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


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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 crystallizes 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 $E_a = 462\, \text{kJ/mol}$ 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, Carbolite BLF 17/3 at $T = 1400\, ^\circ\text{C}$ for $t = 1\, \text{h}$. 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: 

\[ < 0.048, 0.048-0.063, 0.063-0.1, 0.1-0.2, 0.2-0.3, 0.3-0.4, 0.4-0.5, 0.5-0.65, 0.65-0.83 \text{ and } 0.83-1 \text{ mm}. \]

The measurements were performed on a Netsch STA 409EP device by heating a constant sample mass of 100 mg at a rate of \( \beta = 10 ^\circ \text{C/min} \) in the temperature range \( T = 20-800 \text{ °C} \). 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 \( ^\circ \text{C/min} \).

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 \( \beta = 10 ^\circ \text{C/min} \). Before DTA run these samples were thermally treated at selected temperatures of nucleation \( T = 500-620 ^\circ \text{C} \) 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 \( \beta = 10 ^\circ \text{C/min} \) 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 determine the phase composition of the crystallized glass. The XRD patterns were obtained on a Philips PW-1710 automated diffractometer using a Cu tube operated at 40 kV and 30 mA. The instrument was equipped with a diffracted beam curved graphite monochromator and a Xe-filled proportional counter. The diffraction data were collected in the 2\( \theta \) Bragg angle range from 5 to 70\( ^\circ \), counting for 1 s (qualitative identification) and from 10\( ^\circ \) to 110\( ^\circ \) for 4 s (quantitative phase analysis-Rietveld method) at every 0.02\( ^\circ \) step. The divergence and receiving slits were fixed 1 and 0.1, respectively. All the XRD measurements were performed at room temperature 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 FULLPROF programme [8].

A MIRA 3 XMU microscope was used for the SEM investigations, and the fractured bulk samples previously 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 composition 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 \( T = 800 ^\circ \text{C} \) 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.

![Figure 1. XRD pattern of the glass sample annealed at: \( T = 800 ^\circ \text{C} \) for \( t = 100 \) h](image)

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\(_2\) 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\(_4\)] tetrahedron 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

<table>
<thead>
<tr>
<th>Table 1. Chemical analysis of the glass</th>
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<tbody>
<tr>
<td><strong>Oxide content, ( x ) [mol %]</strong></td>
</tr>
<tr>
<td>Li(_2)O</td>
</tr>
<tr>
<td>Nominal</td>
</tr>
<tr>
<td>22.5</td>
</tr>
<tr>
<td>Analysed</td>
</tr>
</tbody>
</table>

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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>LiGe₂(PO₄)₃</td>
<td>a [Å] 8.2648(2)</td>
<td>b [Å] 8.2648(2) c [Å] 20.5696(7)</td>
</tr>
<tr>
<td>GeO₂</td>
<td></td>
<td></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>( T_{p1} [°C] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>629</td>
</tr>
<tr>
<td>10</td>
<td>639</td>
</tr>
<tr>
<td>12</td>
<td>641</td>
</tr>
<tr>
<td>15</td>
<td>645</td>
</tr>
<tr>
<td>20</td>
<td>649</td>
</tr>
</tbody>
</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 \( \beta = 10 °C/min \) in the temperature range 400–800 °C, Fig. 3. All DTA curves show two exothermal 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 LiGe₂(PO₄)₃ crystallized at peak \( T_{p1} \), while the secondary phase GeO₂ is formed at \( T_{p2} \).

![Figure 2. Structure of LiGe₂(PO₄)₃ along b-axes (dark grey GeO₆ octahedra, light grey PO₄ tetrahedra, black spheres Li⁺ ions in cavities) [6]](image)

![Figure 3. DTA curves recorded at a heating rate \( \beta = 10 °C/min \) for glass powder samples with different particle sizes](image)
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Figure 4. SEM micrograph of glass sample heat treated at

\( T = 550 \, ^\circ C \) for \( t = 30 \) min

The characteristic temperatures of glass determined
on DTA curve recorded for the glass sample with
particle sizes < 0.048 mm are: the glass transition tem-
perature \( T_g = 514 \, ^\circ C \), the crystallization peak tempera-
tures \( T_{p1} = 639 \, ^\circ C \), \( T_{p2} = 721 \, ^\circ C \) and liquidus temperature
\( T_l = 1041 \, ^\circ C \).

The kinetic parameters of crystallization were deter-
mined 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 \( T_{p, \beta} \) 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,

\[ \frac{\ln \left( \frac{\beta}{T_{p, \beta}^{n}} \right)}{T_{p, \beta}^{2}} = -\frac{m \cdot E_a}{R} + \text{const.} \tag{1} \]

where \( R \) is the gas constant, and \( E_a \) is activation en-
ergy 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 per-
formed with the glass powder of smallest particle siz-
es (< 0.048 mm) where the surface crystallization dom-
ninates 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 \( \ln \left( \frac{\beta}{T_{p, \beta}^{n}} \right) \) vs. \( 1/T_{p, \beta} \), Fig. 5.

The DTA experiments with the powder glass sam-
ple 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 nu-
cleation and the temperature of maximum nucleation rate
the samples with particle sizes 0.50–0.65 mm previously
nucleated at selected temperatures \( T = 500–620 \, ^\circ C \)

Figure 5. The Kissinger plot \( \ln \left( \frac{\beta}{T_{p, \beta}^{n}} \right) \) vs. \( 1/T_{p, \beta} \) of glass sample
with particle sizes < 0.048 mm

IV. Discussion

Glasses generally crystallize by either surface or vol-
ume 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 \( T^2(\Delta T) \) and the height of the exo-
thermal peak \( (\Delta T) \) 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. Ther-
fore, 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 crys-
tallization 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 crystalli-
ization the equation for the analysis of non-isothermal crys-
tallization derived by Matsumita and Sakka [13] was used:

SEM micrograph of glass sample heat treated at \( T = 550 \)
\(^\circ C\) for 30 minutes is shown. SEM micrographs revealed
the presence of spherically shaped crystallites dimen-
sion 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 in-
dicated a screw dislocations controlled crystals growth
proceeding on crystal/glass interface.
for different times \( t = 15–300 \text{ min} \) were heated in DTA apparatus at heating rate \( \beta = 10 ^{\circ} \text{C/min} \). 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 \( ^{\circ} \text{C} \) shows a maximum at \( T_n = 550 ^{\circ} \text{C} \), commonly called the temperature of maximum nucleation, Fig. 6. At this temperature the nucleation rate \( I_{150} = 6.42 \times 10^{16} \text{m}^{-3} \text{ s}^{-1} \) and crystal growth rate \( u_{150} = 1.42 \times 10^{11} \text{m/s} \) 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 \( 22.5 \text{Li}_2\text{O}-10\text{Al}_2\text{O}_3\cdot30\text{GeO}_2\cdot37.5\text{P}_2\text{O}_5 \) (mol%) prepared by standard melt-quenching technique. The NASICON-type \( \text{LiGe}_2(\text{PO}_4)_3 \) crystals precipitated as a major phase in the glass matrix. The small volume fraction of secondary \( \text{GeO}_2 \) 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 \( T = 510–600 ^{\circ} \text{C} \) and the temperature of maximum nucleation \( T_n = 550 ^{\circ} \text{C} \) 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 mm. The value of activation energy for crystal growth \( E_a = 462\pm11 \text{kJ/mol} \) was determined by using the Kissinger relation.

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