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THERMAL EXPANSION STUDIES ON SOME GAMMA-IRRADIATED BINARY BORATE GLASSES

F. M. Ezz-Eldin

National Center for Radiation Research and Technology, Nasr-City, P.O.Box 29, Cairo, Egypt

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Abstract

The thermal expansion, density and molar volume of some binary borate glasses were measured before and after exposure to a gamma-ray dose of 10^3 kGy. The expansion curves for all glasses, which were measured from room temperature to above the softening temperature, displayed similar characteristics. Increase of the lead oxide content decreased the thermal coefficient of expansion, but the effects of different alkali metal cations were shown to depend on their ionic radii. The various proposed mechanisms of thermal expansion are dealt with. The experimental results could be explained by considering the bond strengths, the polarizing powers of the different cations and the damage produced by radiation. The possible compaction of the structure due to irradiation is also discussed.

Keywords: binary borate glasses, glasses, glass ceramics

Introduction

From a technological point of view, thermal expansion is one of the most important thermal glass properties as it often controls the possibility of bonding by welding to glasses and/or metals.

Thermal properties are directly related to temperature changes. They are essentially the specific heat, the thermal expansion coefficient and the thermal conductivity. Different thermal expansions produce thermal stresses, which strongly influence the mechanical properties of glass articles [1].

The effects of irradiation on glass have been studied extensively and have been critically reviewed by many authors [2–4], but few have discussed the effects of radiation damage on the thermal expansion of glasses and glass ceramics [5, 6]. It has been accepted that glass undergoes compaction when exposed to neutron, ionizing or even ultraviolet radiation. When the absorption coefficient of the material for the radiation is sufficiently small and/or the incident radiation is sufficiently energetic to penetrate through the depth of the sample, uniform compaction occurs. However, if the energy is deposited nonuniformly

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across the surface, or if the radiation does not fully penetrate the material, the resultant nonuniformly compaction can cause sample deformation, especially if the sample is thin [7].

The present investigation was conducted to gain an insight into the effects of gamma irradiation on the glass structure and its response to thermal expansion, and on the densities of alkali metal borate glasses.

Experimental

Glass preparation

All the raw materials used were of chemically pure grade and were finely pulverized. All the batches, after being weighed and well mixed, were melted for 4 h in platinum-2% rhodium crucibles in an electric furnace in the temperature range 1200–1400°C, depending on the glass composition. The amount of glass melted was 100 g in each case. After complete melting, the molten glass was annealed at the appropriate temperature.

Boric oxide was introduced as orthoboric acid, H_3BO_3, lithia, soda and potash were introduced as their respective carbonates and lead was added as red lead oxide (Pb_3O_4).

For thermal expansion measurements, a specimen 1 cm^2 in cross-section and 3 cm in length was required. The ends and the whole bulk of the glass were ground flat and parallel. The glass dimensions were measured with a high-precision micrometer, which was read to three decimal places.

Irradiation procedure

The samples were exposed to gamma radiation at 10^3 kGy, using a ^{60}Co γ-source from a 4000A gamma chamber manufactured by the Atomic Energy Agency of India. The dose rate for irradiation was 1.25 Gy/s. The glass samples were placed in the gamma cell in such a manner that each sample was subjected to the same dose.

Density measurements

The density for each glass sample was determined by the Archimedes method, in which the glass sample was weighed in air and also when immersed in xylene at 20°C. The density was then calculated from the formula

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

where D is the density of the glass sample, a and b are the weights of the glass sample in air and in xylene, respectively, and 0.86 is the density of xylene at 20°C in $g \cdot cm^{-3}$. Duplicate measurements were seen to agree within ±0.005 and the overall accuracy was of the order of ±0.001 $g \cdot cm^{-3}$.

Molar volume calculations

The following formula was used to calculate the value of the molar volume (V) which contains exactly one mole of oxygen ions:

$$V = (M/P) \cdot 1/\Sigma x_i n_i$$

where $M = \Sigma x_i M_i$ = average molar weight of the glass, M_i = molar weight of component i, x_i = molar fraction of component i, n_i = number of oxygen atoms in the oxide and P = density of the glass.

