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Structural Investigations on Sodium Rich Silicate Glass Ceramics

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Abstract

Glasses in the system $x\ (Na_2O)(100-x)\ SiO_2$, ($40 \leq x \leq 65$ mol%) were prepared using ordinary cooling technique. The presence in the silicate network of relatively high concentrations of Na_2O has been found to have a significant influence on its microstructure. Structural changes in the studied glass network were followed by DSC (Differential Scanning Calorimeter), XRD (X-Ray Diffraction), TEM (Transmission Electron Microscopy) and NMR (Nuclear Magnetic Resonance). Addition of up to 50 mol% Na_2O to SiO_2 results in breaking some of Si-O-Si bonds and as a direct result non-bridging oxygen atoms (NBO) are the well-formed species. But in the modifier-rich silicate glasses (Na_2O = 50 and 65 mol%), beside formation of NBO ions, a relatively high portion from Na_2O was consumed to form crystalline clusters species. In such the case, Na^+ ions were proved to have six and seven coordination numbers with oxygen ions as a direct first neighbor. These types of coordinated sodium are evidenced (from ^{23}Na NMR spectroscopy) to be dominant in the modifier rich glasses. The coordination number of Na is increased and the coordination of silicon atoms is decreased with increasing Na_2O content. TEM, (EDP) and XRD spectra in correlation with NMR results have confirmed the presence of crystalline cluster species enriched with Na+ ions.

Keywords

Na Coordination Sites, Clustered Species, Morphological Investigations

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1. Introduction

Oxide glasses which are enriched with modifier oxides have been previously studied [1-7]. It was found that the network of the modified glasses and glass ceramics should contain glass forming atoms like Si atoms bridged to four oxygen atoms. Some of oxygen atoms consumed to bridge between two Si atoms (bridging oxygen, BO) and the rest are bonded to one Si atom (non bridging oxygen, NBO). The modifier cations (Na or Li or Cs, etc.,) are situated in random places throughout the silicon oxygen network to compensate the electric charges. [5-8].

^{29}Si NMR spectroscopy can simply differentiate between different fraction of BO and NBO [2, 4, 5, 7]. On the other hand, alkali-rich glasses can involve an extra type of oxygen species which is consumed to form crystalline clusters [5, 7]. In such case, increasing coordination of oxygen atoms around the alkali ions will result in developing alkali silicate phases such as Li_2SiO_3 or Na_2SiO_3. Formation of these crystalline clusters has to accompanied by formation of alkali-rich percolation channels in the main glass network [3, 4-7]. The simple phases containing some types of crystalline clusters can possess different polymorphs which may play a useful role in changing some of the physical properties such

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as nonlinear optical behavior. The network of the silicate and or telluride glasses can be formed in three different types [2-7] which are BO, NBO and, free O^{2-}. The latter is consumed to form a bridged bond between the alkali ions in the form of six and seven coordination. Specific NMR and FTIR results have indicated that this type was mainly present in alkali rich glasses (glasses rich with modifier oxide) over a wide range of composition and it increases in abundance with increasing modifier content [5, 6, 8, 9].

Majority of the previous studies have concerned with low and intermediate alkali based glasses (≤ 35 mol%. alkali oxide), since both BO and NBO atoms are the main formed types [1, 4, 9]. The situation is different to some extend in the glasses containing higher concentration from the modifier oxide [6]. This may be because a specific concentration of (O^{2-}) species is reported to be present [5, 6, 7, 10]. In this respect, a combined evaluation of ^{23}Na NMR, DSC, XRD, and TEM-ED techniques will be applied to provide a basis for further systematic progress in the field of alkali rich silicate glasses. To our information, this is the first time that the existence of a nanostructure based on Na_2O rich silicate glass ceramics has been inferred in the present study which may provide new ordered materials. The local configurations around sodium ions in the glass and their distributions have strong implications for the dynamic and static properties of the materials which may play an important role in the magmatic processes.

2. Experimental

2.1. Glass Preparation

Glasses in the system x (Na_2O)(100-x) SiO_2, (40≤ x ≤ 65 mol%) have been prepared using the ordinary cooling technique. Reagent grades (Aldrich company) Na_2CO_3 (purity 98.93), and SiO_2 (purity 99.89) are the raw materials used in glass preparation. The glasses were prepared by melting the mixtures in a platinum crucible in an electric furnace. The product was melted between 1350°C to 1550°C for 2 hours depending on the composition. The melts were cooled to reach room temperature by pouring and pressing them between two stainless steel plates. After solidification of the glass, it reheated in an electric furnace at tempering temperature of 250°C for 3 hours to release internal stresses.

