Journal of Non-Crystalline Solids 423–424 (2015) 50–57

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Structure and glass transition temperature of sodium-silicate glasses doped with iron

E.V. Belova [a,*], Ya.A. Kolyagin [b], I.A. Uspenskaya [a]

[a] Lomonosov Moscow State University, Leninskie Gory 1, Building 3, Dept. of Chemistry, Laboratory of Chemical Thermodynamics, Moscow, Russia
[b] Lomonosov Moscow State University, Leninskie Gory 1, Building 3, Dept. of Chemistry, Laboratory of Kinetics and Catalysis, Moscow, Russia

ARTICLE INFO

Article history:
Received 9 February 2015
Received in revised form 11 April 2015
Accepted 24 April 2015
Available online 19 May 2015

Keywords:
Sodium-silicate glass;
Solid-state ^{29}Si NMR;
RS;
Glass local structure;
Glass transition temperature;
Q^n species

ABSTRACT

Glass transition temperature (T_g) of iron-doped sodium silicate glasses $(100 - x)Na_2O \cdot xSiO_2 \cdot yFe_2O_3$ ($x = 75, 78, 81$ mol%, $y = 0.1$–17 wt.%) were determined by DSC method under different pressure (101.325, 5000, 10,000 kPa). DSC experiment showed nonmonotonic behavior (with dominating growth) of T_g and its changes under pressure for iron-doped glass with total iron content. ^{29}Si NMR of glasses with $x = 75$; 81 and y up to 2.75%, and Raman spectroscopy were applied for Q^n structural units estimation. In NMR spectra two signals are detected, average values of the shifts −105 ppm and −93 ppm, corresponding to Q^4 and Q^3. Quantities of the Q^4 and Q^3 units were achieved from spectra fitting, the last one rising with total iron content. Three bands (960–1000 cm^{-1}, 1080–1100 cm^{-1}, 1120–1170 cm^{-1}) were detected in Raman spectra, assigned as vibrations in Q^3 (Si net with Fe), Q^3(Si) and Q^4(Si) respectfully. Specialties in T_g behavior with total iron content correlates with intensity of 1080–1100 cm^{-1} bands in Raman spectra, 960–1000 cm^{-1} band intensity grows proportionally with total iron content. Relative band intensities were used to make half-quantitative calculations of Q^n content in glasses with high iron content. These estimations are compared with calculations from Zachariasen rules, revealing change in Fe(III) role from modifier to net-former.

1. Introduction

Silicate melts, their structure and properties are usual objects of geochemistry, glasses and metallurgical productions. Natural silicate melts often contain alkali, alkaline earth, aluminum and transition metal oxides, e.g. iron oxides, as the main components. In the glass technology iron gets into melt as impurity in trace amounts or specially been added in small quantities to the batch. Transition metals can influence the optical properties of the final glass and viscosity of the melt due to structural changes of matter.

The purpose of this work is to investigate the famous triad "composition–structure–properties" applied to iron-containing sodium-silicate glasses and to reveal some practically useful correlations. Glass transition temperature (T_g) was chosen as a structure sensitive property and solid-state ^{29}Si NMR and Raman spectroscopy were used to characterize local structure properties of iron-containing sodium-silicate glasses with fixed Na_2O/SiO_2 ratio and different iron content. A number of Q^n units (in Zachariasen theory) were applied as a quantitative characteristic of local structure.

Glass transition temperature, being itself a useful parameter in glass technology, is sensitive to structural changes, which can occur due to compositional changes [1–3] or pressure applied [4–10]. We investigated both these factors (x and p) in the present work. Due to relation with viscosity, dependence of T_g vs. composition variation can reveal structure-sensitive changes in viscosity behavior of the silicate at "low" temperatures (below softening point), which are important to the glass preparation procedures and their exploitation. According to IUPAC recommendation, glass transition temperature (T_g) is a temperature when the viscosity of glass becomes equal to 10^{13} P [5,10,11], so the most exact method to determine T_g is a viscosimetry. On the other hand, T_g value can be measured by dilatometry [1] and DTA or DSC [1,3] also, but one problem should be solved in this case. Results of those experiments are dependent on conditions of measuring, primarily, on the rate of scanning. Therefore, correlation between T_g values which had been determined by various techniques must be accounted at comparison of experimental data obtained by dynamic methods in various works. In addition, it should be kept in mind that heat capacity and volume relaxations might occur not at the same point.

