Characterization of Some Chemical and Physical Properties of Lithium Borate Glasses Doped With CuO and/or TeO₂

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Summary: Glasses used in this study are prepared economically at a relatively low melting temperature (650-750°C). Presence of alkalis such as Na_2O works as a flux and enhances the melting process. A Simple comparative study between the effect of doping Cu^{2+} and/or Te^{4+} ions in lithium borate glasses before and after gamma irradiation has been discussed. Density, molar volume, optical UV transmittance, optical band gap energies, DC electrical conductivity and chemical durability of the prepared glasses are measured. It is found that doping with Cu^{2+} ions makes a disruption in the glassy network by increasing the number of non-bridging oxygens (NBO) forming a more open network structure. While doping with the fourfold Te^{4+} ions enhances the crosslinking of the glassy network giving more rigid structure since the relatively high molecular weights of Te^{4+} ions allow them to bond strongly with the glassy network. The last two assumptions can elucidate results obtained from the last measurements.

Key words: Borate glass, Transition metals, Electrical conductivity, Chemical durability, Gamma Irradiation.

Introduction

There are many advantages of using B_2O_3 as a network glass forming oxide. Borate glasses can be easily prepared especially in the presence of flux materials which reduce the required melting temperatures such as sodium carbonates. They are also suitable hosts for many modifier oxides like alkalis and transition metal oxides (TMO). Transition metals containing borate glasses are one of the most commercial materials because of their wide applications in industry, science, and medicine [1]. B_2O_3 forms two main super structural units in borate glass networks; the planar triangle BO_3 and the tetrahedral BO_4 units. These units may be present in many structural groups such as diborate, tetraborate, pentaborate or broxol ring etc based on the percent of bridging or non-bridging oxygens in the glassy network [2]. Generally, the chemical and physical properties of a glass depend mainly on its chemical composition inclusive of both the host glassy network and the modifying ions that introduced in. Introducing of alkali ions in borate glasses creates more cohesive structures because they incorporate into B_2O_3 glasses ionically leading to the change in the coordination number of boron between three and four according to their behavior with the surrounding oxygens [3]. For example, incorporation of Li_2O into borate glasses modifies the host glass structure through the conversion of BO_3 to BO_4 units [2] leading to improving some of glass physical properties such as glass forming capability, chemical durability, and electrical conductivity. Lithium borate glasses are also with interesting semiconducting

properties so they are used widely in the manufacturing of high energy batteries and cathode materials [4] because Li^+ ions are quite mobile in oxide glasses and they act as "charge carriers". Other attractive applications of lithium borate glasses are their using in radiation dosimetry and detecting the penetration of radiation in homeland security [2].

Introducing CuO to lithium borate glasses enhances their semiconducting and super paramagnetic properties. CuO exists in two valence states; monovalent Cu^{1+} ($3d^{10}$) and divalent states Cu^{2+} ($3d^9$) so it can participate in the glass network in the form of CuO_4 or CuO_6 [2]. The presence of Cu^{2+} ions in borate glasses improves their electrical conductivity where the conduction process is controlled by the electronic hopping between Cu^{1+} and Cu^{2+} ions and the total ratio Cu^+ to Cu^{++} controls the conduction mechanism [5]. Lithium tetraborate glasses doped with Cu^{2+} ions has a broad optical absorption band at around 750 nm [6] with intense absorption in the UV region at 350 nm because of the charge transfer band $Cu^{2+} \rightarrow O^{2-}$. Doping with Cu^{2+} ions yields defects in the glass matrix by the creation of more NBO so an obvious decrease in the optical band gap of Cu^{2+}doped glasses would be predicted [7]. TeO_2 belongs to the category of compounds where all atoms are the so-called P-elements having unpaired valence electrons. In the glassy tellurite matrix, the main structural units are the trigonal bipyramid TeO_4 units where their concentration increases with increasing the concentration of the

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introduced modifier ions [8]. Therefore incorporation of tellurium ions into borate glassy systems, especially in presence of TM ions, acquires glasses characteristic chemical and physical properties such as high chemical and thermal stability, low annealing temperature [5] and relatively low electrical resistivity e.g. vanadium tellurite glasses [8].

Improving chemical durability of glasses is extensively required especially when they tend to be used in specific commercial applications. Addition of alkali oxides such as Al_2O_3 and CaO to borate glasses enhances their chemical durability towards moisture and chemical reagents by retarding the work of temperature and chemicals. So a confirmation between durability and workability in commercial glasses should be considered [9]. Gamma irradiation of glasses is believed to change many of their physical and chemical properties. Effect of irradiation on glass depends greatly on three main factors; composition of the host glass; type and dose of radiation; and some physical parameters of the sample such as the specimen state and temperature [4]. According to Friebele, 1991 [10] irradiation with ionizing gamma rays causes displacement of atoms or ions of glasses forming active induced defect centers. The accumulation of theses defects leads to the formation of characteristic color centers such as boron E center, non-bridging hole center, TM defect center etc. These defects are therefore responsible for the variation that takes place in many properties of glasses after irradiation.

