Preparation of chromium doped LiAlSiO₄ glass-ceramics

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Pure and chromium doped homogeneous glasses from the system Li₂O-Al₂O₃-SiO₂-LiBO₂=8.26:28.09:33.05:30.6 wt% are prepared after heating at 1130°C for 24 h. Glass-ceramics with various transparencies are obtained after thermal treatment of the parent glass at different temperatures for different times. The crystallizing phases, the degree of crystallinity and the particle size are determined. Absorption and emission spectra are presented for the glass-ceramic sample with crystallizing phases LiAlSiO₄ and LiBO₂, treated at 500°C during 6 h. The spectra show the co-existence of Cr³⁺ and Cr⁴⁺ ions.

Keywords: LiAlSiO₄, chromium doped glass-ceramics, X-ray diffraction, absorption and emission spectra

INTRODUCTION

Chromium (Cr⁴⁺) doped laser single crystals and glass-ceramics are attractive and important for optical communications, remote sensing and biomedical applications. These lasers operate in the near infrared range, so-called eye-safe wavelength range, which includes wavelengths between 1.1 and 1.6 μm.

It is known that the laser active ion emitting in this range (Cr⁴⁺) has to be in tetrahedral position. Therefore, a suitable laser matrix is particularly important. Different matrices are reported in the literature: Cr⁴⁺:Mg₂SiO₄ [1-3], Cr⁴⁺:Ca₂SiO₄ [4,5], Cr⁴⁺:Ca₂GeO₄ [6,7], Cr⁴⁺:CaMgSiO₄ [8], Cr⁴⁺:Li₂MgSiO₄ [9], Cr⁴⁺:YAG [10, 11].

Another possible material suitable as a matrix for Cr⁴⁺ doping is LiAlSiO₄. This compound is also known as eucryptite.

LiAlSiO₄ is a technologically relevant ceramic, owing to its near to zero thermal expansion coefficient, great thermal and chemical shock resistance, exceptional thermal stability. Up to now, this material is used not only in the field of domestic cookware, but also for various specific applications like heat exchangers, ring laser gyroscopes, precision optical devices and radiation dosimetry purposes. [12] To our knowledge, obtaining of this glass-ceramic doped by chromium is not published so far, probably due to the difficulties to produce homogeneous glasses, since they display both high melting point and high viscosity.

The LiAlSiO₄ structure has been studied by Winkler and has been confirmed by Roy [13, 14]. High eucryptite, LiAlSiO₄, is isomorphous with high quartz, where half of the Si atoms are replaced by Al forming the three-dimensional network of corner-sharing AlO₄ and SiO₄ tetrahedra. The Li⁺ ions are placed in void channels within the spirals of (Si,Al)O₄ tetrahedra. According to Schulz, the unit cell is with hexagonal symmetry (P6222) [15, 16]. The high eucryptite form is stable on cooling even with prolonged heating at low temperatures [17]. Roy also established the reconstructive inversion of the high eucryptite to the rhombohedral phenacite type of low eucryptite (α-eucryptite) at 972° ± 10°C. At about 650°C γ-eucryptite is formed, and its structure is monoclinic with space group Pa. At 900–1000°C γ-eucryptite transforms into the final high-temperature polymorph β-eucryptite [18, 19].

Although the compound appears to be in different structural forms, the presence only of LiO₄, SiO₄ and AlO₄ tetrahedra in the eucryptite structure is favorable for doping with chromium ion in 4+ state of oxidation.

In this paper we report our attempt to prepare chromium doped LiAlSiO₄ glass-ceramics.