Thermal expansion measurements

The specimen was loaded into the chromel-alumina tube dilatometer; its dial gauge with steps of 0.0001 was set to zero and the initial temperature was read and recorded. Heating was controlled automatically. The Shimadzu TMA-30 dilatometer system is a combination of a TMC-30 sample holder, a TM-30 amplifier, a DT-30 control unit and an R-22 T recorder. Temperature was increased at a rate of 10 $deg \cdot min^{-1}$. For each glass specimen, data were obtained from room temperature to the softening point of the glass. At least two measurements were made on each specimen and reproducible results were obtained (±2%). The linear coefficient of thermal expansion (α) was then calculated via the equation $\alpha = \Delta L/L \cdot \Delta T$, in which ΔL is the increase in length, L is the original length and ΔT is the increase in temperature.

Results

Figures 1 and 2 illustrate the thermal expansion curves for all the glasses studied. Some general trends may be observed. During heating from 20 to 100°C, the expansion of the specimen was quite small. This was probably due to the time required for the heat transfer through the quartz tube and for the heating of the specimen to start. In the range 100 to 300°C, the curves exhibit quite linear portions, with slopes depending on the chemical composition. When the curve deviated from linearity, the trend was to a sharply increased expansion rate. This deviation from linearity is referred to as the transformation range of the glass, and is a well-documented phenomenon in various glasses

[6]. There is then an induction period for about 25°C, followed by a sharp decrease, which means that the specimen has reached its softening temperature. The transition temperature T_g and softening temperature T_s also vary with change of the glass composition.

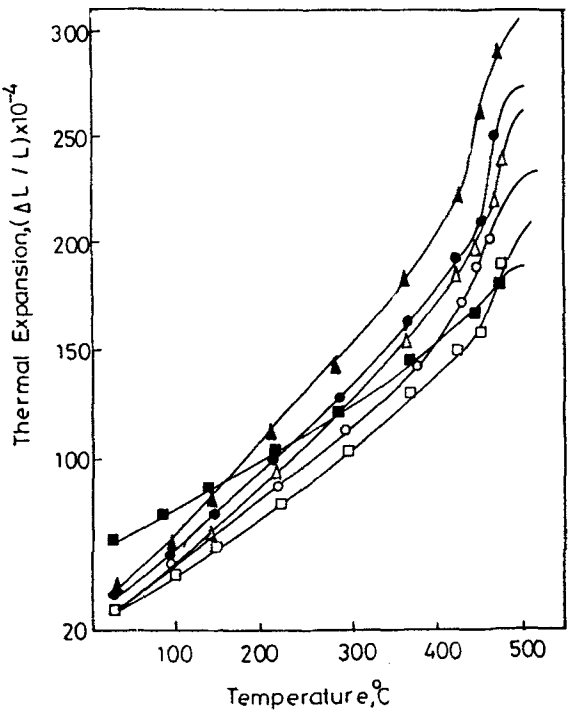

Fig. 1 Relation between thermal expansion ($\times 10^{-4}$) and temperature (°C) for irradiated and unirradiated borate glasses of the following compositions: □ B_2O_3 70%, Li_2O 30%; o B_2O_3 70%, Na_2O 30%; Δ B_2O_3 70%, K_2O 30%. o irradiated • unirradiated

Table 1 Thermal expansion coefficient ($\alpha \times 10^{-6} \cdot K^{-1}$)

Glass	20–100°C		20–200°C		20–300°C		20–400°C	
No.	before irrad.	after irrad.	before irrad.	after irrad.	before irrad.	after irrad.	before irrad.	after irrad.
1.	5.0	5.0	9.0	9.0	12.0	13.0	14.0	17.0
2.	3.4	3.0	12.0	11.0	18.0	12.0	20.0	19.0
3.	7.0	5.0	17.0	12.0	22.0	17.0	26.0	22.0
4.	2.8	4.01	15.5	10.1	21.7	14.5	26.0	17.8
5.	2.8	3.31	15.5	8.8	19.9	12.7	22.9	16.2

