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Effect of irradiation on some optical properties and density of lithium borate glass

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Abstract

Borates and silicate glasses containing boron oxide have been widely used for optical lenses with high refractive index and low dispersion characteristics. Alkali borate glasses are of great technological interest especially lithium borates as solid electrolytes because of their fast ionic conduction. In this study the optical properties including infrared and refractive index and density of lithium borate glass as a base glass were studied. The effect of the presence of either aluminum or lead oxide, or the presence of one of the following transition metal, Fe_2O_3, TiO_2 or V_2O_5 was investigated. The effect of exposing the glass to either gamma, or fast neutron irradiation on the last properties was also studied. The results showed that three main bands appeared due to bending vibration or stretching of either, tetrahedral or triagonal borate units. The addition of alkalies causes only a shift of the bands either to higher or lower wavelength. Glass containing lead oxide had the highest refractive index and density, also the presence of any of the transition metal oxide lowering the average coordination number of oxygen which causes a compaction of the structure hence an increase in the values of density and refractive index. Since irradiation of glass causes compaction of B_2O_3 by breaking the bonds between triagonal elements, the average ring size becomes smaller which leads to an increase in density and refractive index too.

Keywords: Lithium silicate; Optical properties; Density; Gamma rays

1. Introduction

The optical properties of glasses are based on the interaction of the material with the energy of electromagnetic waves. Current use of oxide glasses is based on their good transmission in the optical part of the spectrum (UV+visible+near IR). This 'optical window', corresponding to the spectral sensitivity of the human eye, is bounded at the UV end by electronic transitions from the valence band to the conduction band and at the IR end by natural vibration frequencies of the constituent ions in the network. Absorption in the visible region results from the superposition of the tails of the electronic and vibration transition to which must be added contributions from impurities such as transition element ions and color centers [1].

Min et al. [2] considered that density of the glass is additive and can thus calculated on the basis of the glass composition. Min et al. compared the properties of glasses with different number of glass formers in the system Li_2O–TiO_2–P_2O_5, Li_2O–TiO_2–P_2O_5–SiO_2 and Li_2O–TiO_2–P_2O_5–SiO_2–V_2O_5 and they found that the substitution of TiO_2 for Li_2O and P_2O_5 in the Li_2O–TiO_2–P_2O_5 system results in an increase of the glass density, which implies that the glass intermediate TiO_2 may act as a glass former in this system, and strengths the covalent cross linking of the matrix. On the other hand, the substitutions of P_2O_5 by SiO_2 and SiO_2 by V_2O_5 in the other two series, respectively, just have a small effect on density.

Optical absorption in glass in the visible spectral region colors the glass, leading to applications not only in optic lenses but also for optoelectronic materials such as laser hosts fibers for communications and photonic switches. Borate glasses and silicate glasses containing boron oxide have been widely used for optical lenses with high refractive indices and low dispersion char-

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acteristics to many decorative uses. Absorption and transmission in the visible, infrared and ultraviolet regions are important in optical instruments. Absorption in all three regions can be used to study short-range structure of glasses, that is the immediate surrounding of the absorbing atom [3].

Between density and refractive index there is a close structurally determined connection, for which reason this property along with other optical properties are usually explored. This theme is explored more thoroughly by Fanderlik [4].

If a ray of light enters a glass from air, where it possesses approximately the maximum velocity C_o, then its velocity is diminished to C as a result of the interaction of the light with the ions making up the glass. With vertical incidence of the light the ray path of the light is not altered; with oblique incidence, however, a deviation can occur which is explained by the law of reflection.

$$n = C_o/C = \sin\alpha/\sin\beta$$

where α and β represent the angles of the light ray with respect to the normal in air and glass, respectively and n represent the refractive index of the glass [1].

As the refractive index of the glass is increased, the higher dispersion characteristic valuated by the Abbe number is demonstrated through all of the glass systems. The distinguishing features of borate glasses—relatively high refractive indices and low dispersion—are related to the large number of molecules, n, in a unit volume, compared with those of the other glasses, the number N determined by density measurements is related to the fraction of the four coordinated borons [5].

Alkali Oxide is usually incorporated into B_2O_3 glass ionically. The addition of alkali oxide to B_2O_3 results in quite different behavior from that in the corresponding silicate compositions. The investigated properties indicate that alkali oxide additions create a more cohesive structure while in silicate glass the network is ruptured. The behavior observed in borate glass is initially a change in the coordination number of the boron from three to four as it incorporates the additional oxygen. The bond character becomes three-dimensional and the structure becomes tighter [6].

The response of the glasses to gamma rays irradiation is related to the rate of formation and accumulation of induced defects during progressive irradiation and hence the production of characteristic color center. According to Friebele [7], the color centers may include: silicon E center, boron E center, nonbridging oxygen holes centers this can be defined as HC, hole trapped on a single nonbridging oxygen, and HC_2 hole trapped on two nonbridging oxygen hole center $BOHC_1$ and $BOHC_2$, Pb defect center (Pb^{3+}) and transition metal defect center (i.e. Fe, Ti, V, in this work).

2. Experimental

2.1. Preparation of glass samples

Lithium borate glasses were prepared from chemical grade powders. Boric oxide was introduced in the form of ortho boric acid, and the lithium oxide was introduced in the form of its respective anhydrous carbonate. Alumina oxide was introduced as it is.

Transition metals were added as their respective oxides. Vanadium oxide was introduced as ammonium vanadate, and lead oxide was introduced as red lead oxide. A series of glass samples were melted in batches of 100 g each. The melts were all made in platinum 2% Rh crucibles. In order to reduce the tendency of volatilization, the crucible was initially heated for 1 h. at 300 °C and then transferred to another furnace maintained at 1100 °C and kept there to complete the melting for 2 h. The melt was stirred from time to time to promote complete mixing and was finally poured into moulds made of stainless steel. The samples were then transferred to a muffle, which has already been heated to 300 °C. The muffle was switched off and the samples were maintained to cool down to room temperature at the rate of 30 $°C\,h^{-1}$. The composition of the glass samples is shown in Table 2.

2.2. Infrared measurements

Infrared absorption spectra of powdered glasses were measured in the range 200–4000 cm^{-1} using KBr technique at room temperature. A recording spectrophotometer, type ATI Mattson, Genesis series (Unicom) was used.

