

Journal of Nuclear Materials 303 (2002) 44-51



www.elsevier.com/locate/jnucmat

Effects of fast neutron and gamma irradiation on electrical conductivity of some borate glasses

N.A. Elalaily *, R.M. Mahamed

Department of Radiation Chemistry, National Center for Radiation Research and Technology, P.O. Box 29, Nasr City, Cairo, Egypt Received 20 August 2001; accepted 12 February 2002

Abstract

Electrical conductivity of samples of $Li_2O-B_2O_3$ binary glass system containing Al_2O_3 , PbO, Fe₂O₃, TiO₂ or V_2O_5 was measured at temperatures ranging between 30 and 200 °C before and after irradiation with fast neutrons or γ -rays. Base and Al_2O_3 -containing glasses showed an initial rise in conductivity with the increasing temperature, followed by a steep drop, then a more gradual increase. Glass samples containing lead or one of the transition metal oxides showed a linear pattern of electrical conductivity in response to heating. In these glasses activation energy varied depending on the coordination number of the transition metal lon involved. These changes in electrical conductivity in response to temperature are ascribed to changes in the internal structure of the lithium borate glass, which is also affected by the presence of aluminum, lead or transition metals. The effects of exposing the studied glasses to irradiation were attributed to irradiation-induced changes in the configuration of the glass network, including the formation of matrix defects. © 2002 Published by Elsevier Science B.V.

1. Introduction

In many applications, glass may serve as an electrical insulator or conductor, requiring an understanding of its electrical conductivity. Ionic transport is also taken into account in manufacturing glass for other applications since ionic motion in the amorphous silica layers of silica devices can interfere with their performance and must often be suppressed.

In most oxide glasses, electrical conductivity results from ionic motion. In certain glass compositions containing multivalent oxides, such as vanadium pentoxide or iron oxide, conduction is electronic. Most chalcogenide glasses, which contain pure or combined sulfur, selenium or tellurium, are also electronic conductors. The semiconducting and switching properties of these glasses have excited a great interest in their use in the electronics industries. The 'salt' type glasses of halides, nitrates, sulfates, and aqueous solutions are ionic conductors. Organic glasses can be either electronic conductors or show ionic conduction resulting from impurities.

Ionic conductivity of virtually all oxide glasses results from the transport of monovalent cations. In most commercial glasses the conducting ion is sodium. Faraday's law is found to hold in these glasses and a number of electrolysis experiments [1] have established the ionic nature of the conduction process. It has also been shown that lithium ions are also quite mobile in oxide glasses [1]. In addition, potassium and hydrogen ions are known [1] to sometimes carry current although their mobility is usually lower than that of Na⁺ and Li⁺.

Even in glasses with no nominal addition of monovalent ions, conductivity results from the transport of monovalent cations. In fused silica, electrolysis experiments show that sodium and lithium ions are the conducting species even though they are present only in quantities of few parts per million [2].

Electrical conductivity of a solid conductor can be measured with either direct or alternating currents. In direct current (dc) measurement a space charge is often set up in the glass because of partial blocking of the ionic current by the electrodes. Then the current decreases

^{*} Corresponding author.

rapidly with time, and its value must be extrapolated to zero time if an accurate value of conductivity is desired. To avoid this electrode polarization, alternating current of a frequency from 10^3 to 10^6 Hz is usually used. Silicate glasses show dielectric losses at these frequencies and, therefore, care must be taken to make the measurement over a wide frequency range. If a constant sample resistance is found over several decades of frequency, one can be reasonably certain that an accurate value of conductivity is being measured. Such constancy is often not achieved, making many of the experimental measurements of electrical conductivity of glasses that have been reported in the literature unreliable [2]. The type of electrode and preparation of the glass surface can influence measured conductivity, especially at frequencies below 10 Hz [3]. Accordingly, polishing the glass surface drastically improves the accuracy of conductivity measurements.

Numerous studies [4–6] have been carried out on Li^+ ion glasses because of interest in developing high energy density batteries. The mixing of two glass formers, however, has been found to yield glasses with higher electrical conductivity and better thermal stability compared with the corresponding single former-glasses.

