Journal of Thermal Analysis and Calorimetry, Vol. 77 (2004) 57–63

THERMAL STUDY OF THE INFLUENCE OF CHEMICAL BOND IONICITY ON THE GLASS TRANSFORMATION IN (Na_2O, CaO, MgO)–Al_2O_3–SiO_2 GLASSES

L. Stoch, Irene Wacławska[*] *and M. Środa*

AGH – University of Science and Technology Faculty of Materials Science and Ceramics, al. Mickiewicza 30, 30-059 Cracow, Poland

Abstract

The relation between change of the specific heat (ΔC_p) accompanying the glass transformation and the chemical composition of glasses (Na_2O, CaO, MgO)–Al_2O_3–SiO_2 system has been studied. The exchange of modifiers in the glass structure causes the ΔC_p increase in the sequence Na>Ca>Mg. Change the glass network composition by introducing Al into it makes smaller increase of the ΔC_p values. It has been shown that degree of ΔC_p value changes is dependent on the iconicity/covalence of chemical bonds of cations with oxygen of glass structure network.

Keywords: DTA/DSC/TMA, glass, glass transformation

Introduction

Transformation of the glassy state is regarded as the transition which distinguishes glass from other solid bodies. It is induced by the relaxation processes of internal strains which are the consequence of the disordered arrangement of elements forming the internal structure of glass.

The strains appearing in the glass structure are a feature specific for the particular type of glass (structural stresses), but they depend also on the so-called thermal history of glass (transient stresses).

Relaxation of structural stresses during transition may induce breaking of certain bonds, the visible effect of which is the transition of glass from the state of a solid rigid body into viscoelastic state of viscosity amounting to $10^{13.3}$ dPas at T_g temperature, however the cohesion of the glass structure is still retained. The increase of temperature causes further changes in the glass structure, among others, gradual depolymerization of the glass network which is manifested by a respective decrease of viscosity and the transition of glass into the state of fluid liquid.

Relaxation of strains is accompanied by jump-like changes of certain thermodynamic parameters at the transition temperature T_g, such as: molar heat C_p, coefficient of linear (α) and volume expansion (β) which correspond to the molar volume change.

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[*] Author for correspondence: E-mail: iwac@interia.pl

1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

As it has been already noticed earlier [1], the change in the value of C_p (ΔC_p) accompanying the glass transformation, determined from the DSC curves, is connected with the character of rearrangement of the glass structure in the course of transformation. This is particularly well visible in the case of glasses containing the crystallization activators, with the transformation initiating the crystallization process [2].

As it has been observed earlier [1], the condition for the given substance to assume the glassy form is sufficiently high flexibility of the newly formed amorphous structure. Flexibility has been found to be an indispensable factor for the structure of a solid body to assume and to retain the topological disordering of the elements forming this specific structure for glasses. Elasticity is responsible for the situation that relaxation of internal stresses can proceed by way of reorientation or by rather small displacements of the coordination polyhedra of the polymeric framework, such as the tetrahedra [SiO_4], forming this framework, without disturbing its continuity. This takes place in the course of the glass transformation process.

Elasticity of the structure of oxide glasses is due to the non-directional, ionic bonds or bonds in which partly participate directional covalent bonds, as it occurs in the case of oxygen bridges combining the tetrahedra with each other and with other components of the structure. With increasing covalence of the cation–oxygen bond the structure becomes increasingly more rigid, what with increasing temperature causes the formation of strains inside the structure that can become unloaded only through cracking. This leads to the decomposition of the glass structure and induces its crystallization.

The aim of the investigations was to examine the relation between ΔC_p and ΔV determined from DSC and TMA curves and the glass structure and the type of bonds appearing in it. With this aim in view the chemical compositions of glasses to be examined were selected. It has been also assumed that ΔC_p can be interpreted as the index of the change of the configuration entropy connected with the rearrangement of the glass structure during transformation.

Material and methods

Glasses from the Na_2O–SiO_2 system, modified with CaO, MgO and Al_2O_3 additions, were obtained by preliminary sintering of appropriate powder batches in the form of pastilles, and subsequent melting of the obtained sinters in platinum crucibles, at the temperature 1450°C for 1 h. The obtained glasses were grinded to the grain size 0.1–0.3 mm.

