A NEW LITHIUM ION-CONDUCTING GLASS-CERAMIC WITH NASICON STRUCTURE.

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ABSTRACT

We proposed a new lithium ion-conducting glass-ceramic based on \( \text{Li}_{1+x}\text{Cr}_x\text{(Ge}_y\text{Ti}_{1-y})_2\text{(PO}_4\text{)}_3 \) (LCGTP) system. A particular composition of this system has been synthetized by melt-quenching method followed by crystallization and investigated by using DSC, XRD, SEM and EIS techniques. The main results indicated that the LCGTP glass presents internal nucleation and appreciable glass stability, which allows its development by means of glass-ceramic route. The composition studied forms NASICON \( \text{LiTi}_2\text{(PO}_4\text{)}_3 \)-type phase under heat treatment showing that the proposed system can accommodate Cr, Ti and Ge in octahedral site. The highest room temperature ionic conductivity (6.5 \( \times \) 10\(^{-5}\) \( \Omega \)^{-1}.cm\(^{-1}\)) was found to the glass-ceramic heat treated for 12 hours at 900\(^\circ\)C, which presented a considerably high ionic conductivity related to grain contribution (8.5 \( \times \) 10\(^{-4}\) \( \Omega \)^{-1}.cm\(^{-1}\)). These set of results suggest that the proposed system is promisor to develop fast Li-ion conducting glass-ceramics with a further microestrutural optimization study.

Keywords: Lithium ion-conducting, glass-ceramics, NASICON.

1 INTRODUCTION

Li-ion batteries have an undefeatable combination of high energy and power density, making it the technology of choice for portable electronics, power tools, electric vehicles and large-scale energy production for intermittent power generation. Battery performance depends critically on the materials used and one challenge is the development of safer and more reliable electrolytes to replace the market-leading...
polymeric lithium ion conductors. In this respect, inorganic solid lithium ion conductors present potential advantages, such as, absence of leakage, negligible electronic conductivity and a higher electrochemical and thermal stability (1-6). Among the main lithium ion conductors one can point out sulfides glasses and crystals (7-8), oxides with perovskite-type (9-10) and garnets-type (3, 11) and phosphates with NASICON-type structure (12-14).

The main advantage of NASICON-type lithium ion conductors is its structural versatility regard to a wide range of compositions. The general formula of a NASICON-type electrolyte is LiM\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}, where M is a tetravalent cation (Ge, Ti, Zr, Sn or Hf). The NASICON structure consists of a covalent skeleton containing MO\textsubscript{6} octahedron and PO\textsubscript{4} tetrahedron which form 3D interconnected channels where conductor cations are able to move through. Consequently, the structural and electrical properties of NASICON-type compounds vary with the composition of the framework (4, 5, 12, 15). Among the after mentioned tetravalent cations, titanium (Ti) in LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} (LTP) system shows the highest ionic conductivity and smallest activation energy (6, 15). Additionally, the partial substitution of the M cation by a trivalent cation, A\textsuperscript{3+} (Al, Ga, In, Sc, Y, La, Cr or Fe), generates a deficiency in positive charge, which is compensated by additional Li\textsuperscript{+} ions, leading to the Li\textsubscript{1+x}A\textsubscript{x}M\textsubscript{2-x}(PO\textsubscript{4})\textsubscript{3} system (16).

Due to its particular characteristics, NASICON electrolytes has been synthetized on uncountable chemical compositions by applying different synthesis routes, such as, sol-gel (17-18), solid state reaction (16, 19) and glass-ceramic route (20-22). In this respect, the glass-ceramic route presents clear advantages compare to any route that demand a further sintering stage to consolidate the electrolyte, since one can obtain free porous electrolyte and properly designed its microstructure controlling glass crystallization.

On base of these ideas, the present work introduce a new NASICON series composition based on the Li\textsubscript{1+x}Cr\textsubscript{x}(Ge\textsubscript{y}Ti\textsubscript{1-y})\textsubscript{2-x}(PO\textsubscript{4})\textsubscript{3} system. The substitution of titanium (Ti) by chromium (Cr) based on system Li\textsubscript{1+x}Cr\textsubscript{x}Ti\textsubscript{2-x}(PO\textsubscript{4})\textsubscript{3} (LCTP) has been investigated by Aono (19) resulting in a lithium ion-conducting material with remarkable ionic conductivity (~5x10\textsuperscript{-4} S.cm\textsuperscript{-1}) even though it was obtained by sintering (about 15% of porosity). Unfortunately, the LCTP system has no appreciable glass forming ability due to low glass forming content, thereby rendering electrolyte development by means of glass-ceramic route. On the other hand, germanium oxide is known to be a good glass forming (13, 23) and the Li\textsubscript{1+x}Cr\textsubscript{x}Ge\textsubscript{2-}
The (PO₄)₃ (LCGP) system has already been synthetized by using glass-ceramic route presenting an impressive ionic conductivity in room temperature (~7x10⁻⁴ S.cm⁻¹) (21). However, Cr³⁺ ionic radius in octahedral coordination (0.0755 nm) is much closer of Ti⁺⁴ (0.0745 nm) than Ge⁺⁴ (0.0670 nm) (24). Therefore, chromium insertion does not cause considerable changes in NASICON structure of LTP system (5). Accordingly, the major aim of this work was to investigated the NASICON-type phase formation and its electrical properties in a particular composition (Li₁.₄Cr₀.₄(Ge₀.₄Ti₀.₆)₁.₆(PO₄)₃) of the proposed LCGTP system, by using the glass-ceramic route.

