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Thermal expansion and characteristic points of –Na_2O–SiO_2 glass with added oxides

G. Gavriliu*

Advanced Research Institute for Electrical Engineering (ICPE-CA), 313 Splaiul Unirii, 74204 Bucharest, 3, Romania

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Abstract

A differential method with an optical lever system was used to determine the thermal expansion of the glasses based on Na_2O–SiO_2 and containing the following oxides: Al_2O_3, CaO, TiO_2, ZnO, Al_2O_3–TiO_2, CaO–TiO_2, or ZnO–TiO_2. The determination was carried out on both as-drawn and annealed rods. The influence of the thermal history as well as of the added oxide(s) on the thermal expansion of glasses is dealt with in this paper. The experimental results for the thermal expansion of annealed rods show that the addition of CaO–TiO_2 in the glass has the lowest value while the addition of CaO in the glass has the highest value for the coefficient of linear expansion. At the same time, the characteristic points of the annealed glasses, determined from the expansion-temperature curves, show that the addition of ZnO in the glass has the lowest values while the addition of TiO_2 in the glass has the highest values.

Keywords: Annealing; Glass; Na_2O–SiO_2; Thermal expansion coefficient

1. Introduction

The thermal expansion coefficient of the glass depends on the asymmetry of the amplitude of thermal vibrations in the glass. The amplitudes of the thermal vibrations are small when there are many strong bonds present in the network. As a result, the thermal expansion coefficient decreases as the rigidity of the glass network increases. Modifying cations decrease the rigidity of the glass network by introducing nonbridging oxygen ions, and, therefore, increase the thermal expansion coefficient of the glass. The change in the thermal expansion coefficient of the glass which is caused by different additives is often directly proportional to the amount of the additive.[1]

Kitaigorodsky and Rodin[2] pointed out that the thermal expansion coefficient of the glass depends on its composition, rising with the increase in alkali, lime, and alumina, and falling as the content of silica, zinc oxide, boric oxide, and magnesia increases. Sheen and Turner[3] noticed a considerable reduction in the thermal expansion coefficient which occurs while replacing sodium oxide by titania. The substitution of silica by alumin[4] was without an appreciable effect on the linear coefficient of the thermal expansion. English, Turner and Winks[5] found a linear thermal expansion coefficient of 9.59×10^{-6} K^{-1} for a glass having 73.52 SiO_2, 20.63 Na_2O, 0.88 Al_2O_3 and 4.55 ZnO.

The glass transition temperature depends on the coordination number of the elements in the glass and on the strength of attraction between elements in the glass. Cations which have high coordination numbers and nondirectional bonds raise the glass transition temperature. When different cations which have the same coordination number are used, the glass transition temperature increases as the ionic field strength of the cation increases.[1] The annealing temperature of titania-containing glasses increases rapidly with the increase in the titania content, the rate of increase being higher than that for corresponding glasses containing lime, magnesia or alumina.[3] Replacement of silica by alumina up to 10% results in a slight rise in the annealing temperature; beyond a substitution of 10% the increase rate of annealing temperature is considerably greater.[4] The substitution of sodium oxide by zinc oxide up to 6% led to scarcely perceptible increases of the annealing temperature; up to 10% the effect was not very considerable.[5] Heating and cooling rates are prevailing factors for the glass structure. The

* Tel.: +40-1-3222748; fax: +40-1-3213769.
E-mail address: magnet@icpe.ro (G. Gavriliu).

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structural phenomenon does not represent a fixed point of transformation but has a continuous character and takes place in a temperature range.[6]

Due to the importance of the thermal expansion (or shrinkage) of the glass in different applications, but especially when sealing it with dissimilar materials, the present investigation was undertaken to study the effects of the added oxide(s) and thermal history on the thermal expansion of the added oxide(s)–Na_2O–SiO_2 glass as well as the determination of the characteristic points from its expansion-temperature curve.

