Non-stoichiometric crystallization of Li$_2$SiO$_3$-CaSiO$_3$ glasses: Residual glass composition from ionic conductivity

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A B S T R A C T

All the properties of glass-ceramics are strongly dependent upon their nano or microstructure, including the percentage, composition and, structure of the residual glass phase. Unfortunately, however, determining the chemical composition of residual glass is far from trivial and there are very few publications on this matter. In this paper, we used electrical conductivity measurements by impedance spectroscopy to infer the composition of the residual glass in partially crystallized Li$_2$SiO$_3$-CaSiO$_3$ glasses. The glass-ceramics were obtained by heat-treatment at 560 °C for distinct periods, in conditions where only lithium-metasilicate (Li$_2$SiO$_3$) crystallized. Consequently, residual glasses of the resulting glass-ceramics became depleted in lithium, and their ionic conductivity and the respective activation energies changed accordingly. Therefore, we obtained the compositions of residual glasses by comparing the glass-ceramics ionic conductivities and activation energies with those of reference glasses having known chemical composition. We validated these two methods by comparing the obtained residual glass compositions with those obtained using a technique that relates the glass transition temperature with the ionic conductivity of the parent glass.

1. Introduction

Glass-ceramics are inorganic, non-metallic materials prepared by controlled crystallization of glasses via different processing methods. They contain at least one type of functional crystalline phase and a residual glass. The volume fraction crystallized may vary from ppm to almost 100% [1]. They could be considered composite materials whose properties are synergistically determined by those of crystalline and vitreous phases. In fact, all glass-ceramic properties strongly depend upon their nano or microstructure, including the percentage and composition of the residual glass phase. Unfortunately, however, determining the chemical composition of residual glass is far from trivial and there are only a few works on this matter [2–4].

Even for stoichiometric crystallization, when the compositions of the residual glass and crystal phases are the same, the nucleation and growth of crystals in a parent glass, as well as the evolution of their morphology, including coalescence in the advanced stages, affect the glass-ceramic properties such as the transport properties and, in particular, their electrical conductivity. However, most glasses are non-stoichiometric, and when they are crystallized at adequate temperatures, they lead to one or more crystalline phases whose compositions differ from those of the parent glass. Besides, the nucleation and growth rates of each precipitating phase are different. Thus, the formation of only one phase in the early or middle stages of phase transformation results in a substantial change of the composition of the residual glass. Therefore, because the ionic conductivity of glasses is very sensitive to their composition, the residual glass composition and the crystallization process could, in principle, be followed by ionic conductivity measurements.

The determinations of conductivity were successfully used for monitoring the crystallization kinetic of a Na$_2$O·2CaO·3SiO$_2$ glass [2]. The conclusions based on these measurements were confirmed by optical microscopy, energy-dispersive X-ray spectroscopy (EDS), and differential scanning calorimetry (DSC). In particular, it was shown that, in the advanced stages of phase transition, the conductivity of the residual glass approaches that of the crystalline phase. Measurements of electrical conductivity of the parent and partly crystallized lithium disilicate glasses were used to demonstrate an ionic blocking effect [5].

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Electrical conductivity is also sensitive to the occurrence of the liquid-liquid phase separation (e.g. [6,7]), which often takes place in glass forming systems, and also to structural relaxation [8]. All the above examples indicate that electrical properties can be used to analyze complex multiphase systems, such as glass-ceramics.

In the present work, we investigated the electrical conductivity of glasses with compositions belonging to the meta-silicate joint Li2O·SiO2 - CaO·SiO2, which has a single eutectic, and whose crystallization kinetics was previously studied by some of us [3,4]. Glasses with compositions between 100% Li2O·SiO2 and the eutectic (~50% Li2O·SiO2) undergo internal crystallization of lithium meta-silicate as the unique crystalline phase at the early stages [3]. We emphasize here that, in our case, the main mobile species in the residual glass of glass-ceramics are lithium ions. Therefore, when the degree of crystallization increases, the residual glassy phase becomes progressively lithium-depleted, which strongly affects the ionic conductivity. The aim of the present work was to test whether measurements of ionic conductivity could be used to monitor the evolution of the residual glass composition during crystallization.