EXPERIMENTAL

Li₂CO₃ (p.a), Al₂O₃ (p.a), SiO₂ (p.a.), H₃BO₃ (p.a.) and Cr₂O₃ (p.a.) were used as raw materials. Glass synthesis was carried out in a resistive furnace with Kanthal heating wire permitting maximum working temperature of 1200°C and in a chamber furnace with MoSi₂ heating elements permitting maximum working temperature of 1550°C. The temperature was controlled using a Pt/Pt–10%Rh thermocouple connected to a Eurotherm controller. Glasses of the desired compositions about 30 grams in weight were melted in platinum crucibles. First the mixture was heated at 700°C for decomposition of the carbonate and boric acid and then the melt...
was heated at the proper temperature for homogenization. The obtained glass was cooled to room temperature by quick removal from the furnace. Some of the glasses were quenched by pouring onto a steel plate and pressing with another steel plate. The prepared glasses were thermally treated for establishing the crystallizing phases.

Structural characterization was carried out by powder X-ray diffraction (XRD) using a Bruker D8 Advance powder diffractometer with Cu Kα radiation and SolX detector. X-ray diffractograms were recorded at room temperature. Data were collected in the 2θ range from 10 to 80° with a step of 0.04° and 1 s step−1 counting time. X-ray diffractograms were identified using the Diffracplus EVA program. The mean crystallite size and the unit cell parameters were calculated from the integral breadth of all peaks (Pawley fit) using Scherrer equation and the TOPAS 3 program. The area of the amorphous phase was determined by using a straight line for description of the background and a single line for fitting the amorphous component.

The particle morphology of the glass and glass-ceramic samples was determined using a transmission electron microscope JEOL model JEM 200 CX equipped with EM-ASID3D scanning attachment, working in secondary electron detection mode. Specimens were covered with a carbon-gold film.

The UV–Vis spectra were taken with a Thermo Evolution 300 UV-Vis spectrophotometer equipped with a Praying Mantis device.

The emission spectra in the 1000-1600 nm range were measured with 813.4 nm excitation by the laser diode ATC-C1000-100-TMF-808-10. The rating monochromator SP-150 (Acton Research Corporation) with 32×32 ruled diffraction grating and 300 grooves/mm and 1 μm blaze wavelength was used for the spectra. InGaAs ID-441-C was the detector in the near infrared. The emissions from a black body specimen at determined temperature were utilized for standardization of the data. All spectra were recorded at room temperature.

RESULTS AND DISCUSSION

Glass compositions

As a first step two different compositions from the system Li₂O-Al₂O₃-SiO₂ were selected for preparing the glasses: Li₂O-Al₂O₃·2SiO₂-Li₂O·SiO₂ = 60:40 (C1) and Li₂O·Al₂O₃·2SiO₂-Li₂O·SiO₂ = 65:35 (C2). According to M.K.Murthy and F.A. Hummel, the first composition is eutectic with melting point 1070°C and the second composition is with melting point about 1150°C [20, 21]. For these two compositions the powders was heated at 700°C for 30 min for decomposition of the carbonates. Then the samples were treated at temperatures between 1300 and 1500°C and time between 30 min and 4 h.

It was found that a major factor in obtaining a homogeneous glass in this temperature range is not the temperature, but the treatment time. So in both C1 and C2 compositions treated at 1400 and 1500°C for 30 min inhomogeneous glass with bubbles was obtained, and the temperature treatment at 1350°C for 4 h resulted homogeneous glass, especially for composition C2. The preparation of homogeneous glass during cooling to room temperature proved to be problematic due to the rapid crystallization of the glass during the cooling. An additional problem using these two compositions is the fact that in the glass not only the desired phase, LiAlSiO₄, crystallized, but also two other phases Li₂SiO₃ and Li₂.5Al0.5SiO₄ (Fig.1).

Inability to obtain a homogeneous glass at room temperature was the reason to try obtaining glass with the addition of B₂O₃. It is known from the literature that boron oxide is a good glass former. For the preparation of the glass the composition LiAlSiO₄·LiBO₂ = 69.4:30.6 wt% (Li₂O·Al₂O₃·2SiO₂-Li₂O·SiO₂ = 8.26:28.09:33.05:30.6 wt%) (C3) was selected. The glass with this composition, pure or doped by 2 at% Cr, was successfully homogenized after heating at 1130°C during 24 h and transparent glass was obtained after rapid cooling to room temperature. XRD analyses acknowledged obtaining of glass mass without phases crystallized.
Thermal treatment of the glass

The glass with composition C3 was thermally treated at different temperatures for different times. The results for the crystallizing phases obtained in the glass are presented in Table 1.

