Journal of Non-Crystalline Solids 481 (2018) 403–408

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Network connectivity and properties of non-alkali aluminoborosilicate glasses

Jun Xie, Herui Tang, Jing Wang*, Mengming Wu, Jianjun Han, Chao Liu

State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, 122 Luoshi Road, Hongshan, Wuhan, Hubei 430070, China

ARTICLE INFO

Keywords:
Aluminoborosilicate glasses
Network structure
NMR
Properties

ABSTRACT

The effects of alkaline earth metal oxides (RO) concentrations on the network structure and properties of non-alkali aluminoborosilicate glasses were studied. With the increasing of RO concentrations from 10 to 20 mol%, the number of Q^4 units decreased, while the number of Q^3 units increased. The $[AlO_4]$ units always predominated in Al groups, and the fraction of $[BO_4]$ among B groups increased from 2% to 10%. Meantime, the value of NBO/T increased from 0.48 to 0.70, indicating the weak network connectivity. The depolymerization of T-O-T network resulted in higher coefficient of thermal expansion, lower temperature of transition point, weaker durability in HF acid. While, the increasing in R^{2+} cations and $[BO_4]$ units led to the higher elastic modulus of glasses. The increasing in RO also enhanced the density, dielectric constant and durability in NaOH solution of glasses.

1. Introduction

Non-alkali aluminoborosilicate glasses are an ideal substrate material for TFT-LCD (Thin Film Transistor Liquid Crystal Display) and OLED (Organic Light-Emitting Diode) because of their excellent properties, such as low coefficient of thermal expansion (CTE), low density, high elastic modulus, high chemical durability, high thermal stability and high temperature of strain point [1–4].

The local structure of the network-forming cations (Si^{4+}, B^{3+} and Al^{3+}) in this glasses is still not clear enough, but it plays an important role in many essential physical and chemical performances [5,6]. The close relationships among compositions, structure and properties of traditional borosilicate glasses has been well studied [7–12]. For example, a good prediction of the network connectivity of boron in sodium borosilicate glasses was provided by Dell and Bray model [13], and the prediction of NBO (non-bridging oxygen) contents by using this model was in good accordance with direct ^{17}O NMR results [14]. Abd El-Moneim et al. proposed that the concentration of tetrahedral boron groups and linkages of B-O-Al became higher with the increasing fraction of network modifier cations with higher field strength, which made the connection of tetrahedral units close [15]. In many borate-containing glass systems, boron-11 wide-line MAS NMR was used to determine the fraction of $[BO_4]$ and $[BO_3]$ groups including symmetric and asymmetric trigonal boron groups [16,17]. In the reported paper, the coordination-state of Al^{3+} in aluminosilicate, aluminoborosilicate glasses were investigated by high-resolution NMR [18–26]. For instance, H. Li et al. reported that the increase of $[AlO_5]$ resulted in the enhancement of glass elastic modulus [26].

The structure of aluminoborosilicate glasses is more complicated than that of well-modeled borosilicate glasses because of the variable role of Al^{3+} cations. Non-alkali aluminoborosilicate glasses is also different from that alkali aluminoborosilicate glasses owning to the alkaline earth cations (R^{2+} = Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) with high field strength instead of alkali cations (R'^{+} = Li^{+}, Na^{+} and K^{+}) [27]. The structural differences between alkali aluminoborosilicate and non-alkali aluminoborosilicate glasses were attempted to understand. Lin-Shu Du et al. proposed the network mixing behavior in K-containing quaternary aluminoborosilicate glasses tend to follow the avoidance of linkages between tetrahedral aluminum and tetrahedral boron groups, while Ca-containing glasses prefer random mixing of Si, B, and Al by high resolution ^{11}B, ^{27}Al and ^{17}O MAS NMR [27].