The main objective of this work is to prepare compositions of alkali lithium borate glasses doped with CuO and/or TeO_2 economically at relatively low melting temperature. A simple comparative study between the effect of doping glasses with CuO and/or TeO_2 is argued by characterization some of their chemical and physical properties such as; density, molar volume, electrical conductivity, UV optical properties and chemical durability. Effect of gamma radiation on the previous properties of the prepared glasses is also discussed in order to test their sensitivity to gamma radiation.

Experimental

Preparation of five glasses was carried out by using melting annealing technique. The compositions in wt. % were listed in Table-1; chemicals used in preparation were chemically pure H_3BO_3, Li_2CO_3, Na_2CO_3, $CaCO_3$, $SrCO_3$, Al_2O_3, CuO, and TeO_2. The five batches were accurately weighed by using an electronic balance, mixed thoroughly and grounded to a fine powder, and then they are melted

in porcelain crucibles in an electric furnace at 650-750 ℃ for 90 mins with rotating melts for homogeneity. After casting melts, they were immediately transferred to a muffle furnace regulated at 350 ℃ for annealing. After 1 h, the muffle was switched off to decrease to the room temperature with a rate of 25℃/h.

Table-1: Chemical compositions of the prepared glasses (wt. %).

Glass Composition	B_2O_3	Li_2O_3	Na_2O	Al_2O_3	SrO	CaO	Doping (wt %)
G1	56	25	10	2	2	5	-------
G2	56	25	10	2	2	5	0.1 CuO
G3	56	25	10	2	2	5	$0.5\ TeO_2$
G4	56	25	10	2	2	5	$0.5\ TeO_2$ + 0.1 CuO
G5	56	25	10	2	2	5	$0.5\ TeO_2$ + 0.2 CuO

X-ray Diffraction measurements (XRD) were made by using a Shimadzu XD-DI diffractometer where the X-ray was operated at 40 kV and 30 mA through the measurements.

Density of glasses was measured at room temperature, using the suspended weight method based on Archimedes principle. Xylene was used as the immersion liquid. All measurements were made three times with maximum error 0.0002 g/cm³. Density was calculated according to the following formula:

$$\rho = \{a/ (a-b)\} \times 0.86 \qquad (1)$$

where ρ is the density of the glass sample, a and b are weights of the glass sample in air and xylene respectively. 0.86 is the density of xylene at 20°C.

Molar volume of glasses is also measured by using the formula:

$$Vm = \sum x_i\ M_i /\rho\ cm^3/mol \qquad (2)$$

where x_i is the molar fraction, Mi is the molecular weight of each component of glass and ρ is the density of the glass.

Density and molar volume of glasses were measured before and after gamma irradiation with 1 kGy.

Optical UV transmission spectra of three highly polished samples G2, G3, and G4 with the dimensions 1 X 4 X0.2 cm³ were recorded at room temperature before and after successive gamma

irradiation with 1 and 3 kGy using a recording spectrophotometer in the range 200–1100 nm type JASCO, Corp., V-570, Rel-00, Japan. Optical band gap energies Eopt are also detected before and after gamma irradiation doses.

DC electrical conductivity of the prepared glasses was measured before and after being subjected to 1kGy of gamma radiation. A programmable digital electrometer/high resistance meter (KEITHLY 6517B) was used for the resistivity measurements at constant frequency and voltage with reliable fast response together with a high precision of the power supply. All measurements were carried out in a temperature range from 298 to 473 K and measuring was detected after each 20°C.

Chemical durability of glasses was carried out before and after irradiation glasses with 1 kGy. The leaching experiments were carried out by using cleaned glass slabs, each sample was placed in a 100 ml dis. H_2O in a muffle furnace regulated at 90-100 °C. Weights of samples were then detected many times at different time intervals from 2 to 16 hours. Chemical durability was determined by calculating weight loss% against time of corrosion.

Gamma irradiation source was Co [60] gamma cell (2000 Ci) with a dose rate of 1.5 Gy/s at 30 °C. The glass samples were located into gamma cell in means that each sample was exposed to the required identical dose

Results and discussion

Fig. 1 displays the amorphous structure natures of some prepared glasses where there is a complete absence of any sharp peaks.
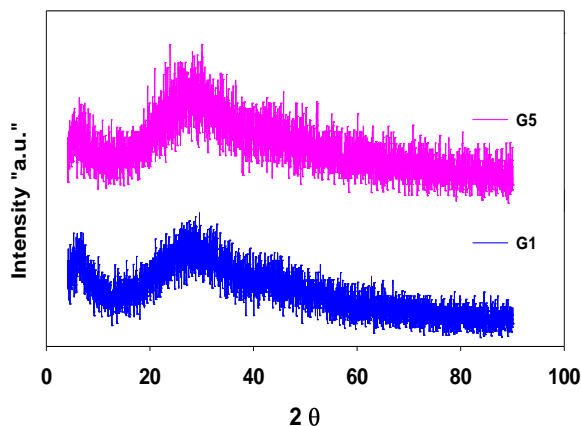

Fig. 1: XRD of some undoped and doped lithium borate glass systems (G1 and G5).

