$  as  $\text{NdF}_3$  content increases from 0.0 to 1.2 mol %, meaning that  $\text{NdF}_3$  didn't act to fill the interstices. Further increase in  $\text{NdF}_3$  content up to 2.98 mol %, resulted in the decrease in molar volume to reach 0.02570  $\text{m}^3/(\text{kg.mol})$ . Shelby [20] reported that if the ionic radius of the modifier ions is smaller than the interstices of the network structure their attraction to the oxygen ions can lead to a decrease in the size of the interstices and consequently decreases the molar volume. Since the ionic radius of  $\text{Nd}^{3+}$  ions (1.0 Å) is larger than that of  $\text{Na}^+$  ions (0.98 Å), therefore the insertion of  $\text{Nd}^{3+}$  ions (with lower oxidation states [17], [27]) from 0 to 1.81 mol % will increase the molar volume. More addition of  $\text{NdF}_3$  up to 2.98 mol % content resulted in the decrease in molar volume values, which means the insertion neodymium ions with higher oxidation states (lower ionic radii) that filled the interstices of the network structure. Moreover, the increase in molar volume may be also due to the decrease in the number of non-bridging oxygens as

reported earlier by [28]. Therefore, it is expected that the presence of  $\text{NdF}_3$  mol % content from 0 to 1.81 as a modifier will decrease the number of non bridging (oxygen & fluorine) atoms to the system, while further increase in  $\text{NdF}_3$  mol % content up to 2.98 will increase the number of non bridging (oxygen & fluorine) atoms.

##### B. Ultrasonic Velocities and Elastic Moduli

Fig. 2 depicts the variation of both longitudinal and shear ultrasonic velocities with  $\text{NdF}_3$  mol % content. A decrease in ultrasonic velocities (both longitudinal and shear) in the glass system under study with the increase of  $\text{NdF}_3$  mol % content. The highest values of velocity (6332 and 3800 m/s for longitudinal and shear waves respectively) were observed at 0.0 mol % content of  $\text{NdF}_3$  as shown in Table II. Insertion of  $\text{Er}_2\text{O}_3$  content to reach 1.2 mol % into the glass network structure will cause a rapid decrease in the values of longitudinal and shear ultrasonic velocities to 5789 and 3518 m/s respectively. Further increases of  $\text{NdF}_3$  content up to 2.98

mol % will slightly decreases the longitudinal and shear ultrasonic velocities to 5763 and 3477 m/s respectively.

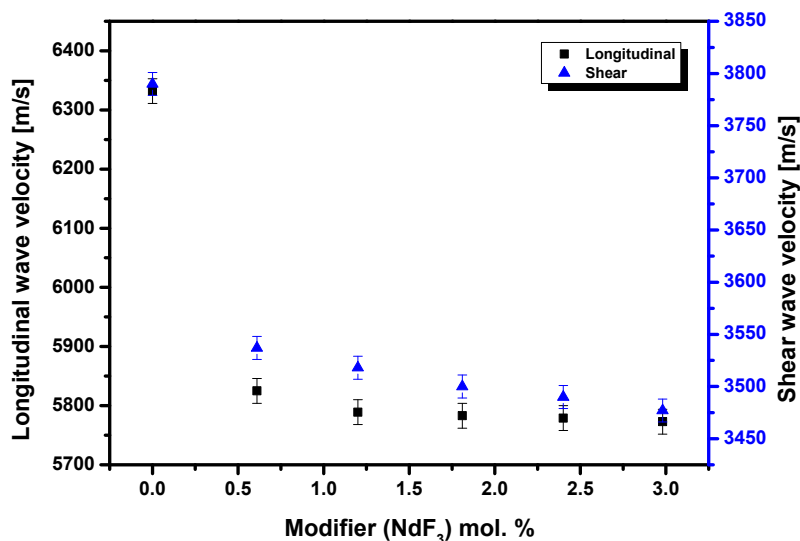


Fig. 2 Variation of longitudinal and shear ultrasonic wave velocities with NdF<sub>3</sub> mol % content

