

Structural Investigation of Na₂O–B₂O₃–SiO₂ Glasses Doped with NdF₃

M. S. Gaafar, S. Y. Marzouk

Abstract—Sodium borosilicate glasses doped with different content of NdF₃ 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 NdF₃ modifier content. Results showed that the elastic moduli, Debye temperature, softening temperature and Poisson's ratio have very slight change with the change of NdF₃ 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 SiO₄ units with four bridging oxygens (Q₄), and with three bridging and one nonbridging oxygens (Q₃).

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

I. INTRODUCTION

MECHANICAL 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 Er₂O₃ or Yb₂O₃. 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 TiO₂–SiO₂ glasses doped with Er³⁺. 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 Er₂O₃ as well as with Yb₂O₃. 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 NdF₃ to the mechanical properties and the network structure of Na₂O–B₂O₃–SiO₂ glasses, using ultrasonic velocity and FTIR spectroscopy.

II. EXPERIMENTAL

A. Preparation of Glasses

SiO₂–Na₂O–B₂O₃ glasses doped with different NdF₃ 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 SiO₂, Na₂CO₃, H₃BO₃, and NdF₃ 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 H₂O and CO₂. 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

M. S. Gaafar. Author is with the Ultrasonic Laboratory, National Institute for Standards, Tersa Str., P. O. Box 136, El-Haram, El-Giza 12211, Egypt. Current address: College of Science, Phys. Dept., Al-Majmaah Univ., Al-Zulfi, Saudi Arabia. (corresponding author; phone: +966598210308; e-mail: m.gaafar@mu.edu.sa).

S. Y. Marzouk. Author is with Arab Academy of Science and Technology, Al-Horria, Heliopolis, Cairo, Egypt (e-mail: samir_marzouk2001@yahoo.com).

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 ₂	Na ₂ O	B ₂ O ₃	Er ₂ O ₃
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 (ρ) 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 ρ_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 Δt 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 cm^{-1} with a resolution of 2 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 SiO₄ tetrahedron as they are the most abundant units in the glass compositions. By knowing the fractions of SiO₄ tetrahedron, (Q₄) and (Q₃), 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, μ 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 (θ_D), softening temperature (T_s), and Poisson's ratio (σ) of SiO₂-Na₂O-B₂O₃ glasses doped with different Er₂O₃ 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/ρ), 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 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 NdF_3 mol % content. The replacement of NdF_3 (with higher molecular weight 201.235 kgm/mol) on the

expense of all SiO_2 , Na_2O , and B_2O_3 (with lower molecular weights 60.084, 61.979, and 69.62 kg/mol respectively) leads to an increase in density from 2418 to 2573 kg/m^3 with the increase of 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 Nd^{3+} ions as reported by [23], [26].

TABLE II
DENSITY (ρ), MOLAR VOLUME (V_a), LONGITUDINAL VELOCITY (U_l), AND SHEAR VELOCITY (U_s)

Glass	Density (ρ) Kg/m ³ ± 5	Molar volume (V_a) m ³ /(kg.mol) ± 0.00003	(U_l) (m/s) ± 21	(U_s) (m/s) ± 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