Thermal measurements were carried out using Perkin Elmer DTA-7 thermoanalyzer, in which after prior calibration there can be obtained data concerning the sample heat flow. Pure aluminum and gold were used for temperature and heat calibration. Glass samples, weighing 60 mg, were heated in platinum crucibles in nitrogen atmosphere, at a rate of 10°C $\min^{-1}$ to the temperature of about 50°C above the transformation temperature, then cooled at the same rate and heated again.

The transformation temperature T_g was determined from the half C_p extrapolated of the heat flow curve. Changes of ΔC_p at the T_g point were determined applying 7 Series/Pyris Thermal Analysis Software Library.

In order to determine the thermal expansion of the glasses the Perkin Elmer TMA-7 thermoanalyzer with an attachment for measuring the changes in volume was used. Glass samples, 3×3×3 mm were placed in the dilatometer accessory barrel together with a known amount of filling medium (Al_2O_3 powder) and closed by the pluger. First, the system was heated at a rate of a 10°C min^{-1} in helium atmosphere, applying 50 mN pressure. After that the glass sample was removed, and second run was done for the same amount of Al_2O_3 to obtain baseline.

The volume expansion occurring in the glass sample during increase ($T_1 \rightarrow T_2$) was calculated from equation:

$$\Delta V_{(T_1 \rightarrow T_2)} = \frac{\pi d^2}{4}(\Delta l_2 - \Delta l_1)$$

where d – diameter of a plunger; Δl – the change in probe position between the baseline and the glass sample with Al_2O_3 line; Δl_2–Δl_1 – the change in probe position due to glass sample expansion going in the transition range (T_1–T_2); T_1–T_2 – temperature range of the glass transformation.

Structural examinations of the obtained glasses were carried out by infrared spectroscopy (FTIR) and nuclear magnetic resonance (MAS-NMR) methods.

The measurements of spectra in the middle infrared were made on FTS-60V spectrometer with Fourrier transform at the Department of the Chemistry of Silicates and Macromolecular Compounds of AGH – University of Science and Technology.

The ^{27}Al MAS-NMR investigations were carried out at the Institute of Nuclear Physics in Cracow, at room temperature, using CMX-400 Chemognetics pulse spectrometer with Bruker 9.4 T superconductive magnet.

Results and discussion

The obtained data (Table 1) show the existence of a definite relation between the value of ΔC_p and the chemical composition of glass and the position of the components in its structure. The base glass for the determination of these dependences was sodium silicate glass of the simple composition $Na_2O \cdot 3SiO_2$ (glass 1). Introduction of aluminum into the structure of glass whose tetrahedra $[AlO_4]$ replace part of the tetrahedra $[SiO_4]$ in the framework (glass 2) causes the increase of the value of ΔC_p. The change of the modifier cation in the newly formed aluminosilicate glass due to the replacement of sodium by calcium is connected also with further increase of this value (glasses 2 and 7). Introduction of magnesium to replace sodium causes almost three-fold increase of ΔC_p (glasses 2 and 6).

Change of the modifiers consisting in the replacement of half of the sodium by calcium (glasses 2 and 4) results in a significant decrease of the value of ΔC_p, whereas the introduction of magnesium in place of half of the amount of sodium is connected with its smaller decrease (glasses 2 and 3). The tendency of these changes is the same as in the case of complete replacement of Na by Ca or Mg. The presence of sodium,

Table 1 Thermal characteristics of glass transformation effect of glasses (Na_2O, CaO, MgO)–Al_2O_3–SiO_2 system

Glass No.	Chemical composition of glass/ mol%	T_g/ °C	ΔC_p/ $J\ g^{-1}\ °C^{-1}$	ΔV/ $mm^3\ mol^{-1}$
1	$Na_2O{\cdot}3SiO_2$	480	0.302	50.55
2	$Na_2O{\cdot}2.5SiO_2{\cdot}0.5Al_2O_3$	531	0.461	27.98
3	$0.5Na_2O{\cdot}0.5MgO{\cdot}2.5SiO_2{\cdot}0.5Al_2O_3$	713	0.435	196.61
4	$0.5Na_2O{\cdot}0.5CaO{\cdot}2.5SiO_2{\cdot}0.5Al_2O_3$	654	0.212	402.50
5	$0.5Na_2O{\cdot}0.5CaO{\cdot}2SiO_2{\cdot}Al_2O_3$	768	0.425	135.00
6	$MgO{\cdot}2.5SiO_2{\cdot}0.5Al_2O_3$	786	1.476	73.60
7	$CaO{\cdot}2.5SiO_2{\cdot}0.5Al_2O_3$	799	0.663	181.28

however, reduces considerably this change. It can be treated as a synergetic interaction of two cations. This is particularly well visible in the case of coexistence of Na and Mg.