2. Materials and methods

2.1. Glass and glass-ceramics synthesis

Glasses were prepared using appropriate amounts of lithium carbonate (Synth, > 99%), calcium carbonate (Mailnickrodt, > 99%) and fumed silica (Aldrich > 99%). Table 1 shows the nominal composition of the glass batches according to their calculated content of Li2O and CaO. A good agreement between chemical analyses and nominal composition was found in our previous work for a similar silicate glass system which was synthesized under comparable conditions with this work [9]. Here, samples were named according to their CaO content. Thus, G-CLS35 means a glass composition with 35 mol% CaO and 65 mol% Li2O. First, solid-state reactions of the starting reagents were performed at temperatures between 800 and 900 °C to eliminate CO2 and form a homogeneous mix. Then, the resulting powder was splat cooled between two brass plates to prevent crystallization. Glass samples of the composition G-CLS35 were submitted to single heat-treatments at 560 °C during 10, 20, 40, 50, 100 and 160 min to obtain partially crystallized glass-ceramics (GC-CLS35). Since this glass composition shows very high homogeneous nucleation rates (about \(10^{14} \text{m}^{-3} \text{s}^{-1} \)) [3]), even the glass obtained via splat cooling had enough crystal nuclei to be developed by a single growth heat-treatment. These heat-treatments were performed in a vertical electric box furnace with temperature pre-stabilized within ± 1 °C. A fully crystallized sample of lithium meta-silicate stoichiometric composition (Li2SiO3) was also prepared with a slow cooling rate from the molten state. This procedure ensured a fully crystallized material with a large crystal size which reduces the contribution of the grain boundary in electrical measurements.

2.2. DSC measurements

Small glass samples of about 30 mg were subjected to differential scanning calorimetry (DSC) analyses in a Netzsch DSC 404 calorimeter equipped with platinum pans and covers, at a heating rate of 10 K min⁻¹. The characteristic temperatures of the precursor glasses, the glass transition temperature (\(T_g\)) and onset temperatures of crystallization peaks (\(T_x\)), were taken from DSC curves. Besides, the onset and offset temperatures of the melting phenomena assigned, respectively, as solidus (\(T_s\)) and liquidus (\(T_l\)) temperatures were also determined based on the DSC thermograms. Finally, the partially crystallized glass-ceramic samples (GC-CLS35) obtained under distinct periods of heat-treatment time (10, 20, 40, 50, 100 and 160 min) were also submitted to DSC scans to determine \(T_s\) of the residual glass phase.

2.3. Electrical measurements by impedance spectroscopy

The ionic conductivity of several glasses (underlined compositions, Table 1) and glass-ceramics were determined via impedance spectroscopy (IS). Before taking the measurements, to ensure that only bulk properties would be investigated, the crystallized surface layers of all samples were eliminated by mechanical polishing. Platinum electrodes were deposited by evaporation on parallel opposite faces of the specimens to ensure electrical contact. The samples were about 0.1 cm thick and had a contact area of around 0.3 cm². IS measurements were conducted using a Solartron impedance analyzer over the frequency range 1 MHz – 10 mHz, with an applied root mean square AC voltage of 500 mV. These measurements were carried out in air, on a two-point cell, at temperatures below \(T_g\) over the range of 323–633 K depending on the resistance of the glass or glass-ceramic samples. The specimens were inserted in a BDS 1200 sample holder in a Novotherm furnace, with a temperature control system allowing maximum temperature variation of ± 0.1 K during the measurements.