2.3. Density measurements

The density of glasses was determined by the Archimedes method in which the glass sample was weighed twice in air and when immersed in Xylene at 20 °C. The density was then calculated from the formula

$$\rho = [a/(a-b)]\times 0.86$$

ρ is the density of the glass sample; a is the weight of the

Table 1
Assignments of the infrared absorption bands of the studied glasses

Peak position (cm^{-1})	Assignment
3200–3000 cm^{-1}	Hydroxyl or water groups
1200–1600 cm^{-1}	Asymmetric stretching of trigonal BO_3
800–1200 cm^{-1}	Stretching of tetrahedral BO_4 groups
700 cm^{-1}	Bending of B–O–B linkages in the borate network

Table 2
Effect of different neutron irradiation fluxes on the glass density in gm cm^{-3}

Composition (wt.%)	ρ Before irradiation	After irradiation			
		ρ at 1.56 $\times 10^{13}$ n cm^{-2}	ρ at 2.08 $\times 10^{13}$ n cm^{-2}	ρ at 3.12 $\times 10^{13}$ n cm^{-2}	ρ at 4.16 $\times 10^{13}$ n cm^{-2}
10 Li_2O·90 B_2O_3	2.1321	2.1398	2.1623	2.1685	2.2019
10 Li_2O·85 B_2O_3·5 Al_2O_3	1.8905	2.1305	2.1589	2.1819	2.1629
10 Li_2O·90 B_2O_3·5 PbO	2.2298	2.2350	2.3505	2.407	2.3941
10 Li_2O·90 B_2O_3.2 Fe_2O_3	2.1723	2.1431	2.1998	2.2093	2.2234
10 Li_2O·90 B_2O_3·2TiO_2	2.1499	2.1295	2.1702	2.1823	2.1950
10 Li_2O·90 B_2O_3·2V_2O_5	2.1587	2.1396	2.1887	2.231	2.1789

glass sample in air; *b* is the weight of the glass sample in Xylene; and 0.86 is the density of Xylene at 20 °C.

2.4. Refractive index

The refractive index of the glass was determined using an Abbe refractometer model 2WAJ. Before measurements, the refractometer was calibrated using a standard specimen, and a drop of a—bromonaphthlene was spread on the surface of the glass sample before measurement.

Special attention was given to the following points during the calibration and manipulations procedures:

1) The glass samples must have a polished surface 1–1.5 cm long, which is accurately plane and at right angle to a small end surface.
2) The intersection between the two polished faces must be free from bevel.

2.5. Irradiation procedure

2.5.1. Fast neutron irradiation

Glass samples were irradiated with neutrons from an Am–Be neutron source of 5 Ci activity (185 Gbq), which has a neutron yield of 0.86×10^7 n s^{-1}. The Am–Be source used in this work was previously used as a neutron logging in Schumberger Co. Plastic detector were exposed to different neutron doses in the range from 0.17 to 4 rem. Four irradiation fluxes of 1.56, 2.08, 3.12, and 4.16×10^{13} n cm^{-2} were used.

2.5.2. Gamma-rays irradiation

A ^{60}Co gamma source from a Gamma chamber 4000A manufactured by Atomic Energy Agency of India was used. The dose rate was 2.5 kGy h^{-1}. The glass samples were irradiated for the necessary time interval to achieve the desired overall dose Table 3. Two irradiation doses of 40 and 80 kGy were used.

Table 3
Effect of different gamma-irradiation doses on the glass density in gm cm^{-3}

Composition (wt.%)	ρ Before irradiation	After irradiation	
		ρ at 40 KGy	ρ at 80 KGy
10 Li_2O·90 B_2O_3	2.1321	2.1489	2.1890
10 Li_2O·85 B_2O_3·5 Al_2O_3	1.8905	2.1304	2.1486
10 Li_2O·85 B_2O_3·5 PbO	2.2298	2.344	2.3424
10 Li_2O·90 B_2O_3·2 Fe_2O_3	2.1723	2.2097	2.2444
10 Li_2O·90 B_2O_3·2 TiO_2	2.1499	2.1805	2.207
10 Li_2O·90 B_2O_3· 2V_2O_5	2.1587	2.1893	2.2199

3. Results and discussion

The spectral infrared absorption curves extending from 200–4000 cm^{-1} region for the pure lithium borate and lithium borate glass containing 5% of either Al_2O_3 or PbO are shown in Fig. 1. While glasses containing 2% of the used transition metal oxides are shown in Fig. 2. The absorption spectra can be classified into three prominent and characteristic regions or groups as tabulated in Table 1. Experimental results indicate that three main IR absorption regions of borate glasses can be identified: the first region at 800–600 cm^{-1} which is due to bending vibration of various borate arrangements, the second at 1200–800 cm^{-1} which is due to B–O stretching tetrahedral units, and the third at 1500–1200 cm^{-1} which is due to B–O stretching of triagonal BO_3 units. According to Mostafa et al. [8] band at about 700 cm^{-1} is due to the presence of pentaborate units present in lithium borate glass.

For the studied lithium borate glasses, in addition to the previous three main groups of bands, there are two extra groups, one in the far infrared ranging from 500–

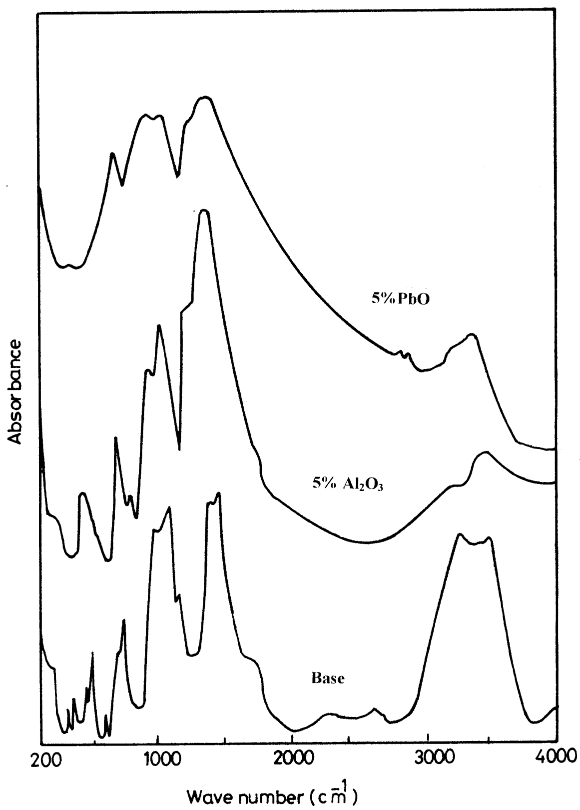

Fig. 1. Effect of replacing 5 wt.% B_2O_3 by either Al_2O_3 or PbO on the infrared spectra.