The solid-state NMR is a common technique in local structure studies of glasses [12–16], but its sensitivity decreases with increasing paramagnetic ions (eg. Fe^{3+}) content. The IR and Raman spectroscopy are also a popular method for investigating local structure in amorphous silicates, alumosilicates, etc. [9,15,17–21]. As was shown, the relations between absolute areas of peaks (assigned as vibrations in Q^n units)

---

* Corresponding author at: Moscow State University, Leninskie Gory 1, Building 3, Dept. of Chemistry, Laboratory of Chemical Thermodynamics, Moscow, Russia.
E-mail addresses: catrine2@td.chem.msu.ru (E.V. Belova), kolyagin@mail.ru (Y.A. Kolyagin), ira@td.chem.msu.ru (I.A. Uspenskaya).

http://dx.doi.org/10.1016/j.jnoncrysol.2015.04.039

and structural units' quantities depend not only on the structural properties, but also on frequency, thickness and form of glass pieces, refraction indexes, baseline, etc. [9,15,18,22]. Therefore, the peak areas ratio is not strictly the same as the Q^i unit ratio (as in the case of NMR method) and preliminary calibration is necessary for quantitate characteristics of structure. Several authors use special corrections for calculating Q^n quantities [18] or ratios of relative areas with one frequency to another [22]. Another way is a calibration of the relative areas by known unit quantities, obtained from NMR experiment or calculated from Zachariasen rules [15]; such approach was used in this work.

2. Experimental

2.1. Glasses

The glasses were prepared in Pt crucibles in air at 1400 °C, with water quenching. This method is analogous to one described in [23], so we believe that compositions of glasses correspond to the initial raw batch. The mixtures were prepared from analytically pure materials. The sodium carbonate, silica, natural iron oxide provided Na_2O, SiO_2 and Fe_2O_3 respectively. The following compositions of glass matrixes $(100 - x)Na_2O/(x)SiO_2$ were chosen for glasses without iron ($x = 73$; 75; 78; 81; 83 mol%) and for iron-doped glasses ($x = 75$; 78; 81 mol%). Variable amount of iron oxide (0.1–17 wt.%) was added to each mixture of Na_2CO_3 and SiO_2 (see Table 1). XRD analysis was performed to all synthesized samples, only glasses without crystalline phase were studied in the present work. NMR method gave additional proof of amorphous state of samples; the peaks of crystalline phase are narrow ones, and they can be easily seen in samples with mixed crystalline and amorphous phases. EDX analysis of some glasses is presented in Table 2.

2.2. MAS NMR

^{29}Si MAS NMR experiments were performed on a Bruker AVANCE-II 400 spectrometer ($v^{29}Si = 79.5$ MHz) by using 4 mm double channel MAS probe with a spinning rate of 8 kHz. The experiments were recorded with π/2 pulse length of 2.5 μs, a recycle delay of 2 s and number of scans of 1024. The chemical shifts were referenced to TMS ($Si(CH_3)_4$). The NMR spectra were fitted with Gauss peaks in Dmfit software vers. dmfit#20111221 [24].

2.3. Raman spectroscopy

The Raman spectra were obtained on Renishaw InVia Raman Microscope (UFC MSU), in the range 100–2000 cm^{-1}, with approximate resolution 2 cm^{-1}. The samples (small chops <0.5 cm in diameter and 1–2 mm thickness) were excited with the 514.0 nm argon laser with a power of 20 mW, using 90° scattering geometry. The spectra were fitted with Gauss peaks in Fityk software, vers. 0.9.8 [25].

Table 1
The batch composition of the studied glasses doped with iron oxide.
(№ — number of sample).