3. Results and discussion

3.1. Residual glass composition estimated by \(T_x\)

The characteristic temperatures of all synthesized glasses were extracted from DSC traces based on the method described in our previous works [3,4]. DSC analyses of glasses from this system have also been published elsewhere [3]. From these analyses, we have determined the glass transition temperature (\(T_g\)), the onset temperatures of the first (\(T_x\)) and second (\(T_x''\)) crystallization peaks, and the onset and offset temperatures of melting, which have been assigned as solidus (\(T_s\)) and liquidus (\(T_l\)) temperature, respectively. Fig. 1 shows the dependence of \(T_s\), \(T_x\) and \(T_x''\), as well as the equilibrium temperatures (\(T_g\) and \(T_l\)) on the glass composition. \(T_s\) exponentially increases with the substitution of Li2SiO3 by CaSiO3. This behavior has previously been found by some of us in the same system [3], and by Neuville through viscosity measurements in soda-lime silicate glasses [10]. Neuville encountered that the supercooled liquid viscosity at low temperatures (around \(T_s\)) decreases rapidly when CaO is replaced by Na2O. This was attributed to a non-ideal mixing entropy, which implies a non-random distribution of Na and Ca in the silicate network [10].

Regarding the onset of the crystallization temperatures, Li2SiO3-CaSiO3 glasses present two DSC crystallization peaks for CaSiO3 content

<table>
<thead>
<tr>
<th>Glass samples</th>
<th>Li2SiO3 (%) mol</th>
<th>CaSiO3 (%) mol</th>
<th>Glass-ceramics</th>
<th>Heat-treatments</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-LS</td>
<td>100</td>
<td>0</td>
<td>GC-LS</td>
<td>From the molten state</td>
</tr>
<tr>
<td>G-CLS15</td>
<td>85</td>
<td>15</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>G-CLS20</td>
<td>80</td>
<td>20</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>G-CLS27</td>
<td>73</td>
<td>27</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>G-CLS35</td>
<td>65</td>
<td>35</td>
<td>GC-CLS35</td>
<td>10, 20, 40, 50, 100, 160 min</td>
</tr>
<tr>
<td>G-CLS40</td>
<td>60</td>
<td>40</td>
<td>–</td>
<td>–</td>
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<td>G-CLS44</td>
<td>56</td>
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<td>47</td>
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<td>–</td>
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<td>G-CLS50</td>
<td>50</td>
<td>50</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>G-CLS55</td>
<td>45</td>
<td>55</td>
<td>–</td>
<td>–</td>
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<td>60</td>
<td>–</td>
<td>–</td>
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<td>67</td>
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<td>75</td>
<td>–</td>
<td>–</td>
</tr>
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<td>G-CLS85</td>
<td>15</td>
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<td>–</td>
<td>–</td>
</tr>
<tr>
<td>G-C</td>
<td>0</td>
<td>100</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
lower than 50%. In our previous work [3], investigation of this behavior led to the conclusion that the first peak is related to the crystallization of Li$_2$SiO$_3$ and the second is related to the concomitant crystallization of Li$_2$SiO$_3$ and CaSiO$_3$ from the residual glass. Above 50% of CaSiO$_3$, these crystallization peaks are overlapped, which impairs the distinction of the two crystallization phenomena. The knowledge of the dependence of the onset temperatures ($T'_{x}$ and $T''_{x}$) on the composition is extremely important if one desires to crystallize the Li$_2$SiO$_3$ crystal phase and avoid CaSiO$_3$ precipitation. Since this is the case here, the G-CLS35 glass composition and the treatment temperature of 560 °C were specifically chosen based on these DSC analyses. Moreover, lines linking the equilibrium temperatures $T_1$ and $T_2$ resemble a typical temperature behavior of a pseudo-binary join having a single eutectic [3]. The latter agrees with the phase diagram of the Li$_2$SiO$_3$-CaSiO$_3$ join constructed by A.R. West in 1978 [11].

