

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 (P62222) [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 carbonates and boric acid and then the melt

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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 K α radiation and SolX detector. X-ray diffractograms were recorded at room temperature. Data were collected in the 2 θ 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 Diffractplus 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.³ – General profile and structure analysis software for powder diffraction data, 2005, Bruker AXS, Karlsruhe, Germany. 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 μ m 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 were 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 Li_{2.5}Al_{0.5}SiO₄ (Fig.1).

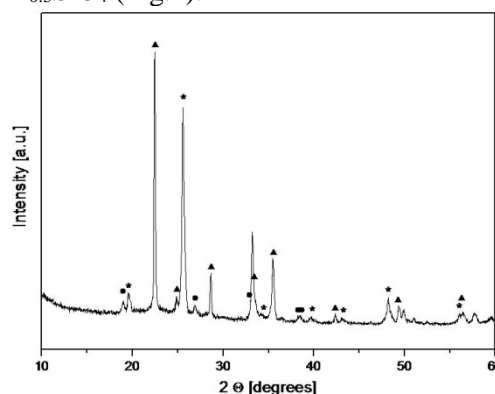


Fig.1. XRD patterns of the phases crystallized in the glass with composition C2 after thermal treatment at 1350°C for 4 h and cooling to room temperature (*-LiAlSiO₄, ●-Li₂SiO₃, ▲-Li_{2.5}Al_{0.5}SiO₄).

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-SiO₂-LiBO₂=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, Li₄B₁₀O₇ 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.

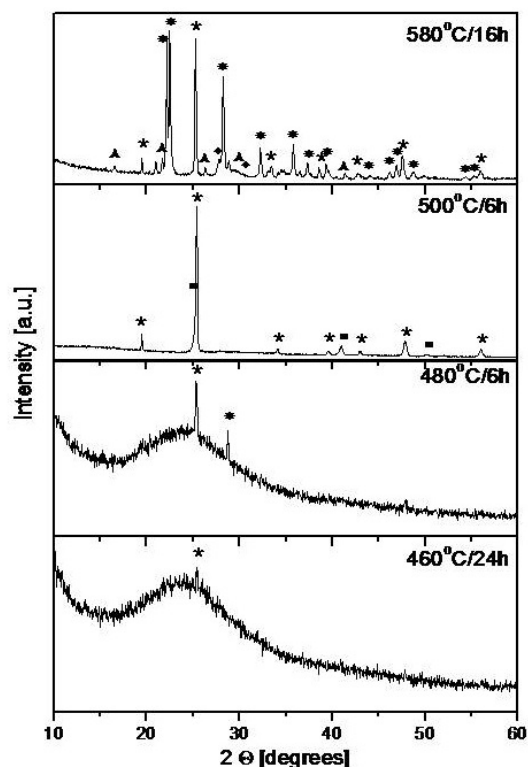


Fig.2. XRD patterns of the glass-ceramics after thermal treatment at different temperatures for different times (★-LiAlSiO₄ hexagonal, * -LiAlSiO₄ monoclinic, ■-LiBO₂, ▲-Li₄B₁₀O₇, ◆-Li₄B₂O₅).

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

Time [h] \ °C	2	4	6	16	24
460	Glass				Glass
480	Glass	Glass	Glass		
	Small peaks of LiAlSiO ₄	Small peaks of LiAlSiO ₄	Small peaks of LiAlSiO ₄ and SiO ₂		
500	LiAlSiO ₄ LiBO ₂	LiAlSiO ₄ LiBO ₂	LiAlSiO ₄ LiBO ₂	LiAlSiO ₄ LiBO ₂	
530	LiAlSiO ₄ LiBO ₂	LiAlSiO ₄ LiBO ₂ Li ₄ SiO ₄		LiAlSiO ₄ LiBO ₂ Li ₄ SiO ₄	
580				LiAlSiO ₄ Li ₄ B ₁₀ O ₇ Li ₄ B ₂ O ₅	

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

Time [h] \ °C	2	4	6	16	24
500	Transparent 29	Transparent 80	Transparent 85	Translucent 87	Opaque
530	Transparent 81				

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]:

Time[h] \ °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.

