A systematic study of glass stability, crystal structure and electrical properties of lithium ion-conducting glass-ceramics of the \( \text{Li}_{1+x}\text{Cr}_x(\text{Ge}_y\text{Ti}_{1-y})_2-\text{x}(\text{PO}_4)_3 \) system

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HIGHLIGHTS

- We synthesize LCGTP glass-ceramics with conductivity higher than \( 10^{-4} \) S cm\(^{-1}\) (R.T.).
- Ionic conductivity of LCGTP glass-ceramics is highly dependent on composition.
- Glass stability of LCGTP system can be improved by increasing Cr and Ge content.
- Unit cell volume of NASICON structure can be tailored by compositional design.
- We find an important correlation between Li ion mobility and unit cell volume.

GRAPHICAL ABSTRACT

ABSTRACT

This study examines the effect of substituting Ti by Cr and Ge on the glass stability of the precursor glass and on the electrical properties of the lithium ion-conducting glass-ceramics of the \( \text{Li}_{1+x}\text{Cr}_x(\text{Ge}_y\text{Ti}_{1-y})_2-\text{x}(\text{PO}_4)_3 \) (LCGTP) system. A set of compositions of this system is synthesized by the melt-quenching method followed by crystallization. The main results indicate that the glass stability of the precursor glasses increases when Ti is replaced by Ge and Cr. After crystallization, all the glass-ceramics present NASICON-type phase, and their lattice parameters decrease with Ge and increase with Cr content, making it possible to adjust the unit cell volume of the NASICON-like structure. Furthermore, the ionic conductivity and activation energy for lithium conduction in the glass-ceramics are notably dependent on the unit cell volume of the NASICON-like structure. The \( \text{Li}_{1.4}\text{Cr}_{0.6}(\text{Ge}_{0.2}\text{Ti}_{0.8})_{1.4}(\text{PO}_4)_3 \) glass-ceramic composition shows the highest overall ionic conductivity \( (2.9 \times 10^{-4} \) \( \Omega \) cm\(^{-1} \)) at room temperature and reveals remarkably high ionic conductivity \( (1.2 \times 10^{-3} \Omega \) cm\(^{-1} \)) and low activation energy \( (0.259 \) eV) regarding grain contribution. The main findings suggest that the proposed system is promising to develop fast Li ion-conducting glass-ceramics, offering a compromise between the glass stability of the precursor glass and the electrical properties of the resulting glass-ceramic.

Keywords:
Li ion-conducting
Glass-ceramic
Glass stability
NASICON-like structure
Ionic conductivity

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1. Introduction

Their unique combination of high energy and power density makes lithium batteries the most attractive technology for several applications, such as portable electronics, power tools, electric vehicles and large-scale energy production for intermittent power generation. Battery life is often limited by side reactions, including decomposition of the electrolyte; however, these reactions rarely take place in inorganic solid electrolyte systems. Since these materials are generally conductors of a single ion species, only lithium ions have significant mobility while other ions form a rigid three-dimensional network, resulting in greater electrochemical and thermal stability. In addition, a variety of inorganic lithium conductors has shown conductivities that are even higher than those of polymeric electrolytes [1–6].

The main inorganic lithium ion conductors include sulfide glasses and crystals [7–9], oxides with perovskite-like [10–13] and garnet-like [3,14,15] structures and phosphates with NASICON-like [16–19] structure. The main advantage of NASICON-type lithium ion conductors is their structural versatility within a wide range of compositions. The base chemical formula of these compounds can be written as LiM2(PO4)3, where M is a tetravalent cation (Ge, Ti, Zr, Sn or Hf). The NASICON-like structure consists of a covalent skeleton containing MO6 octahedra linked by corners to PO4 tetrahedra, which form 3D interconnected channels and two types of interstitial positions in which the mobile cations are distributed. Mobile cations move from one site to another through bottlenecks whose size depends on the framework [4,5,16,20]. Among the aforementioned tetravalent cations, Ti in the LiTi2(PO4)3 (LTP) system leads to the basic NASICON compound [31]. The presence of titanium oxide (TiO2) helps to keep the cell parameters of NASICON-like structure close to those of LTP system. To increase lithium concentration in the NASICON-type phase, chromium oxide (Cr2O3) is chosen as the trivalent doping since the crystal radius of Cr+3 (0.0670 nm) has smaller crystal radius than Ti+4 (0.0745 nm) in octahedral coordination [31], the presence of titanium oxide (TiO2) helps to keep the cell parameters of NASICON-like structure close to those of LTP system. To increase lithium concentration in the NASICON-type phase, chromium oxide (Cr2O3) is chosen as the trivalent doping since the crystal radius of Cr+3 (0.0670 nm) has smaller crystal radius than Ti+4 (0.0745 nm) in octahedral coordination [31], the presence of titanium oxide (TiO2) helps to keep the cell parameters of NASICON-like structure close to those of LTP system. To increase lithium concentration in the NASICON-type phase, chromium oxide (Cr2O3) is chosen as the trivalent doping since the crystal radius of Cr+3 (0.0670 nm) has smaller crystal radius than Ti+4 (0.0745 nm) in octahedral coordination [31].