It is generally believed [7] that the electrical conduction in transition metal oxide (TMO) glasses is due to the hopping of polarons between sites. Mott [8] suggested that the electrical conductivity in alkali borate glasses is due to mobile alkali ions, with conductivity of these glasses being about three orders of magnitude higher than that of barium borate glasses. These materials are, therefore, most suitable for the studying ionic conduction.

Ichinose et al. [9] studied the dc conductivities of glasses in the V_2O_5 -SrO-B₂O₃ system. They suggested that dc conductivity is dependent on the amount of B₂O₃, increasing with the increase in B₂O₃ content and decreasing with the increase in SrO content.

Electrical conductivity measurements [8] of glasses containing vanadium at temperatures higher than room temperature suggest small polaron hopping conduction by the transfer of electrons between V^{4+} and V^{5+} . At temperatures lower than room temperature, conductivity data can be readily fitted to a Mott's variable range hopping model [9].

The effect of irradiation on glasses is believed to depend on the type and energy of irradiation, glass composition and sample parameters such as temperature [10]. It is well established that radiation damage in glass leads to active defects. These defects can be introduced by ionization or atomic displacement mechanisms or via the activation of the preexisting defects [11].

The presence of impurities, such as alkali, alkaline earth and transition metals, in the glass increases radiation-induced defects [12]. These defects may be either permanent or temporary. Defect recovery mechanisms, such as optical bleaching, control the rate of recovery during and after irradiation [13]. Conductivity changes due to irradiation can, therefore, be sensitive to glass composition and temperature, as well as both the magnitude and rate of irradiation dose [14].

The aim of this paper is to study electrical conductivity of lithium borate glass and to investigate how it is affected by the presence of Al₂O₃ or PbO. The effect of introducing small amounts (2%) of a TMO, which can simultaneously exhibit ionic and electronic conduction, is also examined. We also investigate electrical conductivity of these glasses after being exposed to different radiation doses of γ rays or fast neutrons.

2. Experimental

2.1. Preparation of glass samples

Lithium borate glass samples were prepared from chemical reagent grade powders. Boric oxide was introduced in the form of ortho boric acid H₃BO₃, and lithium oxide was introduced in the form of its respective anhydrous carbonate. The composition of the resulting base glass was 10% Li₂O and 90% B₂O₃. Five different glass compositions were then prepared. From the lithium borate base glass mixture, 5% B₂O₃ were replaced by either Al₂O₃ or PbO. TMOs were added to other samples of base glass as 2% additions of either Fe₂O₃, TiO₂ or V₂O₅. Transition metals were added as their respective oxides and vanadium oxide was introduced as ammonium vanadate.

All melts were made in platinum 2% rhodium crucibles placed in an electrical furnace at 1100 °C. The glass mixture was kept in the furnace for 2 h after it was completely melted and they were stirred every half hour. The melt was poured in a stainless-steel disc mold and transferred to a muffle furnace to be annealed at 300 °C for 2 h. The muffle furnace was maintained at this temperature for an hour and then left to cool down to room temperature. The samples were then grind and polished to have a very smooth and flat surface with a thickness of 0.2 cm.

2.2. Irradiation procedure

Glass samples were irradiated with neutrons from a $^{241}\text{Am}\text{-Be}$ neutron source (Schlumberger Co.). The neutron flux was 0.86×10^7 n/s. Fluences of 2.08×10^9 and 4.16×10^9 n/m² were used.

A gamma chamber 4000 A, manufactured by Atomic Energy Agency of India was used as a source of gamma radiation. Glass samples were placed in the gamma cell in a manner that allows each sample to be subjected to the same irradiation dose. The samples were irradiated at a dose rate of 2.27 kGy/h. Two irradiation doses of 40 and 80 kGy were used. All irradiations were carried out in air, at room temperature.