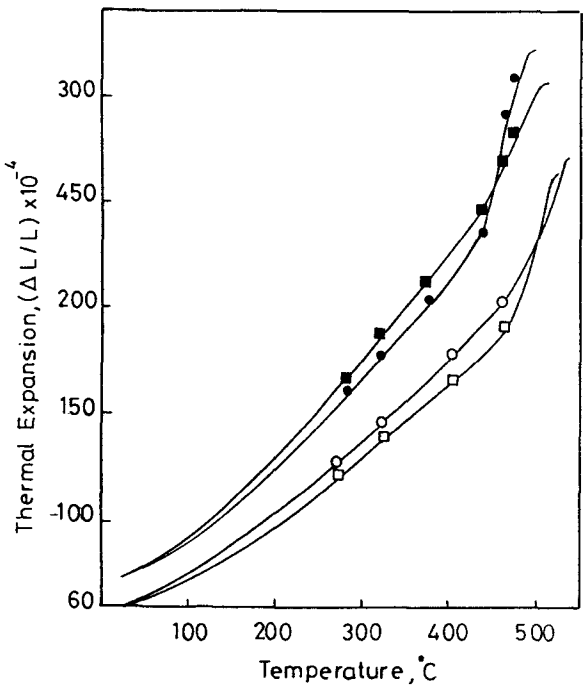

Fig. 2 Relation between thermal expansion ($\times 10^{-4}$) and temperature (°C) for irradiated and unirradiated borate glasses of the following composition: o B_2O_3 55%, PbO 45%; □ B_2O_3 30%, PbO 70%0. o irradiated • unirradiated

Table 2 Glass compositions, density and molar volume

Glass compositions	Density/g·cm^{-3}		Molar volume (V)	
	before irrad.	after irrad.	before irrad.	after irrad.
1. 70 B_2O_3 30 Li_2O	2.0573	2.1731	11.2607	10.6607
2. 70 B_2O_3 30 Na_2O	2.1669	2.2134	12.9986	12.7255
3. 70 B_2O_3 30 K_2O	2.2174	2.2840	14.6192	14.1929
4. 55 B_2O_3 45 PbO	3.1876	3.8890	34.7244	28.4620
5. 30 B_2O_3 70 PbO	4.0572	4.7549	12.2298	10.4354

Upon gamma irradiation with a dose up to 10^3 kGy, the thermal expansion is observed to decrease.

Table 1 lists the average linear coefficients of expansion between 20 and 400°C before and after irradiation for all glasses investigated. The coefficients

of thermal expansion of the glasses are seen to decrease after irradiation, except for the glass containing Li_2O at temperatures higher than 200°C, and to increases with increasing cation size in sequence Li>Na>K in the temperature range 20–400°C; on the other hand, the thermal coefficients decrease with increase of the PbO content.

The densities and molar volumes of the investigated glasses before and after irradiation are given in Table 2. From the data obtained, the density is observed to increase with irradiation, while the molar volume decreases.

Discussion

Effect of irradiation

It is well known that exposure of glasses to radiation affects their physical properties, such as density [6]. Density changes can result in deformation sufficient to cause expansion or compaction of the glass structure [4, 6].

When glasses are irradiated, knock-on displacement of the network atoms can occur as a result of collisions between incident particles or Compton electrons. Likewise, non-radiative decay of excitons formed by much lower-energy photons can cause radiolytic displacement of the atoms [3].

The electron and hole trapping sites in borate glass are believed to arise from the local non-stoichiometry, which is present in the glass as a result of either fabrication or radiation-induced atomic displacement.

Shelby [8] suggested that the boron-oxygen bond is more likely to be affected by irradiation. This indicates that an increase in the boron content causes its radiation sensitivity to increase.

A significant increase in density of a material is an indication of a large change in the structure. Damage by an irradiating species can cause the compaction of B_2O_3 by the breaking of bonds between trigonal elements, allowing the formation of different ring configurations. The average ring size is then smaller, leading to the observed increase in density (Table 2) and the decrease in thermal expansion (Figs 1 and 2).

Effect of temperature

Thermal expansion is closely tied with temperature. The irregularities in the expansion curves are due to rearrangements in the glass structure; these rearrangements occur spontaneously at certain temperatures and reach the point where they can be measured.