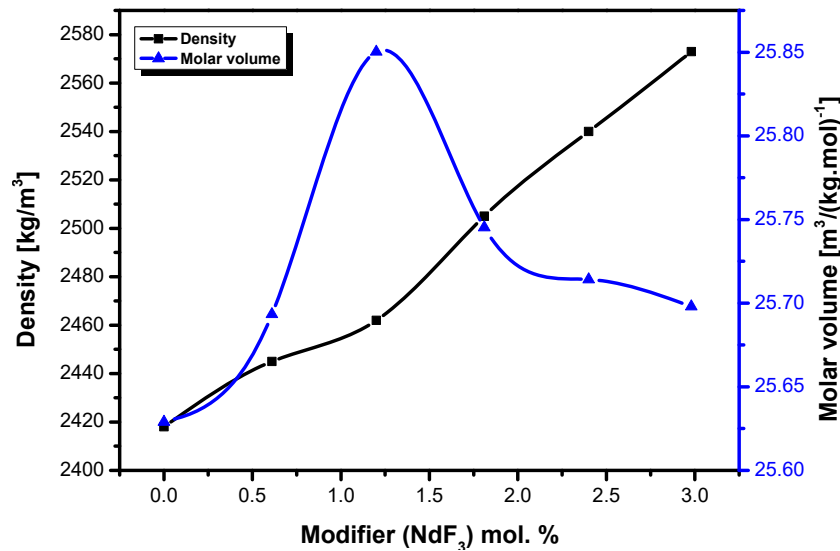


Fig. 1 Variation of density and molar volume with NdF_3 mol % content

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 NdF_3 content increases from 0.0 to 1.2 mol %, meaning that NdF_3 didn't act to fill the interstices. Further increase in 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 Nd^{3+} ions (1.0 Å) is larger than that of Na^+ ions (0.98 Å), therefore the insertion of Nd^{3+} ions (with lower oxidation states [17], [27]) from 0 to 1.81 mol % will increase the molar volume. More addition of 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 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 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 NdF_3 mol % content. A decrease in ultrasonic velocities (both longitudinal and shear) in the glass system under study with the increase of 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 NdF_3 as shown in Table II. Insertion of Er_2O_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 NdF_3 content up to 2.98

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

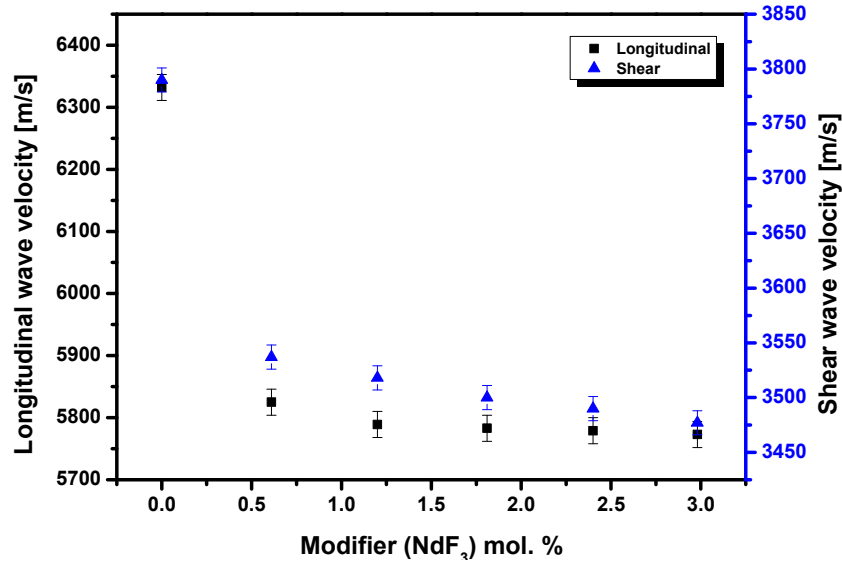


Fig. 2 Variation of longitudinal and shear ultrasonic wave velocities with NdF₃ mol % content