Due to its particular characteristics and ability to form solid solutions, NASICON-type compounds have been synthesized in uncountable chemical compositions by means of different synthesis routes, such as the sol-gel [23–25], solid state reaction [17,21,26] and glass-ceramic routes [18,27,28]. In this respect, the glass-ceramic route offers indispensible advantages over any route that requires a further sintering stage to consolidate the electrolyte, since it allows low porosity electrolytes to be synthesized and the microstructure to be properly designed through controlled glass crystallization. However, the main drawback of the glass-ceramic route is that it requires the glassy state to be reached first, with crystallization occurring only in a subsequent step. Unfortunately, not all NASICON-type compositions can form a glass at the typical cooling rates used in the laboratory or in industrial settings. Moreover, well controlled glass crystallization requires homogenous nucleation of the glass system [18,27,29].

In a previous work [30], we have proposed the new Li1+xCrx(Ge0.8Ti0.2)x(PO4)3 (LCGTP) composition system aiming to synthesize glass-ceramic with NASICON-like crystal phase. The idea behind the proposal of the LCGTP system is based on the rationale that the introduction of germanium oxide (GeO2) increases the glass forming ability of the precursor glass. On the other hand, since Ge+4 (0.0670 nm) has smaller crystal radius than Ti+4 (0.0745 nm) in octahedral coordination [31], the presence of titanium oxide (TiO2) helps to keep the cell parameters of NASICON-like structure close to those of LTP system. To increase lithium concentration in the NASICON-type phase, chromium oxide (Cr2O3) is chosen as the trivalent doping since the crystal radius of Cr+3 (0.0670 nm) has smaller crystal radius than Ti+4 (0.0745 nm) in octahedral coordination [31].

2. Experimental methods

2.1. Preparation of glass and glass-ceramics

In order to cover a representative number of compositions in the Li1+xCrx(Ge0.8Ti0.2)x(PO4)3 (LCGTP) system, x and y were ranged from 0.2 to 0.8, in 0.2 steps, which by simple combination resulted in sixteen compositions. LCGTP samples are labeled according to their x and y values. Table 1 presents all the investigated LCGTP compositions as well as their respective oxide molar ratios. LCGTP precursor glasses

<table>
<thead>
<tr>
<th>Samples</th>
<th>x</th>
<th>y</th>
<th>Li (1 + x)</th>
<th>Cr</th>
<th>Ge (2 – x)</th>
<th>Ti (2 – x)</th>
<th>P</th>
<th>L2O (%)</th>
<th>Ge2O (%)</th>
<th>GeO2 (%)</th>
<th>TiO2 (%)</th>
<th>P2O5 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LC359P0202</td>
<td>0.2</td>
<td>0.2</td>
<td>1.2</td>
<td>0.2</td>
<td>0.36</td>
<td>1.44</td>
<td>3</td>
<td>15.0</td>
<td>2.5</td>
<td>36.0</td>
<td>37.5</td>
<td></td>
</tr>
<tr>
<td>LC359P0204</td>
<td>0.2</td>
<td>0.4</td>
<td>1.2</td>
<td>0.2</td>
<td>0.72</td>
<td>1.08</td>
<td>3</td>
<td>15.0</td>
<td>2.5</td>
<td>18.0</td>
<td>27.0</td>
<td>37.5</td>
</tr>
<tr>
<td>LC359P0206</td>
<td>0.2</td>
<td>0.6</td>
<td>1.2</td>
<td>0.2</td>
<td>1.08</td>
<td>0.72</td>
<td>3</td>
<td>15.0</td>
<td>2.5</td>
<td>27.0</td>
<td>18.0</td>
<td>37.5</td>
</tr>
</tbody>
</table>

Table 1 Nominal glass compositions and their respective oxide molar ratios (%) based on systematic increases of x and y in the Li1+xCrx(Ge0.8Ti0.2)x(PO4)3 (LCGTP) system.
were produced (~15 g by batch) by melting a stochiometric mixture of Li₂CO₃ (99.0%, Synth, Brazil), Cr₂O₃ (99.0%, Aldrich, USA), GeO₂ (99.99%, Alpha Aesar, USA), TiO₂ (99.9%, Aldrich, USA) and NH₄H₂PO₄ (98%, Aldrich, USA). An addition of 5 wt% of NH₄H₂PO₄ was made to compensate evaporation of P₂O₅ at elevated temperatures.

The reactants were homogenized in a planetary mixer for 12 h and the resulting mixture was calcined in a platinum crucible, using a hot plate to decompose NH₄H₂PO₄ and prevent a chemical attack on the platinum crucible at elevated temperatures. Then, the resulting powder was melted at 1450 °C for 30 min and the low-viscosity liquid was splat-cooled in a brass die to prevent crystallization. The quenched glasses were annealed at 550 °C for 2 h to relieve thermal stresses. After cooling, the glass was bubble-free and transparent, exhibiting a greenish color which increased in intensity with increasing Cr content.