2. Experimental procedure

The composition of the chosen glasses is given in Table 1. The mixtures of raw materials, of Analar quality, were melted using a platinum crucible in a gas furnace at a temperature of 1480–1580 °C. The total melting time was about 7 h; for a better homogeneity, after 3 h, the melted glasses were stirred with a platinum sheet for 1 h. Then the melted glasses were poured into a metallic mould. The solid glass samples were remelted in the same crucible and furnace and then the crucible with the melted glass was transferred into an electric furnace having a temperature of 1100–1200 °C. From the melted glasses, with a mechanical device, rods were drawn, with a diameter of about 4 mm. The rods were cut and those free of bubbles were selected for the experimental work.

A differential method was adopted in which the expansion of the rod was compared with that of silica glass.[7–9]

Three different samples from each glass, having the length of the rods of 10 ± 0.03 cm, were used. The measurements were twice carried out on the same glass sample at a heating rate of 3 °C/min; the measurements were performed first on the as-drawn rod and then on the annealed one. The annealing of the glass samples was carried out in the furnace of the thermal expansion apparatus, after the first measurement on the as-drawn rod was performed, the deformation point of the glass was reached and the optical lever system was removed, at a cooling rate of 30 °C/h down to 250 °C and then allowing the sample to cool down freely down in the furnace after the furnace was switched off.

From the expansion-temperature curve of the annealed glasses there were determined the characteristic points of each glass as they are defined.[10]

Table 1
Chemical composition of glasses

Glass name	Composition (wt.%)					
	SiO_2	Na_2O	Al_2O_3	CaO	TiO	ZnO
A	70	22	8	–	–	–
C	70	22	–	8	–	–
T	70	22	–	–	8	–
Z	70	22	–	–	–	8
AT	70	22	4	–	4	–
CT	70	22	–	4	4	–
ZT	70	22	–	–	4	4

3. Results and discussion

The average of the experimental results on the thermal expansion of the glasses for both as-drawn glasses and annealed ones is shown in Figs. 1 and 2, in the form of the expansion–temperature curves, as well as in Fig. 3,

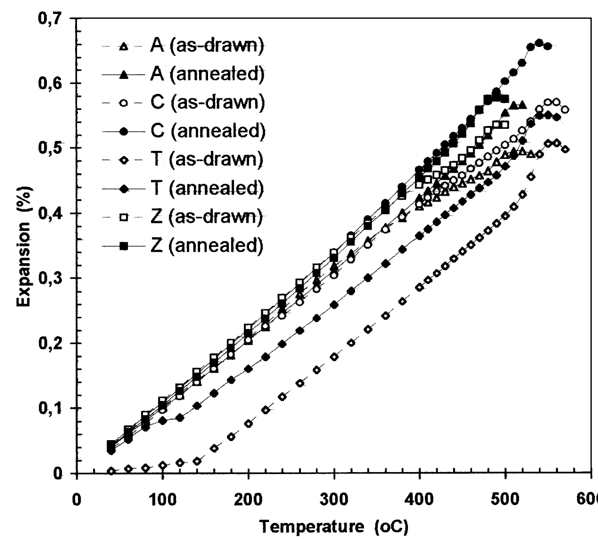

Fig. 1. Effect of thermal history on expansion vs temperature of A, C, T and Z glasses.

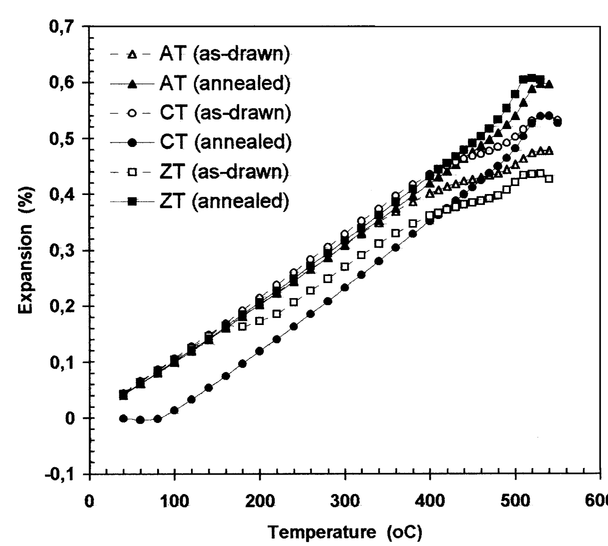

Fig. 2. Effect of thermal history on expansion vs temperature of AT, CT and ZT glasses.