Density and Molar volume

Density of glass is a specific physical property that depends mainly on the way in which atomic groups are placed and interconnected in the glassy network [11]. Usually alkali oxides are incorporated into B_2O_3 glass ionically and they tend to make a more coherent structure by changing the triangle BO_3 to the more congested tetrahedral $[BO_4]^-$ units. This assumption may be related to the change of the boron super structural units from broxol ring which comprises solely of BO_3 units to other super structural units that have more BO_4^- groups. Type and concentration of the introduced alkali ion control this process because in case of high alkali ion concentration, the reverse process may take place by reducing the four coordinated boron concentration $[BO_4]^-$ according to Nattapol L. et al, 2016 [12]. All of oxides; Na_2O, Li_2O_3, Al_2O_3, SrO and CaO are introduced in the prepared glasses as shown in Table-1. The presence of Al_2O_3 tends to increase the strength of the glass by the formation of four-fold AlO_4 groups while the divalent ions SrO and CaO are housed in the interstices – which are a main part of the amorphous structure of the glass – and held strongly more than the monovalent cations Na^+ and Li^+ ions. So the net result would be a mixed cationic structure of more or less regular type surroundings [9]. Then suitable density values are obtained as shown in Table-2. Since the prepared glasses have similar compositions except the doping ions, so the effect controls density would be the type and concentration of the doped ion as well as its behavior with the essential network. It is observed that the undoped G1 has the lowest density value compared with the other four doped glasses. However G3 or Te^{4+} doped glass has the highest density value which may be related to the high atomic weight of tellurium ions ($_{52}Te^{127.8}$) since density depends mainly on the weight of individual components of the glass and defined as the weight per unit volume. On the other hand doping with the TM Cu^{2+} ion as in case of G2 leads to more disruption in the glassy network by creating more non-bridging oxygens NBOs due to the various oxidation states of copper ions Cu^{1+} and Cu^{2+}, then a slightly more open structure with lower density values would be obtained. So the higher the concentration of doped Cu^{2+} ions, the lower the density of its glass so G5 has lower density values than G4. The previous assumptions confirm results shown for G4 and G5 that are doped with both Te^{4+} and Cu^{2+} ions where they have density values lower than G3 but higher than G2 as shown in Table-2. The glass structure can be explained in terms of molar volume rather than density, as the former deals the spatial distribution of the ions forming that structure.

The change in the molar volume with the molar composition of an oxide indicates the preceding structural changes through a formation or modification process in the glass network [13]. According to results shown in Table-2, the molar volumes of the prepared glasses are inversely related to their densities. Doping with copper ions tends to increase the molar volume of a glass doped in, due to the presence of large borate frameworks that are required for accommodation of these ions causing the existence of more NBOs in the borate framework [12]. Table-2 shows also the values of density and molar volume of 1 kGy gamma irradiated glasses where it is obviously shown a slight decrease in their densities and a slight increase in their molar volumes after irradiation. Gamma collisions cause electronic defects and/or breaking bonds of the glassy network thus the formation of more NBOs takes place giving more free electrons that work to open the framework structure and decrease the compaction of the glass. Therefore the net result would be a decrease in density or an increase in the molar volume of the irradiated glasses.

Table-2: Density and molar volume values of Non-irradiated and 1 kGy irradiated glass samples.

Glass no	ρ (g/cm^3)		Vm (cm^3/mol)	
	Un-irradiated	Irradiated (1 kGy)	Un-irradiated	Irradiated (1kGy)
G1	2.3978	2.3406	29.17	29.88
G2	2.4715	2.3589	27.33	28.64
G3	2.6528	2.4440	26.06	28.29
G4	2.5235	2.4153	27.08	28.30
G5	2.5063	2.4125	27.27	28.33

Optical UV transmittance

The change in the glass lattice due to doping of an element or irradiation can be detected by optical UV spectroscopy that gives information concerning to radiation-induced defect centers [14]. For instance, doping with TM ions can deal with intrinsic defects in the glassy matrix by trapping the radiolytic electrons or holes they are so called as potential traps. As well as they can affect the formation rate and intrinsic color centers recovery rates [15]. Trapping or capturing process depends mainly on the type and concentration of the doped TM ion as well as the composition of the host glass. Copper atom, for example, has the electronic structure of [Ar] $3d^{10}$ $4S^1$ so its available oxidation states are; cuprous Cu^{1+} that has five occupied d orbitals so it does not produce any separate coloring, and cupric Cu^{2+} that gives specific coloring centers in the visible region due to the formation of strong tetragonal distortion of Cu^{2+} ion octahedral units [7]. Not only TM ions cause defects in the lattice structure of the glass by creating charge trapping sites or defect color centers but also atoms that are called P- elements such as tellurium oxide TeO_2 where this category of elements have non-

