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ScienceDirect
Journal of Non-Crystalline Solids 354 (2008) 956–961
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

# Effects of mixed alkaline earth oxides additive on crystallization and structural changes in borosilicate glasses

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Received 8 November 2006; received in revised form 14 July 2007
Available online 17 September 2007

**Abstract**

The effects of mixed alkaline earth oxides on crystallization and structural changes in a multi-component borosilicate glass system are studied by using X-ray diffraction (XRD) and transmission electron microscope (TEM). It is found that the crystallization is decreased with increasing alkaline earth oxide content and there are also a series changes occurred in TEM images. This paper introduces the conception that alkaline earth ions tend to occupy their preferred sites regardless of glass systems. This conception is assisted to explain the TEM images to some extent by suggesting a simple structural model about non-bridging oxygen in glass network. The conception also indicates a 'blocking effect' existing in such a multi-component borosilicate glass system, which may be responsible for XRD results in chief. In addition, the structural model suggested by TEM results refers a new unit of Si–O–$M^{2+}$–O–B, which helps in understanding the minimum exhibits in XRD results. Moreover, a dielectric test is taken to study glass properties in detail.


*PACS:* 61.43.Fs; 61.80.Fe; 61.10.Nz; 64.75.+g

*Keywords:* Crystallization; X-ray diffraction; Mixed alkali effect; STEM/TEM; Borosilicates; Short-range order

## 1. Introduction

Nowadays, due to its excellent transparent, low thermal expansion coefficient, high soften temperature, and a high resistance to chemical attack, borosilicate glass plays an outstanding part in a wide variety of technically orientated glass application [1]. In particular, the float borosilicate glass, which is produced by micro-float process, has some remarkable performance in addition, such as excellent transmission, fine surface (very flat and smooth), high quality, extremely fault free [2]. Therefore, it allows access to new and high tech special glass applications, for example: fittings in microwave appliances, special fire-resistant glass, protective panels for spotlights and high-power floodlights, glass for solar collectors, optical filters, display glass, DNA sequencers, etc.

However, up to now, the crystallization is still a serious problem during the manufacture of float borosilicate glass. Many researches have been made to investigate the mechanism of crystallization in borosilicate glass. It was found that cristobalite could be formed when an initially amorphous borosilicate glass was fired at temperatures of 700–1000 °C [3]. Phase separation was the key step in this crystallization, as activation energy analysis [4] suggested that the devitrification is controlled by the transport of alkali ions in borosilicate glass. According to this, several crystalline oxides, such as $Al_2O_3$ [3,5] and $Ga_2O_3$ [6] have been previously identified to inhibit cristobalite forming during firing of the borosilicate glass. Kinetic results showed that these oxides had a strong coupling reaction with alkali ions in the borosilicate glass, diverting the transport of alkali ions from the desired target (cristobalite) to a more attractive but harmless target (crystallization inhibitor). Nevertheless, because of their high electric-filed intensity, the addition of $M^{3+}$ would increase the viscosity of

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doi:10.1016/j.jnoncrysol.2007.08.027

glass notably. Thus, it would increase the working temperature significantly, and then cause a series problems in many aspects during the float borosilicate glass manufacture, e.g. erosion of refractory, corrosion of float medium.

Therefore, proceeding from inhibiting the transport of alkali ions, this study is attempting to find a new way to solve the problem of the crystallization in borosilicate glass. The mixed alkaline earth oxides are adopted here, in the light of that they may work in a similar way like mixed alkali effect (MAE), which would inhibit the transport of alkali ions. In addition, previous studies showed [7] that $Ca^{2+}$ ions would decrease glass viscosity in high temperature range while increase it in low temperature range, so that this study is introducing a mixture of CaO and MgO with the mass ratio of 2:1. Moreover, the kinetic research [8] presented that the precipitation of cristobalite exhibited a characteristic incubation period ranging from 60–120 min at 700 °C to 3–5 min at 1000 °C. Thus, the glass samples are thermal treated at 850, 950 and 1050 °C, respectively for 3.5 h, and then taken an X-ray diffraction (XRD) test in order to examine their crystallizability. Transmission electron microscope (TEM) and dielectric test are also carried out to understand the structure and properties of the samples in detail.