200 cm^{-1} which is due to the vibration of lithium cations in their oxygen sites [9,10], which takes into account two dynamic processes [11], the vibration of lithium ion in a negative site and the jump of the lithium ion between equivalent negative sites.

An absorption band around 3400 cm^{-1} has been also observed for all samples indicating the presence of hydroxyl group and/or B–OH bond within the glass matrix [12]. Experimental results show that the presence of Al_2O_3 in the glass causes the high frequency bands at 1500–1200 cm^{-1} to be highly intensified, the mid frequency bands at 1200–800 cm^{-1} become less intensified, while the band at 700 cm^{-1} remains unaffected. Addition of Al_2O_3 to the borate glasses lowers the conversion rate of BO_4 units that depend on the molar ratio Al_2O_3/Li_2O. It is assumed that the oxygen ions introduced by the modifier oxide are consumed first for the four coordination of aluminum [12] before the conversion of boron from three to four coordination. Upon addition of Al_2O_3 to the lithium borate glass the change in coordination and the inter linking of Al_2O_3, BO_4 and BO_3 are assumed to cause the observed shift.

Lead oxide is supposed to be capable of behaving as a glass former in suitable circumstances. At low content of PbO its bond is ionic, while the formation of BO_4 groups proceeds at the rate of two tetrahedral for each added oxygen. Fig. 1 shows that the band at 1600 shifted

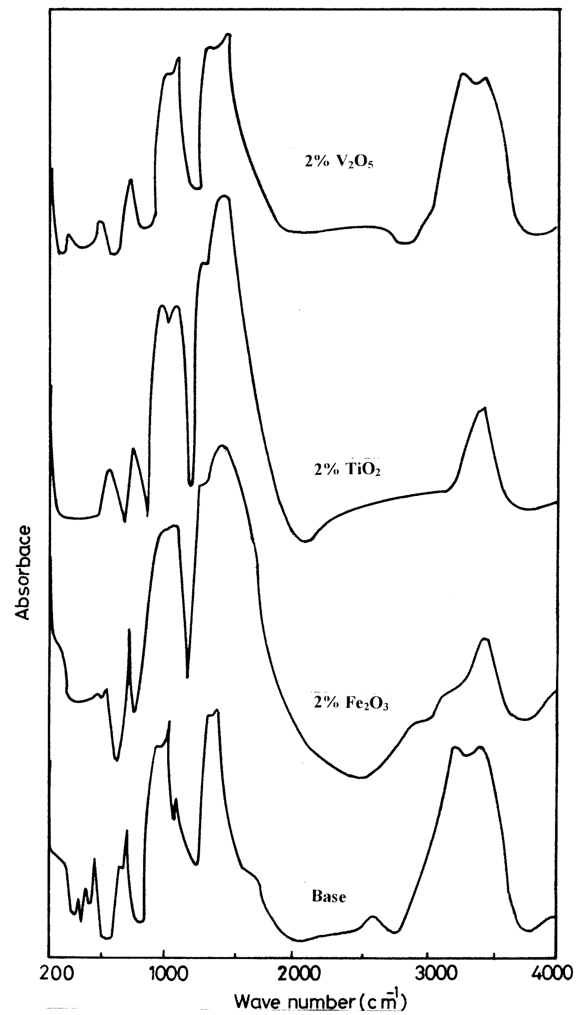

Fig. 2. Effect of adding 2 wt.% transition metal (Fe_2O_3 or TiO_2 or V_2O_5).

to 1393 cm^{-1} due to the substitution of 5% B_2O_3 by pbO.

There is also a shift of the band 1200–800 cm^{-1} to lower frequency at 1071–785 cm^{-1}. Accordingly the results of the infrared spectroscopy revealed that the ionic and covalent PbO bonds might exist in lead borate glass. Tawansi et al. [13] found that at low PbO content the formation of four coordinated borons proceeds the rate of formation of two tetrahedral for each added oxygen. At low PbO content, the lead is assumed to enter the glass as modifier Pb^{2+} ions. The ability of Pb^{2+} to share as glass former Pb^{4+} increase with the higher PbO content.

The addition of iron to lithium borate glass causes a shift accompanied by a decrease in the intensity of the IR spectrum from 1200–800 cm^{-1} to a weak band at 1054–768 cm^{-1} beside the appearance of a strong band located at 1393–1250 cm^{-1}. These new bands may correlate to B–O– and B–O–Fe– vibrations in which boron and iron atoms are coordinated [14]. The band at about 700 cm^{-1}, which represents the bending of B–O–

B linkages in the borate network, remained approximately without any changes in its position.

The addition of TiO_2 causes a shift of the band frequency of the studied glass from 1200–800 to 1054–785 cm^{-1} and the bands at 1600–1200 to 1393–1232 cm^{-1}. The shift of the bands from 700 to 660 cm^{-1} with the addition of 2% TiO_2, encourage the suggestion that titanium is incorporated in the network forming position as TiO_4. Moreover, when Ti^{4+} ions are formed, the polarizability of the oxygen atoms increase, thus the vibrations corresponding to B–O–B and O–B–O groups shift to lower intensities [15].

The absorption spectra of vanadium containing glasses are generally of a very complex nature because of the three valance states of vanadium (V^{3+}, V^{4+}, V^{5+}). These three valances are present all together and usually existing in varying proportions depending mainly on the host glass, the condition of melting and on the concentration of the vanadium in the glass [16]. Ezz Eldin et al. [16] assumed that vanadium ions exhibit a relatively strong distorted symmetry and its spectra have somewhat closer bands, which overlap each other. In borate glass the vanadium ions are verified to exist mainly in lower valance state. Fig. 2 shows infrared bands of lithium borate glass containing 2% V_2O_5 at 1015, 821 cm^{-1} and from 400–500 cm^{-1}. These bands are attributed to the vibration of BO_4 and BO_3 and the presence of VO_4 group where Kulieva et al. [11] found that the stretching V=O band at 1019 and 400–500 cm^{-1}.