Besides the evolution of the $T_x$ for the parent glasses of the Li$_2$SiO$_3$-CaSiO$_3$ system, Fig. 2 also shows the $T_x$ of the residual glass of the GC-CLS35 glass-ceramics (35% of CaSiO$_3$) as a function of the duration of the crystallization heat-treatment at 560 °C. At this temperature and for the chosen durations of heat-treatment, the unique phase to crystallize is Li$_2$SiO$_3$ (see Fig. 1). Thus, as the Li$_2$SiO$_3$ crystal phase evolves, the residual glass in the glass-ceramics becomes lithium-depleted and calcium-enriched, which increases its glass transition temperature (Fig. 2). A quick analysis of Fig. 2 shows that the $T_x$ of the residual glass in the glass-ceramic heat-treated for 160 min is very close to that of the glass composition with 67% of CaSiO$_3$, and thus, the composition of the residual glass in this glass-ceramic is also comparable to that of the glass with 67% of CaSiO$_3$. The dependence of $T_x$ on the chemical composition of simple glasses was fitted using an exponential equation with the numerical purpose of capturing the dependence of $T_x$ in the entire range of compositions to estimate the composition of the residual glasses in the glass-ceramics. This method has been used by some of us before [3,4], and consists of estimating the composition of the residual glass comparing the $T_x$ of the glass-ceramic with the dependence of $T_x$ on the composition of reference glasses (see dotted lines Fig. 2a). It has proven to be effective through the comparison with EDS chemical analyses [3,4].

The changes in $T_x$ of the residual glass caused by precipitation of Li$_2$SiO$_3$ crystal phase are steeper for shorter crystallization time (Fig. 2b). This trend is probably due to the faster growth rates in the initial stages of crystallization, which takes place in a glass richer in Li$_2$O than in later stages. This behavior reflects the overall crystallization kinetics of the lithium meta-silicate crystal phase, which decreases with the CaSiO$_3$ content in the residual glass. The increase in viscosity and decrease in the thermodynamic driving force when the residual glass composition approaches that of the metastable liquidus would be the major causes for the slow crystallization kinetics of Ca-enriched residual glass (see details in [3]).

Once we have determined the composition of the residual glasses of different glass-ceramics comparing the $T_x$ of reference glasses with those of the glass-ceramics, the crystallized fraction ($X_{cc}$) can be determined through Eq. (1). In our case, $C_{CC}$ is the overall composition of the glass-ceramic or the nominal composition of the corresponding parent glass, and $C_{RG}$ the estimated composition of the residual glass, both given in CaSiO$_3$ molar content.

$$X_{cc} = \frac{C_{RG} - C_{CC}}{C_{RG}}$$

(1)

3.2. Residual glass composition estimated by ionic conductivity

We recall that the starting hypothesis of the present work is that the composition of the residual glass in glass-ceramics may also be estimated by electrical conductivity measurements, which has been shown to be a powerful tool for investigating complex heterogeneous systems, such as partially crystallized glasses or glass-ceramics [2,5]. Thus, impedance spectroscopy is widely used in ionic conductor investigations.

Fig. 2. Dependence of $T_x$ on the chemical composition of xCaSiO$_3$ (1 − x)Li$_2$SiO$_3$ glasses (a), and on the duration of the crystallization heat-treatment of the GC-CLS35 glass-ceramics (b). Filled circles correspond to glasses of meta-silicate stoichiometric compositions (G-CS and G-LS), open circles to glasses of intermediary compositions (G-CLS), half-filled circles to glass-ceramics (GC-CLS35). The dotted lines correlate the $T_x$ of the residual glass in the glass-ceramics with their estimated composition.
because it can separate electrical phenomena having different time constants, such as electrode and bulk properties [12,13]. Besides, this technique presents an important advantage since it is a non-destructive method. Impedance data of a homogeneous ionic conducting glass can be represented in the so-called Nyquist diagram (x-axis: the real part; y-axis: the imaginary part of impedance), which is commonly a semi-circle from high to middle-frequency range followed by a characteristic spike in a low-frequency range caused by a ionic blocking effect in the metallic electrode [2,14]. Therefore, the glass resistance (R) is read at the low-frequency intersection of the semi-circle with the x-axis (see Fig. S1). The overall ionic conductivity (σ) is then estimated from the electrical resistance, R, according to Eq. (2), where L is the sample thickness and S is the electrode surface area.

\[
\sigma = \frac{1}{R} \frac{L}{S} \quad \text{(2)}
\]