In the case of glasses with two modifiers the increase of the amount of aluminum in the framework also causes the increase of ΔC_p, similarly as in the case of base sodium silicate glass. Increase in the value of ΔC_p correlates with the increase of T_g (Fig. 1).

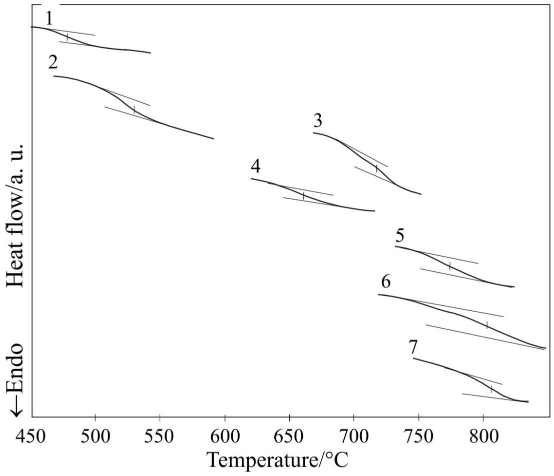

Fig. 1 DSC curves of glasses of (Na_2O, CaO, MgO)–Al_2O_3–SiO_2 system

The effect of the change in the composition and structure on the changes in the molar volume induced by transformation is more complex. Introduction (glasses 1 and 2) as well as increasing amount of aluminum into the glass framework (glasses 4 and 5) causes considerable reduction of the value of ΔV. Replacement of sodium by calcium brings considerable increase of ΔV (glasses 2, 4, 7), whereas the increase caused by magnesium is much smaller (glasses 2, 3, 6).

The value of ΔC_p should be considered in relation to the degree of changes in the structure contributing the glass transformation, which affect the value of the configuration entropy. This comprises the number and the energy of the broken chemical bonds. Change in the value of ΔC_p is dependent on the ionicity of the bond of the cation with the oxygen of the silicon–oxygen network. When searching for this dependence, similarly as in other studies [3] the authors made use of the ionicity of the cation–oxygen bonds, determined by Pauling [4] and Görlich [5] (Table 2).

Table 2 Chemical bonds in glasses of (Na_2O, CaO, MgO)–Al_2O_3–SiO_2 system

Type of bond	Ionicity of bond determined by Pauling	Ionicity of bond determined by Görlich
Si–O	1.7	0.428
Al–O	2.0	0.546
Mg–O	2.3	0.670
Ca–O	2.5	0.707
Na–O	2.6	0.807

The effect of the ionicity of bonds is visible the best in the case of the exchange of modifiers. At the same type of network the ΔC_p increases in the sequence Na>Ca>Mg. This sequence is retained when only half of Na^+ is exchanged, which is characterized by the highest ionicity of the bond with oxygen. Then, however, the value of ΔC_p is appropriately lower. This is evidence of a certain additivity of the interatomic cation-framework interactions. Reduction of the ionicity of the bond and at the same time increased proportion of the covalent bond indicate that the structure becomes more rigid. The results are the structural strains which may cause the cracking of the bonds, what is less probable in the case of bonds of high ionicity, i.e. the non-directional ones, in this way increasing the elasticity of the structure. In accordance with the degree of the covalence of bonds there increases the T_g temperature, necessary to initiate such decomposition of the structure.

The influence of aluminum on the increase of the value of ΔC_p is smaller than it might result from the rather great ionicity of its bonds with oxygen as compared with silica. Its position in the structure, however, is different, since it is present as component of the polymeric silicon–oxygen network, the components of which are connected by relatively elastic but strong oxygen bridges. Decomposition of this framework requires considerable energy and it proceeds step by step with the increase of temperature, which is manifested by the decreasing viscosity of the glass.