2.3. Electrical conductivity measurements

Electrical conductivity measurements of the glass samples were carried out using a specially designed oven constructed and tested to ensure the absence of thermal gradient. Automatic electronic circuitry was used to control the temperature with an accuracy of ± 0.5 °C, while the glass samples were heated in the range from 303 to 573 K (30–200 °C). Conductivity was measured at a stepwise, 10 °C increments in sample's temperature throughout that range.

The direct current conductivity, as a function of temperature, was measured under a steady state condition after attaining the required temperature. In this arrangement, a minimum dc voltage is applied on the glass samples using two, similar and co-axial brass electrodes. The ratio of the cross-sectional area of the sample to the electrode area was 4:1. The contact surfaces were activated using silver paste.

Conductivity of the samples was measured by sandwiching the sample between two copper electrodes. The electrical conductivity was measured using programmable digital electrometer (Model 617 Keithley, USA), which is capable of low current measurements to 1×10^{-15} A with fluctuation errors of about 2.5%. The specific electrical conductivity (σ) of the sample was calculated using the formula

$$\sigma = (L/A)(I/V), \tag{2.1}$$

where L is the sample thickness, A is the cross-sectional area of the brass electrodes in contact with the sample, I is the current flow in the sample and V is the applied voltage.

Activation energy was calculated based on the Arrhenius equation

$$\sigma = \sigma_0 \mathrm{e}^{-E/RT},\tag{2.2}$$

where σ_0 is a constant, *E* is the activation energy of electrical conductivity, *R* is the universal gas constant and *T* is the temperature in K.

3. Results

Our results show that electrical conductivity of glass as a function of temperature is greatly affected by the glass composition. Fig. 1 shows the relationship between the logarithm of σ and $10^3/T$ for all glass samples, where *T* is the temperature in K. For both the base glass and the glass containing 5% Al₂O₃, conductivity was at its minimum value at T = 303 K ($10^3/T = 3.3$). Conductivity increased sharply with the increase in temperature



Fig. 1. Effect of temperature on electrical conductivity of glass samples G2 and G3 (a), and G4, G5 and G6 (b) compared to the base glass G1.

reaching its peak value at 313 K ($10^3/T = 3.19$), but gradually dropped as the temperature continued to increase. A second, rather gradual increase in conductivity then took place. On the other hand PbO-containing glass samples and those containing 2 wt% of one of the TMOs Fe₂O₃, TiO₂ or V₂O₅ showed a more typical steady increase in conductivity as the temperature increases.

Fig. 2 shows the effect of temperature on electrical conductivity of glass samples of different compositions, irradiated with two fluences of fast neutron irradiation. The response of the temperature-conductivity relationship of both the base glass and that containing Al_2O_3 to neutron irradiation was similar (Fig. 2). In these glasses, samples irradiated with the fluence of 2.08×10^9 n/m² showed a gradual linear increase in electrical conductivity with the increasing temperature. This pattern is drastically different from the response of the unirradiated glasses of similar composition, or those irradiated with the larger irradiation fluence of 4.16×10^9 n/m². These glass samples exhibited minimum conductivity value at 303 K ($10^3/T = 3.3$). With increasing temperature, electrical conductivity of these glasses initially showed a sharp increase, and then the conductivity gradually dropped to a minimum value at 423 K $(10^3/$ T = 2.36), before gradual rising again.



Fig. 2. Effect of temperature on electrical conductivity of glass samples of different compositions (G1 to G6) before (o) and following irradiation with fast neutron irradiation fluences of 2.98×10^9 n/m² (\Box) and 4.16×10^9 n/m² (\triangle).

(f)

Temperature-conductivity relationship for glass samples containing PbO, Fe₂O₃, TiO₂ and V₂O₅ showed a different pattern of response, only in the case of samples irradiated with the larger neutron irradiation fluence. Electrical conductivity in this case followed a pattern similar to that of base and aluminum oxide containing glass.

