CRYSTALLIZATION OF $1Na_2O \cdot 2CaO \cdot 3SiO_2$·GLASS MONITORED BY ELECTRICAL CONDUCTIVITY MEASUREMENTS

Ana Candida M. Rodrigues*, Gilberto Tadashi Niitsu, Edgar Dutra Zanotto
Laboratório de Materiais Vítreos, Departamento de Engenharia de Materiais, Universidade Federal de São Carlos, C.P. 676 -13565-905 São Carlos, SP, Brazil
acmr@power.ufscar.br

Miguel Oscar Prado
Comisión Nacional de Energía Atómica-Centro Atómico Bariloche- 8400 S.C. de Bariloche (RN)-Argentina

Vladimir Fokin
S.I.Vavilov's State Optical Institute, Babushkina 36/1, St. Petersburg, 193171 Russia

Compositional changes during the crystallization of stoichiometric $1Na_2O \cdot 2CaO \cdot 3SiO_2$ glass were followed by EDS examination of solid solution crystals. The growth of sodium-enriched crystals in this stoichiometric glass drastically decreased the sodium content in the glassy matrix, confirming previous studies. Glassy, partly crystallized and fully crystallized samples were monitored by electrical conductivity measurements, using impedance spectroscopy. Based on a comparison of the samples' electrical conductivities and activation energies we found that, starting from a crystallized volume fraction of about 0.5, the crystalline phase dominated the electrical conductivity. Electrical conductivity is a highly sensitive property that can indicate changes in the composition of the glassy matrix and contribute to investigations of complex heterogeneous systems such as partly crystallized glasses and glass-ceramics.

(Key words: homogeneous nucleation, crystallization, electrical conductivity, $1Na_2O \cdot 2CaO \cdot 3SiO_2$ glass, impedance spectroscopy)

I. Introduction

The description of the properties of heterogeneous systems is one of the challenging problems of modern materials science and partly crystallized glasses and glass-ceramics are typical, important, heterogeneous systems. In most systems, the composition of the crystal differs from that of the parent glass, which may severely complicate the crystallization pathways. Recently, the formation of $1Na_2O \cdot 2CaO \cdot 3SiO_2$ ($N_1C_2S_3$) crystals in a glass of the same nominal composition was shown to occur via nucleation of solid solution nuclei, which are considerably enriched in sodium, and whose composition varies toward the stoichiometric one during the course of the phase transformation [1]. The deviation of the nuclei's composition from the stoichiometric one was interpreted as resulting from a decrease in the thermodynamic barrier for nucleation as compared with that for stoichiometric nuclei. Thus, crystallization of this particular stoichiometric glass is accompanied by compositional changes of the crystals and glassy matrix! All these changes make this glass quite attractive for investigations into electrical conductivity. This paper presents and discusses electrical conductivity measurements from the parent glass to fully crystallized glass (glass-ceramic) by impedance spectroscopy, together with EDS data on the compositional evolution of crystals and glassy matrix.

II. Experimental

Sample preparation

To obtain samples with different crystallized volume fractions, α, samples of the parent glass were exposed to heat treatments at T=690°C for different periods of time. This temperature considerably exceeds the temperature of the maximum nucleation rate (T_{max}=600°C), hence corresponding mainly to the growth of crystals. Fully crystallized samples were obtained by double heat treatment at T_1=605°C and T_2=690°C.

The α values were estimated by standard methods using optical microscopy. The average compositions of the crystals were analyzed by EDS using a fully crystallized glass as a standard. The compositions of glassy matrix were then calculated based on the parent glass and crystal compositions, taking into account the values of α.