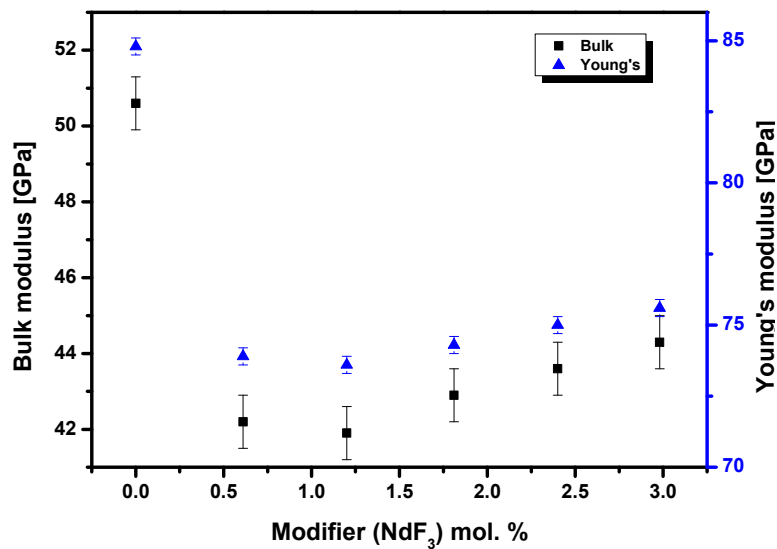


Fig. 3 Plot of bulk and Young's moduli with NdF₃ mol % content

The measured longitudinal and shear ultrasonic velocities of different glass samples investigated showed two regions a) from 0.0 to 1.2 NdF₃ mol % content, and b) from 1.2 to 2.98 NdF₃ 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 NdF₃ 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 (σ), 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 % NdF₃ content. Insertion of the

modifier NdF₃ 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 NdF₃ 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 Er₂O₃ 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 NdF₃ content from 0.0 to 1.2 mol %. Upon the increase of NdF₃ 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 (σ), AND (E/G) RATIO

Glass	L (GPa) ± 0.7	G (GPa) ± 0.2	E (GPa) ± 0.3	K (GPa) ± 0.7	σ ± 0.008	(E/G) ± 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 NdF₃ content from 0.0 to 1.2 mol %. Shear modulus and Poisson's ratio showed very slight increase with increasing NdF₃ 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 NdF₃ content is increased from 0.0 to 1.2 mol %. With further increase of NdF₃ mol % content up to 2.98 mol %, values of ratio (E/G) have increased slightly.

Debye temperature (θ_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 (θ_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 (θ_D)

Glass	(T_s) (K) ± 7	(U_m) (m/s) ± 12	(θ_D) (K) ± 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 NdF₃ 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 NdF₃ to the glass network structure.

It is clearly shown that the addition of rare earth NdF₃ modifier content affects the glass network due to the change in coordination of neodymium atoms with NdF₃ 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 SiO₂-Na₂O-B₂O₃ glasses doped with NdF₃ 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 SiO₂-Na₂O-B₂O₃ glass composition doped with 2.98 mol % content of NdF₃ is shown in Fig. 5. The peak at around 470 cm⁻¹ is assigned to Si-O-Si and O-Si-O bending modes of bridging oxygens (Q₄) overlapped with B-O-B linkages, peak at around 679 cm⁻¹ is assigned to bending vibrations of Si-O-B bridges [32]. The peak at around 770 cm⁻¹ is assigned to Si-O-Er symmetric stretching of bridging oxygens which appears only for the glass compositions containing NdF₃ content. The peak at around 900 cm⁻¹ is assigned to stretching vibrations of B-O bonds in BO₄ tetrahedra. Peak at around 1040 cm⁻¹ accompanied by a broad shoulder centered around 1200 cm⁻¹ (this peak is also overlapped with stretching vibrations of bridging oxygens (BO) of BO₃ triangles) are assigned to asymmetric stretching vibrations of non bridging oxygens of SiO₄⁻ tetrahedra (Q₃) [2]. A peak at around 1430 cm⁻¹ is assigned to stretching vibrations of non bridging oxygens of BO₃ triangles, and the peak at around 1640 cm⁻¹ 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⁻¹. The intensity of the band 470 cm⁻¹ decreases with the increase of NdF₃ concentration from 0.0 to 1.2 mol %. Also the band intensities at 1040 and 1430 cm⁻¹ decreases with increasing NdF₃ mol % content. However, the band intensity at 1640 cm⁻¹ does not show any change with increasing NdF₃ mol % content.