2.2

2 (e)

2.4

2.6

2.8

10³/T(K⁻¹)

3

3.2 3.4

Log o (Ohm⁻¹.cm⁻¹)

-og σ (Ohm⁻¹.cm⁻¹)

Log a (Ohm⁻¹.cm⁻¹)

The effect of temperature on electrical conductivity of glass samples of different compositions, irradiated with two doses of γ -rays is shown in Fig. 3. The figure shows that in all glass samples electrical conductivity response to temperature change followed a trend very similar to that observed following irradiation with the high fluence of neutrons.

Activation energies of the glasses of different composition before and after irradiation are listed in Table 1. The table gives two activation energy values for the unirradiated base glass and that containing Al_2O_3 . The samples irradiated with gamma rays or the higher fluence of fast neutrons also have two values of activation energy.

2.8

10³/T(K⁻¹)

2.6

3.4

3.2

4. Discussion

2.2

2

2.4

4.1. Effect of glass composition

Since the complete dissociation of alkali ions from non-bridging oxygen is not possible in oxide glass, conduction based on random jumps of these ions is not expected to occur [15]. Accordingly, conduction takes place through the movement of the alkali ions in association with the motion of non-bridging oxygens [15].

As the percentage of alkali oxide in the glass increases, glass structure may resemble the modified random network model of Greaves [16]. This model depicts



Fig. 3. Effect of temperature on electrical conductivity of glass samples of different compositions (G1 to G6) before (\circ) and following irradiation with two doses of γ -rays.

Table 1

Activation energies of lithium borate glasses of different composition before and after fast neutrons and irradiation with fast neutrons and γ -rays

Glass no.	Glass composi- tion (wt%)	Activation energy (eV)				
		Before	Fast neutron irradiation		Gamma irradiation	
			$2.08\times10^9~\text{n/m}^2$	$4.16\times 10^9~n/m^2$	40 kGy	80 kGy
G1	$10 Li_2 O \cdot 90 B_2 O_3$	$-5.9561 imes 10^{-4}$	$6.715548 imes 10^{-4}$	-4.071605×10^{-4}	$-1.68114 imes 10^{-4}$	$-1.1125961 imes 10^{-3}$
		$8.56487 imes 10^{-4}$		$4.2006858 imes 10^{-4}$	$5.883312 imes 10^{-4}$	$8.5542706 imes 10^{-4}$
G2	$10 Li_2 O \cdot 85 B_2 O_3 \cdot \\$	$-8.8769 imes10^{-4}$	$8.6727374 imes 10^{-4}$	$-9.5187022 imes 10^{-4}$	$-1.7921979 imes 10^{-4}$	$-1.1455643 imes 10^{-3}$
	5Al ₂ O ₃	$9.85647 imes 10^{-4}$		$8.3838831 imes 10^{-4}$	$9.0424495 imes 10^{-4}$	$7.9026922 imes 10^{-4}$
G3	$10Li_2O \cdot 85B_2O_3 \cdot$	$5.9477 imes 10^{-4}$	$4.8697 imes 10^{-4}$	$-6.575064 imes 10^{-4}$	$-1.4069027 \times 10^{-3}$	-1.570646×10^{-3}
	5PbO			$1.0741192 imes 10^{-3}$	$1.0404954 imes 10^{-3}$	$9.382422 imes 10^{-4}$
G4	$10Li_2O \cdot 90B_2O_3 \cdot$	$4.926119 imes 10^{-4}$	$8.2787366 imes 10^{-4}$	-7.415666×10^{-5}	$-1.531495 imes 10^{-3}$	$-1.388393 imes 10^{-3}$
	$2Fe_2O_3$			$8.564857 imes 10^{-4}$	$9.154425 imes 10^{-4}$	$7.666687 imes 10^{-4}$
G5	$10Li_2O \cdot 90B_2O_3 \cdot$	$5.230113 imes 10^{-4}$	$7.595294 imes 10^{-4}$	$-4.479335 imes 10^{-4}$	$-1.9393563 imes 10^{-3}$	-1.167621×10^{-3}
	2TiO ₂			$1.0769616 imes 10^{-3}$	$9.697933 imes 10^{-4}$	$9.444603 imes 10^{-4}$
G6	$c10Li_2O \cdot 90B_2O_3 \cdot$	$1.3617639 imes 10^{-3}$	$7.4884809 imes 10^{-4}$	$-1.086555 imes 10^{-4}$	$-1.7615647 \times 10^{-3}$	$-1.2139 imes 10^{-3}$
	$2V_2O_5$			$7.975389 imes 10^{-4}$	$8.311527 imes 10^{-4}$	$8.113469 imes 10^{-4}$