All the LCGTP glasses were heat-treated as bulk samples at 900 °C for 2 h. To ensure a near zero impedance contribution from the equipment, a rigorous routine comprising calibration, short cut (closed electrodes) and standard resistor (1000Ω) measurements was established before measuring each sample. EIS measurements were performed in flat polished samples with parallel faces and gold electrodes sputtered on both sides to ensure electrical contact. Samples were about 0.1 cm thick and had a contact area of 0.1–0.2 cm². The spectra were fitted using an impedance spectroscopy software (ZView 3.5b) and a suitable equivalent circuit.

3. Results and discussion

3.1. Chemical analyses

Several acids, mixtures and even bases have been tested to digest the glass samples, but only HF proves to be effective. The samples with higher Cr and Ti content (LCGTP0206, LCGTP0208 and LCGTP0408) have not been digested even after weeks. Therefore, LCGTP0202, LCGTP0404, LCGTP0606, and LCGTP0808 glass samples have been chosen to represent the complete set of compositions, in view of their low Ti or Cr content and the fact that they cover the entire range of x and y values. Table 2 describes the nominal and experimental chemical composition of these samples, in weight percent. As the oxygen content cannot be determined by wet chemical analysis, calculations are made based on a nominal oxygen content. However, this assumption is quite reasonable, since the oxidation state used in the calculation of all the elements is the most common one.

In summary, all the elements show unsystematic discrepancies between nominal and experimental concentrations, but in every case the relative discrepancy is lower than 10%. These discrepancies, which are expected, are attributed to evaporation during melting and to experimental errors intrinsic to chemical analysis. A systematic discrepancy is also detected in the phosphorus content, whose relative percentage in all the analyzed compositions is about 5% higher. This indicates that the 5% addition made in the formulation step is unnecessary, at least when it comes to short melting times. The most important point here is that, in every case, the progressive increase/decrease of Li, Cr, Ge and Ti is maintained (Table 2). This is a crucial point in discussing the properties of these glasses and glass-ceramics. For the sake of simplicity, from now on, all the compositions are discussed based on their nominal content.

3.2. Thermal characterization of LCGTP glass

The DSC analysis indicates that all the LCGTP glasses have showed a clear glass transition and a narrow and very intense crystallization peak. Fig. 1 depicts the DSC curves of four LCGTP glasses (series x = 0.2), showing the glass transition temperature, Tg (Fig. 1a), and the crystallization peak temperature, Tp (Fig. 1b). Note the considerable shift of Tg to lower temperatures as y (proportional to the Ge content) increases, while Tp changes by only a few degrees. All the other LCGTP glass series, x = 0.4, y = 0.6 and x = 0.8, have exhibited essentially the same behavior. Usually, Tg is determined from the inflection point and Tp is ascribed to the crystallization peak temperature on the DSC curve. However, to determine Tg and Tp more precisely and without the influence of the experimenter, we have adopted a more rigorous method than a simple plot visualization. Therefore, the first derivative of the DSC curve is used to ascertain these specific temperatures. In this case, Tg can be determined when the first derivative in the glass transition region reaches a minimum value, while Tp is the temperature at which the first derivative reaches zero in the domain of the crystallization peak (Fig. 1c). In addition, the melting temperature (Tm) of the crystallized phase has been determined by means of optical dilatometry (OD). Fig. 1d shows the shrinkage area of the same four LCGTP glass compositions as a function of temperature. A slight shrinkage of about 1%, attributed to glass crystallization, is visible at around 700 °C, as previously reported [30]. Above this temperature, LCGTP glass-ceramics show only minor dimensional changes until they begin to melt.

<table>
<thead>
<tr>
<th>Samples Nominal (wt.%)</th>
<th>Experimental (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li Cr Ge Ti P</td>
<td>Li Cr Ge Ti P</td>
</tr>
<tr>
<td>LCGTP0202</td>
<td>2.1 2.6 6.6 17.3 23.3</td>
</tr>
<tr>
<td>LCGTP0404</td>
<td>2.4 5.1 11.4 11.3 22.8 2.3 5.0 10.5 10.7 24.5</td>
</tr>
<tr>
<td>LCGTP0606</td>
<td>2.7 7.5 14.7 6.5 22.4 2.7 7.1 14.1 6.4 23.4</td>
</tr>
<tr>
<td>LCGTP0808</td>
<td>3.0 9.9 16.6 2.7 22.1 3.2 8.9 16.1 2.8 23.3</td>
</tr>
</tbody>
</table>
above 1200 °C. Since the Li1-xCrx(GeyTi1-y)2-x(PO4)3 system is a solid solution, the crystallized phase melts within a temperature range of about 30 °C, depending on the chemical composition. Thus, Tm is ascribed to the liquidus temperature (Tl) when the sample has been totally melted (see Fig. 1d, half-filled circles) [30].