Impedance spectroscopy

Electrical conductivity measurements were carried out by impedance spectroscopy, which employs alternating current in variable frequencies. The main feature of this method, which is widely employed in investigations of semiconductors and ionic conductors, is that it allows for the separation of electrical phenomena with different time constants, e.g., electrode and bulk properties [2]. Impedance data of a homogeneous ionic conducting glass, represented as a Nyquist diagram (x–axis: the real part of the impedance; y-axis: the negative of the imaginary part of impedance), commonly show a semi-circle followed by a spike, which is characteristic of ionic conduction. The sample's resistance (R) is read at the intersection of the semicircle with the x-axis at low frequencies. The electrical conductivity σ can thus easily be calculated employing:

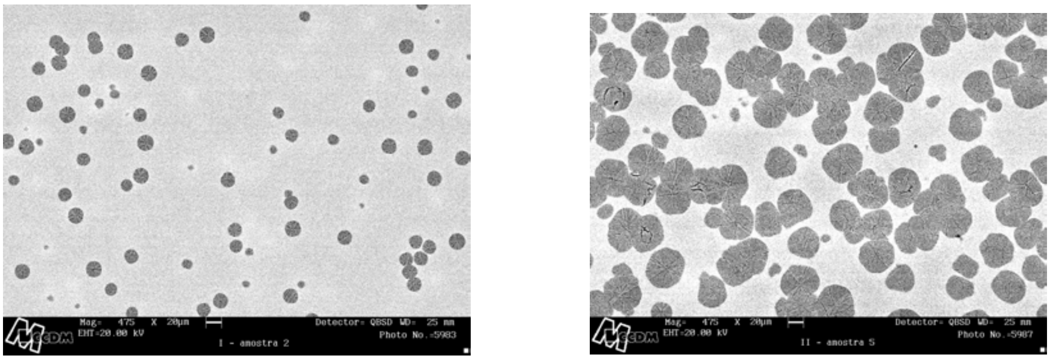
$$\sigma = \frac{1}{R}\frac{L}{S}, \qquad (1)$$

where L is the sample's thickness and S the electrode surface area.

Before taking the measurements, the crystallized surface layer was eliminated by polishing to ensure that only bulk properties would be investigated. Platinum electrodes were then sputtered onto the samples' surfaces to ensure the necessary electrical contact. Measurements were taken in a two-electrode configuration cell, in dry air, using an impedance analyzer HP 4192A, which allows the frequency to vary from a 5Hz to 13MHz. The measurements were taken in the 250 to 600°C temperature range.

III. Results

Partly crystallized $N_1C_2S_3$ glass consists of a glassy matrix with embedded, randomly dispersed, spherical crystals having approximately the same size, as shown in Fig. 1. Fig. 2 shows the evolution of the sodium and calcium contents in the crystals and the sodium content (the main element responsible for electrical conduction) in the glassy matrix with increasing crystal volume fractions. Continuous variations in the crystal's composition are possible because the evolving crystalline phase is a solid solution, $Na_{4+2x}Ca_{4-x}[Si_6O_{18}]$ ($0 \le x \le 1$) [3]. Conductivity data of the studied samples, including the parent glass and the fully crystallized glass, are shown as Arrhenius plots in Fig.3. Note that data on amorphous and fully crystallized samples are congruent with previously published information [4]. The inflection in the Arrhenius plot of the fully crystallized sample at around 500°C was caused by the reversible crystal phase transition that took place in the solid solutions with x up to 0.5 [3].



(a) **(b)**

Fig.1 – SEM micrograph of the cross-sections of glasses treated at 690°C for (*a*) 17 and (*b*) 50 min. Crystallized volume fractions are about (*a*) 0.1 and (*b*) 0.54. The bar has a length of 20 μm. The photo's height is equal to the thickness of the plates used for electrical conductivity measurements.