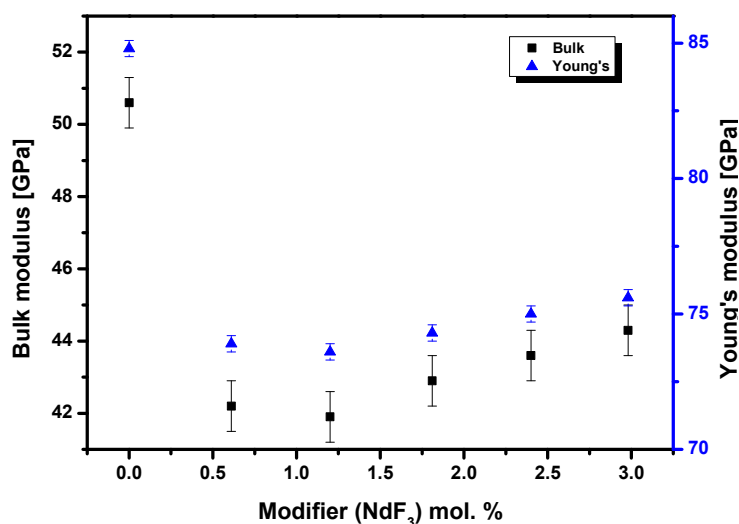


Fig. 3 Plot of bulk and Young's moduli with NdF<sub>3</sub> mol % content

The measured longitudinal and shear ultrasonic velocities of different glass samples investigated showed two regions a) from 0.0 to 1.2 NdF<sub>3</sub> mol % content, and b) from 1.2 to 2.98 NdF<sub>3</sub> mol % content indicating a change in the network structure of these glasses. In general, the decrease of ultrasonic velocity is related to the increase in the inter-atomic spacing due to the addition of NdF<sub>3</sub> with higher bond length instead of the other constituents.

Table III gives the experimentally estimated values of the elastic moduli; longitudinal modulus (L), shear modulus (G), Young's modulus (E), bulk modulus (K), Poisson's ratio ( $\sigma$ ), and (E/G) ratio. As seen from Table III all the elastic moduli values showed the highest values when the sodium borosilicate glass has 0.0 mol % NdF<sub>3</sub> content. Insertion of the

modifier NdF<sub>3</sub> with very low concentrations up to 1.2 mol % (lower coordination equals four) [17] will cause a rapid decrease in elastic moduli due to the decrease in the average number of bonds per unit volume and cross-link density. The addition of NdF<sub>3</sub> content up to 2.98 mol %, will result in a very slight increase in longitudinal (L), Young's (E), and bulk (K) elastic moduli.

Fig. 3 showed the variations of bulk (K), and Young's (E) moduli with Er<sub>2</sub>O<sub>3</sub> mol % content. The behaviour of both bulk and Young's moduli showed rapid decrease from 50.6 and 84.8 GPa to 41.9 and 73.6 GPa respectively, with the increase of NdF<sub>3</sub> content from 0.0 to 1.2 mol %. Upon the increase of NdF<sub>3</sub> concentration to 2.98 mol %, both bulk and Young's moduli showed very slight increase to 44.3 and 75.6 GPa

respectively. It is clear from the elastic moduli results that the type of bonding in the network structure plays a dominant role in deciding the rigidity of these glass structures. It is believed that the behaviour of both bulk and Young's moduli are associated with the change in cross linkage and coordination of the glass network [17] due to the increase of coordination of neodymium atoms [29].