Table 3 summarizes the characteristic temperatures (Tg, Tp and Tm) and thermal parameters (KH and Tgr) obtained for the sixteen LCGTP glasses. Based on the values of Tg from DSC measurements, and of Tm from the OD analysis, it is possible to calculate the reduced glass transition parameter (Tgr) given by the Tg (K)/Tm (K) ratio. This ratio is important because it indicates whether or not a glass presents homogeneous nucleation. A Tgr below 0.6 is a strong indicative that the glass presents homogenous nucleation [32]. As can be seen in Table 3, the sixteen LCGTP glasses under study have showed Tgr < 0.6, indicating that these glass compositions nucleate homogenously, which is desirable to design the final microstructure of a glass-ceramic [18,27].

Another relationship of interest is the Hrubý parameter (KH = T x - Tg/Tm - T x), because it provides information about the glass forming ability of a melt. In fact, the KH parameter is an empirical measure of the stability or resistance of the glass to crystallization under heating [33,34]. However, the correlation between glass stability and glass forming ability has already been established, especially in the case of the KH parameter [33]. Thus, the higher the KH the more easily the glass is formed. For the sake of simplicity, we chose to use Tp instead of the onset crystallization temperature (T x) to calculate KH. As Nascimento et al. [34] have showed, in the glass stability case these terms are interchangeable with no loss of accuracy.

Fig. 2 illustrates the dependence of the KH parameter on x (Cr content) and y (proportional to the Ge content). In summary, the KH values in the entire LCGTP series vary from 0.05 to 0.23, which is...
comparable to well-known glass forming systems such as lithium diborate (KH = 0.096) [34], lithium germanium phosphate (0.11) [27], fresnoite (KH = 0.14) [27] and anorthite (0.25) [34]. As expected, since GeO₂ is a good glass former, the stability of LCGTP glasses increases substantially in response to increasing Ge content, in every x series. Regarding the effect of chromium, the glass stability of the 0.2 y series also seems to increase with Cr content. On the other hand, in the 0.4, 0.6, and 0.8 y series, the glass stability increases with low Cr content, but begins to decrease again after reaching a certain point. It should be kept in mind that the increase of Cr content is followed by a decrease in both Ti and Ge content, according to the chemical formula ([GeyTi1-y]2-x), making this a more indirect analysis.

Because the Ge content is related to y but is also dependent on x (Ge = y[2-x]), the GeO₂ nominal molar content (as shown in Table 1) for each x series (Fig. 3). This enabled us to isolate the effect of GeO₂ from the Cr₂O₃ content. Pearson’s correlation coefficient (R) between the KH parameter and the GeO₂ nominal content of all the LCGTP glasses (Rall = 0.921) indicates a significant correlation between those variables (dashed line, Fig. 3a).

Moreover, when the x series are evaluated separately (R₀₂, R₀₄, R₀₆ and R₀₈), the correlation between KH and GeO₂ content is even higher (solid lines, Fig. 3a). To determine the influence of Cr₂O₃ on the stability of LCGTP glasses, we examined the joint influence of Cr₂O₃ and GeO₂ content on the KH parameter (Fig. 3b). As expected, the correlation within a particular x series (solid lines, Fig. 3b) is the same as the correlation with GeO₂ content. However, an important increase in the R coefficient when all LCGTP glasses are considered (Rall = 0.962) indicates that Cr₂O₃ also plays a positive role in the glass stability parameter (dashed line, Fig. 3b). In conclusion, this result suggests that although Cr is not considered as a glass former like Ge, it might play an intermediate role like Al₂O₃ [35].

### 3.3. Structural characterization of LCGTP glass-ceramics

After crystallization, LCGTP samples become opaque and their greenish color becomes less intense than that of the precursor glass (see Supplementary Fig. 1S). Fig. 1S shows XRD patterns of the sixteen LCGTP glass-ceramics obtained by heat-treating the precursor glass for 2 h at 900 °C. A typical diffraction pattern of NASICON-like structure, LiTi₂(PO₄)₃-type phase (COD card 96-722-2156), was detected in all the LCGTP glass-ceramics. Other diffraction peaks were also indexed as minority phase corresponding to LiCrP₂O₇-type phase (COD card 96-221-2724). Note that the assigned diffraction peaks pertaining to this phase are more intense in series with higher chromium content (Fig. 1S). Moreover, the 2θ angle of diffraction peaks corresponding to NASICON-like structures shifts as germanium content increases, due to changes in interplanar spaces (d). In fact, a progressive shift of the most intense diffraction peak towards higher 2θ is clearly visible in a comparison of all XRD patterns (see guide line, Fig. 1S).