## 2. Experimental

The glass samples, contained (80.4−x) mol% $SiO_2$, 11.2 mol% $B_2O_3$, 2.1 mol% $Al_2O_3$, 4.8 mol% $Na_2O$, 0.8 mol% $K_2O$ and $x$ mol% MO, were prepared by melting at 1700 °C and then annealing at 560 °C for 2 h. Here the symbol 'MO' represents a mixture of CaO and MgO with the mass ratio of 2:1, and the '$x$' represents the total concentration of MO, which is equal to 0.7, 1.3, 1.9, 2.5, 3.0 and 3.6 mol%, respectively.

Then the glass samples were crushed and undergone an isothermal treatment at 850, 950 and 1050 °C, respectively for 3.5 h. The crystallizability of the thermal treated samples was determined by X-ray diffraction (XRD) analysis, using D/max-RA XRD.

The transmission electron microscope (TEM) specimens were prepared by grinding the annealed glass into powders in ethanol and mounting suspended pieces in a holy-carbon-film-covered cope grid. These specimens were then observed by a JEM-100CXII TEM at 160 kV. The dielectric properties of the annealed glass samples were measured by a Precision Impedance Analyzer (HP4294A-LRC).

## 3. Results

### 3.1. TEM results

Fig. 1 shows a series bright-filed TEM images for the samples, which were annealed at 560 °C for 2 h with the concentration alkaline earth metal oxides ranging from 0.7 to 3.6 mol%. All images show the typical image of electron irradiation induced phase separation in glass, consisted with earlier reports [9–12]. However, it is interesting to note that some differences can be observed when the MO amounts are changed. When the content of MO is below 1.9 mol%, as shown in Fig. 1(a)–(c), the phase decomposition occurs only near the edge of powder, while in Fig. 1(d)–(f), it seems that the phase separates more deeply into the inner of the sample, and the dark particles appear more isolated with each other. So that it is indicated that there may be some changes in glass structure occurred with the variation of MO content, which will be discussed below in detail.

### 3.2. XRD results

Fig. 2(a) shows the XRD patterns for the samples thermal treated at 950 °C for 3.5 h with different MO content. Cristobalite is the unique crystallization phase of the borosilicate glasses. It can be found that in Fig. 2(a), the intensity of cristobalite peak continuously decreases with increasing mixed alkaline earth oxide and reaches the minimum at 3.0 mol%. The intensity of (1 1 1) face as a function of MO concentration are shown in Fig. 2(b). A curve fitting of experimental data is made in Fig. 2(b), and it allows extrapolating to zero MO content. This extrapolation suggests that crystallization may be more intense for the glass without any alkaline earth oxide addition.

Furthermore, Fig. 3 presents the XRD patterns of the samples with 1.3 mol% MO contained thermal treated at 850, 950 and 1050 °C for 3.5 h. It shows a direction of temperature changes in the crystallizability. The glass crystallizability increases with the thermal treatment temperature increasing from 850 to 950 °C. While it decreases intensively with the temperature further increasing from 950 to 1050 °C.

### 3.3. Dielectric results

The complex dielectric constant of a material medium is represented by two parts: $\varepsilon = \varepsilon' + j\varepsilon''$, where ε' is the real part (dielectric constant) and ε'' is the imaginary part (dielectric loss). The relation between ε' and ε'' defines a loss tangent $\tan\delta = \varepsilon''/\varepsilon'$. Fig. 4 presents the loss factor tangent tan(δ) versus ln(f) for the annealed glass samples. It is suggested that the relaxation dissipation is the main mechanism for dielectric loss in the studied glass system. The dielectric loss decreases with increasing MO content and the minimum is observed at 3.0 mol% MO content.

## 4. Discussion

### 4.1. Effect of the MO amounts on glass structure

Electron irradiation induced phase separation or decomposition in glasses is a complex phenomenon. In previous studies, Jiang et al. [9,13] suggested that the tendency for the elimination of non-bridging oxygen atoms (NBO) through the removal of cations in several silicate glasses