TABLE III  
EXPERIMENTAL VALUES OF LONGITUDINAL MODULUS (L), SHEAR MODULUS (G), YOUNG'S MODULUS (E), BULK MODULUS (K), POISSON'S RATIO ( $\sigma$ ), AND (E/G) RATIO

Glass	L (GPa) $\pm 0.7$	G (GPa) $\pm 0.2$	E (GPa) $\pm 0.3$	K (GPa) $\pm 0.7$	$\sigma$ $\pm 0.008$	(E/G) $\pm 0.009$
A	96.9	34.7	84.8	50.6	0.221	2.442
B	83.0	30.6	73.9	42.2	0.208	2.416
C	82.5	30.5	73.6	41.9	0.207	2.414
D	83.8	30.7	74.3	42.9	0.211	2.422
E	84.8	30.9	75.0	43.6	0.213	2.426
F	85.7	31.1	75.6	44.3	0.215	2.430

Shear modulus and Poisson's ratio have decreased from 34.7 GPa, and 0.221 to 30.5 GPa, and 0.207 respectively, with the increase of NdF<sub>3</sub> content from 0.0 to 1.2 mol %. Shear modulus and Poisson's ratio showed very slight increase with increasing NdF<sub>3</sub> content from 1.2 to 2.98 mol % due to the increase in cross-link density.

Values of (E/G) ratio decreased from 2.442 to 2.414 when NdF<sub>3</sub> content is increased from 0.0 to 1.2 mol %. With further increase of NdF<sub>3</sub> mol % content up to 2.98 mol %, values of ratio (E/G) have increased slightly.

Debye temperature ( $\theta_D$ ) is an important parameter of solids, which represents the temperature at which nearly all the vibrational modes are excited. Softening temperature ( $T_S$ ) is another important parameter defined as the temperature point at which viscous flow changes to plastic flow. Calculated values of the mean ultrasonic velocity ( $U_m$ ), Debye temperature ( $\theta_D$ ), and softening temperature ( $T_S$ ) are collected in Table IV.

TABLE IV  
SOFTENING TEMPERATURE ( $T_S$ ), MEAN ULTRASONIC VELOCITY ( $U_m$ ), AND DEBYE TEMPERATURE ( $\theta_D$ )

Glass	( $T_S$ ) (K) $\pm 7$	( $U_m$ ) (m/s) $\pm 12$	( $\theta_D$ ) (K) $\pm 3.5$
A	1030	4194	535.4
B	908	3908	498.8
C	910	3887	495.3
D	911	3868	493.8
E	916	3858	492.8
F	921	3845	491.4

It can be observed from Table IV that both Debye and softening temperatures decreased from 535.4 and 1030 K to 491.4 and 921 K respectively, with increasing NdF<sub>3</sub> concentration from 0.0 to 2.98 mol %. The decrease in the mean ultrasonic velocity and consequently the decrease in Debye temperature [24] is mainly due to the increase of the

number of non-bridging oxygens & fluorines as a direct effect of insertion of NdF<sub>3</sub> to the glass network structure.

It is clearly shown that the addition of rare earth NdF<sub>3</sub> modifier content affects the glass network due to the change in coordination of neodymium atoms with NdF<sub>3</sub> concentration. This is in agreement with the results reported by [17], [26], [28].

#### C. Fourier Transform Infrared Spectroscopy (FTIR)

Normalized FTIR absorption spectral curves of the SiO<sub>2</sub>-Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> glasses doped with NdF<sub>3</sub> content from 0.0 to 2.98 mol %, are shown in Fig. 4.

Each spectrum was deconvoluted by using seven symmetrical Gaussian functions considering peak assignment as reported earlier [2], [3], [30]–[36]. The fitting result for SiO<sub>2</sub>-Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> glass composition doped with 2.98 mol % content of NdF<sub>3</sub> is shown in Fig. 5. The peak at around 470 cm<sup>-1</sup> is assigned to Si—O—Si and O—Si—O bending modes of bridging oxygens (Q<sub>4</sub>) overlapped with B—O—B linkages, peak at around 679 cm<sup>-1</sup> is assigned to bending vibrations of Si—O—B bridges [32]. The peak at around 770 cm<sup>-1</sup> is assigned to Si—O—Er symmetric stretching of bridging oxygens which appears only for the glass compositions containing NdF<sub>3</sub> content. The peak at around 900 cm<sup>-1</sup> is assigned to stretching vibrations of B—O bonds in BO<sub>4</sub> tetrahedra. Peak at around 1040 cm<sup>-1</sup> accompanied by a broad shoulder centered around 1200 cm<sup>-1</sup> (this peak is also overlapped with stretching vibrations of bridging oxygens (BO) of BO<sub>3</sub> triangles) are assigned to asymmetric stretching vibrations of non bridging oxygens of SiO<sub>4</sub><sup>-</sup> tetrahedra (Q<sub>3</sub>) [2]. A peak at around 1430 cm<sup>-1</sup> is assigned to stretching vibrations of non bridging oxygens of BO<sub>3</sub> triangles, and the peak at around 1640 cm<sup>-1</sup> is assigned to Si—OH stretching of surface silanol hydrogen bond to molecular water.