islands of network separating narrow conduction channels, which appear at approximately 15 mol% alkali

oxide. These channels provide the conduction pathways along which ion migration occurs. The transport path In ordinary borate and silicate systems containing no transition metal ions, alkali cations are assumed to be the main carrier of the electrical current since anions are condensed to form large, fairly immobile, polyions. For compositions with less than 20% alkali oxide, there exists an evidence for a non-uniform cation distribution in alkali borate. These alkali ions are always located in the neighborhood of borate groups such as BO_4 tetrahedra, with surplus negative charge. In addition, alkali ions tend to attract and share other negative charged groups to screen themselves from an accumulation of the cations in the region of basic composition [17].

Our results (Fig. 1) show that electrical conductivity increases with increasing temperature for all glasses, with the exception of the base and Al_2O_3 glasses, which exhibit a different behavior. In the base glass, three different conduction mechanisms appear to be involved. One mechanism may be attributed to the moisture present within the glass matrix, leading to the formation of lithium hydroxyl and orthoboric acid groups [18]. Evidence of the presence of hydroxyl group within the glass matrices is clear from IR spectroscopy and DTA analysis. The presence of LiOH appears to be responsible for the conduction mechanism in the temperature range from 313 to 413 K (Fig. 1). Through this temperature range, H₃BO₃ begins to dissociate leading to the increase in BO₃ groups with respect to Li⁺ ions and consequently the increase in their recombination. The resulting decrease in free lithium ions leads to the observed lower conductivity. Above 413 K the increased electrical conductivity appears to be due to the presence of a high content of BO₄ groups and low BO₃ with respect to Li⁺ ions. In this case, the activation energy for glass at temperatures above 413 K is the energy needed to activate the ion diffusion and separate one configuration of the borate unit from another [19].

Another possible conduction mechanism may be related to the phase separation process during thermal treatment of the glass, which appears to begin at 413 and 453 K for the base glass and Al₂O₃-containing glass, respectively. This has been discussed by Megahed et al. [20] who postulated that conductivity is initially attributable to the poor conducting B_2O_3 -rich phase. This is then followed by the conducting alkali rich phase, which appears with the increasing temperature. The alkali rich droplets accumulate as Li⁺ and oxygen ions migrate from the glassy matrix to form additional alkali-rich borate droplets. Consequently the separated phase might play an important role in the conduction process and the increased conductivity. According to these authors [20], it may also be assumed that the presence of Al₂O₃ could form droplets suspended in the second phase.

Table 1 shows that the base glass and glass containing aluminum have two values of activation energy. Most of the explanations for the observed composition dependence of ionic conductivity σ of glasses are based on the concepts included in the conductivity model proposed by Andreson and Stuart [21]. According to that model, the activation energy (E_{σ}) of electrical conductivity by alkali ion migration in an oxide glass is the sum of two components: (1) energy of bonding between the mobile cation and its charge compensating center (ΔE_b) and (2) the elastic strain energy (ΔE_s) associated with the distortion of the glass network as the ion jumps from one equilibrium position to the next.

Wakabayshi [22], however, argued that elastic energy is primarily responsible for the variation in E_{σ} with composition since glasses with higher glass-transition temperature ($T_{\rm g}$) have a more compact network structure and hence lower elastic energy for moving lithium ions through the network. This results in the observed decrease in E_{σ} and thus the increased electrical conductivity. He also reported that, upon the substitution of Al₂O₃ for B₂O₃, $\Delta E_{\rm s}$ represents the strain energy that the mobile ion needs to expend in passing through a 'doorway' by elastically deforming the network. In this model, the formula for $\Delta E_{\rm b}$ was derived by mainly considering the Coulombic energy of bonds. The covalency of bonds was included by an empirical constant, which was taken to be the dielectric constant.