Fig. 3 depicts the ionic conductivity at 200 °C of several glass compositions of the Li2SiO3-CaSiO3 join and of GC-CLS35 glass-ceramics obtained after the indicated duration of crystallization heat-treatments. Here, we have also made use of an exponential equation to fit the dependence of the logarithm of ionic conductivity with the nominal composition to have access to such dependency in the entire range of compositions in the Li2SiO3-CaSiO3 system. The ionic conductivity of glasses decreases rapidly with increasing CaSiO3 content (Fig. 3a). In a similar way, the overall ionic conductivity of the GC-CLS35 glass-ceramics also decreases as a function of the duration of heat-treatment (Fig. 3b). The changes in this property are faster for shorter crystallization times and slower for longer heat-treatments (Fig. 3b). This tendency resembles that observed for the dependence of conductivity of glasses and glass-ceramics (Fig. 3a) agree with those estimated by the glass transition temperature (Fig. 2a).

3.3. Residual glass composition estimated by the activation energy for ionic conduction

Although the compositions of the residual glassy phase estimated by ionic conductivity (Fig. 3a) agree with those estimated by the glass transition temperature (Fig. 2a), we should point out that the impossibility of assessing the geometric factor (L/S, Eq. (2)) of the residual glassy phase introduces an error when determining its ionic conductivity. In fact, we stated and justified above, that, because of the much lower conductivity of the crystalline Li2SiO3 phase, the measured ionic conductivity of the glass-ceramic was solely attributed to lithium ions in the residual glassy phase. However, as the crystalline phase is developed, the real geometric factor of the conductive phase changes since the volume fraction of residual glass decreases. In practice, the lithium ions must travel is increased and the effective conductive area is decreased, resulting in an increase of the geometric factor (L/S). As a consequence, there is a tendency to underestimate the conductivity of the residual glass in the glass-ceramic because we are underestimating the term L/S (see Eq. (2)). It is worth mentioning that, even if the crystalline volume fraction and, thus, the volume of the residual glassy phase is known, its geometric factor will remain unknown.

As a plausible alternative to overcome this limitation, we propose using the same rationale as in Fig. 2a and Fig. 3a, but having the activation energy as the key variable, which is independent of the geometric factor of the conductive phase. To have access to the activation energy for ion conduction, it is necessary to measure the ionic conductivity of the residual glassy phase at different temperatures.
conductivity at different temperatures. Fig. 4 presents Arrhenius-like plots of the ionic conductivity of glasses with different CaSiO$_3$ content and of GC-CLS35 glass-ceramics obtained after the indicated duration of crystallization heat-treatment at 560 °C. The dependence of ionic conductivity on the inverse of temperature has been plotted applying the linearized form of the Arrhenius-like relation [15] expressed in Eq.(3):

$$\sigma T = A \exp \left( \frac{E_a}{k_B T} \right)$$

(3)

where $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $A$ is the pre-exponential factor and $E_a$ is the activation energy for ion conduction. Following this approach, the slope of linear fit is proportional to $E_a$, which in turn provides access to the energetic barrier for ionic conductivity.

As shown in Fig. 4a, the slope of the linear fit increases systematically with the increase of CaSiO$_3$ which reflects a decrease in lithium content in the glasses. Similarly, increasing the duration of heat-treatment gradually increases the slope of the linear fit of glass-ceramics (Fig. 4b). As for the logarithm of the pre-exponential term (log A), the values pertaining to glass and glass-ceramic oscillate around the theoretical value [15], ranging from 4.9 to 6.2. For the sake of comparison, in Fig. 4b we also introduced the dependence of ionic conductivity with the inverse temperature for the crystalline Li$_2$SiO$_3$ (C-LS), as well as for the parent glass (G-CLS35) and the glass with 67% of CaSiO$_3$ (G-CLS67). It is important to note that the Arrhenius plot of the glass-ceramic heat-treated for 160 min has nearly the same slope as that of the glass-ceramic with 67% of CaSiO$_3$ content, whereas in the glass-ceramics series the activation energy for ion conduction increases with the duration of heat-treatment. Following this approach, the slope of linear fit is proportional to $E_a$, which in turn provides access to the energetic barrier for ionic conductivity.