bonding valence atoms [16]. Figs. 2, 3, and 4 show the optical transmittance spectra of G2, G3, and G4 respectively before and after gamma irradiation with 1 and 3 kGy. Glasses show high transmittance that may reach 100% before irradiation and decreased gradually as the radiation dose increased. It is obvious during measuring the conversion of the transparent blue color of G2 and G4 to dark blue and the white-yellow color of G3 to brown after each dose of radiation. The color changes may refer to electron trapping in the already exciting defects causing the production of located levels that can absorb light then the formation of color centers [17]. According to results, the order of higher transparency is G3 >G4 > G2 where measuring is carried out by taking G1 as a background in order to refer any changes on the spectra to only the doped metal ions Cu^{2+} and /or Te^{4+} ions. G3 has the highest transmittance since the large Te^{4+} ions can block the glassy network and decrease the number of NBO giving lower electronic transitions than glasses containing Cu^{2+} ions that make a disruption in the lattice causing more defect centers and then absorb light in higher degrees. Figs 2, 3 and 4 show also two essential broad peaks; the first at 330-380 may be related to iron impurities present in the raw materials used in the preparation of glasses even in p.p.m concentrations. The second is a broad band appears at about 650-780 nm in G2 and G4 but disappeared in G3, because it is related to Cu^{2+} ions in the distorted octahedral coordination according to El Batal, F.H. et al, 2008 [15]. Gamma radiation has a significant effect on the optical properties of glasses because it causes the formation of radiolytic defects that may be negative electrons or positive holes. These defects are responsible for the occurrence of color centers by making electronic transitions between the valence and conduction bands causing the appearance of absorption peaks in the UV and visible spectra ranges [17]. Moncke and Ehrt, 2007 [18] have postulated that the formed extrinsic defects after gamma radiation are due to the photochemical reactions (photo-oxidation or photo-reduction) of the transition metal ions. Figs. 2, 3 and 4 show a red shift with the radiation dose which may be attributed to increasing in boron E centers or increasing in the number of NBO resulted from breaking bonds between boron and oxygen atoms after irradiation. It was reported by Singh et al, 2010 [19] that in the high concentrations of tetrahedral BO_4 units the binding forces between the structural units become weaker after irradiation in the order of [BO_3-BO_3] > [BO_3-BO_4] > [BO_4-BO_4]. So that decreasing the transmittance of glasses after gamma irradiation takes place because of creation more defects and color centers. The energy gap between the valence and conduction bands is called the optical band gap Eopt. In amorphous systems, the indirect transition is expected due to the absence of the periodic symmetric structure.

In this case, Eopt can be determined by plotting the linear dependence between $(\alpha h\upsilon)^{1/2}$ (where α is the absorption coefficient) and $h\upsilon$ (the incident photon energy). Mott and Davis, 1979 [20] have suggested the following expression for determining Eopt

$$\alpha h\upsilon = B(h\upsilon - Eopt)^n \qquad (3)$$

where B is a constant called the band tailing parameter and *n* is an index having the values of 1/2, 3/2, 2 and 3, depending on the nature of the electronic transition responsible for the absorption. Fig. 5 shows Eopt values of G2, G3 and G4 before and after irradiation with 1 and 3 kGy where the values ranged from 1.18 to 3.04 eV and it is obvious that G3 or Te^{4+} containing glass has higher Eopt values than Cu^{2+} containing glasses G2 and G4. Previously, it was reported that the addition of CuO decreases the Eopt value by introducing defects in the glassy matrix [7]. After irradiation, there is a change in the oxygen bond strength of the glassy network by increasing the number of NBO because displacement of oxygens from their normal positions causes the formation of more NBO [17]. Consequently more unpaired electrons are formed causing more electronic transitions; this behavior appears in a form of a decrease in Eopt values with the increase in radiation dose as shown in Fig. 5. In other words the optical band gap is related directly to the crosslinking between individual atoms of the glassy matrix or the density of the glass. So it can be assumed that the denser and more compact glass, the higher its Eopt values, this interpretation can be provided by the density results listed in Table-2.
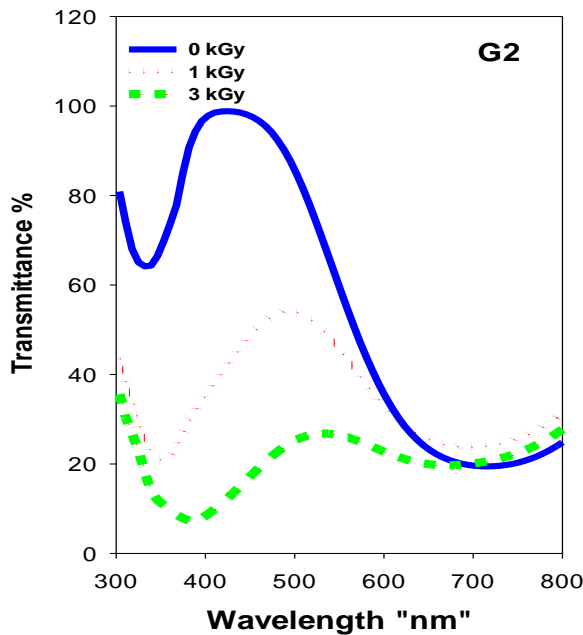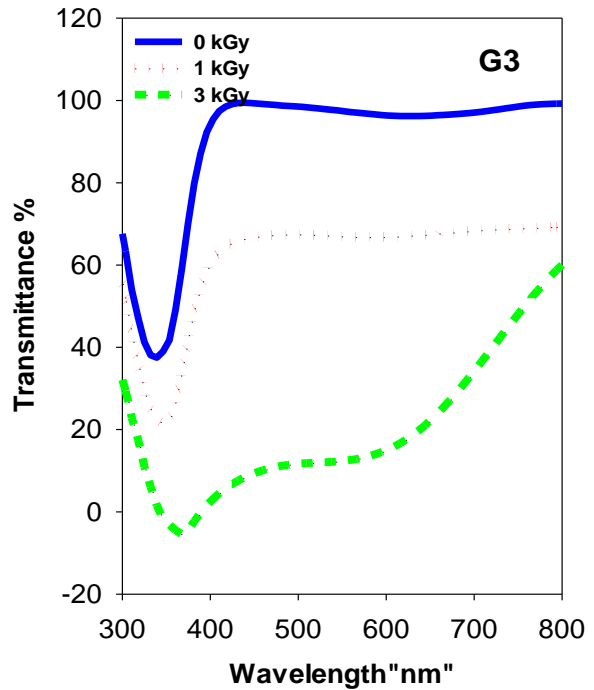