Varshneya [37] stated that in alkali borosilicate glasses there are two network formers: silicon and boron. The added alkali ions (M⁺) may associate either with silicon, creating a NBO as Si⁻M⁺, or with boron presumably converting BO₃ units to BO₄ 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 = [Na₂O] / [B₂O₃]). Thus, it is clear that most of the Na⁺ ions together with Nd³⁺ ions in the investigated glasses have been associated with the with SiO₄ tetrahedra where R ≈ 0.56 and have combined effects in converting the BO₃ to BO₄ units with no non bridging (oxygen & fluorine) atoms.

Table V showed the fractions of SiO₄ units (Q₄) sharing four bridging oxygens (BO) with their neighbors which have

two oxygens per tetrahedron. Also, Table V showed the fractions of SiO₄ units (Q₃) 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+Fs), number of (BOs) per tetrahedron, total number of oxygens & fluorines per tetrahedron and fraction of BO₄ units (N₄) have been shown in Table V. The fraction of Q₃ showed an increase from 0.82 for the glass composition with 0 mol % NdF₃ content to 0.87 for the glass composition with 2.98 mol % of NdF₃ content confirming the observations reported before [16], [17]. Fraction of Q₄ decreased from 0.18 to 0.13 when NdF₃ 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 NdF₃ content from 0.0 to 1.2 mol %. Further increase of NdF₃ 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 BO₄ units was calculated taking into account the ratio (B₂O₃ / (B₂O₃+SiO₂)). It was found to increase from

0.144 to 0.225 with increasing NdF₃ content from 0.0 to 2.98 mol %.

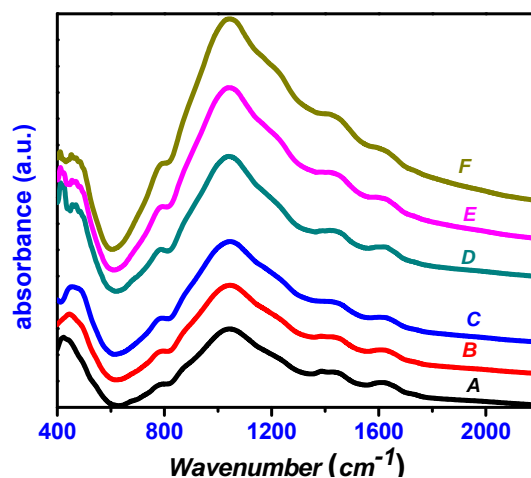


Fig. 4 FTIR absorption spectra of SiO₂-Na₂O-B₂O₃ glasses doped with NdF₃ mol % content

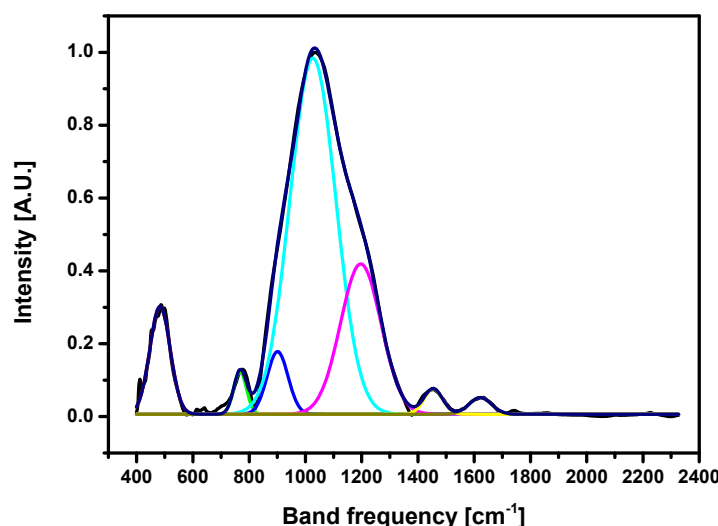


Fig. 5 Deconvoluted FTIR spectrum of SiO₂-Na₂O-B₂O₃ glasses doped with 2.98 NdF₃ mol % content

TABLE V
FRACTIONS OF (Q₃), AND (Q₄), 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 BO₄ (N₄)