Conduction in the glass containing TMOs is generally considered to take place by 'hopping' of carriers from one strongly localized state to another [20]. These two states are the possible two valance or coordination states of the transition-metal ion. Several factors may affect conductivity of such borate glasses containing TMOs. Among these are the co-ordination number of transition metal ions, character of the neighboring oxygen legends or the state of polarizability of the oxygen anions, whether the transition metal ion behaves as a network-former or a network modifier, and valence state of the transition metal ion as governed by oxidationreduction nature of the glass batch constituents and the melting conditions [20].

Accordingly, the increased electrical conductivity in the presence of Fe_2O_3 can be attributed to the increase in the ratio of iron ions in Fe^{2+}/Fe^{3+} states, which in turn causes an increase in the concentration of hopping centers [23]. The general condition for semiconducting behavior is that the transition metal ions should be capable of existing in more than one valence state, so the conduction occurs by movement of carriers from the lower to the higher valance states [19].

Our results show that glass containing TiO_2 gives the highest electrical conductivity, where the glass intermediate TiO_2 may act as a glass former in this system strengthening the covalent cross-linking matrix. The presence of TiO_2 in the $Li_2O-B_2O_3$ system may help the

linking of the broken network structure. It may also be assumed that titanium ions can exist as Ti^{3+} in octahedral environment and as Ti^{4+} in structure building units TiO_4 tetrahedra. The presence of two valence states initiates the 'hopping' or 'transfer of charge carriers' and explains the increased electrical conductivity.

The addition of V_2O_5 to the lithium borate glass causes an increase in the conductivity where the possibility of forming heteropoly-anion molecules due to the interaction between V_2O_5 and LiOH leads to different conduction mechanism characterizing these samples [21]. It has been reported that the maximum electrical conductivity depends on the V⁴⁺ to V_{total} ratio. These materials are electronic conductors in which the transport mechanism involves the exchange of electrons between V⁴⁺ and V⁵⁺ ions as V⁴⁺–O–V⁵⁺ –O–V⁴⁺. In addition, lower valence states e.g., V³⁺ or V²⁺, may also take part in the conduction mechanism [24].

This may indicate that the introduction of mixed glass formers improves of the electrical properties of non-crystalline ionic conductors i.e., lowering the activation energy of ion conduction. In oxide glasses, the mobile cation is bonded to the anionic structural units of the glass network. If more than one structural units are present, the weak electrolyte model [25] predicts that electrical conductivity goes through a maximum value when one structural unit is progressively substituted by another, even if the two units have the same ionic dissociation constant. Such an effect is related to the variation of the entropy of mixing of the two units. Besides, when a single glass former is present, there are few structural units, corresponding to different oxidation states, with well-separated energies. Due to such large separation in energy, the ion migration from one unit to another must overcome a large activation energy. However when more than one glass former is present, the number of structural units increases and their energy separation decreases, which leads to the decrease of the activation energy [24]. It may, therefore, be concluded that the introduction of mixed glass formers can lower the activation energy of the ion migration in a glass system, which provides a new approach for the preparation of ionic conductors with high electrical conductivity. It may be noticed from our results that the addition of lead and titanium, which may act as glass formers, gave the largest electrical conductivity at room temperature.

4.2. Effect of irradiation

It has been suggested that the interaction of fast neutrons with borate glasses results in the rupturing of chemical bonds, the displacement of electrons and ions, and the creation of highly energetic alpha particles [26]. Displaced electrons, ions and recoils, migrate through the glass network until they are trapped by either the matrix defects or the presence of a transition metal element in the lattice, leaving deficient regions [26]. These responses obviously vary according to glass composition. These electronic and ionic rearrangements may provide an explanation of the observed electrical conductivity changes in neutron irradiated glasses. Furthermore, the tendency for neutron irradiation to increase conductivity of glass, has been shown to be related to the gamma irradiation flux accompanying the fast neutrons in the reactor environment [27].