3.1. Effect of irradiation

3.1.1. Neutron irradiation

The IR spectra shown in Figs. 3–8 reveal the effect of exposing the studied glasses to neutron flux for (1.56, 2.08, 3.12 and 4.16) $\times 10^{13}$ n cm^{-2}. Atomic displacement results mainly from the collision of energetic neutrons with the primary displaced atoms dissipate their energy in their passage through the solid. Ionization is known to change the color of vitreous silica and quartz, but more profound changes are found which are attributed to the displacement of atoms from their normal positions in the solid by collision with energetic neutrons [17].

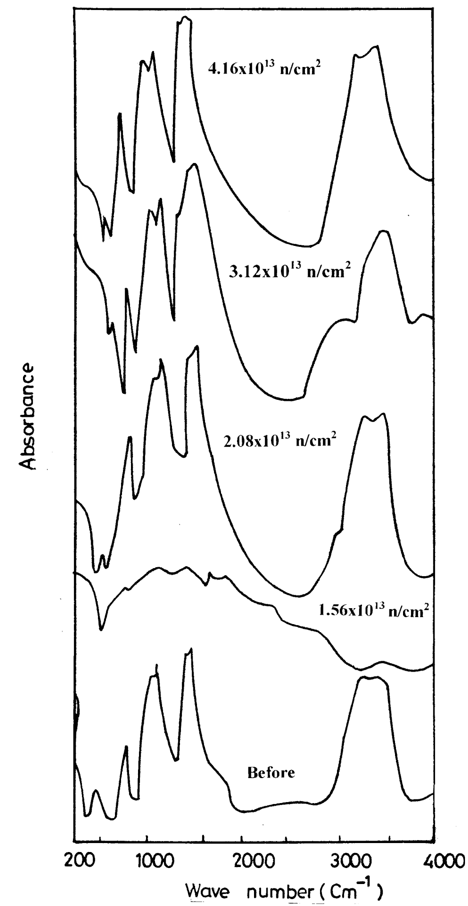

Fig. 3. Effect of neutron flux on infrared spectrum for base glass.

The structure of borate glass is assumed to consist of randomly connected broxol rings together with other tetrahedral units. In the borate conference 1997 it has been confirmed by Golubkov [18] that broxol rings are formed in borate glasses, however, its percentage is still debatable.

The neutron irradiation is said to cause noticeable densfied structural change in glass or a compact state which may include that some bond angles become smaller, change in density and refractive index and induced color centers that is responsible for induced

Table 4
Effect of different neutron irradiation fluxes on the refractive index of the studied glasses

Composition (wt.%)	Before irradiation	After irradiation			
		1.56×10^{13} n cm^{-2}	2.08×10^{13} n cm^{-2}	3.12×10^{13} n cm^{-2}	4.16×10^{13} n cm^{-2}
10 $Li_2O\cdot90\ B_2O_3$	1.5560	1.5563	1.5565	1.5568	1.5600
$10Li_2O\cdot85B_2O_3\cdot5\ Al_2O_3$	1.5465	1.5467	1.5471	1.5475	1.5473
$10Li_2O\cdot85\ B_2O_3\cdot5$ PbO	1.5823	1.5825	1.5829	1.5830	1.5828
$10Li_2O\cdot90\ B_2O_3\cdot2\ Fe_2O_3$	1.5731	1.5730	1.5737	1.5740	1.5742
$10Li_2O\cdot90\ B_2O_3\cdot2\ TiO_2$	1.5563	1.5561	1.5564	1.5567	1.5569
$10Li_2O\cdot90\ B_2O_3\cdot2\ V_2O_5$	1.5593	1.5590	1.5599	1.5602	1.5602

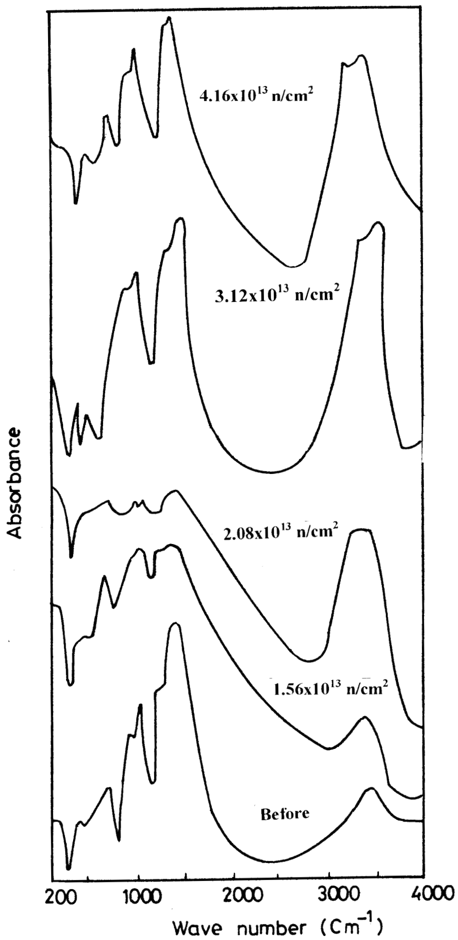

Fig. 4. Effect of neutron flux on infrared spectrum for glass containing 5% Al_2O_3.

absorption bands. In the beginning of the irradiation, the majority of neutrons will be captured close to the glass surface causing the surface to expand or contract while the center remains unaffected [19] (Table 4).

3.1.2. Effect of gamma irradiation

Figs. 9–14 show the effect of exposing glasses to gamma rays at a dose of 40 and 80 kGy Table 5. It can be noticed that the exposure of the glass to irradiation did not give a sharp change in their IR spectra.

The liberated electron from photoelectric effect may be trapped by either the glass matrix defects or by M^{X+} ion to produce $M^{X+(+)}$ ion [20]. This suggestion may give a plausible explanation for the change in absorption with irradiation dose. Several processes may occur in glasses containing transition metal ions upon gamma ray irradiation:

1) Transition metals may capture the charge carriers before they are trapped in defect originally present in the glass.