Fig. 4 shows the most intense diffraction peak (2θ ∼ 25°) of twelve LCGTP glass-ceramics. In the 0.2 x series (Fig. 4a), the increase in y (proportional to Ge content) causes the diffraction peak to shift to higher angles. Based on Bragg’s law (n.λ = 2.d.sinθ), this shift indicates smaller interplanar distances. These results are in perfect agreement with the previous assumption, which justified the investigation of the LCGTP system. As Ge⁴⁺ has a smaller crystal radius (0.0670 nm) than Ti⁴⁺ (0.0745 nm) [31], the substitution of Ti⁴⁺ by Ge⁴⁺ in this series leads to a smaller interplanar spacing. The same applies to the 0.8 x series (Fig. 4b), albeit with smaller shifts, since the effective Ge content here is lower because x is higher (Ge = y[2-x]). On the other hand, when the 0.2 y series is analyzed as a function of x (Cr content), the shift is almost imperceptible (Fig. 4c). As the Ge content in this series is low, Cr (0.0745 nm) replaces mostly Ti (0.0745 nm) and no shift is
Conversely, if the Ge content is high, like in the 0.8 y series (Fig. 4d), an increase in Cr content shifts the most intense diffraction peak to lower 2θ angles because the interplanar spacing increases, since the crystal radius of Cr$^{+3}$ (0.0745 nm) is larger than that of Ge$^{+4}$ (0.0670 nm).

As the NASICON-like structure has a rhombohedral lattice (space group R3c, trigonal system), its cell parameters can also be represented on hexagonal axes [36]. Thus, the lattice parameters and unit cell volume of NASICON-like structure can be estimated applying Bragg’s law to the diffraction angle of its atomic planes, followed by the use of Eq. (1) and Eq. (2), respectively. In fact, it is possible to determine a and c parameters by knowing the diffraction angle of only two atomic planes. Even though, we chose to use a fitting tool so-called “profile matching with constant scale factor”, available in Full Prof Suite software. This fitting tool uses all reflections generated from the space group which confers better accuracy to the analysis. In addition to the cell parameters, also zero shift and Caglioti’s coefficients were refined. A second phase (space group P 1211, monoclinic system) corresponding to the LiCrP$_2$O$_7$ compound has also been added to get more reliable fitting.

For all sixteen glass-ceramics, agreement between experimental and calculated XRD patterns is reasonable good, with $\chi^2$ lower than 7 and Bragg R-Factor for the NASICON-like phase lower than 0.5. Fig. 2S shows experimental and calculated XRD pattern of glass-ceramic sample LCGTP0602.

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$  \hspace{1cm} (1)

$$V = \frac{\sqrt{3} a^2 c}{2}$$  \hspace{1cm} (2)

Fig. 5 illustrates the dependence of the unit cell volume of NASICON-like structure on x and y. An analysis of the unit cell volume in the 3D plot in Fig. 5a clearly indicates that the unit cell volume decreases when y increases in every x series. As stated earlier, this effect is smaller in the 0.8 than in the 0.2 x series because the effective Ge content (y[2-x]) is lower in 0.8 than in 0.2 x series. In the case of Cr content, the increase in x causes practically no change in the unit cell volume of the 0.2 y series, but significantly increases the volume in the 0.8 y series. To gain a clear understanding of how the unit cell volume of a NASICON-like structure changes with Cr and Ge content, we have also plotted the unit cell volume as a function of the effective Ge content and its respective difference (Cr plus Ti content), since Cr$^{+3}$ and Ti$^{+4}$ have comparable crystal radii (Fig. 5b). Note that the sum of Cr, Ge and Ti is always 2 because of the proportion of the octahedral site in the LCGTP system. Pearson’s correlation coefficient (R) shows a
negative dependence ($R = -0.991$) of the unit cell volume on the effective Ge content ($y(2-x)$). Hence, the enhancement of Ge content indeed decreases the unit cell volume. Consequently, the correlation coefficient between the unit cell volume and Cr plus Ti content ($x + [1-y][2-x]$) is the same, but positive ($R = +0.991$). Moreover, the intercepts where Ge content ($1.314 \pm 0.002$ nm$^3$) and Cr plus Ti content ($1.198 \pm 0.004$ nm$^3$) are zero, match fairly well with the unit cell volume of LiTi$_2$(PO$_4$)$_3$ (1.310 nm$^3$) and LiGe$_2$(PO$_4$)$_3$ (1.207 nm$^3$) [28], respectively. Therefore, notwithstanding some spurious phases, it is highly likely that Ge, Ti, and Cr share the octahedral sites of NASICON-like structures in all the LCGTP compositions. In summary, these results are consistent with our previous prediction that the lattice parameters and unit cell volume of the proposed Li$_{1+}[Cr(Ge,Ti)_{1-y}^{2-x}](PO_4)_3$ system could be tailored by means of compositional design. In addition, the unit cell volume of LCGTP glass-ceramics of the 0.2 $y$ series is only slightly lower (1.290–1.300 nm$^3$) than that of LiTi$_2$(PO$_4$)$_3$ (1.310 nm$^3$).

