Preparation of glass-ceramic in Li$_2$O-Al$_2$O$_3$-GeO$_2$-P$_2$O$_5$ system

Jelena D. Nikolić, Sonja V. Smiljanjić, Srdan D. Matijašević, Vladimir D. Živanović, Mihajlo B. Tošić, Snežana R. Grujić, Jovica N. Stojanović

1Institute for the Technology of Nuclear and other Mineral Raw Materials, 86 Franchet d’Esperey St, 11000 Belgrade, Serbia
2Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia

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Abstract
The results of preparation and structural characterization of glass-ceramics from the system Li$_2$O-Al$_2$O$_3$-GeO$_2$-P$_2$O$_5$ are shown in this paper. The crystallization behaviour of the selected glass was examined under non-isothermal and isothermal crystallization conditions. DTA, XRD and SEM methods were employed for analyses. It was confirmed that this glass crystallizes by the volume crystallization mechanism. The results also showed that the glass crystallize by primary crystallization. As a primary phase the LiGe$_2$(PO$_4$)$_3$ is formed and the traces of GeO$_2$ as a secondary one is present. The crystallization process occurred at a high homogeneous nucleation rate and the spherical morphology of crystal growth. By applying the Kissinger relation the activation energy of crystal growth $E_a = 462$ kJ/mol was determined.

Keywords: germanium phosphate glass, crystallization, kinetics, crystal growth

I. Introduction
High lithium ionic conducting solids are potential electrolyte materials for high energy density batteries and other electrochemical devices [1]. Based on conducting properties one of most promising materials for such purpose is the glass-ceramic prepared from Li$_2$O-Al$_2$O$_3$-GeO$_2$-P$_2$O$_5$ glassy system. These materials can be usually obtained by the classical powder sintering route, sol-gel method and common glass-ceramic processes [2]. Because of several technological advantages the glass-ceramics process was frequently used for fabrication of lithium ionic conducting materials [3,4]. The studies of crystallization of Li$_2$O-Al$_2$O$_3$-GeO$_2$-P$_2$O$_5$ glasses showed that one of dominant crystal phase precipitated in glass matrix is NASICON-type LiGe$_2$(PO$_4$)$_3$ crystals. Also, it was found that in this composition, the partial substitution of tetravalent germanium ions by trivalent aluminium allows more Li$^+$ into the crystal structured that causes an increase in ionic conductivity of the prepared glass-ceramics [5,6]. Therefore, to fabricate appropriate lithium ion conducting glass-ceramics it is necessary to study in detail the crystallization behaviour of lithium germanium phosphate glasses of different composition. In this paper the glass with composition 22.5Li$_2$O·10Al$_2$O$_3$·30GeO$_2$·37.5P$_2$O$_5$ (mol%) prepared by standard melt-quenching technique was investigated.

II. Experimental procedure
Li$_2$O-Al$_2$O$_3$-GeO$_2$-P$_2$O$_5$ glass was prepared by the standard melt-quenching technique. Reagent grade Li$_2$CO$_3$, Al$_2$O$_3$, GeO$_2$ and (NH$_4$)$_2$HPO$_4$ were mixed and homogenized in agate mortar and the mixture was melted in covered Pt-crucible in an electrical furnace, Carbolute BLF 17/3 at $T = 1400$ °C for $t = 1$ h. The melt was cast and cooled between two steel plates. The solidified glass sample was transparent, light yellowish in colour and without residual bubbles. The chemical analysis was determined using spectrophotometer AAS PERKIN ELMER Analyst 300.

Crystallization behaviour under non-isothermal crystallization conditions was investigated and for this one part of bulk glass sample was crushed in agate mortar and then sieved to appropriate particle sizes. To determine crystallization mechanism the DTA experiments were...
used and the following glass granulations were chosen: 
< 0.048, 0.048–0.063, 0.063–0.1, 0.1–0.2, 0.2–0.3, 0.3–
0.4, 0.4–0.5, 0.5–0.65, 0.65–0.83 and 0.83–1 mm. The
measurements were performed on a Netsch STA 409EP
device by heating a constant sample mass of 100 mg at
a rate of $\beta = 10{^\circ C}/\text{min}$ in the temperature range $T = 20–
800{^\circ C}$. The glass granulation < 0.048 mm was used for
determination of kinetic parameters of crystallization and
the DTA crystallization peaks were recorded at several
heating rates 5, 10, 12, 15 and 20 °C/min.