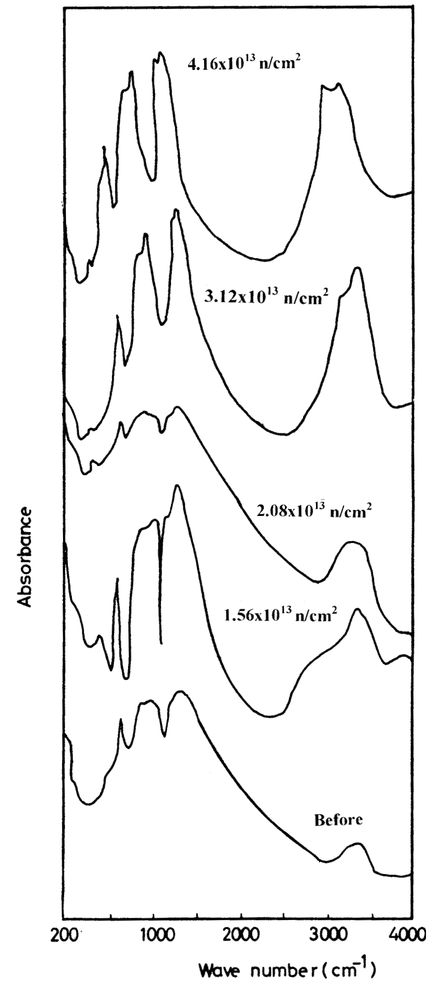

Fig. 5. Effect of neutron flux on infrared spectrum for glass containing 5% PbO.

2) Transition metal may trap holes, which endow it with a high recombination cross-section so those electrons are annihilated before they are trapped.
3) Transition metal may increase the recombination of carriers by decreasing their mean free path.

The shift of the absorption edge to lower wavelength can be due to a transfer of some boron atoms from the

Table 5
Effect of different gamma-irradiation doses on the refractive index of the studied glasses

Composition (wt.%)	Before irradiation	After irradiation	
		40 KGy	80 KGy
$10Li_2O \cdot 90B_2O_3$	1.5560	1.5565	1.5570
$10Li_2O \cdot 85B_2O_3 \cdot 5Al_2O_3$	1.5465	1.5467	1.5473
$10Li_2O \cdot 85\ B_2O_3 \cdot 5PbO$	1.5823	1.5825	1.5829
$10Li_2O \cdot 90B_2O_3 \cdot 2Fe_2O_3$	1.5731	1.5735	1.5739
$10Li_2O \cdot 90B_2O_3 \cdot 2TiO_2$	1.5563	1.5598	1.5607
$10Li_2O \cdot 90B_2O_3 \cdot 2V_2O_5$	1.5593	1.5598	1.5607

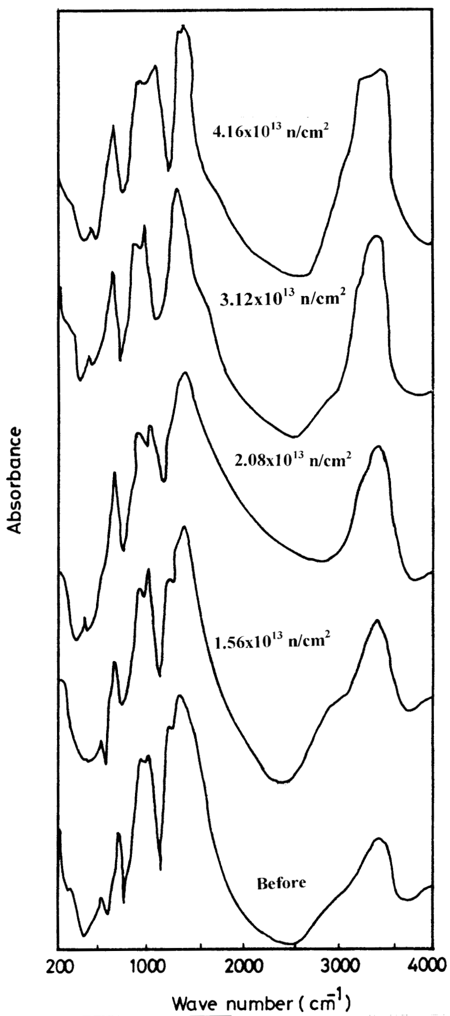

Fig. 6. Effect of neutron flux on infrared spectrum for glass containing 2% Fe_2O_3.

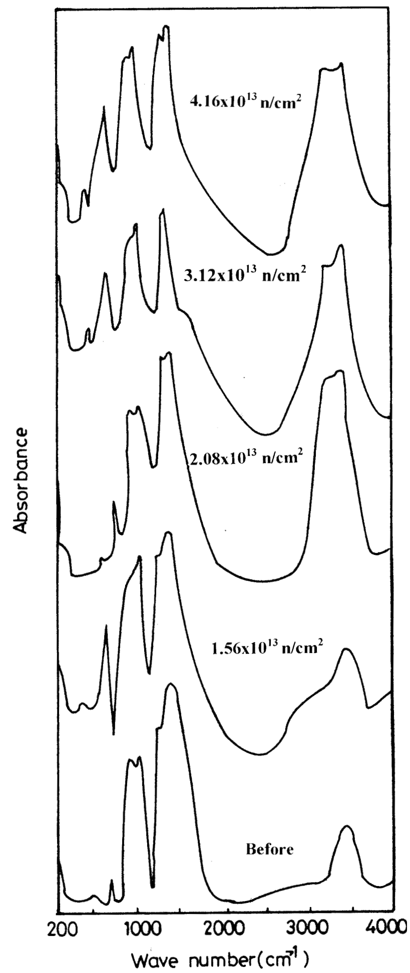

Fig. 7. Effect of neutron flux on infrared spectrum for glass containing 2% TiO_2.

triangular BO_3 group to the tetrahedral BO_4 one, particularly at high γ-ray doses [21].

3.2. Effect of glass composition on density

The increase of the density of glass with higher content of Li_2O may be due to the effect of Li ions which are situated in rooms or cavities in the empty spaces of the network, recognizable by the decline in the molar volume [1]. In the binary alkali metal borate systems, a transition into three-dimensional cross-linking takes place with high alkali metal content through the coordination shift $(BO_3) \rightarrow (BO_4)$. The tetrahedral BO_4 groups are strongly bonded than the triangular BO_3 groups and hence a compact structure is expected leading to a higher density. As seen in Table 1 glass containing lead had the highest density. In borate glasses containing low proportion of lead oxide, it would be expected that some of the lead ions will exist as PbO_4 groups, while the remaining lead ions can exist as bridges between BO_3 and BO_4 groups or enclosed in the interstices in the glass structure as Pb^{2+} ions [22]. Also it can be noticed that glass containing 5% Al_2O_3 has the lowest density. This result can be understood in the light of the decrease of the coordination shift of BO_3 to BO_4. The presence of Al_2O_3 in the glass causing an increase in the BO_3 units where it consumes some of the available oxygen atoms in the Li_2O which are required to covert BO_3 to BO_4, where the priority become to change AlO_3 to AlO_4. This in tern led to increase in the glass volume, which means a decrease in the glass density.