2.2. Experimental Techniques

The amorphous or crystalline nature of material structure was examined by X-ray diffraction measurements which were carried out on the powdered samples. The measurements were carried out at (Metallurgical Institute, El-Tebbeen-Helwan, Cairo) using a Bruker D8 Advance powder XRD system with a Cu Kα radiation. The range of the diffraction angle (2θ) was changed from 4° to 70° using a dwell time of 0.4 seconds.

Transmission electron microscopy was widely used to examine the morphology in the bulk of the sample. The measurements were carried out on TEM unit (Mansura University) equipped with electron diffraction apparatus of type (JEOL-JSM-6510 LV Model) with a working accelerating voltage of 200 kV and an increasing size image up to 300.000X.

^{23}Na MAS NMR measurements were carried out using solid state MAS NMR technique (JEOL RESONANCE GSX-500 spectrometer, Mansoura University, EGYPT). The obtained spectra were recorded at magnetic field (11.747 T). The resonance frequency was approximately 132.3 MHz and the applied spinning frequency was 14 KHz. 90° pulses of acquisition time of 2.7 μs are applied. The cycle times of 5s. and 200 scans have been taken. The chemical-shift was referenced to NaCl whose chemical shifts was set at 0 ppm.

3. Results and Discussion

3.1. DSC, XRD and TEM-EDP Analysis

The DSC curves of the investigated glasses are shown in Figure 1. They showed some resolved exothermic peaks corresponding to the crystallization processes. As a result, the glass phase in the sample containing 40 and 50 mol% Na_2O is transformed into some crystalline phases represented by the appearance of more new exothermic peaks in glasses enriched with alkali oxides (65 mol% Na_2O). Such exo-peaks (at 600°C and 775°C) are typical for glasses with a high crystallization tendency [11-13] and formation of clustered species from sodium silicate species [11].

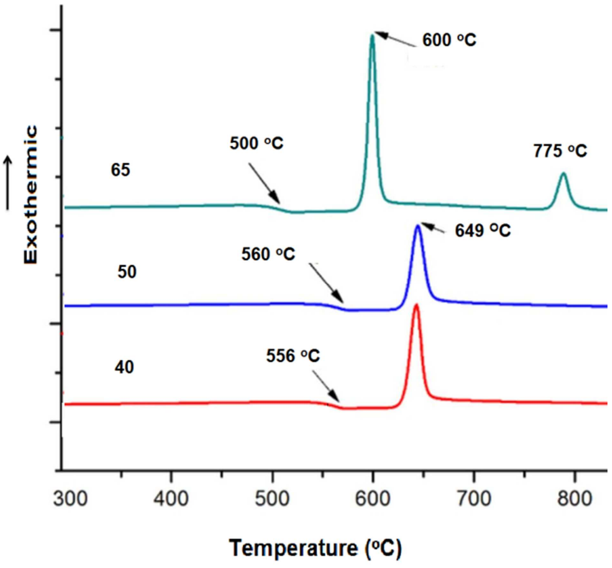

Figure 1. Differential scanning calorimetric plots (DSC) for glasses containing 40, 50 and 65 mol% (Na_2O).

The increase of crystalline species leads to the conversion of amorphous glass to glass ceramics [3, 11-13]. Appearance of the well resolved exothermal peaks around 647°C and at 649°C in the spectrum of glass containing 40 and 50 mol% sodium oxide, respectively reflects the precipitation of some crystalline structure [11, 12]. It also can be noticed that these exothermic peaks are shifted from their position with increasing Na_2O concentration. This shift (600°C and 775°C) may be attributed to the formation of new nano-size clusters or crystallites Na_2SiO_3 whose concentration increases with increasing the alkali content [6, 13, 14]. Presence of more than one exothermic peak in glasses of higher Na_2O content (65 mol%) may be attributed to a transformation of Q^4 (four coordinated silicon) to another SiO_4 units (Q^3, Q^2 and Q^1) containing more non-bridging oxygen atoms (NBO). Increasing of the latter, results in increasing the concentration of modifier ions of Na^+ to compensate the charge of NBO atoms. It can be suggested that glass containing 65 mol% Na_2O contains two separated phases, one is enriched with Na^+ cations (at 600°C) and the other is silica rich (at 775°C). From NMR results, it was found that the coordination number of the Na^+ ions is increased with modifier addition which may play the main role in increasing the crystallization ability [1, 3, 6, 12, 14]. As a result, different exothermic peaks have appeared in DSC curve of the Na- rich glasses.