In this work, the non-alkali aluminosilicate glasses with different RO concentrations were prepared. The chemical environments of network-former cations were investigated by ^{29}Si, ^{27}Al, ^{11}B NMR. And the density, dielectric constant, elastic modulus, CTE, T_g and chemical durabilities of glasses were characterized. Furthermore, the relationships among compositions, network connectivity and properties of glasses were discussed.

* Corresponding author.
E-mail address: wangj@whut.edu.cn (J. Wang).

https://doi.org/10.1016/j.jnoncrysol.2017.11.023
Received 23 August 2017; Received in revised form 3 November 2017; Accepted 10 November 2017
Available online 16 November 2017

Table 1
Compositions of glass samples (mol%). The molar ratios of MgO:CaO:SrO are 4:3:3.

Glasses	Oxide composition						*x* value
	SiO_2	Al_2O_3	B_2O_3	MgO	CaO	SrO	
R_{10}	71.0	11.0	8.0	4.0	3.0	3.0	10
R_{12}	69.0	11.0	8.0	4.8	3.6	3.6	12
R_{14}	67.0	11.0	8.0	5.6	4.2	4.2	14
R_{16}	65.0	11.0	8.0	6.4	4.8	4.8	16
R_{18}	63.0	11.0	8.0	7.2	5.4	5.4	18
R_{20}	61.0	11.0	8.0	8.0	6.0	6.0	20

2. Experimental

2.1. Glass preparation and characterization

The nominal compositions of glasses were $(81 - x)$ SiO_2-$11Al_2O_3$-$8B_2O_3$ − xRO (in mol%), and the detailed oxide compositions were listed in Table 1. The oxides were introduced by analytical reagents of SiO_2 (≥ 99%), Al_2O_3 (≥ 99%), B_2O_3 (≥ 98%), MgO (≥ 98.5%), $CaCO_3$ (≥ 99%) and $SrCO_3$ (≥ 99%) respectively. The well-mixed glass batches were melted at 1640 °C for ~2 h in a Pt-Rh (Pt:Rh = 9:1) crucible to obtain the bubble-free glassy melt. Then the melts were quickly poured onto a preheated foundry iron mould to form glasses. The as-prepared glasses were annealed at 650–700 °C for 2 h to eliminate the thermal stress.

It was likely that a significant proportion of boron volatilized at high temperature, and caused deviations from nominal compositions. When taking into account this, each sample was added an additional 15% B_2O_3 to compensate for the volatilization before melting. For example, the 8 mol% B_2O_3 of R_{10} were equivalent to 8.46% in weight of oxides, and additional 8.46 × 15% grams of B_2O_3 were added to the well-mixed batches per 100 g of oxide. The practical proportions and volatility of B_2O_3 measured by methods of chemical analysis were listed in Table 2. The test method was followed the national standard method of China. From the results of quantitative analysis, the volatiles of B_2O_3 in all samples were not exactly the same, but the practical concentrations of B_2O_3 were close to nominal values. As given in Table 2, the deviations of boron content were no > 5%. So the deviations from nominal compositions were neglected in the calculation to simplify the process of understanding.

2.2. Nuclear magnetic resonance spectroscopy

High-resolution solid NMR is one of the most effective methods to study the microstructure of glasses at the atomic scale [28–30]. NMR is a precise detection of atomic selective technology. When the atoms are placed in a stabled strong magnetic field, they can generate a resonance signal with a pulse of particular frequency because of every atomic specie have a nuclei possessing a non-zero spin (the nuclear spin I). The essential information of different atomic chemical environment can be acquired through NMR study. In this work,we have selected the important nucleus of network-former cations: ^{29}Si (I = 1/2), ^{27}Al (I = 5/2) and ^{11}B (I = 3/2) for NMR detection.