3.3. Effect of irradiation on the glass density

Irradiation with neutron or γ-rays are assumed to create displacements, electronic defects and/or breaks in the network bonds, which allow the structure to relax and fill the relatively large interstices that exist in the interconnected network of boron and oxygen atoms

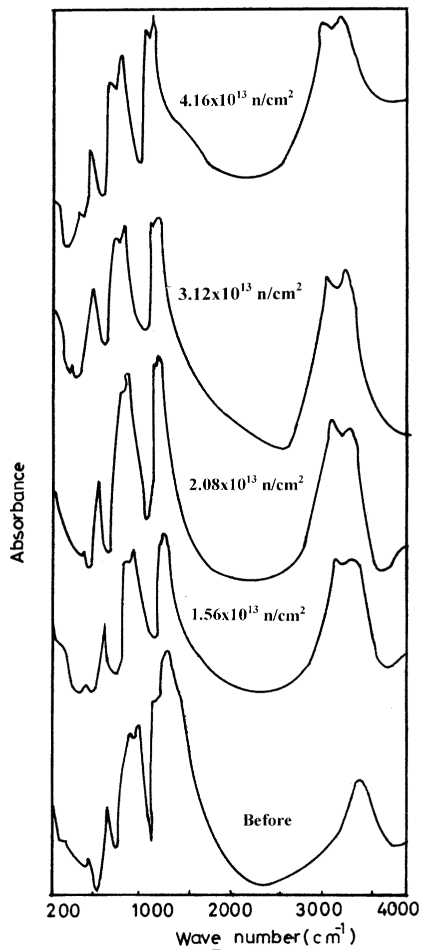

Fig. 8. Effect of neutron flux on infrared spectrum for glass containing 2% V_2O_5.

causing expansion followed by compaction of the volume [20]. Shelby [23] suggested that the boron–oxygen bond is more likely to be affected by irradiation. Damage by an irradiation species can cause the compaction of B_2O_3 by the breaking of bonds between triagonal elements, allowing the formation of tetrahedral BO_4.

This can explain the increase in the density of the glass with irradiation. As shown from Tables 1 and 2, the densities of the glasses increase with the increase of irradiation dose, which is represented, by increasing of the exposure time to the irradiation source. This result is in agreement with the results obtained by Ezz Eldin et al. [16] where they found that nuclear irradiation is believed to cause noticeable structural changes, which may comprise:

a) Some bond angles become smaller, i.e. a compact state are produced.
b) Increase or decrease in density depending on composition or state of aggregation.
c) Induced damage that is responsible for induced color centers.

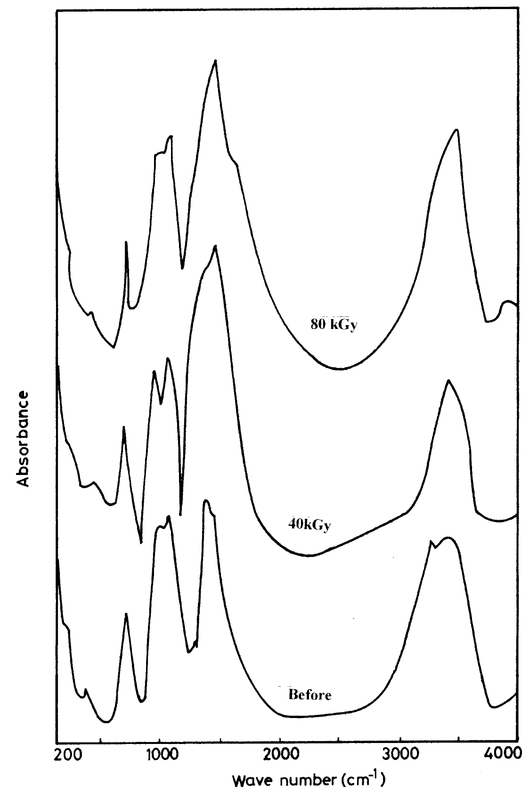

Fig. 9. Effect of gamma irradiation-dose on the infrared spectrum for base glass.

The observed increase in density of glasses as irradiated with neutron flux is accounted to be due to a tightening effect or compaction of the glass structure.

The decrease in the glass density at the first neutron flux can be attributed to the absorption of the neutrons in the surface of the glass. In the glass surface the transition metals present in the glass can change its coordination and prevent the neutrons from attacking the glass center. This means that there was an expansion in the glass which in tern causing a decrease in the glass density.

3.4. Effect of composition on refractive index

The distinguished features of borate glasses are their relatively high refractive indices and low dispersion values, which are related to the large number of groupings in a unit volume, compared with those of the other glasses. The number of molecules in a unit volume is related to the fraction of the, four coordinated borons as mentioned by Fujino et al. [5]. Many authors [1,20] have investigated the binary alkali-borate glasses. Those authors found that the system containing Li_2O shows the highest refraction, this is because the refractive index is determined not only by the polarizability but the molar volume M/ρ can also play a role such that, the index of refraction increases with decreasing the molar volume, and thus a dense structure is expected.

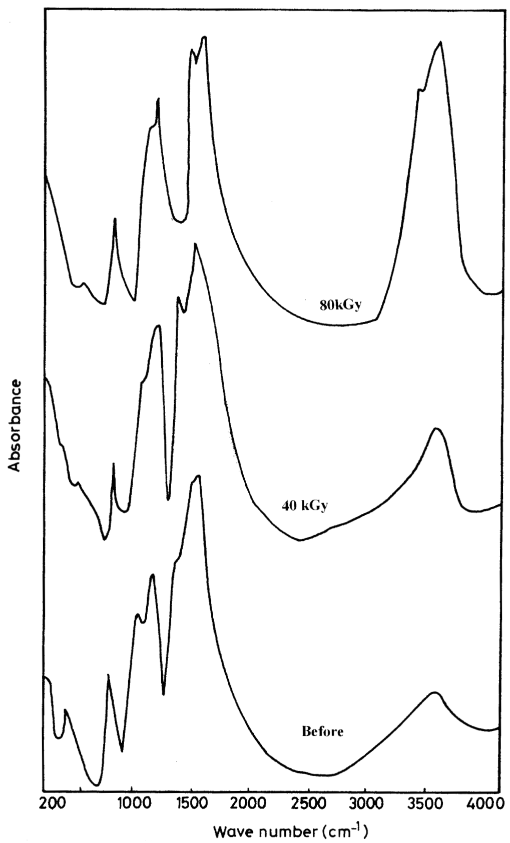

Fig. 10. Effect of gamma irradiation-dose on the infrared spectrum for glass containing 5% Al_2O_3.