It can be observed from Fig. 4 that the FTIR absorption spectra of the investigated glasses have main four absorption bands at around 470, 1040, 1430, and 1640 cm<sup>-1</sup>. The intensity of the band 470 cm<sup>-1</sup> decreases with the increase of NdF<sub>3</sub> concentration from 0.0 to 1.2 mol %. Also the band intensities at 1040 and 1430 cm<sup>-1</sup> decreases with increasing NdF<sub>3</sub> mol % content. However, the band intensity at 1640 cm<sup>-1</sup> does not show any change with increasing NdF<sub>3</sub> mol % content.

Varshneya [37] stated that in alkali borosilicate glasses there are two network formers: silicon and boron. The added alkali ions (M<sup>+</sup>) may associate either with silicon, creating a NBO as Si<sup>-</sup>M<sup>+</sup>, or with boron presumably converting BO<sub>3</sub> units to BO<sub>4</sub> units and creating no NBO in the process. Furthermore, the alkali ion prefers to associate with the boron as long as R < 0.5 (where R = [Na<sub>2</sub>O] / [B<sub>2</sub>O<sub>3</sub>]). Thus, it is clear that most of the Na<sup>+</sup> ions together with Nd<sup>3+</sup> ions in the investigated glasses have been associated with the with SiO<sub>4</sub> tetrahedra where R ≈ 0.56 and have combined effects in converting the BO<sub>3</sub> to BO<sub>4</sub> units with no non bridging (oxygen & fluorine) atoms.

Table V showed the fractions of SiO<sub>4</sub> units (Q<sub>4</sub>) sharing four bridging oxygens (BO) with their neighbors which have

two oxygens per tetrahedron. Also, Table V showed the fractions of  $\text{SiO}_4$  units ( $Q_3$ ) sharing three bridging oxygens and one non bridging oxygen or fluorine (NBO+F) which have 2.5 oxygens & fluorines per tetrahedron. Moreover, the fractions of (NBO+F)s, number of (BOs) per tetrahedron, total number of oxygens & fluorines per tetrahedron and fraction of  $\text{BO}_4$  units ( $N_4$ ) have been shown in Table V. The fraction of  $Q_3$  showed an increase from 0.82 for the glass composition with 0 mol %  $\text{NdF}_3$  content to 0.87 for the glass composition with 2.98 mol % of  $\text{NdF}_3$  content confirming the observations reported before [16], [17]. Fraction of  $Q_4$  decreased from 0.18 to 0.13 when  $\text{NdF}_3$  concentration is increased from 0.0 to 2.98 mol %. The fraction of NB(O+F)s and total number of oxygens & fluorines per tetrahedron have decreased from 0.205 and 2.410 to 0.202 and 2.405, respectively with the addition of  $\text{NdF}_3$  content from 0.0 to 1.2 mol %. Further increase of  $\text{NdF}_3$  content up to reach 2.98 resulted in an increase of NB(O+F)s and total number of oxygens & fluorines per tetrahedron to 0.217 and 2.434, respectively, confirming the behavior of molar volume. This observation agrees well with previous works [16], [17], [38]–[41]. The fraction of  $\text{BO}_4$  units was calculated taking into account the ratio ( $\text{B}_2\text{O}_3 / (\text{B}_2\text{O}_3 + \text{SiO}_2)$ ). It was found to increase from

0.144 to 0.225 with increasing  $\text{NdF}_3$  content from 0.0 to 2.98 mol %.