The spectrums of ^{27}Al and ^{29}Si MAS NMR were obtained on a Bruker VANCE III 400 spectrometer (B_0 = 9.6 Tesla), while ^{11}B data were recorded by a Bruker AVANCE III 600 spectrometer. The frequency of ^{27}Al, ^{29}Si, ^{11}B data were 104.26 MHz, 79.49 MHz, 192.41 MHz respectively. Spinning speeds of 12 kHz, 6 kHz, 18 kHz at magic angle and 4 mm, 7 mm, 6 mm rotors were chosen for ^{27}Al, ^{29}Si, ^{11}B separately. The pulse sequences for ^{27}Al, ^{29}Si, ^{11}B data collection were single pulse, with the relaxation delays of 2s, 5s, 10s.

2.3. Glass properties characterizations

Some typical physical and chemical properties of glasses were tested, such as density, coefficient of thermal expansion, elastic modulus, dielectric constant and chemical durability. The densities of glasses were carried out on the basis of Archimedes drainage with an analytical scale by neglecting the buoyancy of air. The thermal expansion curves of glasses were collected on a dilatometer (DIL402C, NETZSCH, German), and the characteristic temperatures of T_g (temperature of glass transition) were determined from the thermal expansion curves. The elastic modulus of glasses was collected on a ceramic experimental system (MTS810 100KN, MTS Inc. America). The dielectric constants of glasses were obtained on an impedance analyzer (HP4294A, Agilent Technologies Inc. America). The glasses were cut into the dimensions 30 mm × 10 mm × 2 mm and optical polished for chemical durability test. Some of the glass sheets were dipped into 10 vol% HF solution at 20 °C for 20 min, and some of the glass sheets were dipped into 5 wt% NaOH solution at 95 °C for 6 h. The values of weight loss ratio (WLR) were calculated by followed formulation (1).

$$WLR = (m_0 - m_1)/S \times 100\% \quad (1)$$

m_0: the mass of ultrasonic cleaning before etching.
m_1: the mass of ultrasonic cleaning after etching.
S: the surface area of each sheet.

3. Results and discussion

3.1. Aluminum-27 NMR

The ^{27}Al MAS NMR spectra of glasses with 10–20 mol% RO were showed in Fig. 1. Al (I = 5/2) is one kind of quadrupole nuclei (I > 1/2), that the spectra are subjected to a quadrupole expansion even under MAS NMR [26]. However, the position of main peaks was still clearly presented in spectroscopy. The typical chemical shift δ_{iso} (ppm) of ^{27}Al NMR spectrum normally centered around 50 ppm–70 ppm (four-coordination, [AlO_4]), 30 ppm–40 ppm (five-coordination, [AlO_5]) and 0 ppm–20 ppm (six-coordination, [AlO_6]), and the predominant of [AlO_4] groups among Al groups also reported when (R′$_2$O or RO)/Al_2O_3 > 1 [27,25,31]. In many investigated aluminosilicate glasses, δ_{iso} of ^{27}Al decreases by about 5 ppm for each [SiO_4] connected to [AlO_4] [32]. As shown in Fig. 1, the main peaks of each spectrum from our glasses located around 50 ppm, which indicated the vast majority of Al^{3+} formed [AlO_4] groups. The widened signal at lower chemical shift δ_{iso} was mainly attributed to the second-order quadrupole effect [22], and the signal from [AlO_5] and [AlO_6] were not detected. The small and sharp peaks at about − 20 ppm were mainly caused by background signal from the rotor.

Table 2
The quality content of B_2O_3 in all samples (wt%). All data are calculated only for oxides.

Sample NO.	R_{10}	R_{12}	R_{14}	R_{16}	R_{18}	R_{20}
Nominal ratio (%)	8.46	8.45	8.44	8.43	8.42	8.41
Proportion before melting (%)	9.61	9.60	9.58	9.57	9.56	9.55
Measured proportion after melting (%)	8.69 ± 0.13	8.80 ± 0.15	8.77 ± 0.18	8.75 ± 0.18	8.83 ± 0.12	8.81 ± 0.10
Volatility (%)	9.57	8.33	8.46	8.57	7.64	7.75