Original Paper

Crystallization, microstructure and properties of selected glasses and glass-ceramics in the $SiO_2-Li_2O-ZnO-K_2O-P_2O_5$ system

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The crystallization behavior of selected glasses in the multicomponent $SiO_2-Li_2O-ZnO-K_2O-P_2O_5$ system was investigated using high-temperature X-ray diffraction and differential scanning calorimetry. Proceeding from a dental model glass with the molar composition 63.2 SiO₂, 29.1 Li₂O, 3.3 ZnO, 2.9 K₂O and 1.5 P₂O₅, 20 glasses were melted, varying the concentrations of the single components systematically. Glass compositions mainly influenced the formations and dissolutions of metastable and stable phases in the temperature range of 480 to 1100 °C. In the majority of the glasses lithium disilicate (Li₂Si₂O₅) precipitated as the main crystal phase during heating, while lithium metasilicate, lithium orthophosphate, cristobalite and quartz crystallized as secondary phases. After a one-step heat treatment microstructures of glass-ceramics and morphologies of Li₂Si₂O₅ crystals were characterized by scanning electron microscopy. With few exceptions glass-ceramics showed a finegrained microstructure with interlocking, rodshaped Li₂Si₂O₅ crystals with 0.5 to 10 µm in length. The corresponding glass-ceramics were processed by a hot-pressing technique to test samples for mechanical and optical measurements. Concentration variations of the base glasses caused bending strengths between 224 and 675 MPa. Within a comparison of translucency according to dental standard BS 5612 contrast ratios between 0.3 and 0.8 were determined.

1. Introduction

The binary Li₂O·SiO₂ system is regarded as the basic system of multi-component lithium silicate glasses. Nucleation and crystallization of the stoichiometric Li₂O·2SiO₂ system has been investigated very intensively and was discussed controversially [e.g. 1 to 5]. The multicomponent SiO₂-Li₂O-ZnO-K₂O-P₂O₅ system has been used as a model system of dental materials in some previous studies concerning glass-ceramics with favorable mechanical and optical properties [e.g. 6 to 8]. It was proved that the properties of these glass-ceramics depend on the composition of the initial glass and the heat treatment process during the manufacture of the final products. Crystal phase formation in multi-component systems is on the one hand a very complex process which offers on the other hand possibilities for the production of polyphase glass-ceramics obtained by controlled crystallization [6]. Relating to the above mentioned complex lithium silicate glass-ceramic system Hing and McMillan [9] stated that the properties of the glass matrix of binary lithium silicate glasses can be strongly influenced by additions of ZnO, K₂O, and P₂O₅. Moreover the

Presented in German at: 75th Annual Meeting of the German Society of Glass Technology (DGG) on 23 May 2001 in Wernigerode (Germany). resulting morphology of the $Li_2Si_2O_5$ crystals can be changed by the nucleation agent concentration from a coarse spherulitic to needle-like fine-crystalline microstructure.

The present investigations focus on the crystallization behavior of selected glasses of the multi-component $SiO_2-Li_2O-ZnO-K_2O-P_2O_5$ system in dependence on the glass composition. In addition the resulting differences in the morphology of the glass-ceramics after a one-step heat treatment was investigated. Furthermore this research shows a correlation between glass composition and mechanical as well as optical properties of glass-ceramics in the scope of the five-component system. Samples for mechanical and optical measurements were processed by a dental hot-pressing technique [10].