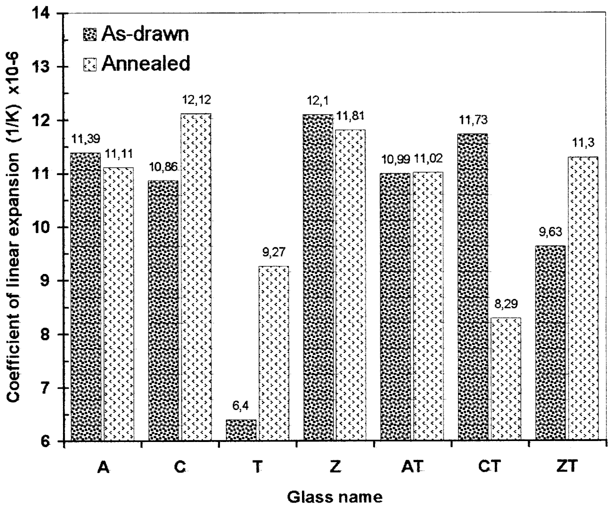

Fig. 3. Effects of added oxide(s) and thermal history on the coefficient of linear expansion of glasses determined over the temperature range from 20 to 300 °C.

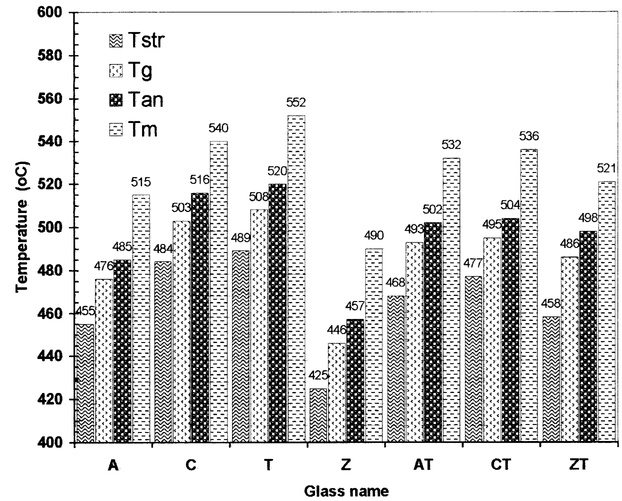

Fig. 4. Effect of added oxide(s) on the characteristic points of annealed glasses (T_{str}—strain point; T_g—glass transition temperature; T_{an}—annealing point; T_m—deformation point).

in the form of the linear thermal expansion coefficients over the temperature interval from 20 to 300 °C.

From the expansion–temperature curves as well as from the linear thermal expansion coefficients it is pointed out that their values are strongly dependent on the added oxide(s) in the glass. Also, on the same glass, the thermal history of the glass has, generally, less influence at lower temperatures (Fig. 3) but sensible differences at higher temperatures (Figs. 1 and 2) on the thermal expansions of the glasses.

The thermal expansion curves of the A, AT, Z and ZT glasses, as-drawn and annealed, present a certain superposing over a larger or shorter temperature range as the thermal expansion curves of the C, T and CT glasses are completely out of superposing.

The results point out that the thermal expansions of the annealed glasses are generally greater than those of the as-drawn glasses but especially at higher temperatures.

The characteristic points of the annealed glasses, determined from the expansion–temperature curves, are shown in Fig. 4. These results represent a clear proof that the characteristic point depends on the type of added oxide(s).

The influence of 8% of the added oxide(s) in the glasses seems to have an important effect on the thermal expansions, the coefficients of the linear expansion, as well as the characteristic points. This influence on both the thermal expansion and the coefficient of linear expansion of the annealed glasses, when one oxide is added, shows the following increasing order: TiO_2, Al_2O_3, ZnO, and CaO; on the characteristic points the order is: ZnO, Al_2O_3, CaO, and TiO_2. When two oxides are added the influence on the thermal expansions and the coefficients of linear expansion of the annealed glasses are shown in the following increasing order: CaO–TiO_2, Al_2O_3–TiO_2, and ZnO–TiO_2 on the characteristic points the order is: ZnOTiO_2, Al_2O_3–TiO_2, and CaO–TiO_2. The results are generally between that of TiO_2 alone and that of the glass with the other added oxide.