Fig. 5 shows the calculated values of $E_a$ for glasses and glass-ceramics obtained from slopes of linear fits (Fig. 4). A nearly linear relationship (Fig. 5a) is found for glasses of intermediate composition (27–75% of CaSiO$_3$), although the binary stoichiometric meta-silicate glasses, Li$_2$SiO$_3$ (G-LS) and CaSiO$_3$ (G-CS), are not included in this trend. As expected, and contrary to the ionic conductivity, the activation energy for ion conduction in this glass series increases with the CaSiO$_3$ content, whereas in the glass-ceramics series the activation energy increases with the duration of heat-treatment (Fig. 5b), reflecting, in both cases, a decrease in lithium content, respectively in the crystalline Li$_2$SiO$_3$ crystals never percolate (see Fig. S2). Therefore, the proposed Maxwell-Wagner model describes fairly well the microstructure of the glass-ceramic system presented here.

3.4. Correction of the ionic conductivity of the residual glass by the effective medium theory

Another possibility to determine the ionic conductivity of the residual glass through the overall ionic conductivity of the glass-ceramic is by applying models derived from the effective medium theory. Several models have been derived using this approach and one of the most used is the Maxwell–Wagner model [13]. This model has been derived for complex conductivity but can be reduced to the dc conductivity. The expression derived from this model adapted for our case is presented in Eq. (4). Here, $X_v$ is the crystalline volume fraction, and $\sigma_{GC}$, $\sigma_{RG}$ and $\sigma_C$ are the ionic conductivity of the glass-ceramic, the residual glass and the crystalline Li$_2$SiO$_3$ phase, respectively. It should be noted that this approach makes certain implicit assumptions about the microstructure, especially regarding the continuity of the constituent phases. In this case, the model considers a dispersion of spheres of one phase in a continuous medium of the second phase [13]. In the present case, the crystals of lithium meta-silicate are surrounded by diffusion zones, which prevent them from touching [3]. Thus, in the investigated glass-ceramics, the Li$_2$SiO$_3$ crystals never percolate (see Fig. S2). Therefore, the proposed Maxwell-Wagner model describes fairly well the microstructure of the glass-ceramic system presented here.

$$\sigma_{RG} = \frac{2\sigma_{RG} + \sigma_C - 2X_v(\sigma_{RG} - \sigma_C)}{2X_v + \sigma_C + X_v(\sigma_{RG} - \sigma_C)}$$

(4)

Since the ionic conductivity of the glass-ceramics ($\sigma_{GC}$) and of the crystalline phase ($\sigma_C$) are known, the conductivity of the residual glass ($\sigma_{RG}$) becomes only dependent on the crystalline volume fraction ($X_v$). Neglecting the small differences in density of crystal and glass, $X_v$ may be reduced to the crystalline fraction ($X_v$) from Eq. (1). To propose a method using only ionic conductivity data, we chose to estimate $X_v$ by means of Eq. (1) using the residual glass composition ($C_{RG}$) assessed in Fig. 3a and the overall composition of GC-CLS35 glass-ceramics ($C_{GC}$) assessed in Table 1. Table 2 shows the input values used to solve Eq. (4), as well as the obtained value of the ionic conductivity of the residual glass. As we predicted before based on changes in the geometric factor of the residual glass (L/S) due to an increase in the volume of the crystalline phase, the estimated ionic conductivity of the residual glass is always higher than that of the measured overall conductivity of the
The activation energy for ionic conductivity on the chemical composition of \( x \text{CaSiO}_3 \) \( - (1-x) \text{Li}_2\text{SiO}_3 \) glasses (a) and on the time of crystallization.

**Fig. 6:** Dependence of the activation energy for ionic conductivity on the chemical composition of \( x \text{CaSiO}_3 \) \( - (1-x) \text{Li}_2\text{SiO}_3 \) glasses (a) and on the time of crystallization (b).

