Journal of Thermal Analysis and Calorimetry, Vol. 64 (2001) 1017–1024

THE ROLE OF TRIVALENT ELEMENT OXIDES IN CaO (Na_2O)–M_2O_3–SiO_2 GLASSES FROM T_g

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Abstract

In this paper T_g values of calcium (sodium) silicate glasses containing added with oxides of trivalent elements are reported. The plots of T_g as a function of composition or *vs.* the ionic field strength prove to be useful in discussing the role of the oxides in the glass structure. It is found that, at least in the studied composition range, Sc_2O_3, Y_2O_3, La_2O_3, and In_2O_3, behave as network modifier oxides.

In the compositional ranges studied, the hypothesis based on them well agree with the expectations based on the known criteria reported in literature and on FTIR spectra.

Keywords: glass structure, glass transformation temperature, silicate glasses

Introduction

Recently several papers have been published reporting on the effect of adding oxides of trivalent elements to silicate glasses. Y_2O_3 and La_2O_3 were recently added to silicate and alumino silicate glasses, allowing to improve the alkaline durability [1] and to obtain exceptionally high glass transformation temperatures (T_g), high refractive indices, very low electrical conductivity and moderate thermal expansion coefficients. These properties make them a good alternative to borosilicate glasses currently used for sealing glass to tungsten and molybdenum [2].

It is also known that CaO and SiO_2 are the basic components of bioactive glasses and glass-ceramics, i.e. ceramics able to bond to living bone. They are of great interest for the repair and reconstruction of deseased or damaged parts of the muscle-skeletal system [3, 4]. It is also known that the addition of M_2O_3 oxides does allow to obtain bioactive materials, as long as no too great amounts are added [5, 6]. However, other properties are expected to be significantly changed in the view of the above reported remarks.

All this stimulated research on the structural role of M_2O_3 in silicate glasses. Several criteria, predicting the role of the oxides, are available [7–9]. However, the role, in the case of the oxides of formula M_2O_3, is questioned.

In this paper, while discussing the role of oxides in the glassy structures, the usefulness of the plots of the T_g values that are easily taken from DTA curves is shown.

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

Glasses of composition

$$(1–x)Na_2O{\cdot}x/nM_mO_n{\cdot}SiO_2 \qquad \text{(I)}$$

$$(2.5–x)CaO{\cdot}x/3M_2O_3{\cdot}2SiO_2 \qquad \text{(II)}$$

(M=Y^{3+}, La^{3+}, In^{3+}, Sc^{3+}, Al^{3+}, Ga^{3+}, Ba^{2+}, K^+) were prepared by melting analytical grade reagents Al_2O_3, Ga_2O_3, Y_2O_3, La_2O_3, In_2O_3, Sc_2O_3, $CaCO_3$, $BaCO_3$, Na_2CO_3 $K_2CO_3$and SiO_2 in a platinum crucible in an electric oven for 4 h at 1550°C. The melt was quenched by plunging the bottom of the crucible into cold water.

Differential scanning calorimetry was carried out by means of a Netzsch heat flux apparatus model 404M, on about 50 mg powdered samples (63–90 μm) at a heating rate β=10°C min^{-1}. Powdered Al_2O_3 was used as reference material.

Fourier transform infrared (FTIR) transmittance spectra were recorded in the 400–1200 cm^{-1} region using a Mattson 5020 system, equipped with a DTGS KBr (deuterated triglycine sulphate with potassium bromide windows) detector, with a resolution of 2 cm^{-1} (20 scans). KBr pelletised disks containing 20 mg of sample and 200 mg KBr were made. The FTIR spectra have been elaborated by means of a Mattson software (FIRST Macros).

Results

The glass transformation temperature, T_g, was taken from the differential thermal analysis derivative (DDTA) curve, as illustrated in Fig. 1, as the inflection point of the DTA curve at the lower end of the glass transformation temperature range, where the DTA curve shows a slope change.

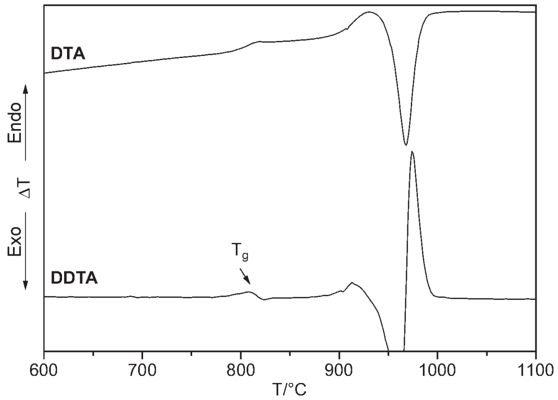

Fig. 1 Typical DTA curve and its derivative (DDTA)

T_g is plotted in Figs 2–4 as a function of composition expressed by means of the x values of the general formulas. Different trends are observed, both linear and non-linear, depending on the type of substituent.