Fig. 3: Optical UV transmittance of G3 before and after gamma irradiation.

Fig. 4: Optical UV transmittance of G4 before and after gamma irradiation.
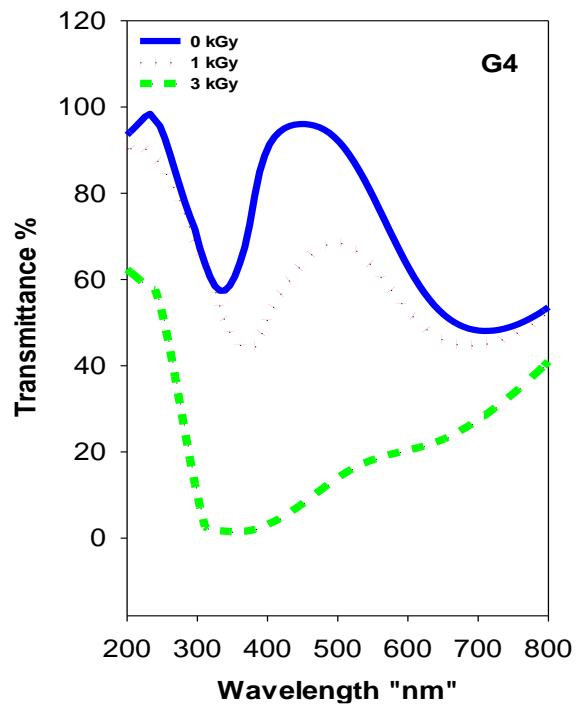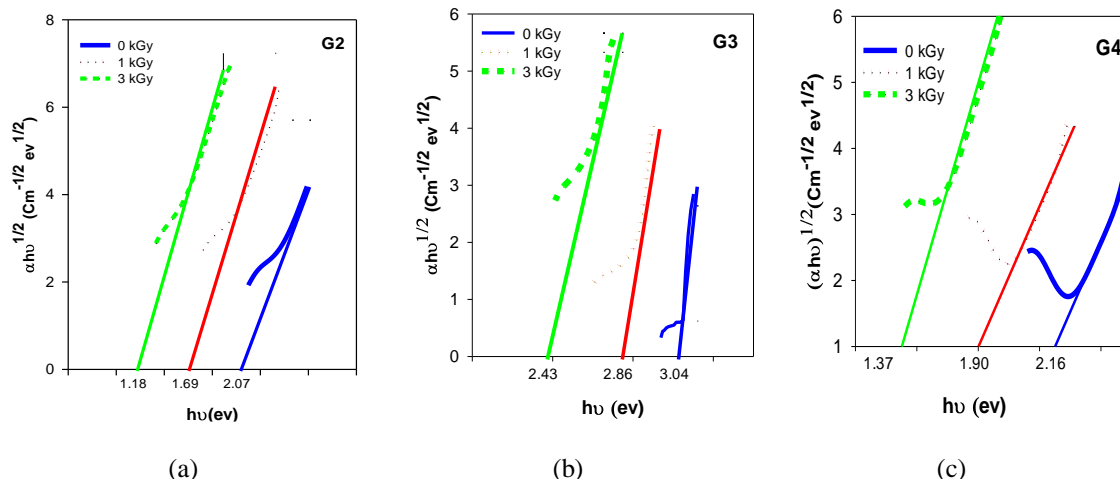

Fig. 2: Optical UV transmittance of G2 before and after gamma irradiation.

Fig. 5: Plots of $(\alpha h\upsilon)^{1/2}$ against $h\upsilon$ for Non-irradiated and irradiated glass samples G2, G3 and G4.