2. Experiments

Proceeding from a lithium silicate model composition (in mol%) for dental glass-ceramics [8] (63.2 SiO₂, 29.1 Li₂O, 3.3 ZnO, 2.9 K₂O and 1.5 P₂O₅), 20 samples were melted, varying the single components or rather the SiO₂/Li₂O molar ratio systematically, indicated by the sample designation table 1). The molar ratios of the remaining components were kept constant. A comparison

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Table 1. Batch compositions (in mol%) of samples; random errors $< 2.5 \%$					
sample	SiO_2	Li ₂ O	ZnO	K ₂ O	P_2O_5
model glass	63.2	29.1	3.3	2.9	1.5
0.0 P ₂ O ₅	64.2	29.5	3.4	2.9	0.0
$0.5 P_2 O_5$	63.9	29.3	3.4	2.9	0.5
1.0 P ₂ O ₅	63.5	29.2	3.4	2.9	1.0
$2.0 P_2 O_5$	62.9	28.9	3.3	2.9	2.0
2.5 P ₂ O ₅	62.6	28.7	3.3	2.9	2.5
0.0 K ₂ O	65.1	29.9	3.4	0.0	1.6
1.5 K ₂ O	64.1	29.5	3.4	1.5	1.5
4.5 K ₂ O	62.1	28.6	3.3	4.5	1.5
6.0 K ₂ O	61.2	28.1	3.2	6.0	1.5
0.0 ZnO	65.4	30.1	0.0	2.9	1.6
1.7 ZnO	64.3	29.5	1.7	2.9	1.6
5.0 ZnO	62.1	28.6	5.0	2.8	1.5
6.6 ZnO	61.0	28.1	6.6	2.8	1.5
8.3 ZnO	60.0	27.6	8.3	2.7	1.4
1.9 SiO ₂ /Li ₂ O	60.5	31.8	3.3	2.9	1.5
$2.0 \operatorname{SiO}_2/\operatorname{Li}_2O$	61.8	30.8	3.3	2.9	1.5
$2.1 \operatorname{SiO}_2/\operatorname{Li}_2O$	62.5	29.7	3.3	2.9	1.5
$2.3 \operatorname{SiO}_2/\operatorname{Li}_2O$	64.3	28.0	3.3	2.9	1.5
$2.4 \operatorname{SiO}_2/\operatorname{Li}_2O$	65.2	27.1	3.3	2.9	1.5

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of batch compositions with analyzed (X-ray fluorescence, atomic absorption spectroscopy) glass compositions stated random errors of single components smaller than 2.5 %.

Figure 1. Hot-pressing furnace (EP 500, Ivoclar Vivadent AG, Schaan, (Liechtenstein)).

2.1 Sample preparation and heat treatment

2.1.1 Glass samples

Homogeneous glasses in 200 g scales were prepared from reagent-grade raw materials (SiO2, Li2CO3, Li₃PO₄, K₂CO₃ and ZnO) and poured into cylindrical stainless steel moulds as described in [8]. The cast samples were cooled from 450 °C to room temperature at a rate of 2 K/min to relieve internal stress. A part of each batch was quenched into water to form glass granules differential scanning calorimetry (DSC) for analysis.

For the high-temperature X-ray diffraction experiments, glass discs of 1.2 mm thickness with polished surfaces were prepared.

2.1.2 Glass-ceramic samples

Ceramming heat treatment of the glass samples was carried out according to the thermal analysis results. The samples were subjected to a one-step holding stage treatment for 30 min, while the selected temperature was about 80 K less than the endothermal peak of the DSC

measurements. Specimens were placed directly in an electric furnace at the temperature of the holding stage (810 to 900°C).

For SEM investigations polished glass-ceramic samples were etched with a ceramic etching solution (Ceramex, Renfert, Hilzingen, (Germany)) in an ultrasonic bath for 30 s.

2.1.3 Hot-pressed glass-ceramic samples

Test specimens (bars, discs) for mechanical and optical investigations were obtained by shaping glass-ceramic ingots by a hot-pressing process via the lost wax technique [10] in a dental furnace (EP 500, Ivoclar Vivadent, Schaan (Liechtenstein)) (figure 1) in the temperature range of 840 to 950 °C. The detailed specimen preparation is described elsewhere [8].

2.2 Measurement techniques

The thermal, microstructural, mechanical and optical properties of the investigated samples were analyzed by means of the following techniques:





Figure 2. DSC measurements of selected samples; heating rate 1 K/min; curves are deliberately displaced along the vertical axis for better clarity.