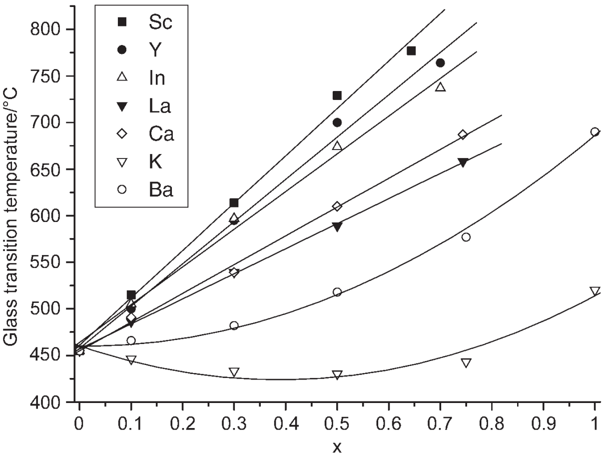

Fig. 2 T_g *vs.* composition curves of glasses of series I (*M*=Sc, Y, La, In, Ca, Ba, K)

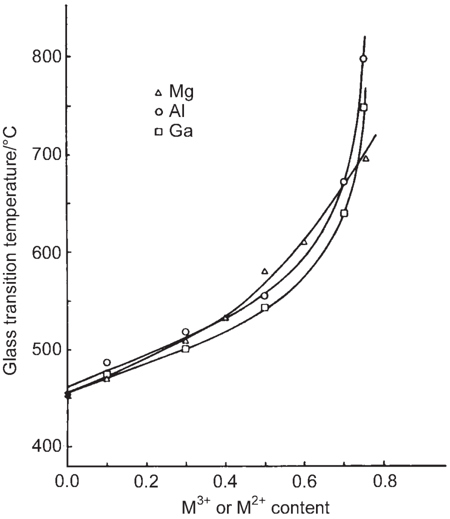

Fig. 3 T_g *vs.* composition curves of glasses of series I (*M*=Al, Ga, Mg)

A useful parameter, when discussing the role played by the oxides in the glass structure, is the ionic field strength, Z/r^2, which is the ratio of the cation charge, Z, to the square of its radius. In particular McMillan found [8] that the network modifier cations have $Z/r^2<5$ Å^{-2}. In Figs 5 and 6 T_g of the glasses with the least substitution (x=0.1 in the case of series I and x=0.2 for the series II) is plotted *vs.* the ionic field strength. It can be seen two different linear relationships are obtained depending on the value of $Z/r^2<4.6$ Å^{-2} or $Z/r^2>4.6$ Å^{-2}.

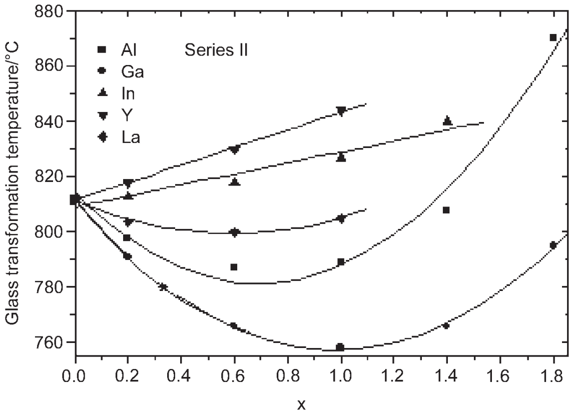

Fig. 4 T_g *vs.* composition curves of glasses of series II

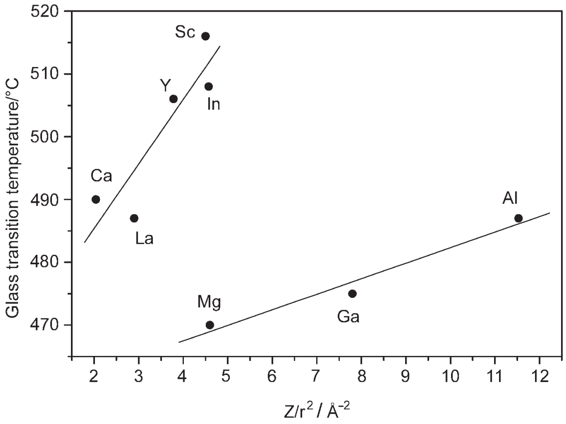

Fig. 5 T_g *vs.* ionic field strength of glasses of series I (*x*=0.1)