Electrical conductivity

Fig. 6 shows dc electrical conductivity values of the prepared glasses with raising the temperature in the range from 298 to 473 K. Fig. 6 shows that G1 has the highest conduction values where G3 has the lowest value; in addition there is a continuous increase in conduction values with temperature. Generally, traditional commercial glasses are poor conductors at least at room temperature but this behavior can be changed under certain conditions. It was assumed by Doremus, 1994 [21] that the electrical conduction in almost all oxide glasses containing alkali oxide is due to the motion of alkali ions present in the interstitial positions within the glass network. The monovalent Na^+ and Li^+ ions are the most popular conducting species in commercial glasses because such cations are quite mobile and able to escape from their sites into the surrounding vacancies or interstices of the glassy network so they are called current carrier ions [22]. However anions are not observed to move so conduction in oxide glasses is essentially ionic. Glass compositions listed in Table-1 show the presence of a mixture of multivalent alkali ions, so the conduction mechanism can be described by jumping the mobile alkali ions especially Li^+ and Na^+ ions along the interstices or holes within the glass network [22]. Additionally, the incorporation of TM ion can be described by the mechanism of hopping of small polarons among its different valence states, this polaron hopping mechanism depends greatly on the concentration of the doped TM ion. Increasing the concentration of TM ion leads to more disruption in the glass lattice by increasing the number of NBO then openness of the network and weakening of the borate structure. This behavior gives the chance for the present alkali mobile ions to move more freely which explains

why G5 with 0.2wt. % CuO has higher conduction values than G4 with 0.1wt. % CuO. On the other hand it was reported by Bazan et al,1996 [23] that there is a deep minimum in conductivity isotherm of glassy system Li_2O:WO_3: P_2O_5 due to the strong coupling of the oppositely charged current carriers and this effect is considered to be as ion-polaron effect because the mobility of ions and electrons are comparable in magnitude. Tsuchiya and Moriya, 1975 [24] have also observed a mixed electronic and ionic conduction in copper phosphate glasses existing in sites with different bending forces. The last two assumptions can interpret that glasses containing both alkali and TM ions (G2, G4, and G5) have lower conduction values than that containing only alkali mobile ions (G1). Doping with Te^{4+} ions makes a blocking or retarding effect because of their large atomic radii that inhibit the movement of alkali current carries therefore relatively low conduction values. So G3 has the lowest conduction values among all other prepared glasses however glasses containing both Cu^{2+} and Te^{4+} ions (G4 and G5) have lower values than those containing only Cu^{2+} ions (G2). It is well known that resistivity of glasses decreases with increasing temperature because raising temperature facilitates the motion of alkali current carriers so increasing in conduction values takes place. In other words at low temperature the electric field in the sample will respond to the applied field simultaneously because there is no charge piling up at sites with high free energy barriers, while with raising temperature the charges will pile up at sites with high free energy barriers then the electric field in the sample will not respond to the applied field at high frequency [25]. Fig. 7 shows the electrical conductivity values of the prepared glasses after irradiation with 1 kGy where there is a slight increase in conduction values after irradiation. It is generally accepted that ionizing radiation causes mainly

excitation and ionization leading to atomic or lattice displacement. Therefore increasing the number of vacancies and vacancy interstitials recombine or vacancies immigrate to the glass surface. This behavior allows the mobile alkali ions to emigrate much easier through the glass matrix causing a remarked increase in the electrical conductivity values [26]. Increasing of electrical conductivity after irradiation may be also related to decreasing in the glass densities since the open networks produce easier paths for the current flow through the samples so the net result will be an increase in the conduction values [4].
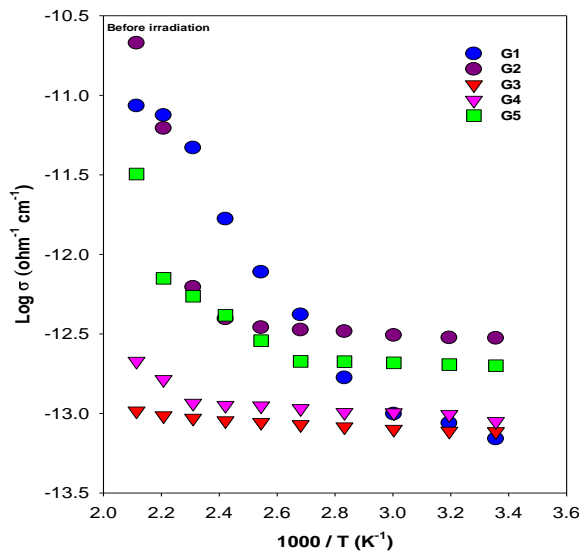

Fig. 6: Temperature dependence of dc electrical conductivity of Non- irradiated glass samples.
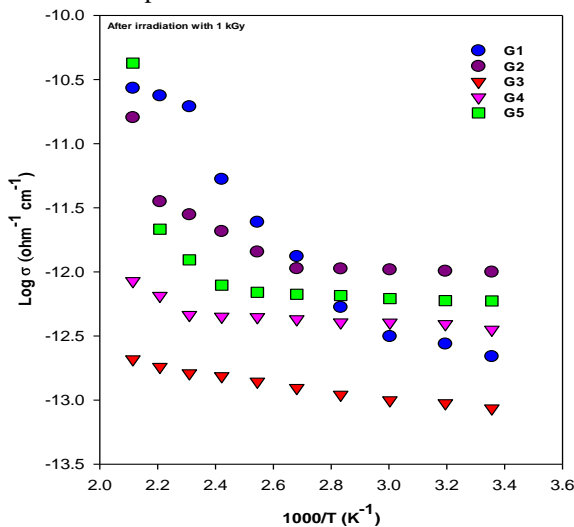

Fig. 7: Temperature dependence of dc electrical conductivity of 1 kGy irradiated glass samples.