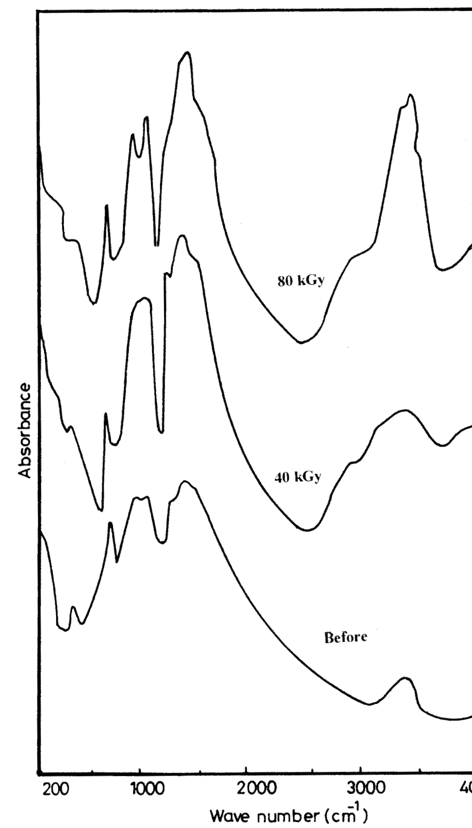

Fig. 11. Effect of gamma irradiation-dose on the infrared spectrum for glass containing 5% PbO.

The B_2O_3 glass with free OH groups, attains a denser structure through increased formation of nonbridging oxygens and thus higher index of refraction. This influence, however decreases with increasing alkali content in the binary R_2O–B_2O_3 [24].

According to Fanderlik [4] where the glass density is connected to the refractive index, the glass containing Al_2O_3 has a relatively large ion size besides in the studied glass Al_2O_3 acts as a glass modifier and not as a glass former. While, lead oxide gives the highest density and the highest refractive index because it enters the glass network mainly as glass forming PbO_4 groups. The refractive index of the glass containing transition metal, like V_2O_5 and TiO_2 is high, and this may be because vanadium and titanium ions lower the average coordination number of oxygen. This results in the compacting of the structure, which is in tern reflected in the increase of the refractive index.

3.5. Effect of Irradiation

The values of refractive index of the irradiated glasses increase when the glass is irradiated either with neutrons or γ-rays. The increase of the density and refractive index of the glass with irradiation may be due to ionization or atomic displacements that resulted from gamma rays collision with the glasses, which may materially alter or change the internal structure in the glass. Also the recoiled oxygen ions from the sample may give an explanation for the volume changes [25].

Towards the end of its track the gamma rays irradiation produce a large number of displacements creating an area of highly disturbed material. Within these ‘displacement spikes’ individual displacements have no meaning [20]. This disturbed region can be considered as quenched glass and is, therefore, an area of volume expansion. This expanded region will exert pressure on the surrounding material, which will become compacted while any resulting strain is released by plastic flow. The outer area, therefore, can be considered as a region of annealed glass of higher density and refractive index. These effects do not reach their maximum at the same level of irradiation, depending on the size of the displacement spikes, and the zone of compaction [9]. The significant increase in density of a material is an indication of a large change in the structure. As mentioned before induced damage by an irradiating species can cause the compaction of B_2O_3 by the breaking of bonds between triagonal elements, allowing the formation of different ring configuration. The average ring size is then decreased, leading to the

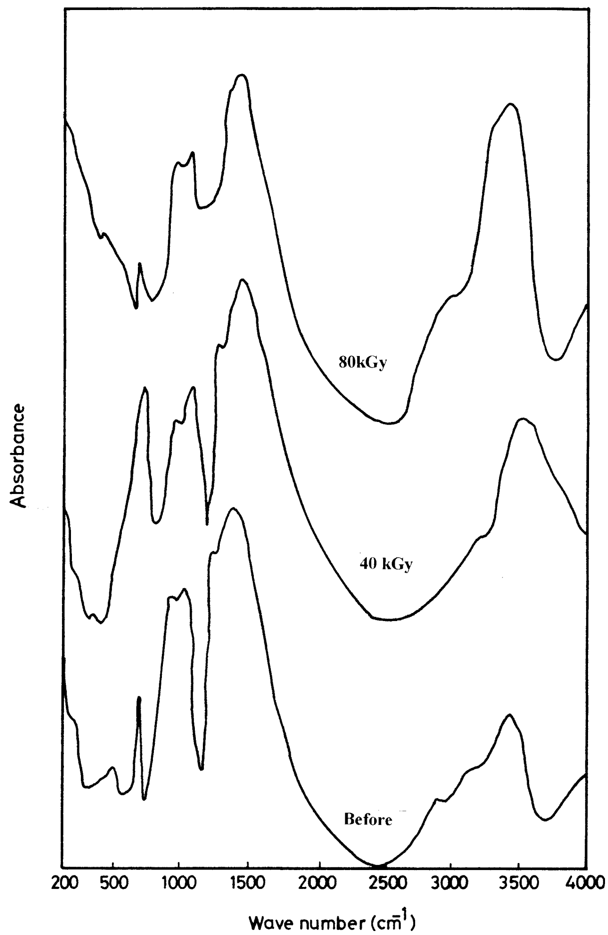

Fig. 12. Effect of gamma irradiation-dose on the infrared spectrum for glass containing 2% Fe_2O_3.