The effect of the cation modifiers and aluminum on the glass structure is evidenced by ^{27}Al MAS-NMR spectra (Fig. 2). Sodium aluminosilicate glass (glass 2) gives a sharp line at +50 ppm which is probably characteristic of aluminum in the IV coordination with respect to oxygen. Introduction of calcium into this glass causes the broadening of this line towards negative values which is an indication of the

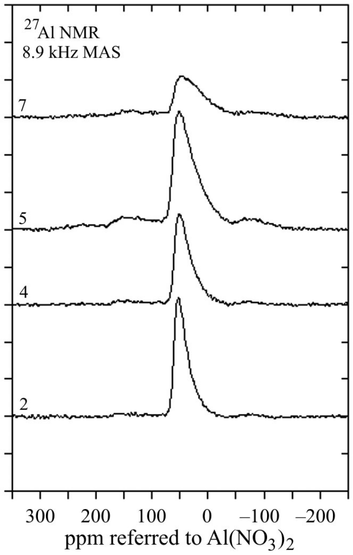

Fig. 2 ^{27}Al MAS NMR spectra of glasses of (Na$_2$O, CaO, MgO)–Al$_2$O$_3$–SiO$_2$ system

appearance of the change of aluminum coordination number. This indicates that Ca^{2+} besides Na^+ participates in the compensation of electrical charge deficiency of [AlO$_4$] tetrahedra. Replacement of sodium by calcium induces considerable changes in the glass structure reflected in ΔC_p value (Table 1).

FTIR spectra of silicate and alumino-silicate glasses are characterized by three bands deriving from the oxygen bridges. These are: stretching (about 1000 cm^{-1}), bending (700–800 cm^{-1}) and rocking (500–429 cm^{-1}). The first of these bands is the most sensitive on the network structure changes and it usually represents a superposition of some bands situated close to each other [6].

Increase of aluminum content into the silicate network shifts the position of the absorption band towards smaller wavenumbers (glasses 4 and 5) (Fig. 3).

FTIR spectra of the examined alumino-silicate glasses containing sodium (glasses 3 and 4) are characterized by the bands 1013 and 1019 cm^{-1}, respectively. Increased proportion of Al in the network shifts this band to 989 cm^{-1} (glass 5), whereas the effect of calcium and magnesium on the spectrum is not very noticeable.

In sodium-free glass, containing magnesium (glass 6), the band about 1000 cm^{-1} becomes divided into three bands: 938, 1081 and 1214 cm^{-1}. In the glass containing calcium (glass 7) there occur the bands: 924, 988 and 1214 cm^{-1}. The bands 938 cm^{-1} and 924 cm^{-1} can be ascribed to asymmetric stretching vibrations of the terminal Si–O bonds which occur through breaking of a part of the oxygen bridges and partial depolymerization of the network under the influence of the modifiers.

As it is seen, the results of FTIR study are in agreement with the above presented structural interpretation of the dependence between the value of ΔC_p accompanying the

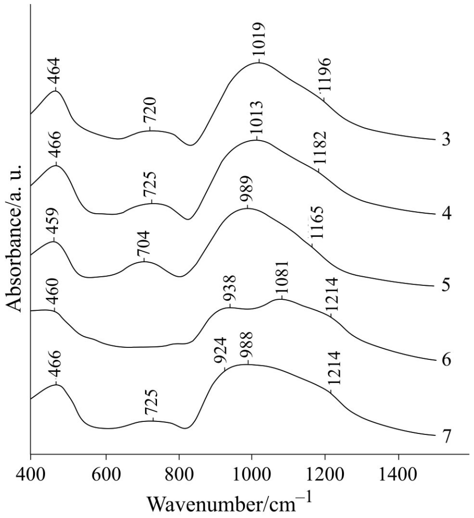

Fig. 3 FTIR spectra of glasses of (Na_2O, CaO, MgO)–Al_2O_3–SiO_2 system

glass transformation effect and the role of ionicity/covalence of bonds between the cations and the oxygens of the network and the resulting rigidity of the glass structure.

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The work was supported by the State Committee for Scientific Research (Grant No. PBZ/KBN/13/T08/99/34). Additional information on the nanomaterials project is obtainable on www.inwat.pw.edu.pl/nanomaterialy/

References

1 L. Stoch, J. Therm. Anal. Cal., 54 (1998) 9.
2 L. Stoch, J. Therm. Anal. Cal., 77 (2004) 7.
3 I. Wacławska, M. Środa and L. Stoch, J. Therm. Anal. Cal., 65 (2001) 661.
4 L. Pauling, Nature of the chemical bonds, Cornell Univ. Press. Ithaca 1950.
5 E. Görlich, Z. Phys. Chem., 271 (1990) 169.
6 L. Stoch and M. Środa, J. Mol. Struct., 511–512 (1999) 77.