3.4. Electrical characterization

We have analyzed the sixteen LCGTP glass-ceramics by electro-chemical impedance spectroscopy (EIS) at six different temperatures, making a total of 96 measurements. In every case, the EIS analysis reveals the typical behavior of an ionic conductive electrolyte with a spike of points at low frequency (see Fig. 6a), which is characteristic of an ionic polarization effect [18,27,28,37]. This result indicates that the main charge carrier in this glass ceramic are ions and the electronic conductivity can be neglected. Fig. 6 shows a representative set of data obtained from the EIS analyses of LCGTP glass-ceramics. Here, the complex impedance ($Z^*$) plots have been normalized by the shape factor ($\ln(S)$, thickness/area) of each sample given arise what we have called specific impedance ($Z_{sp}$). This approach allows one to make direct comparisons of differences in the electrical behavior of samples, since the resistivity of samples can be promptly read on the real axis ($Z_{sp}$). An analysis of Fig. 6a, which shows impedance data of LCGTP0602 glass-ceramics recorded at 300 K, reveals three distinct contributions, namely, in the low frequency range ($10^5–1$ Hz), a spike related to lithium ions being blocked by the sputtered gold electrodes; in the medium frequency range ($10^2–10^5$ Hz), a depressed semi-circle related to grain boundary resistance; and in the high frequency range ($>10^8$Hz), a partial semi-circle related to grain resistance. All the LCGTP glass-ceramics have exhibited these behaviors, although the frequency range in which they are observed varied, since the resistivity of LCGTP glass-ceramics also varied considerably.

The strong dependence of the electrical properties of LCGTP glass-ceramics on their composition can be directly observed in the specific complex impedance plots. Fig. 6b presents $Z_{sp}$ plots of LCGTP glass-ceramics of the 0.6 $x$ series. As can be seen, while the total resistivity of the LCGTP0608 glass-ceramic (higher Ge content) is higher than 35 kΩ cm (Fig. 6b), that of the other glass-ceramics of the 0.6 $x$ series is lower than 10 kΩ cm (insert Fig. 6b, 10X zoom). Moreover, the grain resistivity of the LCGTP0608 is in the same order of magnitude as the total resistivity of the other glass-ceramics (insert Fig. 6b, 10X zoom). In contrast, the LCGTP0602 glass-ceramic has presented the lowest resistivity (about 3 kΩ cm) at room temperature (300 K) among all the LCGTP glass-ceramics studied here (Fig. 6a and b). As the temperature of measurement is increased the resistivity of the samples decreases. Fig. 6c shows $Z_{sp}$ plots of LCGTP0602 glass-ceramics measured at six different temperatures. As the theory predicts, the decrease in resistivity as a function of temperature is not linear but logarithmic.

In order to properly separate and quantify grain and grain boundary contributions, the impedance data are fitted with an equivalent circuit comprising a parallel combination of a resistance ($R_g$) and a capacitance ($C_g$) attributed to the grain contribution; in series with a parallel combination of a resistance ($R_{gb}$) and a constant-phase element (CPE$_{gb}$) attributed to the grain boundary contribution; and a constant-phase element (CPE$_{eq}$) that accounts for the electrode polarization effects in the low frequency region (see Fig. 6a). The impedance of the constant-phase element (CPE) is given by Eq. (3), where $\omega$ is the angular frequency and $Q$ and $n$ are fitting parameters related, respectively, to capacitance and depression angle ($n \leq 1$), [26,37,38].

$$Z_{CPE} = \frac{1}{Q(\omega)^n}$$

(3)

$$C_{\phi} = \frac{(R\phi Q_{\phi})^{-\alpha}}{R_{\phi}}$$

(4)

Note that the equivalent circuit used here (Fig. 6a) does not comprise an $R_0$ circuit element related to the resistance and/or inductance of the cell measurement or equipment. Although, the use of $R_0$ is very common in the literature [19,39,40], this approach can lead to misinterpretation, since this $R_0$ parameter is normally unknown and is usually a floating parameter in fitting procedures. Thus, the impedance of the equipment can be overestimated in detriment to that of the sample, which leads to an overestimation of the sample’s conductivity. This is particularly true when samples are highly conductive and the frequency range used in the measurement is not broad enough to
encompass all the electrical behavior of the grain contribution. In this work, we chose to ensure a near zero equipment impedance by means of calibration, which allows us to work with an equivalent circuit without \( R_0 \). It is worth to note that this approach can lead to an underestimation of total conductivity but never an overestimation.

Fig. 6a shows the resulting fit obtained for the impedance data of sample LGCTP0602. The goodness of fit is remarkably high (\( \chi^2 = 0.0006 \), in this case) indicating that the chosen equivalent circuit can describe very well the impedance data.