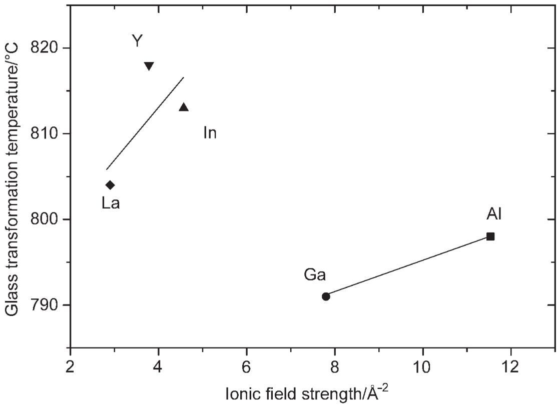

Fig. 6 T_g *vs.* ionic field strength of glasses of series II (*x*=0.2)

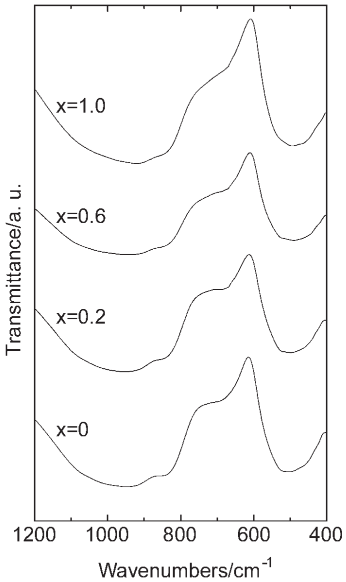

Fig. 7 FTIR spectrum of Al_2O_3 containing glasses of series II

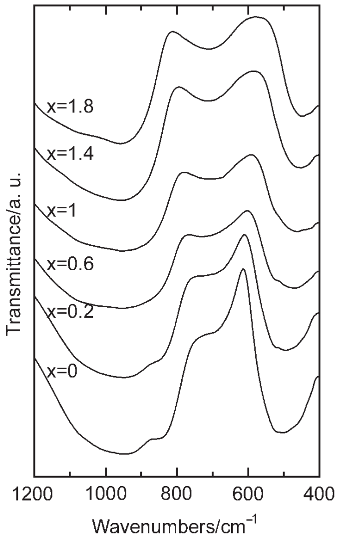

Fig. 8 FTIR spectrum of La_2O_3 containing glasses of series II

In Figs 7 and 8 the FTIR spectra of the glasses of the II series, obtained when the substituents are La_2O_3 and Al_2O_3, are reported. In all the cases, the broad band in the higher wavenumber range, linked to the stretching vibration modes of the SiO_4 tetrahedra [10–12], partially overlaps the band at ~700 cm^{-1}, due to bending vibration modes of Si–O–Si [13, 14]. The band at ~500 cm^{-1} can be attributed to bending vibration modes of the silicatic structure [10–12]. As can be seen, the stretching vibration band is not affected by the substitution of M_2O_3 to CaO, in the case of La_2O_3; in the case of Al_2O_3, instead, it sharpens and shifts towards higher wavenumbers the greater is the substituted CaO amount. FTIR spectra of the Y_2O_3 and In_2O_3 containing glasses are very similar to those for the La_2O_3 containing ones.

Discussion

It is known that the silica glass structure is constituted of SiO_4 tetrahedra sharing the corners. When a 'network modifier oxide', like CaO or Na_2O, is added, the cations are hosted in the holes of the structure and extra oxygens allow that some oxygens bridges between the tetrahedra are broken: it is said that bridging oxygens are substituted by couples of 'non-bridging oxygens' the charge of which is compensated by the cations in the holes of the structure. A mixed covalent-ionic structure is obtained.

It's also worth remembering that following Ray [15] T_g depends on:

a) the density of covalent cross-linking;
b) the number and strength of cross-links between the cation and oxygens.

When the well-known network modifying cations, Ca^{2+} and Na^+, are substituted with a network forming cation M^{3+}, MO_4 tetrahedral units are formed substituting the SiO_4 ones [7, 8]; therefore non-bridging oxygens are converted into bridging ones; however, owing to the need of an extra oxygen to construct these MO_4 tetrahedra and their need of charge compensation, some of the remaining modifying oxide, CaO or Na_2O, is subtracted to its role; therefore, the density of covalent cross-linking is changed and a twofold dependence on the composition, expresssed as the x value of the formulas, is expected. As a consequence a non-linear trend of the plots of Figs 2–4 is expected.