2 EXPERIMENTAL METHODS

LCGTP precursor glass was obtained by melting a mixture of reagents with an oxide molar ratio of 15.5Li₂O-5Cr₂O₃-16GeO₂-24TiO₂-37.5P₂O₅, based on the stoichiometric chemical formula Li₁.₄Cr₀.₄(Ge₀.₄Ti₀.₆)₁.₆(PO₄)₃. Li₂CO₃ (99.0%, Synth), Cr₂O₃ (99.0%, Aldrich), GeO₂ (99.99%, Alpha Ceasar), TiO₂ (99.9%, Aldrich) and NH₄H₂PO₄ (98%, Aldrich) were used as raw materials. These reactants were homogenized in a planetary mixer for 12 hours and the resulting mixture was calcined in a platinum crucible using a hot plate in order to decompose NH₄H₂PO₄ and prevent chemical attack of platinum crucible in higher temperatures. Thus, the resulting powder was melted at 1450°C for 30 min and the low-viscous liquid was splat-cooled in a brass die in order to avoid crystallization of the super-cooled liquid. The quenched glass was annealed at 550°C for 2 h to relieve thermal stresses. After cooling, the glass was bubble-free, transparent but with an intense green color (see Fig. 2), probably caused by chromium content. The obtained LCGTP glass was heat treated as bulk samples based on DSC analysis at Tp (HT700) and also at 800°C (HT800), 900°C (HT900), and 1000°C (HT1000) for 12 hours.

Differential Scanning Calorimetry (DSC) analyses were performed in a glass bulk sample under heating rate of 10 K.min⁻¹ using a Netzsch DSC 404 equipment supplied with platinum pans and covers. The characteristic temperatures of the precursor glasses, such as, the glass transition temperature (Tg), the crystallization onset (Tx) and the crystallization peak temperature (Tp) were taken from DSC curves. In addition, glass crystallization was monitored by means of optical dilatometry (OD) using an equipment Misura (model 444) also under heating rate of 10 K.min⁻¹. The melting temperature (Tm) of the full crystalline glass-ceramic was
also estimated by using optical dilatometry under the same heating rate. In order to confirm the glassy nature of LCGTP glass, X-ray diffractions analysis were performed in a bulk glass sample in a Rigaku Ultima IV diffractometer with Cu Ka radiation under a continuous scan with speed of 0.02º/s in the range of 5 to 90º.

X-ray diffraction (XRD) analyses under the after mentioned conditions were also performed in all glass-ceramics heat treated for 12 hours. Electrical conductivity was measured by electrochemical impedance spectroscopy (EIS) using a Novocontrol-Alpha impedance analyzer in the frequency range of $10^7$–$1$ Hz, voltage amplitude of 500mV and at temperature range of 300-400K. EIS measurements were conducted in flat and polished samples with parallel faces and gold sputtered in both sides to ensure electrical contact. Samples were about 0.1cm thick and had a contact area between 0.1 and 0.2 cm². The obtained results were fitted by means of appropriated software of impedance spectroscopy (Zview 3.2b) using an equivalent circuit. Fracture surface were prepared by breaking the glass-ceramics and sputtering gold on the fractured surface. Micrographs were taken by using a Scanning Electron Microscope (SEM) equipment FEI Inspect S50.

3 RESULTS AND DISCUSSION

DSC and DO curves of LCGTP bulk sample are presented in Fig. 1. DSC analysis of LCGTP glass shows a clear Tg (Fig. 1a, zoon in) and a very intensive and narrow crystallization peak, which become easy Tx and Tp identification (Fig. 1a). The shrinkage area of LGTP sample as a function of temperature shows two characteristic events (Fig. 1b). The first event at 695ºC is a very small shrinkage of about 1% (Fig. 1b, zoom in) in the same range of Tp determined from DSC analysis. Thus, this shrinkage is related to the crystallization process and shows that the density of crystallized phase is slightly smaller than the parent glass. The second event happens after 1330ºC when the sample start to melts. As the Li$_{1.4}$Cr$_{0.4}$(Ge$_{0.6}$Ti$_{0.4}$)$_{1.6}$(PO$_4$)$_3$ system is a solid solution the crystallized phase starts to melt at about 1330ºC and finishes at 1346ºC when the entire sample is liquid (Fig. 1b). The latter is related to the liquidus temperature and was taken as Tm.
Fig. 1. DSC (a) and DO (b) curve of LCGTP precursor glass in bulk sample under heating rate of 10K.min⁻¹. Tg, Tp, Tx and Tm are indicated in plots.