When T_g is exceeded, no special rearrangements in structure occur, but rather an intensified opening of the bonds. In this way, the cohesion of the struc-

ture is diminished, the thermal vibration can have a stronger impact, and the expansion becomes greater. Coenen [9] has related this process to the elastic forces in the glass and shown that the difference below and above T_g is much larger as the structure becomes weaker, i.e. the lower T_g is. Sanditov and Mantatove [10], who are respective to this idea, pointed out in particular the connection with the Poisson ratio, since this varies little for glasses.

The abnormal behaviour for the glass containing lithia can be discussed according to Griscom [11], who suggested that radiation-produced electrons are trapped on clusters of alkali metal ions in alkali borate glasses and that the number of alkali metal ions and electrons per cluster may increase with increasing temperature, which may lead to an increase in expansion coefficient at higher temperature.

Another postulation can be advanced, which suggests that the glasses containing Li_2O have a tendency to be easily internally phase-phase separated [12]. Such suggestions can explain the observed results.

Effect of composition

To discuss the influence of chemical composition, one may go back to the principle cited earlier, according to which thermal expansion is determined by anharmonic lattice vibrations. To a first approximation, one can expect the coefficient of expansion to become much smaller as the glass network produces fewer non-bridging oxygens [13]. Not only the quantity of non-bridging oxygens is significant, however, but also the type of network modifiers present, which, according to Lisenenko [14], determine the symmetry of the close-range order.

Since the linking of the individual (BO_3) groups in B_2O_3 glass occurs only at three places, the cross-linking is chiefly two-dimensional.

Thus, vibration of the groups relative to one another becomes possible, which leads to the high expansion.

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)→(BO_4), in this way a decrease in expansion occurring. Correspondingly, α should decrease and then increase again as the four-coordination of boron falls with still higher alkali metal contents and non-bridging oxygen therefore forms. Moreover, the alkali metal ions introduced in greater amounts cause an increase in asymmetry, which produces an increase in expansion.

At the same alkali metal content, the influence becomes greater as the bonding strength diminishes, and thus as the field strength of the cation in question decreases. At constant alkali metal content, α increases in the sequence Li–Na–K, the sequence of increasing ionic radius.

Soda is considered destructive and lead oxide is constructive for the glass network. If Na^+ ions destroy the bridging oxygen bonds, then the negative contribution to the thermal expansion will be much reduced as a greater proportion of such bonds are attacked. In contrast, Pb^{2+} ions may damp but not completely destroy the transverse vibrational modes [15].

It has been assumed [16] that, for lead glasses in which the PbO content is low, the Pb^{2+} ions will mostly be enclosed within the interstices formed between the glass former. In glasses containing a larger amount of PbO, some of the lead atoms apparently act as network formers. The increase in the transformation temperature with the PbO content of the glass may be attributed to the less rigid or loosely compact nature of the structure [18].

Density and molar volume

Irradiation creates 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, causing a compaction of the volume [18, 4]. Rajaram *et al.* [7] observed a linear relationship between the concentration of non-bridging oxygen hole centres and the depth of the surface deformation due to compaction induced by electron exposure in glass ceramic materials. A reasonable conclusion is that the compaction of the glass network under radiation is related to the formation of induced defect centres.

The densities are not alone indicative of the actual correlations. For this, it would be better to return to the molar volume, which contains exactly one mole of oxygen ions. It can be assumed that all additional network modifiers find room in the empty spaces of the network [19].

From the data in Table 1, it can be seen that the increase in the molar volume depends on the composition as follows: in the case of Na_2O–B_2O_3 glass, on the incorporation of Na^+ ions the network at first undergoes little change in volume, but it is then somewhat expanded. The expansion is even more pronounced in the case of the larger K^+ ion. On the other hand, the Li_2O show that the Li^+ ion not only finds room in the empty spaces of the network, but also produces a contraction of the network, recognizable by the decline in the molar volume [19].