2.2.1 Differential scanning calorimetry (DSC)

The thermal behavior of the glasses was analyzed by differential scanning calorimetry (DSC 404, Netzsch, Selb (Germany)) in N₂-atmosphere. Crystallization temperatures of the precipitating crystalline phases were evaluated from 450 up to $1000 \,^{\circ}$ C with a heating rate of 1 K/min, comparable to the high-temperature X-ray diffraction (HT-XRD) measurements.

As development and change of phases occurred within a narrow temperature range, the DSC plots were helpful in interpreting the HT-XRD data. The single measurements in figure 2 were deliberately displaced along the vertical axis for better clarity.

2.2.2 High temperature X-ray diffraction (HT-XRD)

A diffractometer (D 5005, Bruker AXS, Karlsruhe (Germany)) with CuK_{α} radiation in combination with a high-temperature chamber (HTK 1200) was chosen for HT-XRD analysis. A total of 36 measurements per sample was recorded in steps of 20 K (diffraction angle 2θ from 10° to 60°, step size 0.015°, step time 0.5 s). Continuous XRD patterns were obtained by evaluation and extrapolation of the single measurements (DIF-FRAC^{plus}, Bruker AXS, Karlsruhe (Germany)). As the main diffraction peaks of the crystal phases occurred be= tween $15^{\circ} \leq 2 \theta \leq 40^{\circ}$, this range was chosen in the figures of section 3.1.2 for better clarification. The mean heating rate in the temperature range of 400 to 1100 °C was calculated as 1 K/min. The utilization of the continuous XRD patterns allowed a qualitative characterization of the precipitated crystal phases and phase successions during heating. Moreover the exothermal and endothermal effects observed in the DSC plots could be explained in a structural way.

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2.2.3 Scanning electron microscopy (SEM)

Microstructures of glass-ceramics and morphologies of $Li_2Si_2O_5$ crystals after a one-step heat treatment of initial glasses was investigated using a scanning electron microscope (LEO DSM 962, Zeiss, Oberkochen (Germany)). As a result of the etching procedure described in section 2.1 the glassy matrix as well as the lithium metasilicate and lithium orthophosphate crystal phases were dissolved a few microns from the surface area while the $Li_2Si_2O_5$ crystals protruded from the sample surface.

2.2.4 3-point flexural strength test

Flexural strengths of the hot-pressed glass-ceramics were determined according to European ceramic standard DIN EN 843-1 [11] with a universal testing apparatus (1455, Zwick, Ulm (Germany)). Twelve glass-ceramic rods (2.0 x 2.5 x 25) mm³ per group were hot-pressed and ground with SiC 600 grinding paper. The 3-point flexural strength test was conducted with a span length of 20 mm and a crosshead speed of 1.5 mm/min.

2.2.5 Contrast ratio

A translucency comparison of the hot-pressed glass-ceramic samples was carried out according to dental standard BS 5612 [12] using a spectral colorimeter (CR 300, Minolta, Tokyo (Japan)). The contrast ratio measurement includes two single measurements, i.e. a black ceramic specimen and a white ceramic specimen placed behind the testing sample were colorimetrically recorded $(Y_{\rm b}, Y_{\rm w})$. The reflexion/absorption takes place at the black/white ceramic specimen when it is a highly translucent testing sample. On the other hand the reflexion/absorption takes place at the testing sample itself when it is a low-translucent material. The contrast ratio (CR) is given as the quotient of the measurement with black and the measurement with white background (CR = Y_b/Y_w). A contrast ratio of 1 would represent a 0 % translucent and a value of 0 would characterize a 100 % translucent material. For dental applications contrast ratios of about 0.2 to 0.7 (sample thickness 1 mm) would be practice relevant, dependent on the indication. For full anatomically produced dental restorations a higher translucency is required to obtain a chameleon effect. Using the lithium disilicate glass-ceramic as a framework material which gets veneered with a high-translucent glass-ceramic demands lower translucencies to cover the natural tooth abutment.