To determine the temperature range of nucleation and the
temperature of maximum nucleation rate the samples with the
granulation 0.50–0.65 mm (100 mg) were heated in DTA
apparatus at heating rate $\beta = 10{^\circ C}/\text{min}$. Before DTA run these samples were ther-
mally treated at selected temperatures of nucleation $T = 500–620{^\circ C}$ for different times $t_n = 15, 30, 60, 120,
180 and 300 minutes.

The experiments under isothermal condition were
performed in one-stage regime with bulk glass samples
which were heated at heating rate $\beta = 10{^\circ C}/\text{min}$ up to
the chosen temperature in the range 500–800 °C and
then held at these temperatures for different times from
15 min to 100 h. The XRD method was used to deter-
mine the phase composition of the crystallized glass.
The XRD patterns were obtained on a Philips PW-
1710 automated diffractometer using a Cu tube operat-
ed at 40 kV and 30 mA. The instrument was equipped
with a diffracted beam curved graphite monochroma-
tor and a Xe-filled proportional counter. The diffraction
data were collected in the $2\theta$ Bragg angle range from 5
to 70°, counting for 1 s (qualitative identification) and
from 10° to 110° for 4 s (quantitative phase analysis-Ri-
etveld method) at every 0.02° step. The divergence and
receiving slits were fixed 1 and 0.1, respectively. All
the XRD measurements were performed at room tem-
perature in a stationary sample holder. The quantitative
amounts of crystalline phases in the glass sample were
determined using the full structure matching mode of
the Rietveld refinement technique [7], using the FULL-
PROF programme [8].

A MIRA 3 XMU microscope was used for the SEM
investigations, and the fractured bulk samples previous-
ly sputtered with gold were used.

III. Results and discussion

The results of the chemical analyses of the glass are
presented in Table 1. It can be seen that the glass com-
position is close to the nominal one.

X-ray powder diffraction (XRD) analysis confirmed
the quenched melts to be amorphous. The XRD method
was used to determine the phase composition of the
crystallized glass (Fig. 1.) and the quantitative volume
fractions of crystalline phases were obtained by the
Rietveld analysis of XRD pattern for the fully crystallized
glass sample annealed at $T = 800{^\circ C}$ for $t = 100 h$ (Table
2). The XRD results revealed the primary crystallization
of this glass with precipitation of primary LiGe$_2$(PO$_4$)$_3$
crystalline phase (rhombohedral crystal system, space
group R3c (167) [9]. According to the JCPDS card there
is no aluminium in the structure of LiGe$_2$(PO$_4$)$_3$, it is
believed that aluminium can be present in solid solution
within this structure. The formation of a solid solution
can exist due to the similar ionic radii of Al$^{3+}$ and Ge$^{4+}$.
The partial substitution of Ge$^{4+}$ by Al$^{3+}$ induces more Li$^{+}$
into the crystal structure and, therefore, increased ionic
conductivity of the resulting glass-ceramics. As shown
in Table 2, the secondary GeO$_2$ phase [10] appeared
in a small volume fraction (2.41 %) in the crystallized
sample.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{XRD pattern of the glass sample annealed at:
$T = 800{^\circ C}$ for $t = 100 h$}
\end{figure}

It may be considered that the crystal structure of
the main crystal phase LiGe$_2$(PO$_4$)$_3$ of this glass sample
consists of GeO$_6$ octahedra and PO$_4$ tetrahedra (Fig. 2).
Both units are linked by their corners to form a three-
dimensional network structure and this structure results
in cavities where lithium ions reside and in bottlenecks
in which they pass through. Asymmetry of [PO$_4$] tetra-
hedron unit of phosphate glasses is believed the origin
of their many specific properties. Three oxygen atoms
are connected by single bonds to the phosphor atom and

\begin{table}
\centering
\caption{Chemical analysis of the glass}
\begin{tabular}{lcccc}
\hline
 & Oxide content, $x$ [mol %] \\
 & Li$_2$O & Al$_2$O$_3$ & GeO$_2$ & P$_2$O$_5$ \\
Nominal & 22.5 & 10 & 30 & 37.5 \\
Analysed & 21.98±1.0 & 9.37±0.5 & 32.54±0.5 & 36.11±0.5 \\
\hline
\end{tabular}
\end{table}
via them the tetrahedron is connected to neighbouring tetrahedra.