We extrapolated the fit to a frequency (10 GHz) out of the measured frequency range just to clearly show the grain contribution, which agrees very well with the high-frequency experimental data where the grain contribution is significant. The grain contribution becomes more obvious in analysis of more resistive samples such is the case of LCGTP0608 sample (insert Fig 6b, 10X zoom). The results of fitting of grain capacitance (\( C_g \)) at 300 K of all the LGCTP glass-ceramics range from \( 2.5 \times 10^{-12} \) to \( 1.5 \times 10^{-11} \) F. As for grain boundary, capacitance (\( C_{gb} \)), which has been determined using Eq.(4) [26,37], is found to range from \( 3.2 \times 10^{-11} \) to \( 3.0 \times 10^{-10} \) F, while the parameter \( n_{gb} \) is fitted between 0.46 and 0.81. All the results of fitting are reasonable for polycrystalline ionic conductors [41], demonstrating that the equivalent circuit employed here can provide a good description of the electrical behavior of the investigated electrolytes.

The grain (\( \sigma_g \)) and grain boundary (\( \sigma_{gb} \)) contributions to the ionic conductivity, as well as the total ionic conductivity (\( \sigma_t \)) of LGCTP glass-ceramics, were determined by applying the relationship \( \sigma = 1/\rho \) [26,37] to the values of \( R_g \), \( R_{gb} \) (obtained by fitting) and \( R_g + R_{gb} \), respectively. As the impedance data have previously been normalized by the sample’s shape factor, the values obtained by fitting directly indicate the resistivities (\( \rho \)). As a matter of fact, since the geometrical factor (1/S) of grains and grain boundaries is unknown, only their apparent contribution can be estimated based on the shape factor of the entire sample.

The dependence of ionic conductivity on the inverse of temperature has been plotted following the Arrhenius relation expressed in Eq.(5) [23,42], 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.

\[
\sigma T = A \exp\left(\frac{-E_a}{k_B T}\right)
\]  

Arrhenius plots of grain and grain boundary apparent contribution of ionic conductivity for LGCTP glass-ceramics of the 0.6 x series are shown in Fig. 6d. Both grain and grain boundary apparent contributions present an Arrhenius behavior. Fig. 6d clearly shows that the grain apparent conductivity of LGCTP0602 is higher than that of LGCTP0608. The grain boundary apparent conductivity of LGCTP0602 is even higher than the grain apparent conductivity of LGCTP0608 glass-
ceramics. Thus, the increase of Ge content seems to impair both grain and grain boundary conductivities. Indeed, this behavior generally has prevailed throughout the entire LCGTP glass-ceramic system.

Fig. 7 shows the dependence of total ionic conductivity ($\sigma_t$) at 300 K on x and y, as well as the grain ($\sigma_g$) and grain boundary ($\sigma_{gb}$) apparent contribution. As can be readily seen in Fig. 7a, an increase in y (proportional to Ge content) decreases the total ionic conductivity of every x series. On the other hand, looking at the y series, the enhancement of x (Cr content) seems to increase the total ionic conductivity up to a certain limit ($x = 0.6$). After this point, the enhancement of Cr content decreases the total ionic conductivity of every y series. The highest total ionic conductivity is found to be $2.9 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ ($\log [\sigma_t] = -3.53$) for the LCGTP0602 glass-ceramic. Half of all the LCGTP glass-ceramics, namely, LCGTP0402, LCGTP0404, LCGTP0602, LCGTP0604, LCGTP0606, LCGTP0802, LCGTP0804 and LCGTP0806, have presented a total conductivity higher than $10^{-4} \Omega^{-1} \text{cm}^{-1}$ at 300 K. One can also see that the tendency and magnitude of total ionic conductivity is mostly limited by the grain boundary apparent contribution (Fig. 7c). However, special attention should focus on the grain apparent contribution, which is higher than $10^{-2} \Omega^{-1} \text{cm}^{-1}$ in the LCGTP glass-ceramics of the 0.2 y series (Fig. 7b). The apparent grain conductivity decreases in response to increasing y in every x series. On the other hand, increasing x does not change substantially the apparent grain conductivity of the 0.2 and 0.4 y series, but increases it sharply in the 0.6 and 0.8 y series.