The effect of fast neutron irradiation on the electrical conductivity of alkali borate glass is reported to be independent of neutron fluence [27]. However, our results show that the two neutron irradiation fluences result in different effects on electrical conductivity of the studied glasses. On one hand, the initially decreased electrical conductivity due to the lower dose of neutron irradiation may be a result of the redistribution of impurities. On the other hand, the smaller initial increase in electrical conductivity of glass irradiated with the higher dose of fast neutrons is possibly the result of permanent disorder in the glass structure caused by the higher gamma irradiation emission in response to the fast neutrons.

Gamma irradiation of glass, on the other hand, is reported to lead mainly to surface damage, unstable charging, and migration of mobile (non-network) cations [28]. The electron hole trapping sites in borate glass are believed to arise from the local non-stoicheometry, which is present in the glass as a result of either fabrication or radiation induced atomic displacement [29].

The abnormal behavior of electrical conductivity with temperature in γ -irradiated glass containing lithia can be explained on the basis of Griscom's suggestion [30] that electrons released due to irradiation become trapped on clusters of alkali metal ions. The number of alkali metal ions and electrons per cluster increases with increasing temperature, leading to the observed decrease in electrical conductivity. An alternative explanation suggests that Li₂O-containing glass has the tendency to be internally phase–phase separated, which can readily explain our observed results.

The effect of increasing the electrical conductivity of the glass irradiated with γ -rays at a dose of 80 kGy may be attributed to the initial formation of the induced color centers and the decrease in the number of the intrinsic defects that have no trapped electrons or holes in the glass network structure [17].

The increased electrical conductivity of the glass subjected to the higher γ -irradiation dose may also be due to the decreased density of the medium, which permits higher transition metals coordination numbers and the continuous running of ions through holes in the glass network. Alternatively, this decreased density may offer an easier path for current flow through the specimens. The net result in both cases is the attainment of higher value of electrical conductivity. However, the number of entities oriented by the dc field is increased by the action of the higher gamma radiation dose [31].

Taking into consideration the above discussion, our results can be interpreted on the premise that when glass was exposed to γ rays, transient defects were produced. At moderate temperature (313 K), there was a considerable increase in electrical conductivity. This may be due to the enhanced movement of the defects formed in the glass matrix upon irradiation. These defects may include vacancies or vacancy-interstitial pairs and the formation of electrets. Upon heating, such defects are believed to affect the movement of ionic species, which are responsible for the conduction mechanism. However, the electronic transient defects are gradually eliminated as temperature increases to 423 K. This is responsible for the decrease in electrical conductivity with heating.

The values of electrical conductivity obtained at temperatures above 387 K are appropriate when compared with those of unirradiated glass, where conductivity increases with the increase of temperature. In other words, the observed decrease in conductivity of the irradiated glass upon heating may also be due to the bleaching of the induced defects. Accordingly, upon further heating, the glass returns to its initial state where ions can freely move at high temperature causing the observed increase in conductivity with the increasing temperature.

5. Conclusions

Electrical conductivity changes of lithium borate glass in response to temperature are clearly affected by the glass composition. With the increase in temperature from 303 to 573 K base and Al₂O₃-containing glasses exhibited one pattern of response where conductivity undergoes an initial rise followed by a steep drop before assuming a more gradual increase. A linear pattern of electrical conductivity response to heating was observed in glass samples containing lead or one of the transition metal ions used in this study. In these glasses, however, activation energy varied according to the coordination number of the transition metal ions involved. In general, these patterns of change in electrical conductivity in response to temperature may be explained by transient changes in the internal structure of the lithium borate glass, which is again affected by the presence of aluminum, lead or transition metals.

The results also showed that irradiation of glass samples with either fast neutrons or γ -irradiation clearly affected electrical conductivity response to heating. The effect of both types of irradiation varied according to the glass composition and the irradiation dose. Irradiationinduced changes in these configurations of the glass network, including the formation of matrix defects may cause the observed electrical conductivity changes.