Glass-ceramic discs for contrast ratio evaluation were hot-pressed, divested, ground and polished (1 μ m diamond suspension) to a diameter of 16 mm and a thickness of (1.0 ± 0.02) mm. For contrast ratio comparisons of different materials importance has to be attached to parallel sample planes and uniform sample thicknesses.



Figure 3. Continuous X-ray diffraction pattern of the model glass; mean heating rate 1 K/min; measurements in steps of 20 K; angle range 15° to 40° ; step size 0.015° ; measuring time 0.5 s; main diffraction peaks are marked.

3. Results

3.1 Crystallization

3.1.1 Differential scanning calorimetry

The strong influence of the composition on the crystallization of investigated glasses is indicated by selected DSC curves in figure 2. It can be clearly seen that, in comparison to the DSC plot of the model glass, especially the variation of the P_2O_5 and K_2O concentration had a strong effect on the thermal behavior of the samples. A different number and shape of exothermal crystallization peaks and endothermal melting peaks was observed during the heating of the glasses. Moreover the varying energy changes during crystallization processes signalize variable crystal contents of the glass-ceramics.

3.1.2 High temperature X-ray diffraction

The qualitative characterization of the crystalline phases was carried out by continuous HT-XRD experiments which show the precipitating cristalline phases as a function of increasing temperature. Parallel vertical lines indicate the existence of a crystalline phase over a certain temperature range during heating. The intensity of a diffraction peak is expressed by the gray shade. Figure 3 represents the continuous XRD pattern of the model glass. At about 500 °C, lithium metasilicate (ICDD 29-0828) [13] and lithium disilicate (ICDD 40-0376) start to precipitate with low intensity. Between 630 and 660°C, cristobalite (ICDD 27-0605) is present besides the two prior phases. At 660°C, lithium metasilicate and cristobalite decompose while the amplitudes of the lithium disilicate peaks increase until the phase dissolves at about 960 °C. The crystallization of lithium phosphate (ICDD 15-0760) begins after the transformation of lith-



Figure 4. Continuous X-ray diffraction pattern of sample 0.5 P_2O_5 ; mean heating rate 1 K/min; measurements in steps of 20 K; angle range 15° to 40°; step size 0.015°; measuring time 0.5 s; main diffraction peaks are marked.



Figure 5. Continuous X-ray diffraction pattern of sample SiO_2/Li_2O 1.9; mean heating rate 1 K/min; measurements in steps of 20 K; angle range 15° to 40°; step size 0.015°; measuring time 0.5 s; main diffraction peaks are marked.

ium metasilicate and cristobalite. Li_3PO_4 dissolves during further heating at about 1050 °C.

A reduction of the nucleation agent (P_2O_5) content to 0.5 mol% leads to a completely different diffraction pattern (figure 4). Over a broad diffraction area no signals or just very weak signals were recorded while the (002)-peaks of the Li₂SiO₃ and Li₂Si₂O₅ phases were emphasized.

The higher SiO₂ concentration of sample SiO₂/Li₂O 1.9 results in a primary cristallization of the Li₂SiO₃ phase which stays thermally stable up to 970 °C (figure 5). The thermal behaviors of the glasses with K₂O limiting values 0.0 and 6.0 mol% strongly differed from the behavior of the model glass. While a low K₂O content favors the intensive primary crystallization of the Li₂. Si₂O₅ phase (figure 6), a high K₂O content, i.e. a high network modifyer concentration and therefore a lower viscosity of the glass matrix, causes the crystallization of Li₂SiO₃ as main crystal phase (figure 7).



Figure 6. Continuous X-ray diffraction pattern of sample 0.0 K_2O ; mean heating rate 1 K/min; measurements in steps of 20 K; angle range 15^{∞} to 40^{\circ}; step size 0.015^{\circ}; measuring time 0.5 s; main diffraction peaks are marked.