The activation energy for ionic conductivity of grain and grain boundary apparent contributions has been calculated for all the LCGTP glass-ceramics by using the fitting results of Arrhenius-type plots. Fig. 8 shows the dependence of activation energy related to grain contribution ($E_{ag}$) as a function of x and y, as well as the effective Ge content ($\xi(y(2-x))$). The increment of y causes an increase in $E_{ag}$ in every x series, while the increment of x does not show a regular tendency, exhibiting a different trend for each y series (Fig. 8a). Nonetheless, the 0.2 y series, which presents apparent grain conductivity higher than $10^{-3}$, shows the lowest $E_{ag}$ (< 0.27 eV). Additionally, 10 of the 16 LCGTP glass-ceramics present $E_{ag}$ lower than 0.30 eV. As we have previously done with the unit cell volume in section 3.3, the correlation between effective Ge content and $E_{ag}$ for all the LCGTP glass-ceramics has also been evaluated based on Pearson’s coefficient (R). Here, we find a positive and significant correlation (0.9713), indicating that the Ge content causes structural changes that hamper the movement of lithium ions in NASICON-like structure. Considering the negative correlation ($-0.991$) between Ge content and unit cell volume shown in the previous section, we can safely infer that there is also a correlation between the unit cell volume and $E_{ag}$, in which an increase in the unit cell volume tends to cause a decrease in $E_{ag}$. The relationship between unit cell volume and activation energy for ion conduction has already been reported for other systems. However, this reported correlation contemplates a broad range of cell volumes with only tetravalent cations (Ge, Ti, and Hf) and suggests an optimum volume to a lower $E_{ag}$ [5]. In this study, we extended this investigation considering also a trivalent cation (Cr$^{3+}$), but we use a narrower range of cell volumes. However, notwithstanding the correlation we found, another structural issue other than just the cell volume may play a role in the $E_{ag}$ since there is a considerable dispersion in $E_{ag}$ data. As for the pre-exponential term, A, the values pertaining to grain contribution ($\log A_g$) ranges from...
The charge carrier concentration (\( n = \frac{e \lambda^2 \nu}{6k_B} \)), where \( n \) is the charge carrier concentration (\( \sim 10^{-3} \text{ions/cm}^2 \)), \( e \) is the electronic charge of an electron (\( 1.6 \times 10^{-19} \text{C} \)), \( \lambda \) is the jump distance (\( \lambda \sim 1 \times 10^{-8} \text{cm} \)) and \( \nu \) is the attempt frequency (\( \nu = 10^{13} \text{Hz} \)) [18].

Values of activation energy (\( E_{A,gb} \)) and log pre-exponential term (\( \log A_{gb} \)) related to grain boundary contribution are identified, ranging from 0.36 to 0.49 eV and from 3.8 to 6.5, respectively. In the case of \( E_{A,gb} \), no important correlation relating to Ge content (\( R < 0.05 \)) has been found. In the case of the LCGTP0602 glass-ceramic, which exhibited the highest grain boundary conductivity, \( E_{A,gb} \) is found to be 0.42 eV and \( \log A_{gb} \) is at the upper limit (\( \log A_{gb} = 6.5 \)). Although it is tempting to attribute the high grain boundary conductivity of the LCGTP0602 sample to its high \( A_{gb} \) value, it should be kept in mind that the grain boundary conductivity calculated here is based on the shape factor of the whole sample. Therefore, the grain boundary conductivity calculated here is simply the apparent grain boundary conductivity, thus precluding an in-depth discussion of the differences found in the \( A_{gb} \) term [37]. The real shape factor of the grain boundary depends on the microstructure of the glass-ceramics. In this regard, the reason why some glass-ceramics of this system present higher grain boundary conductivities than others is still unknown, but the microstructure and spurious phase should play a significant role. However, since this issue falls outside the scope of this study, we consider it an open question for further investigation.

4. Conclusions

We have investigated the influence of substituting Ti by Cr and Ge on the glass stability of precursor glasses and the electrical properties of glass-ceramics of the \( \text{Li}_{1+x}\text{Cr}_{x}\text{(Ge}_y\text{Ti}_{1-y})_{2-x}\text{PO}_4 \_3 \) system. The glass stability of LCGTP glasses can be enhanced with Ge and Cr content. The crystallization temperature of all the LCGTP glasses was found to range from 700 to 730 °C. Thus, after heat treatment at 900 °C for 2 h, all the LCGTP glasses became crystallized. All the glass-ceramics presented the NASICON-type phase and their lattice parameters decreased with Ge and increased with Cr content, enabling adjustment of the unit cell volume of the NASICON-like structure. Furthermore, the total ionic conductivity of the glass-ceramics, which showed a strong dependence on Cr and Ge content, varied from 2.9 \( \times 10^{-4} \text{Ω}^{-1} \text{cm}^{-1} \) (LCGTP0602) to 2.9 \( \times 10^{-7} \text{Ω}^{-1} \text{cm}^{-1} \) (LCGTP0208) at 300 K. The activation energy for lithium conduction related to grain contribution increased with Ge content. The LCGTP0602 glass-ceramic showed the highest grain ionic conductivity (\( 1.2 \times 10^{-3} \text{Ω}^{-1} \text{cm}^{-1} \)) at room temperature. This specific composition also presented the lowest activation energy relating to grain contribution (0.26 eV). The main findings suggest that the LCGTP system is promising for the development of fast Li ion-conducting glass-ceramics, offering a compromise between the glass stability of the precursor glass and the electrical properties of the resulting glass-ceramics. Further microstructural optimization studies are expected to drive this system toward even higher ionic conductivities. The system’s electrochemical stability window is also under study.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2017.10.020.

References