The fourth oxygen atom is connected by a double bond to phosphor atom [11].

To determine the dominant crystallization mechanism of this glass, DTA curves of the glass powder samples with particle sizes of 0–1 mm were recorded at a heating rate \( \beta = 10 \, ^\circ\text{C}/\text{min} \) in the temperature range 400–800 \(^\circ\text{C} \), Fig. 3. All DTA curves show two exothermic temperature peaks \( T_p1 \) and \( T_p2 \) representing the glass crystallization. The higher peaks \( T_p1 \) appeared at lower temperatures while only the peaks height is changed while their positions do not change markedly by increasing of the glass particle size. Similar peaks behaviour was registered for all glass samples studied. Based on phase composition of crystallized glass sample determined by XRD it can be considered that LiGe\(_2\)(PO\(_4\))\(_3\) crystallized at peak \( T_p1 \), while the secondary phase GeO\(_2\) is formed at \( T_p2 \).

Table 2. The most important crystallographic parameters for crystalline phases, obtained from Rietveld refinement of XRD pattern

<table>
<thead>
<tr>
<th>Phase</th>
<th>Unit cell parameters</th>
<th>Quantitative volume fraction [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiGe(_2)(PO(_4))(_3)</td>
<td>( a = 8.2648(2) ) A, ( b = 8.2648(2) ) A, ( c = 20.5696(7) ) A</td>
<td>97.59</td>
</tr>
<tr>
<td>GeO(_2)</td>
<td>( a = 5.003(2) ) A, ( b = 5.003(2) ) A, ( c = 5.580(5) ) A</td>
<td>2.41</td>
</tr>
</tbody>
</table>

Table 3. The crystallization peak temperature \( T_{p1} \) for different heating rates \( \beta \) of the powder samples having particle sizes < 0.048 mm

<table>
<thead>
<tr>
<th>( \beta ) [°C/min]</th>
<th>5</th>
<th>10</th>
<th>12</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{p1} ) [°C]</td>
<td>629</td>
<td>639</td>
<td>641</td>
<td>645</td>
<td>649</td>
</tr>
</tbody>
</table>

Figure 2. Structure of LiGe\(_2\)(PO\(_4\))\(_3\) along b-axes (dark grey GeO\(_6\) octahedra, light grey PO\(_4\) tetrahedra, black spheres Li\(^+\) ions in cavities) [6]

Figure 3. DTA curves recorded at a heating rate \( \beta = 10 \, ^\circ\text{C}/\text{min} \) for glass powder samples with different particle sizes
The characteristic temperatures of glass determined on DTA curve recorded for the glass sample with particle sizes < 0.048 mm are: the glass transition temperature $T_g = 514 ^\circ C$, the crystallization peak temperatures $T_{p1} = 639 ^\circ C$, $T_{p2} = 721 ^\circ C$, and liquidus temperature $T_l = 1041 ^\circ C$.

The kinetic parameters of crystallization were determined by using the DTA data of the glass powder with particle sizes < 0.048 mm heated at heating rates $\beta = 5, 10, 12, 15$ and $20 ^\circ C/min$. In Table 3 the crystallization peak temperatures $T_{p1}$ for different heating rates $\beta$ are shown.

To study the microstructure of isothermally treated bulk samples in the temperature range of 500–800 $^\circ C$ for different times the SEM method was employed and the surface of crushed samples were recorded. In Fig. 4, SEM micrograph of glass sample heat treated at $T = 550 ^\circ C$ for $t = 30$ min is shown. SEM micrographs revealed the presence of spherically shaped crystallites dimension of 30–50 nm in glass matrix. According to XRD analysis, Fig. 1 these crystals belong to LiGe$_2$(PO$_4$)$_3$. The crystal number density was increased with the increase of temperature and the duration of thermal treatment. The spherical growth morphology of these crystals indicated a screw dislocations controlled crystals growth proceeding on crystal/glass interface.