Figure 7. Continuous X-ray diffraction pattern of sample 6.0 K_2O ; mean heating rate 1 K/min; measurements in steps of 20 K; angle range 15° to 40°; step size 0.015°; measuring time 0.5 s; main diffraction peaks are marked.

3.2 Morphology

The influence of the composition of initial glasses on the $\text{Li}_2\text{Si}_2\text{O}_5$ crystal morphology will be described here for the $P_2\text{O}_5$ and $K_2\text{O}$ concentration series. The dominance of surface crystallization was observed in the samples with lowest $P_2\text{O}_5$ contents (figures 8a and b). Crystals grow radially from the cylindrical surface into the sample volume with lengths up to 500 µm. This phenomenon explains the distorted diffraction pattern of sample 0.5 $P_2\text{O}_5$ in figure 4. Crystals in the volume of the samples 0.0 $P_2\text{O}_5$ and 0.5 $P_2\text{O}_5$ were spherulitic with diameters up to 400 µm. An increase of the nucleation agent $P_2\text{O}_5$ from 1.0 to 2.5 mol% caused a decrease of $\text{Li}_2\text{Si}_2\text{O}_5$ crystal lengths from about 8 to 0.5 µm (figures 8c to f).

The influence of K_2O on the microstructure of the complex glass-ceramics after a ceramming treatment can be estimated by figures 9a to e. Only the samples with K_2O concentrations 1.5 and 2.9 mol% showed a fine-crystalline $Li_2Si_2O_5$ microstructure. Coarsening and

cracking was observed for sample $0.0 \text{ K}_2\text{O}$, as the developed internal strains during crystallization could not be relieved by viscous flow. In sample $6.0 \text{ K}_2\text{O}$, Li₂SiO₃ represents the main crystal phase, which was dissolved during etching (figure 9e).

The majority of the investigated glass-ceramics showed volume crystallization and a microstructure of interlocking lath-like lithium disilicate crystals with crystal lengths ranging from 1 to 10 μ m and aspect ratios between aproximately 2 and 6. Astonishingly no significant changes of the Li₂Si₂O₅ morphology were observed in dependence of the ZnO content [14] and the SiO₂/Li₂O [8] ratio variation.

3.3 Flexural strength

The dependency of the P_2O_5 concentration on the flexural strengths of the multi-component glass-ceramics is shown in figure 10. Strengths of the samples increased sligthly from 467 to 581 MPa with increasing P_2O_5 concentration or with decreasing crystal length respectively. Samples without P_2O_5 and with 0.5 mol% P_2O_5 showed porosity after ceramming treatment and were not further processed via hot-pressing procedure.

The influence of the K_2O concentration on the strength of the hot-pressed glass-ceramics is demonstrated in figure 11. Solely the glass-ceramics with medium K_2O contents showed high strengths of about 550 MPa which can be related to the fine-crystalline microstructure. The main crystal phase Li_2SiO_3 of sample 6.0 K_2O was responsible for the lowest flexural strength of 224 MPa within the scope of these investigations.

Homogeneously distributed small Li₂SiO₃ crystals within the interlocking Li₂Si₂O₅ crystal microstructure resulted in residual stresses after cooling and caused the highest strength (674 MPa) of sample SiO₂/Li₂O 1.9 (figure 12). Figure 5 demonstrated the presence of Li₂SiO₃ at the ceramming temperature of about 900 °C. The decreasing Li₂SiO₃ crystal content leads to a decreasing strength from sample SiO₂/Li₂O 1.9 to sample SiO₂/Li₂O 2.4.

With increasing ZnO concentration the flexural strengths of hot-pressed glass-ceramics decreased from 600 MPa (sample 0.0 ZnO) to 440 MPa (sample 8.3 ZnO) [8].