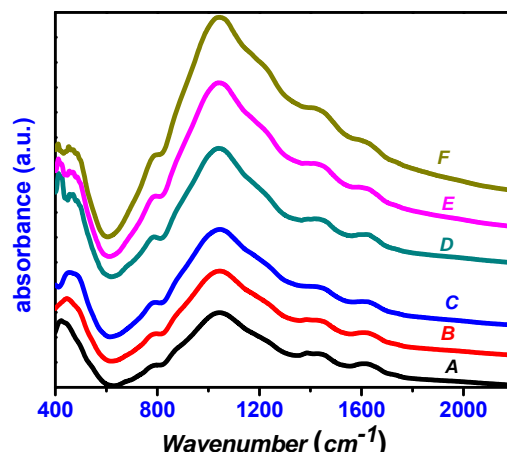


Fig. 4 FTIR absorption spectra of  $\text{SiO}_2$ - $\text{Na}_2\text{O}$ - $\text{B}_2\text{O}_3$  glasses doped with  $\text{NdF}_3$  mol % content

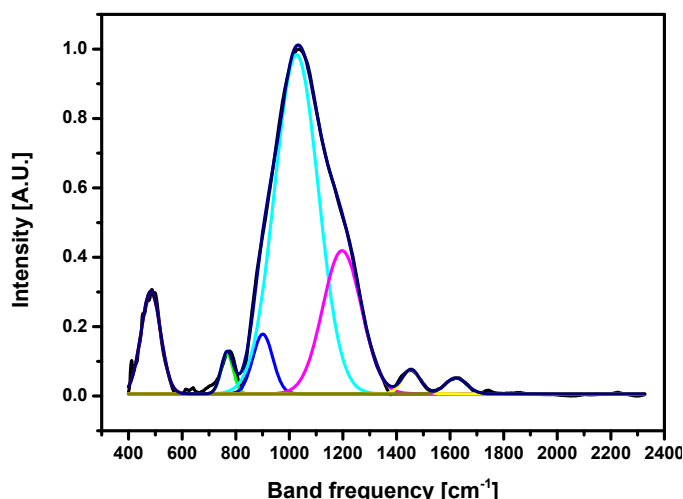


Fig. 5 Deconvoluted FTIR spectrum of  $\text{SiO}_2$ - $\text{Na}_2\text{O}$ - $\text{B}_2\text{O}_3$  glasses doped with 2.98  $\text{NdF}_3$  mol % content

TABLE V  
FRACTIONS OF ( $Q_3$ ), AND ( $Q_4$ ), FRACTION OF NON-BRIDGING OXYGENS PER TETRAHEDRON (NBO/(BO+NBO)), NUMBER OF BRIDGING OXYGENS PER TETRAHEDRON (BOs/(TETRAHEDRON)), TOTAL NUMBER OF OXYGENS PER TETRAHEDRON (OXYGENS/(TETRAHEDRON)), AND FRACTION OF  $\text{BO}_4$  ( $N_4$ )

Glass	$Q_3$ $\pm 0.02$	$Q_4$ $\pm 0.02$	(NBO+F)/ (BO+(NBO +F)) $\pm 0.005$	BOs/ (tetrahedron) $\pm 0.02$	O+F / (tetrahedron) $\pm 0.01$	$N_4$ $\pm 0.02$
A	0.82	0.18	0.205	3.18	2.41	0.14
B	0.81	0.19	0.203	3.19	2.41	0.21
C	0.81	0.19	0.202	3.19	2.40	0.25
D	0.85	0.15	0.212	3.15	2.42	0.22
E	0.87	0.13	0.217	3.13	2.43	0.22
F	0.87	0.13	0.217	3.13	2.43	0.22

It is clear from the FTIR results that  $\text{Na}_2\text{O}$ - $\text{B}_2\text{O}_3$ - $\text{SiO}_2$  glasses doped with  $\text{NdF}_3$  are mainly composed of  $\text{SiO}_4$  units ( $Q_4$ ) with 4 bridging oxygens & fluorines and ( $Q_3$ ) with 3 bridging oxygens & fluorines and one non bridging oxygen or fluorine. Moreover, addition of the rare earth  $\text{NdF}_3$  will acts as a network modifier transforming the basic structural units  $Q_4$  to  $Q_3$ , and  $\text{BO}_3$  units to  $\text{BO}_4$ .