By using the Tg from DSC and Tm from OD analysis we are able to calculate the reduced glass transition parameter (Tgr) given by relation Tg/Tm. In this case the ratio found was 0.553 which is a strong evidence that the studied glass present homogenous nucleation (20, 22). The Hruby parameter (Kh) is another relation (Tx-Tg/Tm-Tx) of interest because bring information about the glass forming ability of a particular glass (25-26). The higher Kh values, higher is glass forming ability. The Kh value found for the studied glass was just reasonable (0.105) but comparable to well-known glass system as lithium disilicate (0.163) and lithium diborate (0.096) (25).

In order to achieved highly crystalline glass-ceramics, LCGTP glass samples were also crystallized for 12 hours in different temperatures. XRD results for the LCGTP glass sample and glass-ceramic samples heat treated at 700°C (HT700), 800°C (HT800), 900°C (HT900) and 1000°C (HT1000) for 12 hours are presented in Fig. 2. As can be seen, LCGTP glass sample shows no XRD pattern. Besides this, NASICON LiTi2(PO4)3-type phase (JCPDS card 35-754) forms in all glass-ceramic and the intensity of XRD pattern also increases as heat treatment temperature get higher. An image of the LCGTP glass and HT700 glass-ceramic over the word NASICON shows that while LCGTP glass is transparent is totally opaque.
Fig. 2. XRD patterns of LCGTP glass and LCGTP glass-ceramics heat treated for 12 hours in bulk sample at different temperatures: HT700, HT800, HT900 and HT100.

Electrochemical impedance spectroscopy (EIS) analyses of the LCGTP glass and all glass-ceramics showed a typical behavior of ionic conductor with a spike of points in low frequency showing an ionic polarization effect \(^{(13, 21-22)}\). In order to separate grain and grain boundary contributions, the impedance data were fitted based on 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 with a constant-phase element \((CPE_e)\) accounts for electrode polarization effects in the low frequency region\(^{(23, 7)}\). In case of glass sample, the equivalent circuit used has only a parallel combination of a resistance \((R_a)\) and a constant-phase element \((CPE_a)\) in series with a constant-phase element for electrode \((CPE_e)\). Fig. 3 shows a complex impedance plot including experimental and fitted data, as well as the used equivalent circuit. Total ionic conductivity of glass and glass-ceramics were determined by applying equation \((A)\) \(^{(23, 27)}\) to resistance fitting results, where \(t\) denotes the thickness and \(S\) the area of the sample.

\[
\sigma_t = \frac{1}{\frac{R_g}{R_{gb}} + \frac{t}{S}}
\]  

\((A)\)
Fig. 3. Complex impedance plot for sample SHT700 recorded at room temperature (300K) and fitted based on showed equivalent circuit.

The dependence of total ionic conductivity with the inverse of temperature were plot based on the Arrhenius relation expressed in equation (B) \(^{(13, 22)}\), where \(k_b\) is Boltzmann’s constant, \(T\) is the absolute temperature \(E_a\) is the activation energy to ion conduction and \(\sigma_0\) is the pre-exponential factor.

\[
\sigma_t = \sigma_0 \exp\left(\frac{-E_a}{k_b T}\right)
\]  

(B)

In Fig. 4, it is showed an Arrhenius plot of total ionic conductivity \((\sigma_t)\) for all glass-ceramics and also for LCGTTP glass. Ionic conductivity in glass-ceramics is up to 5 magnitude orders higher than the parent glass. This result demonstrated how particular is the NASICON structure since in general a glass has higher conductivity than its isochemical crystal \(^{(15)}\). Additionally, the ionic conductivity increases as a function of heat treatment temperature with the exception of the heat treatment conducted at 1000°C (HT-1000). Activation Energy \((E_a)\) to ion conduction are calculated for LCGTTP glass and all glass-ceramics by means of equation (B). In Table 1 are summarized the grain, grain boundary and total ionic conductivity at room temperature (300K) as well as the \(E_a\) and \(\sigma_0\) term related to total contribution.
Based on total contribution results is clear that the main difference between LCGTP glass and glass-ceramics lies in $E_a$, since $\sigma_0$ has comparable values for glass and glass-ceramics. The separate contributions of grain and grain boundary conductivity show that the grain boundary is the limiting factor. The highest value of ionic conductivity at room temperature (6.5 x10$^{-5}$ $\Omega^{-1}.cm^{-1}$) was found to HT900 glass-ceramic, which presents a notably grain conductivity of 8.5 x10$^{-4}$ $\Omega^{-1}.cm^{-1}$. On the other hand, sample HT1000 shows the lower ionic conductivity, which is probably due to porous or cracks introduced in heat treatment step. In fact, while all glass-ceramics have appreciable mechanical strength, HT1000 sample was fragile and used to break easily under manipulation.