The table shows that after thermal treatment of the glass below 500°C, samples with small peaks of the desired phase are obtained. In all other regimes of thermal treatment addition of different phases to the desired phase occurred. For example, after thermal treatment at 500°C LiBO₂ crystallized as a second phase. After thermal treatment above this temperature Li₄SiO₄, Li₄B₁₀O₁₇ and Li₄B₂O₅ occurred (Fig. 2).

For further investigations samples with a second phase of LiBO₂ were chosen. The presence of more than one non-desired phase implies obtaining the desired phase in a lower concentration which reduces the optical properties of the glass-ceramic.

Transparency and degree of crystallization of the glass-ceramics after thermal treatment:

Transparency of the glass-ceramics and the degree of crystallization are presented in Table 2.

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### Table 1. Crystallizing phases obtained in the glass with composition C3 after thermal treatment at different temperatures for different times.

<table>
<thead>
<tr>
<th>°C</th>
<th>Time [h]</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>16</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>460</td>
<td>Glass</td>
<td>Glass</td>
<td>Glass</td>
<td>Glass</td>
<td>Glass</td>
<td></td>
</tr>
<tr>
<td>480</td>
<td>Glass</td>
<td>Small peaks of LiAlSiO₄</td>
<td>Small peaks of LiAlSiO₄</td>
<td>Small peaks of LiAlSiO₄ and SiO₂</td>
<td>Glass</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>LiAlSiO₄</td>
<td>LiAlSiO₄</td>
<td>LiBO₂</td>
<td>LiBO₂</td>
<td>LiAlSiO₄</td>
<td></td>
</tr>
<tr>
<td>530</td>
<td>LiAlSiO₄</td>
<td>LiAlSiO₄</td>
<td>LiBO₂</td>
<td>LiBO₂</td>
<td>LiAlSiO₄</td>
<td></td>
</tr>
<tr>
<td>580</td>
<td>LiBO₂</td>
<td>LiBO₂</td>
<td>Li₄SiO₄</td>
<td>Li₄SiO₄</td>
<td>Li₄SiO₄</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2. Transparency of the glass-ceramics and degree of crystallization [%]:

<table>
<thead>
<tr>
<th>°C</th>
<th>Time [h]</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>16</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>Transparent 29</td>
<td>Transparent 80</td>
<td>Transparent 85</td>
<td>Translucent 87</td>
<td>Opaque</td>
<td></td>
</tr>
<tr>
<td>530</td>
<td>Transparent 81</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
As can be seen from the table, the glass-ceramics are transparent up to the crystallization degree of about 85%. At higher degrees of crystallization the glass-ceramics becomes translucent or opaque. The crystallization degree slightly depends on the thermal treatment time and more on the thermal treatment temperature.

**Particle size:**

Particle size of the glass-ceramics depending on the thermal treatment conditions is presented in Table 3.

The particle size is about 50 nm and slightly depends on the thermal treatment time, but depends on the treatment temperature. This result is in agreement with the crystallization degree values.

| Table 3. Particle size of the glass-ceramics [nm]: |
|---|---|---|---|---|
| °C | 2 | 4 | 6 | 16 |
| 500 | 22 | 53 | 48 | 51 |
| 530 | 52 |

According to the results obtained, after the beginning of the crystallization, the increased time of treatment probably does not lead to expanding of the nucleated seeds, but to arising of new seeds. This can be seen also from the patterns of the glass-ceramics treated at 500°C for 2, 4, 6 and 16 h and of glass-ceramics treated at 500 and 530°C for 2 h (Fig. 3). No significant difference can be seen between XRD patterns of the samples treated for 6 and 16 h at 500°C, but there is a significant difference in the XRD patterns for the samples treated at 500 and 530°C for 2 h.

**Absorption and emission**

Fig. 5 presents the absorption and the emission spectra of the glass-ceramics treated at 500°C for 6 h.