Glass	Q ₃ ± 0.02	Q ₄ ± 0.02	(NBO+F)/ (BO+(NBO +F)) ± 0.005	BOs/ (tetrahedron) ± 0.02	O+F / (tetrahedron) ± 0.01	N ₄ ± 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 Na₂O-B₂O₃-SiO₂ glasses doped with NdF₃ are mainly composed of SiO₄ units (Q₄) with 4 bridging oxygens & fluorines and (Q₃) with 3 bridging oxygens & fluorines and one non bridging oxygen or fluorine. Moreover, addition of the rare earth NdF₃ will act as a network modifier transforming the basic structural units Q₄ to Q₃, and BO₃ units to BO₄.

Values of the effective band frequencies of Q₃, Q₄, BO₃, and BO₄, were employed to obtain the bond lengths of Si-O_{BO}, Si-O_{NBO}, and B-O in both BO₃, and BO₄ units with mol % content of NdF₃. 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 (ℓ), average stretching force constant (\bar{F}), average cross-link density (\bar{n}_c), and total number of cations per glass formula (η). 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 (ν) 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	ν_{Q_4} cm ⁻¹ ± 1	ν_{Q_3} cm ⁻¹ ± 4	$Si-O_B$ (nm) ± 0.0001	$Si-O_{NB}$ (nm) ± 0.0001	ν_{BO_3} cm ⁻¹ ± 8	ν_{BO_4} cm ⁻¹ ± 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 (\bar{F}) will also decrease from 379 to 362 Nm^{-1} as shown in Fig. 6. Furthermore, the number of cations per glass formula unit (η) 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 (ℓ) 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 (ℓ) 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 BF's. The increase of NdF_3 content from 1.2 to 2.98 mol % caused a decrease in (K_{bc} / K_{exp}) ratio and (ℓ) 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 (\bar{n}_c). It was found that (\bar{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 (ℓ), AVERAGE STRETCHING FORCE CONSTANT (\bar{F}), AVERAGE CROSS LINK DENSITY (\bar{n}_c), TOTAL NUMBER OF CATIONS PER GLASS FORMULA UNIT (η), AND THEORETICALLY CALCULATED POISSON'S RATIO (σ_{th})

Glass	K_{bc} (GPa) ± 0.8	K_{bc} / K_{exp} ± 0.04	n_b $\times 10^{28}$ (m^{-3})	ℓ (nm) ± 0.002	\bar{F} (N.m^{-1}) ± 1	\bar{n}_c	η	σ_{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

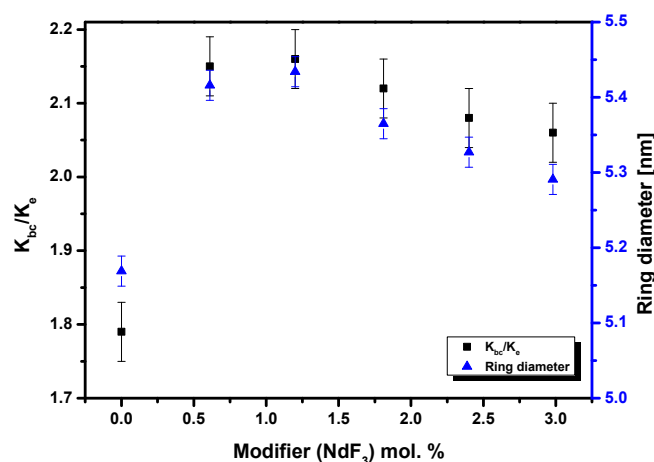


Fig. 6 Variation of K_{bc}/K_e and average ring diameter with NdF_3 mol % content