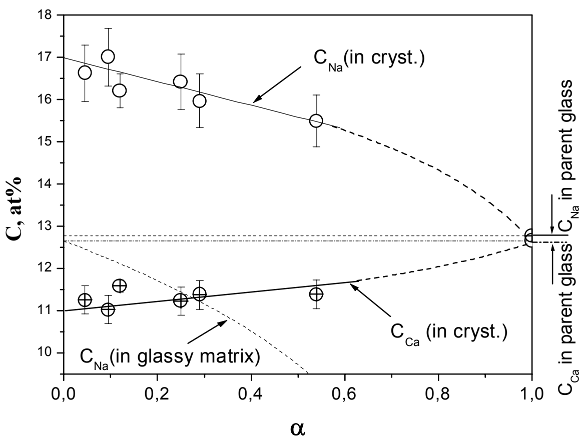


Fig.2 – Average compositions of the crystalline phase (points), measured by EDS, and glassy matrix, calculated from the crystallized volume fractions and the parent glass composition, *versus* volume crystallized at T=690°C.

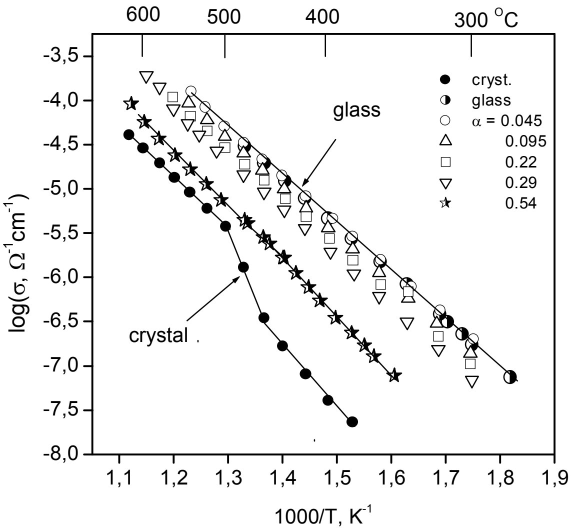


Fig.3 – Electrical conductivity of glass, partly crystallized glasses, and polycrystal *versus* reverse temperature.

IV. Discussion

In agreement with Ref. [1], partly crystallized glass is composed of sodium-enriched crystals as compared to the parent glass and glassy matrix. According to Fig. 2, the sodium content in the crystals exceeds that of the parent glass, drastically exhausting the sodium ions in the glassy matrix. In the course of crystallization, the crystal compositions approach that of the parent glass

To further improve our investigation, glasses with similar compositions to that of different glassy matrix and crystals found during crystallization were also synthesized. Glasses containing more sodium than the $N_1S_2S_3$ composition were, furthermore, fully crystallized. These standard crystals and glasses were then also subjected to electrical conductivity measurements. Fig.4 presents electrical conductivities at a fixed temperature of glasses, partly crystallized samples and crystals as a function of their sodium content. In the case of partly crystallized samples, the sodium content refers to the glassy matrix. At first sight, the conductivity of partly crystallized samples, σ_{pcs}, up to α~0.54 is mainly due to the glassy matrix, since its conductivity is analogous to that of the pure glass with similar sodium content (Fig.4). However, according to Fig.2, the crystals contain much more sodium than the respective glassy matrix. Since sodium enhances the conductivity of the crystals, the result is that σ_{cr} is close to that of the glassy matrix (at α≤0.3) or slightly exceeds it (at α~0.54) (see Fig.4).

To further analyze the electrical conductivity behavior of partly crystallized samples, $\sigma_{pcs,}$ we calculated the activation energy for the electrical conductivity of crystals and glasses and also for that of partly crystallized samples. These data are plotted in Fig. 5 versus sodium content which, in the case of partly crystallized glasses, refers to the glassy matrix.