Table 1. Ionic conductivity at room temperature ($\sigma_{300K}$) for grain, grain boundary and total contribution, as well as $E_a$ and the log[$\sigma_0$] relate to total contribution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grain $\sigma_{300K}$ ($\Omega^{-1}.cm^{-1}$)</th>
<th>Grain Boundary $\sigma_{300K}$ ($\Omega^{-1}.cm^{-1}$)</th>
<th>Total $\sigma_{300K}$ ($\Omega^{-1}.cm^{-1}$)</th>
<th>Log[$\sigma_0$]</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>-</td>
<td>-</td>
<td>4.2 x10$^{-10}$</td>
<td>2.34(4)</td>
<td>0.700(3)</td>
</tr>
<tr>
<td>HT700</td>
<td>2.7 x10$^{-4}$</td>
<td>2.8 x10$^{-5}$</td>
<td>2.6 x10$^{-5}$</td>
<td>1.93(3)</td>
<td>0.365(2)</td>
</tr>
<tr>
<td>HT800</td>
<td>4.1 x10$^{-4}$</td>
<td>3.4 x10$^{-5}$</td>
<td>3.1 x10$^{-5}$</td>
<td>2.23(1)</td>
<td>0.402(1)</td>
</tr>
<tr>
<td>HT900</td>
<td>8.5 x10$^{-4}$</td>
<td>7.1 x10$^{-5}$</td>
<td>6.5 x10$^{-5}$</td>
<td>2.11(2)</td>
<td>0.399(1)</td>
</tr>
<tr>
<td>HT1000</td>
<td>-</td>
<td>-</td>
<td>2.9 x10$^{-8}$</td>
<td>1.71(4)</td>
<td>0.440(3)</td>
</tr>
</tbody>
</table>

Fig. 4. Arrhenius plot of total ionic conductivity as a function of inverse temperature for the precursor LCGTP glass and all glass-ceramics.
In Fig. 5 are shown SEM micrographs of fracture surface for all studied glass ceramics under different magnification, 100,000X to HT700 (a), 50,000X to HT800 (b), 15,000X to HT900 (c) and 10,000X to HT1000 (d). HT700 and HT800 samples show an irregular fracture surface with underdeveloped grains, without defined shape and grain size smaller than 1 um. On the other hand, HT900 and HT1000 samples showed a typical NASICON cubic-shaped grains (17, 21, 27) and higher than 1 um. Moreover, HT1000 glass-ceramic showed a very regular surface fracture typical from intergranular fracture which justify its poor mechanical strength and also may explain the drop in ionic conductivity.

Fig. 5. SEM micrographs of surface fracture of LCGTP glass-ceramics heat treated at a) 700°C, b) 800°C, c) 900°C, and d) 1000°C.
4 CONCLUSIONS

We proposed here a new NASICON series based on the Li_{1+x}Cr_x(Ge_yTi_{1-y})_2 PO_4_3 system with great potential to be synthetized through glass-ceramic route. We have investigated a particular composition of this system with regard to crystallization behavior, formation of NASICON-type structure and electrical properties of the obtained glass-ceramics. The studied LCGTP glass shows internal nucleation and presents thermal stability parameters (T_{gr} and K_{hi}) compared with other self-nucleating glasses. Besides, NASICON LiTi_2(PO_4)_3-type phase forms without presence of phases related to germanium chromium and titanium oxide. Ionic conductivity of glass-ceramics is up to 5 order of magnitude higher than the precursor glass and is dependent of heat treatment temperature. The highest room temperature ionic conductivity (6.5 x 10^{-5} \Omega^{-1}.cm^{-1}) was found to the glass-ceramic heat treated for 12 hours at 900°C. Its high ionic conductivity related to grain contribution (8.5 x 10^{-4} \Omega^{-1}.cm^{-1}), suggest that the proposed system is promisor to develop fast Li ion conducting glass-ceramics by optimizing its microstructure. Further compositional adjustment could provide a compromise between glass stability (Ge addiction) and the lattice parameter of NASICON structure (Ti and Cr addiction).

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