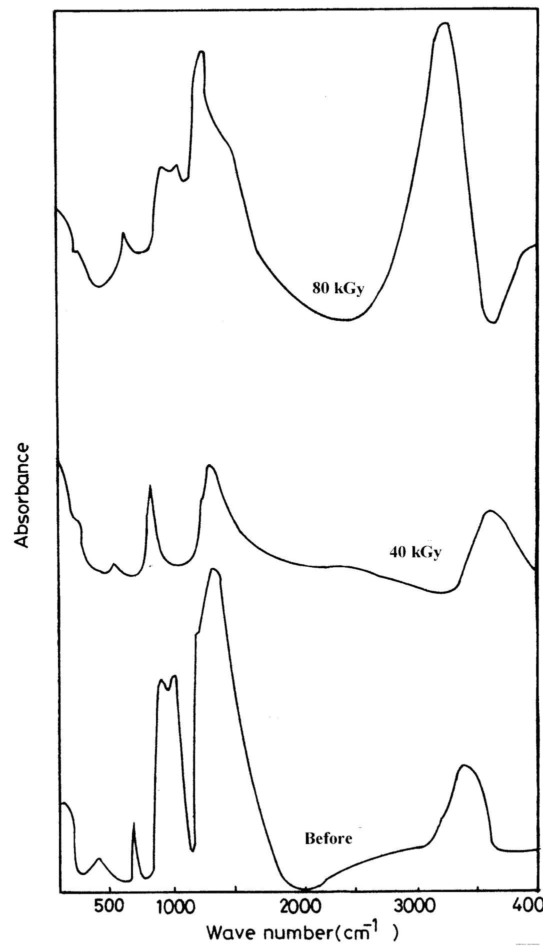

Fig. 13. Effect of gamma irradiation-dose on the infrared spectrum for glass containing 2% TiO_2.

observed increase in density and therefore, increase in the refractive index [2].

4. Summary remarks

The IR spectra of lithium borate glass showed the main bands of borate glass. The substitution of 5% B_2O_3 by Al_2O_3 in the base glass causes a shift of the bands, this shift assumed to be due to the change in the coordination and the inter linking of Al_2O_3, BO_4 and BO_3. The substitution of 5% B_2O_3 by PbO causing a shift to the lower wavelength which may reveal the presence of both ionic and covalent PbO bonds in lead borate glass. The addition of 2% Fe_2O_3 to the base glass caused the appearance of a new band at 1393–1250 cm^{-1} which may correlate to B–O and B–O–Fe vibrations in which boron and iron atoms are coordinated. By the addition of 2% TiO_2, the shift of the band at 700–660 cm^{-1} encourage the suggestion that the titanium ion is incorporated in the network forming position as TiO_4 where Ti^{4+} ions causing increase in the polarizability of oxygen atoms, thus the vibration corresponding to B–O–B and O–B–O groups shifted to lower intensity. The presence of 2% V_2O_5 causes a shift to lower wavelength where the stretching V=O band occurs at 1019 and 400–500 cm^{-1}.

The highest glass density is given for the glass containing 2% lead oxide, where lead ions can exist as PbO_4 and as bridges between BO_3 and BO_4 groups. The lowest density of the studied glasses is given by glass containing 5% Al_2O_3 where the presence of Al_2O_3 in the glass causing an increase in the BO_3 units because it consume some of the available O_2 in Li_2O which are required to convert BO_3 to BO_4 where the priority become to change AlO_3 to AlO_4 this cause an expansion of the glass volume.

The density increases for all of the studied glasses when subjected to irradiation, (either with neutron flux or γ rays). It can be noticed that the density of the glass containing transition metal decreases when it irradiated with the lowest neutron flux, this may be due to the absorption of the neutrons in the glass surface causing a displacement of the ions, so the oxygen ions can be used to change the valence of the transition metal ions to a

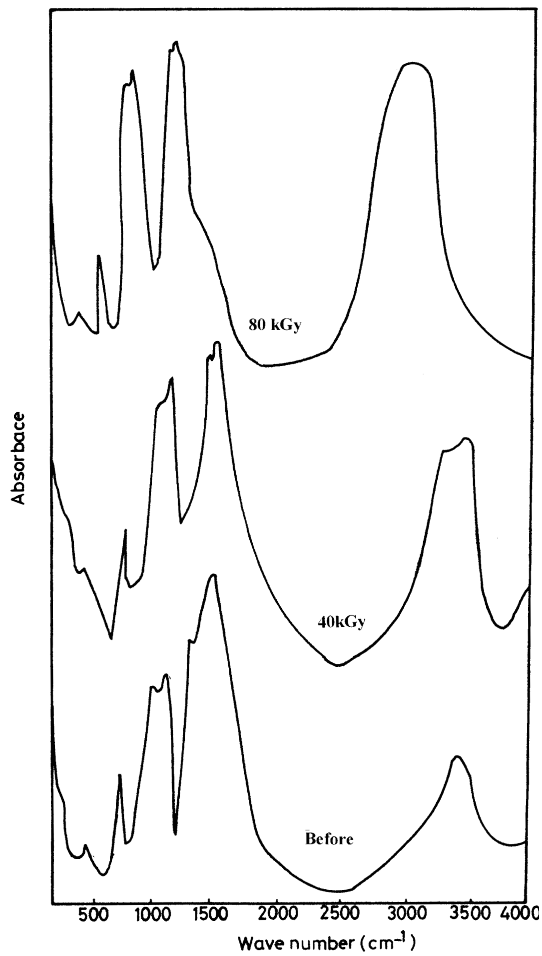

Fig. 14. Effect of gamma irradiation-dose on the infrared spectrum for glass containing 2% V_2O_5.

higher valence and bigger size instead of consuming this oxygen as bridges between BO_3 and BO_4. At higher irradiation doses, the irradiation species can cause the compaction of B_2O_3 by breaking the bonds between triagonal groups allowing the formation of different ring configurations.

Also it can be noticed that the glass containing alumina is the most affected glass when subjected to irradiation, where it gives the highest rate of increase either in density or refractive index values. This can be attributed to the large size of AlO_4, which causes an expansion of the glass volume as mentioned before, when this glass is subjected to irradiation there will be a displacement and AlO_4 ion which has large size will cause a compaction to the surrounding ions causing an increase in both the glass density and refractive index values. The same results where achieved for glass containing transition metal ions, which lower the average coordination number of oxygen, however, these large configurations resulted in a compaction of the surrounding structure.

Generally borate glasses have high refractive index, the presence of Li_2O in the studied glass increasing the refractive index value. AS the refractive index increase relatively with the increase of the density, the same results of the glass density is obtained with refractive index.

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