References

- [1] E. Warburg, Ann. Phys. 21 (1954) 622.
- [2] R.H. Doremus, Glass Science, 2nd Ed., Wiley Interscience, New York, 1994.
- [3] M.D. Ingram, Phys. Chem. Glasses 28 (1987) 215.
- [4] A. Magistris, G. Hiodelli, M. Villa, J. Power Sources 14 (1985) 87.
- [5] M. Tatsumisago, Y. Komada, M. Minam, Phys. Chem. Glasses 28 (1988) 136.
- [6] B.V.R. Chowdari, K.I. Tan, W.T. Chia, R. Gopalakrishnam, J. Non-Cryst. Solids 128 (1991) 18.
- [7] A.K. Bandyopadhyay, J.O. Isard, J. Parke, J. Phys. D 11 (1987) 2559.
- [8] N.F. Mott, Metal–Insulator Transition, Taylor and Francis, London, 1990.
- [9] N. Ichinose, Y. Nakai, J. Non-Cryst. Solids 203 (1996) 353.
- [10] M. Rajaram, E.J. Friebele, J. Non-Cryst. Solids 1081 (1989) 1.
- [11] A. Agrawal, M. Tomazawa, J. Non-Cryst. Solids 209 (1996) 166.
- [12] E.J. Friebele, M.E. Gingerich, K.J. Long, Appl. Opt. 21 (1982) 547.
- [13] H. Henschel, O. Kohn, H.U. Schmidt, I. Trans, Nucl. Sci. 43 (1996) 1050.
- [14] V.A. Mashkov, W.R. Austin, L. Zhang, R.G. Leisure, Phys. Rev. Lett. 76 (1996) 2926.
- [15] P. Balaya, C.S. Sunandana, J Non-Cryst. Solids 175 (1994) 51.
- [16] G.N. Greaves, in: D.R. Uhlmann, N.Y. Kreidel (Eds.), Glass Science and Technology, vol. 4B, Academic, New York, 1990.
- [17] F.M. Ezz Eldin, A.H. Zahran, N.A. El-Alaily, Ind. J. Pure Appl. Phys. 31 (1993) 481.
- [18] F.A. Cotton, F.R.S. Wilkinson, Advanced Inorganic Chemistry, John Wiley, London, 1972.
- [19] M.A. Zaki Ewiss, S.A. Abu Mansoor, Phys. Stat. Sol. A 156 (1996) 421.
- [20] A.A. Megahed, I.A. Gohar, A. Atta, M.S. Meikhal, Nuova Cim. 14D (8) (1992) 789.
- [21] O.L. Anderson, D.A. Stuart, J. Am. Ceram. Soc. 37 (1954) 573.
- [22] H. Wakabayshi, Phys. Chem. Glasses 30 (1989) 51.
- [23] I. Kashef, H. Farouk, S.A. Aly, A.A. Abdel-Rahman, M. Sanad, E.E. Assem, Mater. Sci. Eng. 10 (1991) 1.
- [24] J.R. Min, J. Wang, L.Q. Chen, R.J. Xue, W.Q. Cui, J.K. Liang, Phys. Stat. Sol. A 148 (1995) 383.
- [25] J.M. Cowly, A.F. Moodi, Acta Crystallogr. 10 (1957) 609.
- [26] A.M. Nassar, M.A. Fadel, J. Phys. D (1983) 16431.
- [27] L.L. Hench, J. Non-Cryst. Solids 2 (1970) 250.
- [28] F.M. Ezz Eldin, N.A. El-Alaily, H.A. El-Batal, Ind. J. Pure Appl. Phys. 30 (1992) 443.
- [29] J.E. Shelby, J. Appl. Phys 51 (5) (1980) 2561.
- [30] D.L. Griscom, J.Non-Cryst. Solids 6 (1971) 275.
- [31] M.M. Abu Sekina, M.A. Ewida, N.A. Ghoneim, Thermochim. Acta 30 (1984) 307.