From these experimental results on both the thermal expansions and the characteristic points it is pointed out that a change in the added oxide(s) as well as in the thermal history, changes the thermal properties of glasses within larger or closer limits, determined by the chemical composition of the glass on the one hand, and by the resulting structure of glass on the other band.

The basic oxides in the studied glasses are SiO_2 and Na_2O. The glasses are thus rich in Si–O–Si and Si–O–Na linkages. When the added oxide is included, other linkages appear. Thus, for one added oxide (for example, Al_2O_3) other linkages such as Si–O–Al and Al–O–Na can appear. For two added oxides (for example, Al_2O_3–TiO_2) other linkages such as Si–O–Ti and Ti–O–Al can also occur. The same type of linkages but with Ca, Ti, or Zn instead of Al could appear when other added oxides are included. Concentrations of the various linkages are determined by the composition and relative energies of the linkages.[11,12]

Table 2 shows some structural characteristics on both the coordination number of the chemical elements (M) and the coordination number, electrostatic field and single-bond strength regarding the M_xO_y groups, possibly and/or probably in the elaborated glasses.[6,13–16]

From these data, the experimental results on the thermal expansions and the characteristic points of the annealed glasses (Figs. 1, 2 and 4) as well as the electrostatic field and single-bond strength (Table 2), we can notice that the effect of the added oxide(s) on the thermal expansions of glasses is close, physically and mathematically, to an inverse ratio to both the single-bond

Table 2
Some structural characteristics

Chemical element (M)		Oxide (M_xO_y)			
		Coordination number			
Symbol	Observed coordination number	Predicted	Observed	Electrostatic field $Z/a^2 \times 16\ cm^{-2}$	Single-bond strength (kcal/mol)
Si	4,5,6,8	4	4,6	1.57	106
Na	3,4,6.7,8,9,10,11,12	6	4,6,8	0.19	20
Al	4,5,6,8,12	4	4,5,6	0.96–0.84	108– 79
		6			53–67
Ca	6,7,8,9,10,11,12	6,8	6,7,8,9	0.33	32
Ti	4,5,6,7,8,12	6	6	1.25	73
Zn	2,4,5,6,8,12	2	2,4		72
		4		0.59	36

strength and the electrostatic field. On the other hand the effect of the added oxide(s) on the characteristic points of glasses is in direct ratio to both the single-bond strength and the electrostatic field. Thus, the thermal expansion response of the glasses is bigger at both lower values of the electrostatic field and lower values of the single-bond strength or smaller at both higher values of the electrostatic field and higher values of the single-bond strength. At the same time, the characteristic point response of glasses is smaller at both lower values of the electrostatic field and lower values of the single-bond strength or bigger at both higher values of the electrostatic field and higher values of the single-bond strength. There are, however, exceptions in the case of C and CT glasses due to, probably, the coordination number of Ca, when one oxide is added, or Ca and Ti, when two oxides are added.

As Figs. 1–3 show, for as-drawn glasses, the thermal expansions and the coefficient of linear expansions values are in an uncontrolled response. This appears, certainly, due to the different solidification of the structure from the outside to the inside of the glass rods, resulted in their drawing process by uncontrolled and rapid cooling.

4. Conclusions

The experimental results for the thermal expansions and the characteristic points of the added oxide(s)–Na_2O–SiO_2 glasses showed the effects on these properties due to both the added oxide and the thermal history.

The effect of 8% of the added oxide(s) {Al_2O_3, CaO, TiO_2, ZnO, Al_2O_1–TiO_2, CaO–TiO_2, or ZnO–TiO_2}, at the other 92% of Na_2O and SiO_2, in the annealed glasses, is close to an inverse ratio in the case of the thermal expansions and a direct ratio in the case of the characteristic points to both the single-bond strength and the electrostatic field.

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