X-ray powder diffraction is a powerful method used to identify ordered clusters in the tested samples. XRD spectra of the investigated glasses are shown in Figure 2. The spectrum of the glass containing 40 mol% Na_2O contains peaks which are less resolved than those of glasses of higher Na_2O concentration. Extra well-resolved diffractions patterns were observed only for glasses which are enriched with Na_2O (50 and 65 mol%). It can be noticed from this Figure that with increasing Na_2O/SiO_2 molar ratio, the intensity of the diffracted peaks increases. The height of the peaks (intensity) depends on the number of crystallites diffracting the X-rays. Thus a sample containing more finely ordered crystals will give higher and narrower peaks than that containing coarsely and disordered structure [3, 7, 12, 15]. This consideration is further supported by the argument presented previously on alkali rich glasses [3, 7, 6, 15].

The spectra presented in Figure 2 clearly indicate that all of the three samples were crystallized but to a different extend. The lowest degree of crystallization is observed in the sample containing 40 mol% Na_2O, since only one well-formed peak and a pronounced halo typical for the vitreous state are the dominant features of the spectrum. The sample with 50 mol% Na_2O has crystallized to a noticeably larger extent (a larger set of peaks and a hardly noticeable halo). The sample with 65 mol% Na_2O seems to be completely crystalline (a large set of well- defined peaks and absence of any halo).

In this respect, it can be suggested that sodium rich glasses (Na_2O > 40 mol%) can contain crystalline structures as the dominant species. While at lower concentrations, the modifier oxide is consumed to form NBO atoms in silicate network through the transformation of SiO_4 to another units containing more NBO atoms. The formation of crystallites from Na cations may be considered as the main reason for resolving of the XRD bands in the glass containing 65 mol% Na_2O.

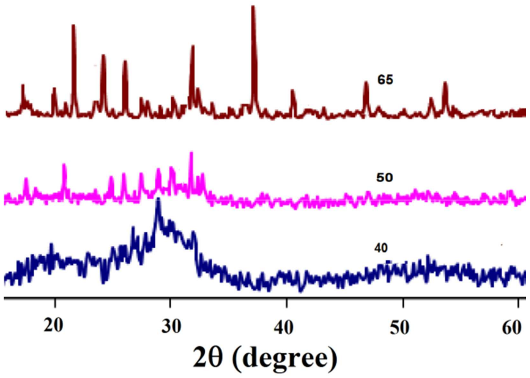

Figure 2. XRD patterns for glasses of different sodium oxide concentrations.

The interpretations presented above are confirmed by TEM-EDP micrographs (Figures 3 and 4), since the EDP (Electron Diffraction Pattern) of selected species of the network presents a highly crystalline structure of the glass containing 65 mol% sodium oxide. TEM micrograph in Figure 4 (a) and (b) showed more accumulated crystalline species than that in Figure 3 (a) and (b), which showed less ordered structure at lower Na_2O concentration (40 mol% Na_2O).

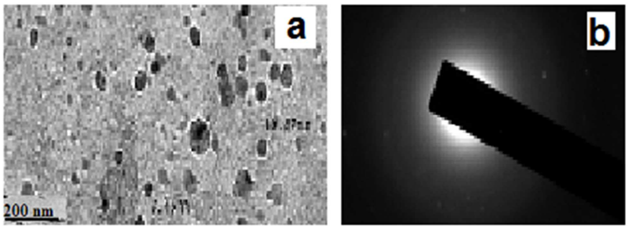

Figure 3. (a) TEM and (b) EDP micrographs of glass containing 40 mol% sodium oxide.

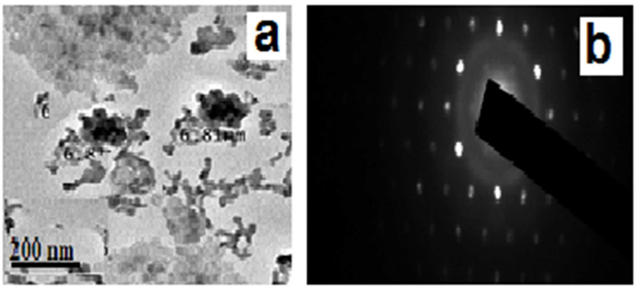

Figure 4. (a) TEM and (b) EDP micrographs of glass containing 65 mol% sodium oxide.