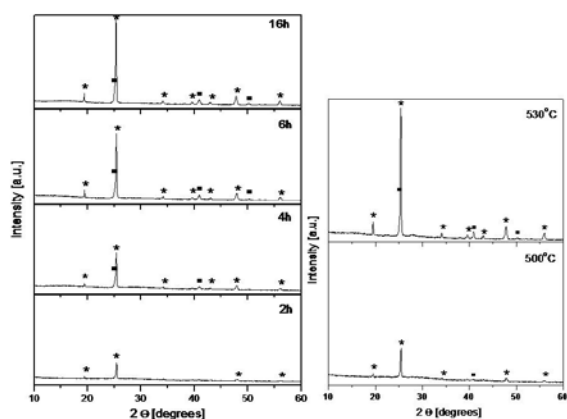


Fig. 3. XRD patterns of the glass-ceramics treated at different conditions (★-LiAlSiO₄, ■-LiBO₂).

Fig.4 presents the SEM micrographs of the initial glass and glass-ceramics. As can be seen, the particle size is from 30 to 50 nm. This result is in accordance with the particle size calculated by the Scherrer equation.

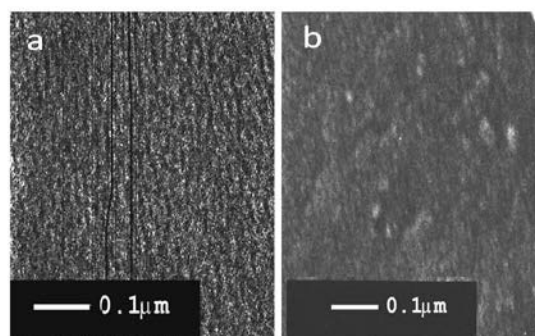


Fig. 4. SEM micrographs of the initial glass (a) and the glass-ceramic (b).

Absorption and emission

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

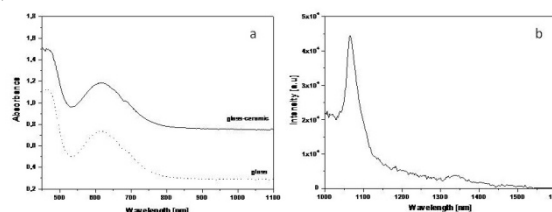


Fig. 5. Absorption (a) and emission (b) spectra of the glass-ceramic treated at 500°C for 6 h.

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 ⁴A₂→⁴T₂ of Cr³⁺. 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 ³A₂→³T₁ of Cr⁴⁺ with energy-level splitting in a distorted tetrahedron. The ³A₂→³T₁ absorption band of the tetrahedral Cr⁴⁺ centers overlap with the ⁴A₂→⁴T₂ absorption band of octahedral Cr³⁺ centers. Since there are both Cr³⁺ and Cr⁴⁺ ions, these absorption bands are not pure Cr⁴⁺ bands. Another band from 800 to 1100 nm is ascribed to ³A₂→³T₂ of Cr⁴⁺. 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 ⁴T₂→⁴A₂ of Cr³⁺ ions and the second peak is attributed to ³T₂→³A₂ of Cr⁴⁺ in tetrahedral

occupation. Such emission spectrum is expected [22], taking into account the existence of three matrices (residual glass, LiAlSiO₄ and LiBO₂), where the chromium ion could be incorporated.

CONCLUSION

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 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 LiAlSiO₄ appears. Except LiAlSiO₄, different 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 thermal treatment time, but depends on the treatment temperature. Absorption and emission spectra are presented for the sample with crystallizing phases LiAlSiO₄ and LiBO₂ treated at 500°C for 6 h. The spectra show the co-existence of the Cr³⁺ and Cr⁴⁺ ions.

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ПОЛУЧАВАНЕ НА ДОТИРАНА С ХРОМ СЪГЛОКЕРАМИКА СЪДЪРЖАЩА LiAlSiO₄

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(Резюме)

Синтезирани са чисти и дотирани с хром хомогенни стъкла от системата Li₂O-Al₂O₃-SiO₂-LiBO₂=8.26:28.09:33.05:30.6 wt% след 24 часова нагряване при 1130°C. Прозрачни стъклокерамики са получени след термично третиране на стъклата при различни температури и с различна продължителност. Определени са кристализиращите фази, степента на кристализация и размерът на частиците. Представени са спектри на абсорбция и емисия за стъклокерамични образци с кристализиращи фази LiAlSiO₄ и LiBO₂ термично третиращи при 500°C за 6h. Спектрите показват едновременното присъствие на йони Cr³⁺ и Cr⁴⁺.