№	Fe_2O_3, wt.%	Na_2O, mol.%	SiO_2, mol.%	Fe_2O_3, mol.%	№	Fe_2O_3, wt.%	Na_2O, mol.%	SiO_2, mol.%	Fe_2O_3, mol.%
Matrix (mol.%)					Matrix (mol.%)				
19% Na_2O/81% SiO_2					22% Na_2O/78% SiO_2				
1	0.1	18.99	80.97	0.04	11	0.15	21.98	77.96	0.06
2	0.25	18.98	80.92	0.09	12	0.65	21.95	77.81	0.24
3	0.55	18.96	80.83	0.21	13	1.5	21.88	77.56	0.56
4	1	18.93	80.70	0.38	14	2.75	21.77	77.20	1.03
5	1.5	18.89	80.54	0.56	Matrix (mol.%)				
6	4.5	18.68	79.65	1.67	25% Na_2O/75% SiO_2				
7	7	18.51	78.92	2.57	15	0.1	24.99	74.97	0.04
8	11.4	18.22	77.66	4.12	16	0.25	24.98	74.93	0.09
9	13	18.11	77.21	4.68	17	0.55	24.95	74.84	0.21
10	17	17.85	76.12	6.03	18	1.00	24.90	74.72	0.38
					19	2.75	24.74	74.23	1.03
					20	4.50	24.58	73.75	1.67
					21	7.00	24.35	73.07	2.58
					22	13.0	23.82	71.49	4.69

Table 2
Chemical analysis of some glasses.

Sample	Batch composition. mol.%			Glass composition. mol.%		
	Na_2O	SiO_2	Fe_2O_3	Na_2O	SiO_2	Fe_2O_3
No markings	17	83	0	15.4 ± 3	84.6 ± 3	0
	22	78	0	21.9 ± 2	78.1 ± 2	0
	25	75	0	23.8 ± 1	76.2 ± 1	0
	27	73	0	27.6 ± 3	72.4 ± 3	0
4	18.93	80.69	0.38	19.3 ± 1	80.0 ± 3	0.7 ± 0.2
7	18.51	78.91	2.58	19.3 ± 3	77.0 ± 3	3.7 ± 1

2.4. XRD

The X-ray powder diffraction analysis was carried out using a STADI-P (STOE) diffractometer (CuKα_1 radiation, $\lambda = 1.54059$°A) under ambient conditions ($T = 295$ K).

2.5. SEM-EDX

The ratio of Na/Si in the samples was determined using energy dispersive X-rays spectrometer INCA Energy 350 Premium with a silicon drift detector. Coverage was done at a working distance of 10 mm at a voltage of 30 kV in the "all-element" mode. The data accumulated in 90 points were processed statistically.

2.6. DSC and TG

DSC method was used for the glass transition measurements at the 204 HP Phoenix high pressure calorimeter (NETZSCH) in argon atmosphere with scanning rate 10 $K \cdot min^{-1}$. For all samples, the following thermal treatment and scanning program were used: heating up to 590 °C, isothermal annealing at 590 °C within 10 min, cooling to 400 °C, isothermal annealing at 400 °C within 10 min, and glass transition temperature registration in the heating process of the sample from 400 °C to 590 °C. TG analysis was made for some sodium-silica glasses quenched to water and in air. The measurements were performed under a high purity argon flow on a NETZSCH TG 209 F1 Iris instrument at a heating rate 10 $K \cdot min^{-1}$ from 40 °C up to 700 °C. The calorimeter was calibrated on the phase transition points of reference substances with the ISO 11357–11 standard for the temperature and heat flow. The results of thermoanalytical experiments were analyzed according to ISO 11357–1, 11357–2 and ASTM E-1269-95 standards using the NETZSCH Proteus Thermal Analysis software package.

3. Results

3.1. Glass transition temperature measurements

Two types of measurements were performed: at atmosphere and high pressure. The samples with matrix ratio $Na_2O/SiO_2 = 19/81$ were investigated at $p = 101.325$ kPa, 5000 kPa and 10,000 kPa; glasses with other sodium oxide/silica ratio were tested at normal pressure only. Excess pressure was created by inert gas with high purity (residual content of oxygen was 10^{-5}%). Experimental data were approximated with NETZSCH Proteus Thermal Analysis software. The glass transition temperature was determined as $T_{midpoint}$ — the point at which the curve is intersected by a line that is equidistant between two extrapolated baselines, according to ISO 11357-2.