Values of the effective band frequencies of  $Q_3$ ,  $Q_4$ ,  $\text{BO}_3$ , and  $\text{BO}_4$ , were employed to obtain the bond lengths of  $\text{Si}-\text{O}_{\text{BO}}$ ,  $\text{Si}-\text{O}_{\text{NBO}}$ , and  $\text{B}-\text{O}$  in both  $\text{BO}_3$ , and  $\text{BO}_4$  units with mol % content of  $\text{NdF}_3$ . These values are collected and given in Table VI.

It is of great interest to interpret the variation in the experimental elastic behaviour observed in this study with the

bulk compression model put forward by [19] and extended by [1], [42] for predicting the compositional dependence of elastic moduli of poly component oxide glasses. Table VII gives the values of theoretical bond compression bulk modulus ( $K_{bc}$ ), ratio of ( $K_{bc} / K_{exp}$ ), number of bonds per unit volume ( $n_b$ ), ring diameter ( $\ell$ ), average stretching force constant ( $\overline{F}$ ), average cross-link density ( $\overline{n_c}$ ), and total number of cations per glass formula ( $\eta$ ). It is quite clear from Table VII that the value of the bond compression bulk modulus ( $K_{bc}$ ) slightly increases from 90.5 GPa, for the glass

with 0.0 mol % of the modifier  $NdF_3$ , to 91.0 GPa as a direct effect of insertion of  $NdF_3$  modifier content up to 2.98 mol % into the glass network. This increase in  $K_{bc}$  is expected since  $K_{bc}$  depends on the number of the network bonds per unit volume ( $n_b$ ), and the average bond lengths, which is related to the first order stretching force constant. The presence of the modifier  $NdF_3$  with its lower coordination [17], [27] in the glass network structure will cause the number of bonds per unit volume to increase.

TABLE VI  
THE EFFECTIVE BAND FREQUENCY ( $\nu$ ) OF  $Q_4$ ,  $Q_3$ ,  $BO_3$ , AND  $BO_4$ , AND BOND LENGTH OF  $Si-O_B$ ,  $Si-O_{NB}$ , AND  $B-O$  IN  $BO_3$  AND  $BO_4$  UNITS

Glass	$\nu_{Q_4}$ cm <sup>-1</sup> ± 1	$\nu_{Q_3}$ cm <sup>-1</sup> ± 4	$Si-O_B$ (nm) ± 0.0001	$Si-O_{NB}$ (nm) ± 0.0001	$\nu_{BO_3}$ cm <sup>-1</sup> ± 8	$\nu_{BO_4}$ cm <sup>-1</sup> ± 2	$B-O$ in ( $BO_3$ )(nm) ± 0.0001	$B-O$ in ( $BO_4$ ) (nm) ± 0.0001
A	454	1038	0.1653	0.1663	1209	891	0.1365	0.1673
B	471	1033	0.1611	0.1669	1199	899	0.1373	0.1663
C	490	1032	0.1571	0.1669	1197	905	0.1374	0.1656
D	485	1030	0.1580	0.1671	1194	899	0.1376	0.1663
E	485	1029	0.1581	0.1673	1197	900	0.1374	0.1662
F	483	1027	0.1585	0.1675	1197	901	0.1374	0.1661