Absorption spectra of the glass and glass-ceramic samples show similar Cr ions absorption bands assigned to different types of chromium ions. The absorption spectra consist of strong absorption bands between 520 and 800 nm and a weak one near infrared absorption between 800 and 1100 nm. According to the literature [7], in the region 520-800 nm a strong band exists ascribed to the transition of $^3A_2 \rightarrow ^3T_2$ of Cr$^{3+}$. A maximum at 615 nm in our glass and glass-ceramic is observed. Multiplet bands at 680 nm may be ascribed to the transition of $^3A_2 \rightarrow ^3T_1$ of Cr$^{4+}$ with energy-level splitting in a distorted tetrahedron. The $^3A_2 \rightarrow ^3T_1$ absorption band of the tetrahedral Cr$^{4+}$ centers overlap with the $^4A_2 \rightarrow ^4T_2$ absorption band of octahedral Cr$^{3+}$ centers. Since there are both Cr$^{3+}$ and Cr$^{4+}$ ions, these absorption bands are not pure Cr$^{4+}$ bands. Another band from 800 to 1100 nm is ascribed to $^3A_2 \rightarrow ^3T_2$ of Cr$^{4+}$. There is more intense absorbance in the glass-ceramic sample compared with the initial glass.

The emission spectra overlap from 1000 to 1550 nm. There is a strong peak at 1065 nm and a weak, broad one at 1340 nm. The absorption spectra show different oxidation states of the chromium ions in the glass-ceramic samples. In accordance to the absorption spectra the first emission peak could be attributed to $^4T_2 \rightarrow ^4A_2$ of Cr$^{3+}$ ions and the second peak is attributed to $^3T_2 \rightarrow ^3A_2$ of Cr$^{4+}$ in tetrahedral
occupation. Such emission spectrum is expected [22], taking into account the existence of three matrices (residual glass, LiAlSiO$_4$ and LiBO$_2$), where the chromium ion could be incorporated.

**CONCLUSION**

Pure and chromium doped homogeneous glasses from the system Li$_2$O-Al$_2$O$_3$-SiO$_2$-LiBO$_2$=8.26:28.09:33.05:30.6 wt% are prepared after 24 h heating at 1130°C. Glass-ceramics with various transparencies are obtained after thermal treatment of the parent glass at different temperatures and times. The crystallizing phases, the degree of crystallinity and the particle size are determined. In all thermal regimes LiAlSiO$_4$ appears. Except LiAlSiO$_4$, different crystallizing phases crystallize depending on the treatment conditions. The glass-ceramics are transparent to the crystallizing phases crystallize depending on the treatment conditions. The glass-ceramics are transparent to the crystallization degree of about 85%. The particle size is about 50 nm and slightly depends on the treatment time, but depends on the treatment temperature. Absorption and emission spectra are presented for the sample with crystallizing phases LiAlSiO$_4$ and LiBO$_2$ treated at 500°C for 6 h. The spectra show the coexistence of the Cr$^{3+}$ and Cr$^{4+}$ ions.

**REFERENCES**


ПОЛУЧАВАНЕ НА ДОТИРАНА С ХРОМ СТЪКЛОКЕРАМИКА СЪДЪРЖАЩА LiAlSiO$_4$

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(Резюме)

Синтезирани са чисти и дотирани с хром хомогенни стъкла от системата Li$_2$O-Al$_2$O$_3$-SiO$_2$-LiBO$_2$=8.26:28.09:33.05:30.6 wt% след 24 часово нагряване при 1130°C. Прозрачните стъклокерамики са получени след термично третиране на стъклата при различни температури и с различна продължителност. Определени са кристализиращите фази, степента на кристалзация и размерът на частиците. Представени са спектри на абсорбция и емисия за стъклокерамични образци с кристализиращи фази LiAlSiO$_4$ и LiBO$_2$ термично третирани при 500°C за 6h. Спектрите показват едновременното присъствие на йони Cr$^{3+}$ и Cr$^{4+}$. 

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