As mentioned before, in the lead borate glasses containing a 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. In the glasses containing a high proportion of lead oxide, it would be expected that more easily polarizable oxygen ions can exist. The two outer electrons of the lead ion are

easily repelled by the field of the negative oxygen ion. The lead ion loses its spherical symmetry and its electron distribution shifts towards the oxygen ion. The density therefore tends to increase [20], i.e. a decrease in molar volume (V) is expected with the gradual increase of PbO content.

Conclusion

Gamma irradiation of some binary borate glasses decreases the thermal expansion coefficient. The extent of this decrease depends on the type of cation introduced. Further, the densities and the calculated molar volumes of these glasses were found to change on irradiation.

The data are interpreted by comparing the bond strengths between the respective cations and the oxygens together with the state of polarizability of the oxygen ions. The possible creation of an induced radiation-compaction state in the glasses upon gamma-ray irradiation is discussed.

References

1 J. Zarzuci, Glasses and Vitreous State, Cambridge Univ. Press, Cambridge, UK, 1991.
2 F. M. Ezz-Eldin, Indian J. Pure and Appl. Phys., 28 (1990) 251.
3 J. A. Ruller and E. J. Friebele, Non-Cryst. Solids, 136 (1991) 163.
4 F. M. Ezz-Eldin, N. A. Elalaily and H. A. El-Batal, Radioanalytical and Nucl. Chem., 163 (1992) 299.
5 M. Rajaram and E. J. Friebele, Non-Cryst. Solids, 108 (1989) 1.
6 F. M. Ezz-Eldin and H. A. El-Batal, Non-Cryst. Solids, 152 (1993) 195.
7 M. Rajaram, T. Tsai and E. J. Friebele, Adv. Ceram. Material, 3 (1988) 598.
8 J. E. Shelby, J. Appl. Phys., 51, (5), 2561, (1980).
9 M. Coenen, Glastech Ber., 50, 74, (1977).
10 D. S. Sanditov and V. V. Mantatov, Sov. J. Glass Phys. Chem., 10 (1984) 29.
11 D. L. Griscom, J. Non-Cryst. Solids, 6 (1971) 275.
12 W. H. Zachariasen, Acta Crystallogr., 17 (1964) 749.
13 T. Kawaguchi, J. Non-Cryst. Solids, 82 (1986) 50.
14 A. A. Lisenenko, Sov. J. Glass Phys. Chem., 12 (1986) 105.
15 R. D. Greenough, P. Dentschulk and S. B. Polmer, J. Mater. Sci., 16 (1981) 599.
16 M. Leventhal and P. J. Bray, Phys. Chem. Glasses, 6 (1965) 113.
17 T. Furukawa, S. A. Brawer and W. B. White, J. Mater. Sci., 13 (1978) 268.
18 W. Primak and E. Edwards, Phys. Rev., 128 (1962) 2580.
19 H. Sholze, Glass Nature, Structure and Properties, Springer-Verlag, N. Y. Inc., USA, 1991.
20 F. A. Khalifa, Z. A. El-Hadi, F. A. Moustaffa and N. A. Hassan, Indian J. Pure Appl. Phys., 27 (1989) 279.

Zusammenfassung — Es wurden Wärmeausdehnung, Dichte und molares Volumen einiger binären Boratgläser vor und nach einer Gammastrahlungsdosis von 10^3 kGy gemessen. Die für den Temperaturbereich von Raumtemperatur bis Erweichungspunkt vermessenen Ausdehnungskurven für alle gemessenen Gläser zeigen ähnliche Züge. Ansteigender Bleioxidgehalt erhöht den Wärmeausdehnungskoeffizient, für den Einfluß verschiedener Alkalikationen wurde Abhängig-

keit vom Ionenradius nachgewiesen. Die verschiedenen vorgeschlagenen Mechanismen für die Wärmeausdehnung wurden verbessert und die experimentellen Ergebnisse konnten unter Berücksichtigung von Bindungsstärke, Polarisierungskraft auf die verschiedenen Kationen und die durch die Bestrahlung hervorgerufenen Störungen erklärt werden. Weiterhin wurde in Verbindung mit der Bestrahlung die mögliche Kompaktheit der Struktur diskutiert.