The increase of  $NdF_3$  modifier content from 0.0 to 2.98 mol % will cause the number of bonds per unit volume to increase from  $8.069 \times 10^{28} \text{ m}^{-3}$  to  $8.261 \times 10^{28} \text{ m}^{-3}$ . The average stretching force constant ( $\overline{F}$ ) will also decrease from 379 to 362  $\text{Nm}^{-1}$  as shown in Fig. 6. Furthermore, the number of cations per glass formula unit ( $\eta$ ) increased from 1.278 to 1.270 with increasing the modifier  $NdF_3$  content from 0.0 to 2.98 mol %. For the glass composition with 0.0  $NdF_3$  mol %, the values of ( $K_{bc} / K_{exp}$ ) ratio and ( $\ell$ ) were 1.788 and 5.169 nm respectively, and addition of  $NdF_3$  up to 1.2 mol % will increase ( $K_{bc} / K_{exp}$ ) ratio and ( $\ell$ ) to 2.165 and 5.434 nm indicating the decrease in elastic moduli (see Fig. 6) and therefore the structure becomes more open structure. This observation is mainly due to the increase in molar volume and the decrease of  $NB(O+F)$ s as the  $NdF_3$  modifier enters the glass structure with 3 BFs. The increase of  $NdF_3$  content from 1.2 to 2.98 mol % caused a decrease in ( $K_{bc} / K_{exp}$ ) ratio and ( $\ell$ ) to reach 2.056 and 5.291 nm respectively, confirming the slight increase of the elastic moduli which is due to the increase in  $NB(O+F)$ s and consequently the decrease in molar volume, as the  $NdF_3$  started to fill the interstices. Poisson's ratio is defined for any structure as the ratio between lateral and longitudinal strain produced when tensile force is applied. For tensile stresses applied parallel to the chains, the produced longitudinal strain will be the same and is unaffected by the cross link density. The lateral strain is greatly affected by the cross-link density ( $\overline{n_c}$ ). It was found that ( $\overline{n_c}$ ) increased from 1.594 to 1.673 with the increase of  $NdF_3$  modifier from 0.0 to 2.98 mol % as shown in Fig. 6.

Theoretically estimated values of longitudinal, shear, bulk, and Young's moduli are given in Table VIII. They showed quite similar trends to the experimentally obtained elastic moduli. Fig. 7 showed good agreement between the

experimental bulk modulus ( $K_{exp}$ ) and the theoretical bulk modulus ( $K_{th}$ ).

TABLE VII  
THEORETICAL BOND COMPRESSION BULK MODULUS ( $K_{bc}$ ), ( $K_{bc} / K_{exp}$ ) RATIO, NUMBER OF BONDS PER UNIT VOLUME ( $n_b$ ), AVERAGE RING DIAMETER ( $\ell$ ), AVERAGE STRETCHING FORCE CONSTANT ( $\overline{F}$ ), AVERAGE CROSS LINK DENSITY ( $\overline{n_c}$ ), TOTAL NUMBER OF CATIONS PER GLASS FORMULA UNIT ( $\eta$ ), AND THEORETICALLY CALCULATED POISSON'S RATIO ( $\sigma_{th}$ )

Glass	$K_{bc}$ (GPa) ± 0.8	$K_{bc} / K_{exp}$ ± 0.04	$n_b$ $\times 10^{28}$ ( $\text{m}^{-3}$ )	$\ell$ (nm) ± 0.002	$\overline{F}$ ( $\text{N.m}^{-1}$ ) ± 1	$\overline{n_c}$	$\eta$	$\sigma_{th}$
A	90.5	1.79	8.069	5.169	379	1.594	1.278	0.249
B	90.8	2.15	8.096	5.416	378	1.618	1.276	0.248
C	90.6	2.16	8.075	5.434	380	1.633	1.275	0.248
D	90.9	2.12	8.177	5.365	370	1.651	1.273	0.247
E	90.8	2.08	8.204	5.327	366	1.656	1.271	0.247
F	91.0	2.06	8.261	5.291	362	1.673	1.270	0.246