**IV. Discussion**

Glasses generally crystallize by either surface or volume mechanism. The one of the procedure convenient for evaluating the dominant crystallization mechanism of glass powder is differential thermal analysis (DTA) [12]. The DTA parameters $T/(\Delta T)_p$ and the height of the exothermic peak $(\delta T)_p$ reflect dependency on glass particle size. Since the volume fraction of the secondary phase GeO$_2$ is 2.41% (Table 2) it has no significant impact on the overall process of crystallization of the glass. Therefore, the behaviour of the first exothermal peak $T_{p1}$ which belongs to the main LiGe$_2$(PO$_4$)$_3$ crystalline phase was analysed. The results of DTA experiment with different glass particle size (Fig. 3) showed that in the range of the smallest granulations the surface mechanism of crystallization is dominant. With increasing particle size the surface mechanism of crystallization is replaced by the volume one, and in the size range > 0.4 mm the volume mechanism of crystallization prevails.

For determination of the kinetic parameters of crystallization the equation for the analysis of non-isothermal crystallization derived by Matusita and Sakka [13] was used:

$$\ln \frac{\beta^n}{T_{p}^{2}} = - \frac{m \cdot E_a}{R \cdot T_p} + \text{const} \quad (1)$$

where $R$ is the gas constant, and $E_a$ is activation energy of crystal growth. The values of the parameters $n$ and $m$ depend on the rate controlling mechanism of the crystallization kinetics. The DTA experiment was performed with the glass powder of smallest particle sizes (< 0.048 mm) where the surface crystallization dominates and the number of nuclei is constant during DTA run at different heating rates $\beta$. In this case $n = m = 1$ and equation (1) becomes the same as the well-known Kissinger equation [14]. Using the DTA data (Table 3), the activation energy of crystal growth of $E_a = 462 \pm 11$ kJ/mol was calculated from the slope of the line of the Kissinger plot $\ln(\beta/T_{p}^{2})$ vs. $1/T_{p}$, Fig. 5.

The DTA experiments with the powder glass samples revealed that in the particle size range > 0.4 mm the volume mechanism of crystallization is dominant for this glass. To determine the temperature range of nucleation and the temperature of maximum nucleation rate the samples with particle sizes 0.50–0.65 mm previously nucleated at selected temperatures $T = 500–620 ^\circ C$.
for different times $t_i = 15–300 \text{ min}$ were heated in DTA apparatus at heating rate $\beta = 10 \text{ °C/min}$. A plot of inverse exothermal peak temperature $T_{p}^{-1}$ vs. nucleation temperature $T_n$ produces a nucleation rate-like which agree reasonable with the determined temperature range of nucleation and the temperature of maximum nucleation rate [15]. In Fig. 6 the dependence of $T_{p}^{-1}$ on $T_n$ for the glass sample nucleated for $t = 30 \text{ min}$ is shown. The nucleation-like curve in the temperature range from 510 to 600 °C shows a maximum at $T_n = 550 \text{ °C}$, commonly called the temperature of maximum nucleation, Fig. 6. At this temperature the nucleation rate $I_{550} = 6.42 \times 10^{-16} \text{ m}^{-2}\text{ s}^{-1}$ and crystal growth rate $u_{550} = 1.42 \times 10^{-11} \text{ m/s}$ were determined by using the SEM analysis of isothermally heated bulk glass samples.

V. Conclusions

The glass-ceramics was obtained by crystallization of the parent glass composition of 22.5Li$_2$O·10Al$_2$O$_3$·30GeO$_2$·37.5P$_2$O$_5$ (mol%) prepared by standard melt quenching technique. The NASICON-type LiGe$_3$(PO)$_4$ crystals precipitated as a major phase in the glass matrix. The small volume fraction of secondary GeO$_2$ phase was detected in the samples. SEM analyses showed that the crystallization process occurred with high homogeneous nucleation rate and spherical crystal growth morphology. The nanostructured glass-ceramics samples were obtained. The temperature range of nucleation $T = 510–600 \text{ °C}$ and the temperature of maximum nucleation $T_n = 550 \text{ °C}$ were determined for the parent glass. It was shown that the mechanism of crystallization depends on glass particle size and the dominant volume one was determined for the glass with particle sizes $>0.4 \text{ mm}$. The value of activation energy for crystal growth $E_g = 462\pm11 \text{ kJ/mol}$ was determined by using the Kissinger relation.

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