<table>
<thead>
<tr>
<th>Glass-ceramics</th>
<th>Input parameters ( X_v )</th>
<th>( \sigma_{GC} ) ( (\Omega^{-1} \cdot \text{cm}^{-1}) )</th>
<th>( \sigma_{C} ) ( (\Omega^{-1} \cdot \text{cm}^{-1}) )</th>
<th>Calculated</th>
<th>( \sigma_{RG} )</th>
<th>( \sigma_{GC} )</th>
<th>( \sigma_{RG}/\sigma_{GC} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC-CLS35-10 min</td>
<td>0.080</td>
<td>2.53E-8</td>
<td>2.95E-10</td>
<td>2.86E-6</td>
<td>1.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GC-CLS35-20 min</td>
<td>0.226</td>
<td>5.05E-7</td>
<td>2.95E-10</td>
<td>7.27E-7</td>
<td>1.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GC-CLS35-40 min</td>
<td>0.383</td>
<td>2.73E-6</td>
<td>2.95E-10</td>
<td>5.24E-8</td>
<td>1.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GC-CLS35-50 min</td>
<td>0.414</td>
<td>1.17E-5</td>
<td>2.95E-10</td>
<td>2.37E-8</td>
<td>2.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GC-CLS35-100 min</td>
<td>0.480</td>
<td>1.15E-4</td>
<td>2.95E-10</td>
<td>2.26E-8</td>
<td>1.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GC-CLS35-160 min</td>
<td>0.509</td>
<td>3.17E-4</td>
<td>2.95E-10</td>
<td>3.42E-10</td>
<td>1.08</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2**

Input parameters \( (X_v, \sigma_{GC} \text{ and } \sigma_{C}) \) and calculated ionic conductivities for the residual glass (\( \sigma_{RG} \)) applying the Maxwell-Wagner equation (Eq. (4)). \( X_v \) was calculated by Eq. (1) using the composition of the residual glass estimated from Fig. 3a. The \( \sigma_{RG}/\sigma_{GC} \) ratio is also shown since it gives a direct comparison between \( \sigma_{GC} \) and \( \sigma_{RG} \).

A better way to visualize the evolution of the \( \sigma_{RG}/\sigma_{GC} \) ratio as a function of heat-treatment time is by dividing both sides of the Maxwell-Wagner equation by \( \sigma_{C} \) and rearranging Eq. (4) to introduce the \( \sigma_{RG}/\sigma_{GC} \) ratio:

\[
\frac{\sigma_{RG}}{\sigma_{GC}} = \frac{\frac{2 \sigma_{C}}{\sigma_{GC}} + 1 + X_v \left( \frac{\sigma_{C}}{\sigma_{GC}} - 1 \right)}{2 \sigma_{C} \left( \frac{\sigma_{C}}{\sigma_{GC}} - 1 \right)}
\]

(5)

From Eq. (5), we are able to represent the dependence of \( \sigma_{RG}/\sigma_{GC} \) ratio on \( \sigma_{RG}/\sigma_{GC} \) ratio and \( X_v \). We propose this exercise to rationalize the effect of each parameter on the conductivity of the resulting inhomogeneous media, in our case, the glass-ceramics with a variable fraction of the crystalline phase and the composition of the residual glass. Fig. 6 shows the dependence of \( \sigma_{RG}/\sigma_{GC} \) ratio on \( \sigma_{RG}/\sigma_{GC} \) ratio for crystalline fractions between 0 and 0.5, as well as the dependence of the \( \sigma_{RG}/\sigma_{GC} \) ratio on the duration of heat-treatment. The ratio plot (Fig. 6a, full lines) is constructed simply by feeding Eq. (5) with values of \( \sigma_{RG}/\sigma_{GC} \) from 1 to \( 10^5 \) for different values of \( X_v \) (from 0 to 0.5). The key role of this plot is to make the Maxwell-Wagner equation more intuitive showing that the ratio between the ionic conductivity of the residual glass and the overall conductivity of the glass-ceramic (\( \sigma_{RG}/\sigma_{GC} \)) increases as the ratio between the conductivity of the residual glass and the crystal phase (\( \sigma_{RG}/\sigma_{GC} \)) increases, up to a certain value, and then becomes constant. Besides, it shows that this dependence is strongly influenced by the crystalline volume fraction (\( X_v \)).