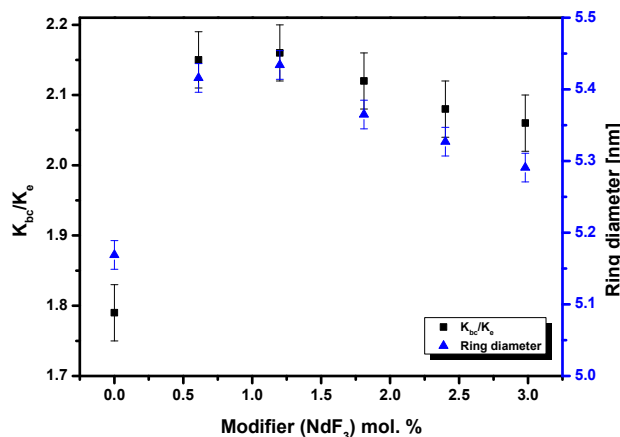


Fig. 6 Variation of  $K_{bc}/K_c$  and average ring diameter with  $NdF_3$  mol % content

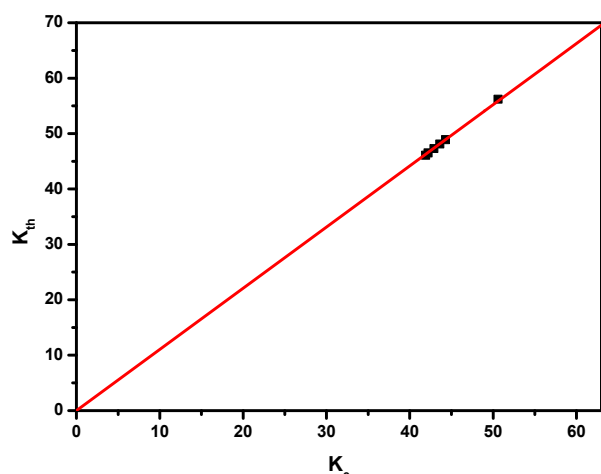


Fig. 7 Agreement between theoretically and experimentally estimated Bulk moduli as a function of NdF<sub>3</sub> mol % content

TABLE VIII  
THEORETICALLY ESTIMATED LONGITUDINAL (L), SHEAR (G), YOUNG'S (E), AND BULK (K) MODULI

	L	G	E	K
Glass	(GPa)	(GPa)	(GPa)	(GPa)
	± 0.5	± 0.2	± 0.4	± 0.3
A	101.2	33.8	84.5	56.2
B	83.8	28.1	70.2	46.5
C	83.2	28.0	69.7	46.1
D	85.5	28.8	71.8	47.3
E	87.1	29.3	73.1	48.1
F	88.7	29.9	74.5	48.9

## V. CONCLUSIONS

The density, ultrasonic velocities, elastic properties, and FTIR studies on the network structure of Na<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glasses doped with NdF<sub>3</sub> have revealed the following conclusions:

- 1- The density of the glass system studied is increased with the increase in mol percentage of NdF<sub>3</sub>.
- 2- Ultrasonic velocities (both longitudinal and shear), Debye and softening temperatures values decreased with increasing mol % content of NdF<sub>3</sub>, which is interpreted in due to the increase in average bond length of the network structure.
- 3- Elastic moduli and Poisson's ratio decreased for glasses having low NdF<sub>3</sub> concentration, while an increase of NdF<sub>3</sub> concentration will slightly increase the elastic moduli, and Poisson's ratio increases slightly. The number of bonds per unit volume and cross-link density also increase which is the reason for the slight increase of Poisson's ratio with the increase of NdF<sub>3</sub> mol %.
- 4- Analysis of the deconvoluted FTIR spectra, showed an increase in the fraction of non bridging (NBO+Fs) with the increase of NdF<sub>3</sub> mol % content. Moreover, the increase in molar volume for lower NdF<sub>3</sub> content glasses leads to the decrease in elastic moduli of these glasses as evidenced by Bridge and Patel theoretical model. The increase of NdF<sub>3</sub> content to the glass leads to a decrease in

molar volume and consequently slight increase in elastic moduli is resulted.

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