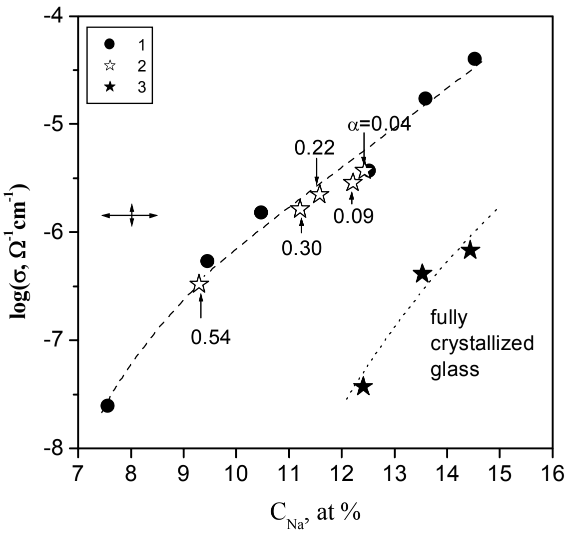


Fig. 4 – Electrical conductivity at T=394°C of glasses (*1*), fully crystallized samples (*3*) and partly crystallized glass of $N_1C_2S_3$ composition (*2*) versus sodium content, which refers, in case (*2*), to the glassy matrix. The numbers close to the open stars denote crystallized volume fraction.

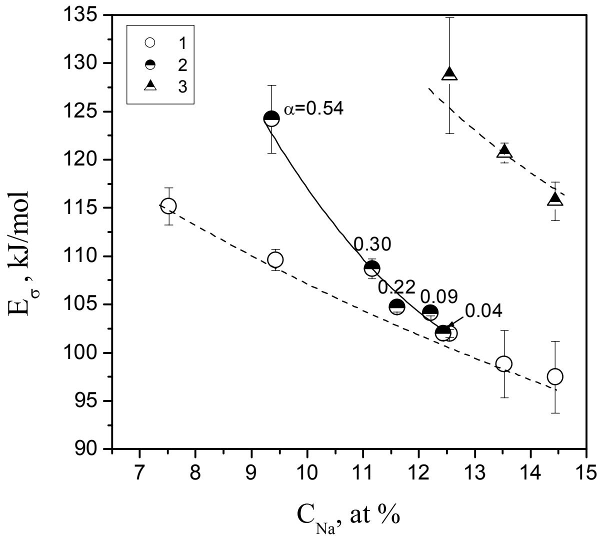


Fig.5 – Activation energy for electrical conductivity in glasses (*1*), crystals (*3*), and partly crystallized samples (*2*) versus sodium content. In the case of partly crystallized glasses, the sodium content corresponds to glassy matrix. The numbers close to the points denote crystallized volume fractions.

Although the conductivity of the sample with α~0.54, σ_{pcs}, is close to the conductivity of a glass having the same sodium content as the glassy matrix (Fig. 4), its activation energy is higher and close to that of the crystals (Fig. 5). This tendency already becomes apparent at α~0.30. Thus, the comparison between the values of conductivity and activation energy of partly crystallized samples, glasses, and crystals allows us to conclude that the electrical conductivity of partly crystallized glasses, beginning with α~0.54, is dominated by the crystals. This conclusion is corroborated by a weak inflection in the Arrhenius plot of a sample with α~0.54 (Fig.3), which is attributed to the high-low inversion in the crystalline phase. It should be noted that the higher the sodium content in the solid solution, the weaker the signal of the reversible crystal phase transformation [3]. Therefore, the absence of inflection in an Arrhenius plot is insufficient to conclude that the crystals do not affect the sample's conductivity.

V. Conclusions

Electrical conductivity measurements of partly crystallized samples corroborated EDS evidence of a variation in the compositions of both glassy phase and crystals during crystallization of a $1Na_2O{\cdot}2CaO{\cdot}3SiO_2$ glass. In this particular case, electrical conductivity was dominated by the glassy phase up to α~ 0.30, and by the crystals from α~0.54 on. These findings were confirmed by independent analyses of electrical conductivities of glasses and crystals having sodium contents as in partly crystallized samples, and were substantiated by the analysis of the activation energies. For samples with higher crystallinities, the Arrhenius plot showed a change in slope due to a phase transition occurring in crystals, confirming that electrical conductivity is dominated by the crystals. Electrical conductivity proves to be a very sensitive property that can indicate changes in the glassy matrix composition, and should contribute to investigations of complex heterogeneous systems such as partly crystallized glasses.

Acknowledgments

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VI. References

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