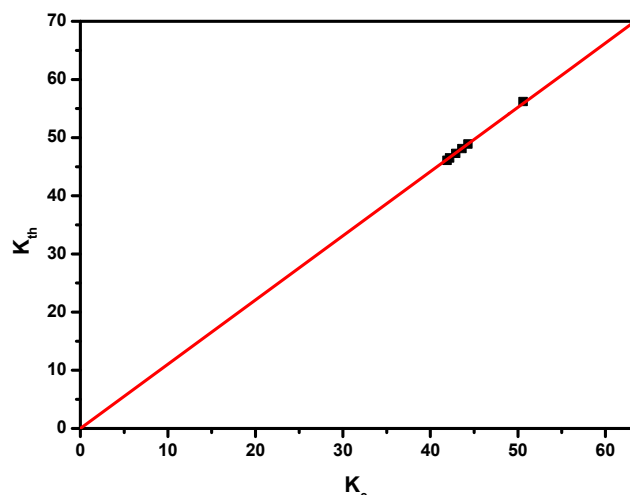


Fig. 7 Agreement between theoretically and experimentally estimated Bulk moduli as a function of NdF₃ mol % content

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

Glass	L (GPa) ± 0.5	G (GPa) ± 0.2	E (GPa) ± 0.4	K (GPa) ± 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 Na₂O–B₂O₃–SiO₂ glasses doped with NdF₃ have revealed the following conclusions:

- 1- The density of the glass system studied is increased with the increase in mol percentage of NdF₃.
- 2- Ultrasonic velocities (both longitudinal and shear), Debye and softening temperatures values decreased with increasing mol % content of NdF₃, 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 NdF₃ concentration, while an increase of NdF₃ 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 NdF₃ mol %.
- 4- Analysis of the deconvoluted FTIR spectra, showed an increase in the fraction of non bridging (NBO+Fs) with the increase of NdF₃ mol % content. Moreover, the increase in molar volume for lower NdF₃ content glasses leads to the decrease in elastic moduli of these glasses as evidenced by Bridge and Patel theoretical model. The increase of NdF₃ content to the glass leads to a decrease in

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

ACKNOWLEDGMENT

The authors wish to express their gratitude to college of science - Majmaah University for supporting this search work.