However, as in the studied series the molar ratio O/Si is remained constant throughout the substitution, no change of the density of covalent cross-linking is expected in the case of the introduction of network forming cations. In this case the T_g changes are due to differences in the number and strength of the cross-links between the cation and oxygens. Non-linear trends can be expected when the substituent cation does not perform, at low substitution (when the structure is primarily determined by the substituted cation) to achieve its own coordination shell and this changes progressively along the substitution. As long as the ionic field strength is a measure of the electrostatic force that the ion can exert upon neighboring oxygens, it is reasonable to think that the difference of its values between the substituent and substituted cations should be determinant: non-linear trends would be expected when the difference of the Z/r^2 values is low. As a matter of fact, non-linear trends are observed in Figs 2–4 when CaO or Na_2O are substituted with the well-known network former oxides Al_2O_3 and Ga_2O_3 or when they are substituted with the well-known network modifier oxides BaO or K_2O, with K^+ and Ba^{2+} and the substitued cation having close values of the ionic field strengths.

Therefore, taking into account the high value of Z/r^2=4.60 for Mg^{2+}, the non-linear trend of the curve for the MgO containing glasses implies a role of network former oxide for it. The linear trends obtained in the cases of Sc_2O_3, Y_2O_3, La_2O_3, In_2O_3, are indicative of the network modifier role in the studied composition range.

In Figs 5 and 6 two distinct behaviors are observed: when Z/r^2>4.6 Å^{-2} (Al^{3+}, Ga^{3+}, Mg^{2+}), the T_g falls to lower values instead of continuing to grow. This is easily explained if it is admitted that Al^{3+} , Ga^{3+} and Mg^{2+} act as network forming ions, while the other ones as network modifying ions. When entering as a network modifying ion, in fact, a mean coordination number close to the one in the pure oxide structure, reported in Table 1, can be expected. Therefore, according to Ray, greater values of T_g are expected for them than in the case of ions entering the silicate glass structure as network forming ions, in fourfold coordination. Therefore, also in this way a network forming role is expected for Al_2O_3, Ga_2O_3, and MgO and a network modifier role for the others. All this is in good agreement with the expectations based on several criteria reported in literature [7–9] predicting the role of the oxides in the silicatic glass structure. In particular, it is confirmed that, as reported by McMillan [8], starting from Z/r^2≅5 Å^{-2} the cations enter as network formers.

Table 1 Coordination number in the oxide (*CN*), radius (*r*) and ionic field strength of cations

M	*CN*	*r*/Å	Z/r^2/Å^{-2}
Al (+3)	6	0.51	11.53
Ga (+3)	6	0.62	7.80
In (+3)	6	0.81	4.57
Y (+3)	8	0.89	3.78
La (+3)	7	1.02	2.90
Ca (+2)	8	0.99	2.04
Na (+1)	6	0.97	1.06
K (+1)	9	1.33	0.56
Mg (+2)	6	0.66	4.60
Ba (+2)	8	1.34	1.11

FTIR spectra reported in Figs 7 and 8 give evidence of the correctness of the structural hypothesis based on the plots of T_g as a function of the composition and *vs.* the ionic field strength.

The changes of the band in the range 800–1100 cm^{-1} appear relevant to the above reported discussion. It is known that SiO_4 stretching vibration modes of fused silica give rise to a sharp band at 1100 cm^{-1} [10, 11]. When a network modifying oxide is added, it shifts towards lower wavenumbers progressively and broadens [10, 12]. This is due [10, 12] to the build up of SiO_4 tetrahedral units bearing a progressively higher number of non-bridging oxygens. Therefore, the lack of modification, when La_2O_3, Y_2O_3 and In_2O_3 are substituted, well agrees with the hypothesis that they enter as network modifying oxides. In fact, because the substitution is that kind the ratio O/Si is not changed, no changes in the number of the non-bridging oxygens are expected. The case of the M_2O_3 oxides entering as network forming oxides is different. In particular, when $CaO/M_2O_3=1$, all the oxygens should become bridging and the stretching band is expected to be the result of the overlapping of the ones of SiO_4 and MO_4 tetrahedra bearing only bridging oxygens. Therefore, a progressive sharpening is expected as it is observed for Ga_2O_3 and Al_2O_3 containing glasses.

Conclusions

The plots of T_g as a function of the composition or *vs.* the ionic field strength prove to be useful in discussing the role of the oxides in the glass structure.

In the compositional ranges studied, the hypothesis based on them well agree with the expectations based on the known criteria reported in literature and on FTIR spectra.

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