Chemical durability

Chemical durability of glasses refers to the ability of their surfaces to resist different chemical reagents such as acids, alkalis, moisture or any substance in contact with them. Mechanisms of corrosion process in glass are generally described by two stages; leaching and etching mechansims. The first mechanism depends on the ion exchange process between alkali mobile ions present on the glass surface (e.g. Na^+ or Li^+) and hydrogen H^+ or hydronium ions H_3O^+ of the attacking leaching solution. The second mechanism takes place when the pH of the solution increased in the later stages of leaching, where the OH groups cause dissociation or bond breaking of the glassy network. The kinetic of leaching reaction of the glass depends greatly on many factors such as its composition, pH of the leaching medium, temperature, time of leaching as well as surface area and specimen state of tested samples. Leaching process of borate glasses containing monovalent sodium ions in water takes place by the inward-diffusion of water molecules that react with the alkali cations in order to achieve the electrical neutrality through the following reaction

$$= B\_ O^- Na^+ + H_2O \rightarrow\ = B\_OH + Na^+ + OH^- \qquad (4)$$
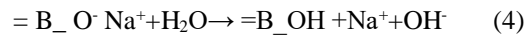
The rate of boron leaching process depends on the concentration of triangle BO_3 and tetrahedral BO_4 groups. The BO_4 groups are closely bonded in all four directions and nearby alkali ions to neutralize the excess of negative charges. This process also depends mainly on alkali diffusion process of the mobile Na^+ ions because such modifying metal ions occupy the percolation channels spreading through the glassy network [27] and the easier their migration from these channels to the solution, the faster the rate of leaching process. The water hydronium ions can penetrate the glass surface lattice and exchange with mobile ions present in the interstitial positions of the glassy matrix. The continuity of this reaction allows H_3O^+ ions to react with the internal building groups that forming the glassy network (BO_3 and BO_4) then the formation of large molecular islands that may cause bond breaking, dissociation of the matrix or dissolving of borate glasses into the solution. Therefore, ion exchange process is ionic selective method while hydrolysis of the glass network occurs in the later stages and leads to glass congruent release of ions with time [28].

$$= B\_ O\_B = + H_2O \rightarrow 2 = B\_ OH \qquad (5)$$

$$= B\_ O\_B = + OH^- \rightarrow\ = B\_OH + = B\ O^- \qquad (6)$$
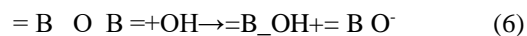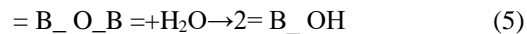
In fact, borate glasses have low durability because of their weak and hygroscopic structure but their durability can be improved by the addition of some alkali ions during the preparation process such as CaO and Al_2O_3 oxides. These oxides have a comparatively large molecular size so the presence of these ions inhibits the progress of leaching mechanism to a certain extent because they make more closed glassy network by blocking the routes of diffusion of alkali ions to the attacking leaching solution. For instance, Al^{3+} ions may found in the form of fourfold coordination AlO_4 groups which strength and compact the glass network while the divalent Ca^{2+} ions are strongly held or attached to the network interstices [9]. So there is a direct relation between the crosslinking density of the glass and its chemical durability. Fig. 8 shows the relation between weight loss percent of glass samples versus time at 90 °C. It is known that testing the durability of a glass for 16 hours during heating at 90-100 °C in a certain solution compensates its durability test for one year in the same solution. It is observed from Fig. 8 that G3 has the highest durability because of its high crosslinking density that delays the inter-diffusion process between Na^+ or Li^+ ions in the glass and H_3O^+ ions of the attacking aqueous solution. However, G1 is the most corroded glass where there are more chances for the mobile ions to diffuse into the solution and enhance the ion exchanging process. By comparing the durability of G2 with that of G4 and G5; it is obvious that the two later glasses have better durability than G2 because they contain the large Te^{4+} ions which plug the interstitial positions or the routes of diffusions in which alkali mobile ions move from. This leads to the inhibition of ion migration during the corrosion process then give a more durable glass. However, G2 that doped only with Cu^{2+} ions has lower durability than G4 and G5 because of the more disruption in its network that allows the formation of interstitial channels and facilitates the ion exchanging process. Effect of gamma radiation on chemical durability of the glass can be displayed by considering the effect of radiation on glass itself as it was mentioned before. Fig. 9 shows that the rate of corrosion in the prepared glasses increases slightly after irradiation with 1 kGy. The released electrons from irradiation process are trapped at impurity atoms or imperfections leading to the formation of induced defect centers. Consequently, the rate of corrosion should be enhanced by facilitating the penetration of H^+ or H_3O^+ ions from the solution to the formed defects.
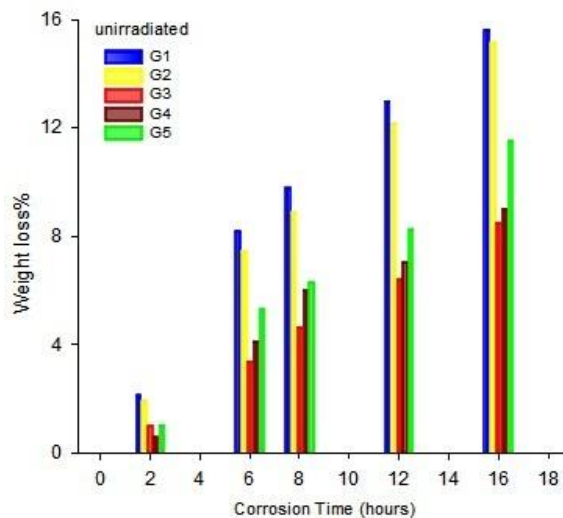