REFERENCES

- [1] A. Abd El-Moneim, *Physica B*, 325, 319, (2003).
- [2] K. El-Egili, *Physica B*, 325, 340, (2003).
- [3] L. G. Protasova, V. G. Kosenko, *Glass and Ceramics*, 60, 164, (2003).
- [4] M. J. Weber, *J. Non-Cryst. Solids*, 42, 189, (1980).
- [5] C. Spielmann, F. Krausz, T. Brabec, E. Winter, A. Shmidt, *J. Quantum Electron.*, 27, 1207, (1991).
- [6] M. Oomen, *Adv. Mater.*, 3, 403, (1991).
- [7] A. J. G. Ellison, P. Hess, *J. Geophys. Res.*, 95, 15717, (1990).
- [8] T. Schaller, J. F. Stebbins, M. C. Wilding, *J. Non-Cryst. Solids*, 243, 146, (1999).
- [9] L. -G. Hwa, C. L. Lu, L. -C. Liu, *Mater. Res. Bull.*, 35, 1285, (2000).
- [10] A. Makishima, J. D. Mackenzie, *J. Non-Cryst. Solids*, 12, 35, (1973).
- [11] A. Makishima, J. D. Mackenzie, *J. Non-Cryst. Solids*, 17, 147, (1975).
- [12] T. Y. Wei, Y. Hu, L. -G. Hwa, *J. Non-Cryst. Solids*, 288, 140, (2001).
- [13] A. Abd El-Moneim, I. M. Youssof, M. M. Shoaib, *Mater. Chem. Phys.*, 52, 258, (1998).
- [14] L. -G. Hwa, K. Hsieh, L. Liu, *Mater. Chem. Phys.*, 78, 105, (2002).
- [15] L. -G. Hwa, T. Lee, S. Szu, *Mater. Res. Bull.*, 39, 33, (2004).
- [16] J. A. Sampaio, M. L. Baesso, S. Gama, A. A. Coelho, J. A. Eiras, I. A. Santos, *J. Non-Cryst. Solids*, 304, 293, (2002).
- [17] C. Bernard, S. Chaussedent, A. Monteil, M. Montagna, L. Zampedri, M. Ferrari, *J. Sol-Gel Sci. and Technol.*, 26, 925, (2003).
- [18] Y. B. Saddeek, *Physica B*, 363, 19, (2005).
- [19] B. Bridge, N. D. Patel, D. N. Waters, *Phys. Stat. Sol. (a)*, 77, 655, (1983).
- [20] James, E. Shelby, "Introduction to Glass science and technology", The Royal Society of Chemistry, UK, (1997).
- [21] Y. D. Yiannopoulos, G. D. Chryssikos, E. I. Kamitsos, *Phys. Chem. Glasses*, 42, 164, (2001).
- [22] D. L. Pavia, G. M. Lampman, G. S. Kriz, "Introduction to spectroscopy", W. B. Saunders Co., London, (1979).
- [23] M. A. Sidkey, M. S. Gaafar, *Physica B*, 348, 46, (2004).
- [24] O. L. Anderson, "Physical Acoustics", Warren P. Mason ed., Academic Press, New York, (III) B, 45, (1965).
- [25] V. Kh. Nikulin, L. M. Prusakova, O. S. Viktorova, *Soviet J. Glass Phys. Chem. (USA)*, 7 / 4, 287, (1981).
- [26] A. A. Higazy, B. Bridge, A. Hussein, M. A. Ewida, *J. Acoust. Soc. Am.*, 86 (4), 1453, (1989).
- [27] M. S. Gaafar, S.Y. Marzouk, *Physica B*, 388, 294, (2007).
- [28] F. A. Khalifa, Z. A. El-Hadi, F. A. Moustaffa, N. A. Hassan, *Indian Journal of Pure & Applied Physics*, 27, 279, (1989).
- [29] K. J. Rao, B. G. Rao, *Bul. Mat. Sci.*, 7(3&4), 353, (1985).
- [30] K. M. El-Badry, F. A. Moustafa, M. A. Azooz, F. H. El-Batal, *Indian Journal of Pure & Applied Physics*, 38, 741, (2000).
- [31] A. Adamczyk, M. Handke, *Journal of Molecular Structure*, 596, 47, (2001).
- [32] M. Handke, M. Sitaz, M. Rokita, E. Galuskin, *Journal of Molecular Structure*, 651 – 653, 39, (2003).
- [33] P. Muralidharan, M. Venkateswarlu, N. Satyanarayana, *Solid State Ionics*, 166, 27, (2004).
- [34] K. Annapurna, Maumita Das, P. Kundu, R. N. Dwivedi, S. Buddhudu, *Journal of Molecular Structure*, 741, 53, (2005).
- [35] M. Abd El-Baki, F. A. Abd El-Wahab, F. El-Diasty, *Materials Chemistry and Physics*, in press, (2005).
- [36] E. I. Kamitsos, J. A. Kapoutsis, H. Jain, C. H. Hsieh, *J. J. Non-Cryst. Solids*, 171, 31, (1994).
- [37] A. K. Varshneya, "Fundamentals of Inorganic Glasses", Acad. Press, New York, (1994).
- [38] Hong Li, Yali Su, Liyu Li, Denis M. Strachan, *J. Non-Cryst. Solids*, 292, 167, (2001).
- [39] H. Li, L. Li, J. D. Vienna, M. Qian, Z. Wang, J. G. Darab, D. K. Peeler, *J. Non-Cryst. Solids*, 278, 35, (2000).

- [40] Byeongwon Park, Hong Li, L. Rene Corrales, J. Non-Cryst. Solids, 297, 220, (2002).
- [41] A. Bonamartini Corradi, V. Cannillo, M. Montorsi, C. Siligardi, A. N. Cormack, J. Non-Cryst. Solids, 351, 1185, (2005).
- [42] A. Abd El-Moneim, L. Abd El-Latif, Phys. Chem. Glasses, 44 (6), 446, (2003).