Now, by applying values of conductivities and crystalline volume fractions from Table 2 we can add to the ratio plot (Fig. 6a) the experimental values of \( \sigma_{RG}/\sigma_{GC} \) ratio for GC-CLS35 glass-ceramics. The dependence of the \( \sigma_{RG}/\sigma_{GC} \) ratio on the duration of heat-treatment increases in the initial stages of crystallization, goes through a maximum and then, decreases for longer times of heat-treatment (Fig. 6b). This behavior can be rationalized considering that, in the early stages of crystallization, the residual glassy phase is richer in lithium and its conductivity is much higher than that of the \( \text{Li}_2\text{SiO}_3 \) crystalline phase. Longer heat-treatments lead to an increase in \( X_v \) (see optical micrographs, Fig. 6b) but also decrease \( \sigma_{RG} \) because the residual glass becomes impoverished in lithium. Therefore, competition between these two parameters (\( \sigma_{RG} \) and \( X_v \)) leads to a maximum of the \( \sigma_{RG}/\sigma_{GC} \) ratio for intermediary heat-treatments (40–100 min), where the estimated conductivity of the residual glass is about twice the measured overall conductivity of the glass-ceramics. Finally, using the corrected conductivity of the residual glass, its composition can be estimated by comparing it with the conductivity of reference glasses of known chemical composition.

### 3.5. Comparison between the three methods

The ultimate goal of this work is to compare the \( T_g \)-method to estimate the composition of the residual glassy phase with the two methods proposed here using conductivity data. Fig. 7 shows the estimated composition of the residual glass in the GC-CLS35 glass-ceramics using the glass transition temperature (\( T_g \)), the activation energy for ionic conductivity (\( E_a \)) and ionic conductivity at 200 °C of the glass-ceramic (\( \sigma_{GC} \)) and of the residual glass corrected by the Maxwell-Wagner model (\( \sigma_{RG} \)). The overall tendency follows the same behavior regardless of the property used, with the composition of the residual glass changing sharply for shorter than for longer crystallization times. The agreement between the \( T_g \)-method and the proposed methods are quite good (\( R^2 = 0.997 \) for \( T_g \) vs \( E_a \), \( R^2 = 0.988 \) for \( T_g \) vs \( \sigma_{GC} \) and \( R^2 = 0.994 \) for \( T_g \) vs \( \sigma_{RG} \)), with discrepancies smaller than 5% between all methods, and smaller than 2% between the \( T_g \) and \( E_a \) methods. In addition, the use of the Maxwell-Wagner correction brings the estimates of the residual glass composition using conductivity data closer to the \( T_g \) and \( E_a \) methods (discrepancies smaller than 2%), except for the longest heat-treatment (160 min). A reasonable explanation for this limitation of the Maxwell-Wagner model for 160 min of growth heat-
We tested three different methods to estimate the chemical composition of the residual glass in partially crystallized glass-ceramics. These techniques are based on the same reasoning, i.e., comparing a particular property of a glass-ceramic with that same property of reference glasses having a known composition. The procedure using glass transition temperature has been validated through EDS chemical analyses in a previous study. Here we proposed and tested two innovative approaches to determine the composition of the residual glass by using electrical conductivity measurements. In the first approach, we compared the ionic conductivities of certain glass-ceramics with those of reference glasses. The agreement between this method and the \( T_g \) technique was reasonably good, with differences within 5%. Moreover, by applying corrections using the Maxwell-Wagner equation, which is adequate for glass/crystal composites, these discrepancies reduced to 2% for glass-ceramics having crystallized fraction lower than 0.5.

The second approach relies on determining the ionic conductivity as a function of the temperature and calculating the activation energy for ionic conduction in reference glasses of known composition and in the glasses-ceramics. The agreement between this method and the \( T_g \) technique was also quite good, with discrepancies smaller than 2%.

These novel methods yield similar results to the procedure using the glass transition temperature. However, these electrical property techniques are non-destructive and can be used to follow the crystallization process in situ.

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**Appendix A. Supplementary data**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jnoncrysol.2019.01.022.

**References**