Fig. 8:   Corrosion behavior of Non- irradiated glass samples immersed in dis. H_2O at 90° C for 16 hours.
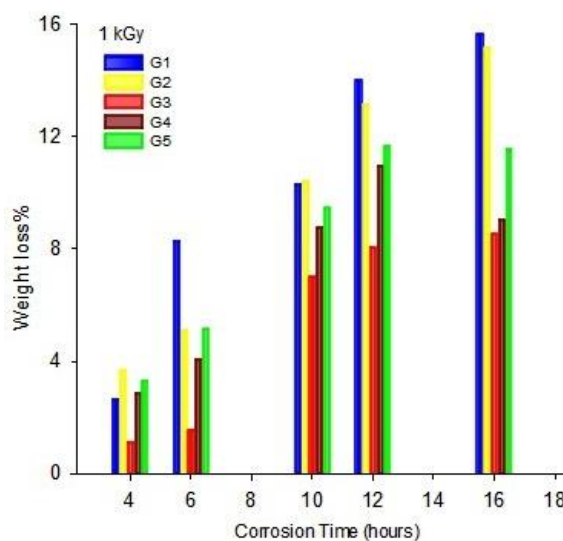

Fig. 9:   Corrosion behavior of 1 kGy irradiated glass samples immersed in dis. H_2O at 90° C for 16 hours.

Conclusion

There is a different behavior between doping borate glasses with Cu^{2+} and/or Te^{4+} ions. The fourfold Te^{4+} ions are not only strongly attached to borate network but also have high molecular weights enough to increase the density of glasses that doped with. While glasses containing Cu^{2+} and Te^{4+} ions together or Cu^{2+} ions only have lower densities than those containing only Te^{4+} ions since such a TM makes a disruption in borate network by creating

more NBO then more open structure would be released. The prepared Cu^{2+} and Te^{4+} doped borate glasses are highly transparent however they become darker with irradiation due to the formation of radiolytic defects and trapping of electrons or holes. Trapping of electrons produces located levels that are responsible for absorbing light leading to the formation of color centers. Therefore the appearance of UV peak at 650-780 nm in Cu^{2+} containing glasses because of the distorted octahedral coordination of Cu^{2+} ions. Glasses doped with CuO have lower Eopt than those doped with TeO_2 where more disruption is caused by doping with Cu^{2+} ions but more crosslinking is caused by doping with Te^{4+} ions. As the radiation dose increases the Eopt decreases because of the change in oxygen bond strength and increasing number of NBO, so the net result will be more unpaired electrons with more electronic transitions and lower Eopt. The conduction mechanism takes place by jumping of mobile ions Na^+ and Li^+ ions along the interstices or holes within the glass network. The disturbance of the network forms an open structure by the formation of more NBO thus moving of current carries takes places easier giving an increase in conduction. This behavior is enhanced by introducing Cu^{2+} ions by the hopping mechanism of small polarons through different valence states of such a TM. However, glasses doped with Te^{4+} ions have relatively low conduction because these large ions block the interstices in the glassy matrix and retard the mobility of charge carriers. This performance can describe also the leaching process of the prepared glasses that depends on the rate of diffusion of alkali mobile ions from the glass network to the leaching solution through ion exchange mechanism. So it can be concluded that, the more compact and crosslinked structure as in case of glass doped with Te^{4+} ions, the lower electrical conductivity, and corrosion rates. While those containing Cu^{2+} ions have both higher conduction values and leaching rates. Generally gamma irradiation causes electronic displacement and/or bond breaking in the glass network so an increase in NBO takes place leading to changing in some of the chemical and physical properties of the studied glasses such as a decrease in density, optical transmittance, Eopt and chemical durability or an increase in molar volume and electrical conductivity.

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