3.2. ^{23}Na NMR Spectroscopy

The strong differences between NMR spectra of glasses containing 40 and those containing 65mol% Na_2O (Figure 5) affirm that ^{23}Na MAS NMR spectroscopy at a high field (11.74 T) is an effective probe for local Na ion environments and their distributions in SiO_2 glass network. The distributions of Na-O distances in sodium silicate glasses can be obtained from the distribution of the isotropic chemical shift (δ_{iso}) which in most cases is mainly due to differences in distances between Na cation and {Si-O-Si}. In addition, the difference in chemical shift values between glasses of 40 and 65 mol% Na_2O can be attributed to the changes of the type of oxygen clusters around Na ions. The variation of bond length reflects the different degree of interaction between Na and each type of BO. The d (Na-O) is compositional dependent and manifests the differential reactivity between Na and the different types of BO or NBO oxygens. This trend can be found in the binary silicate glasses, in which d (Na-BO) is apparently longer than the d (Na-NBO). In this study, we provide new insights into the nature of Na cations distribution in sodium rich glasses [5, 16-20]

The present data together with those from the literature, suggest that the ^{23}Na isotropic chemical shift correlates well with both the Na coordination and the degree of polymerization (characterized by NBO/Si) of glasses. The presence of dissimilar network formers such as silicate, borate and borosilicate affects the ^{23}Na isotropic chemical shift [16-24]. Thus it appears that the average Na coordination environments are more sensitive to the presence of high concentration of the alkali oxides. Further studies on silicate glasses containing sodium oxide are necessary to confirm this conclusion.

Figure 5 represents ^{23}Na NMR spectra of glasses of the low modifier content (40 mol% Na_2O) and of crystalline glass (65 mol% Na_2O), respectively. As shown in this Figure, two different resolved resonance peaks appear in the spectrum of Na_2O rich glass. This suggests the presence of different sites or coordination of Na ions in the crystal (both 6 and 7 coordination) [19, 20]. The two coordination of sodium atoms are represented by the peaks centered at different values of chemical shift. The two obtained values of chemical shift may refer to the coordination of Na ions [20, 24]. In the glass of 65 mol% sodium oxide, both six and seven coordinated Na in crystalline clusters are suggested to be present. The well-formed crystalline species in the glass of 40 mol% sodium oxide is lower, since the presence of a broad spectrum of extremely high area at chemical shift (1 ppm) confirms the distribution of Na cation in the vicinity of NBO atom as a charge compensator only [25]. On the other hand, the area of this resonance is abruptly decreased upon addition of 65 mol% Na_2O and a more intense resonance at about 10 ppm is resolved when it is compared to that of the glass containing 40 mol% Na_2O. A slight shift to more negative values of the broad ^{23}Na resonance indicates an increase in the mean coordination number of sodium in glasses by increasing alkali oxide concentration from 40 to 65 mol% Na_2O. This probably arises from the decrease in sodium content within the silicate rich phase due to the separation of most of Na_2O to form Na_2SiO_3 crystalline clusters.

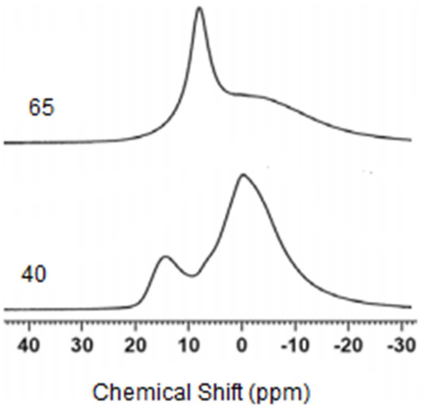

Figure 5. ^{23}Na MAS NMR spectra of glasses containing 40 and 65 mol% Na_2O.

4. Conclusions

Addition of Na_2O to SiO_2 glass increases NBO concentrations. Addition of up to 50 mol% Na_2O to SiO_2 results in breaking some of Si-O-Si bonds and as a direct result non-bridging oxygen atoms (NBO) are the well-formed species. The sodium rich silicate glasses (Na_2O > 40 mol%) have been found to contain nano-cluster which is related to presence of crystalline species of Na_2SiO_3 species. The DSC results suggest that glass containing 65 mol% Na_2O contains two separated phases, one is enriched with Na^+ cations (at 600°C) and the other is silica rich (at 775°C). TEM-EDP, and XRD spectroscopic analysis have revealed that, the nano-crystalline species are congregated with one another severely to make a large region of clusters. ^{23}Na NMR spectroscopy has confirmed that both 6 and 7 coordinated sodium are formed as the base structure of the clustered sodium silicate phases. The coordination number of Na is increased and the coordination of silicon atoms is decreased with increasing Na_2O content.

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