3.4 Contrast ratio

The influence of composition variation on the translucency of the hot-pressed glass-ceramics is demonstrated here exemplary for the K_2O and the ZnO series according to BS 5612 [12]. Crystal size and crystal kind



Figures 8a to f. Morphology of glass-ceramics with P_2O_5 variation from 0.0 to 2.5 mol%; SEM pictures of etched samples; temperature treatment at 880 °C for 30 min.

influenced the contrast ratio measurements of hotpressed glass-ceramics with variable K_2O concentration. Decreasing and increasing the K_2O content of the initial glasses proceeding from the model glass lead to a higher contrast ratio or a lower translucency respectively (figure 13). The contrast ratio values were calculated in the The variation of the ZnO concentration of the initial glasses strongly affected the contrast ratio, i.e. the translucencies of the corresponding hot-pressed glass-ceramics (figure 14). The lowest contrast ratio 0.34, which characterizes the highest translucency, was measured for the glass-ceramic of the model glass. Increasing and











e)





d)

Figures 9a to e. Morphology of glass-ceramics with K_2O variation from 0.0 to 6.0 mol%; SEM pictures of etched samples; temperature treatment at 810 to 890 °C for 30 min.

reduction of the light transmittance of the glass-ceramics up to a contrast ratio value of 0.76.

4. Discussion

Variations of the single components or rather the SiO₂/ Li₂O molar ratio affected the crystallization of the glasses in the SiO₂-Li₂O-ZnO-K₂O-P₂O₅ multicomponent system in the temperature range of 480 to with limiting values of K_2O , lower P_2O_5 and high ZnO [14] contents showed deviations from the phase formations of the model glass during heating.

As the viscosity of the glass matrix of the sample without K_2O was too high, through initial crystallization induced strains could not be relieved by viscous flow, and coarsening of the material was observed. The low viscosity of sample 6.0 K_2O was responsible for the crystallization of Li₂SiO₃ as main crystal phase as well as



Figure 10. Flexural strengths of glass-ceramics with P_2O_5 variation from 0.0 to 2.5 mol% following EN 843-1 [11]; sample size: (2.0 x 2.5 x 25) mm³; span length: 20 mm; crosshead speed: 1.5 mm/min; n = 12.



Figure 11. Flexural strengths of glass-ceramics with K₂O variation from 0.0 to 6.0 mol% following EN 843-1 [11]; sample size: (2.0 x 2.5 x 25) mm³; span length: 20 mm; crosshead speed: 1.5 mm/min; n = 12.



Figure 12. Flexural strengths of glass-ceramics with SiO_2/Li_2O molar ratio variation from 1.9 to 2.4 following EN 843-1 [11]; sample size: (2.0 x 2.5 x 25) mm³; span length: 20 mm; cross-head speed: 1.5 mm/min; n = 12.

With increasing amount of nucleation agent P_2O_5 from 0.0 to 2.5 mol% the tendency to surface crystallization of initial glasses was decreased or rather suppressed. During heating, samples with P_2O_5 concentrations of



Figure 13. Contrast ratios of glass-ceramics with K_2O variation from 0.0 to 6.0 mol% following BS 5612 [12]; sample thickness 1.0 ± 0.02 mm.



Figure 14. Contrast ratios of glass-ceramics with ZnO variation from 0.0 to 8.3 mol% following BS 5612 [12]; sample thickness 1.0 ± 0.02 mm.

about 1.5 to 2.5 mol% precipitated the transition-phase cristobalite within a solid state reaction $Li_2SiO_3 + SiO_2$ \rightarrow Li₂Si₂O₅ prior to the main crystallization of Li₂Si₂O₅ and Li₃PO₄. Cristobalite occurred over a temperature range of approximately 30 to 40 K. This reaction mechanism, in which lithium metasilicate and cristobalite restructure to lithium disilicate, is not known from literature in this way. As indicated by Holland et al. [15] in the scope of ²⁹Si-NMR investigations of Li₂O·2SiO₂ glasses containing P_2O_5 as nucleation agent, no Li₃PO₄ crystals could be detected as heterogeneous nuclei of the Li2-Si₂O₅ crystallization. Heterogeneous nucleation of Li₂ SiO₃ and Li₂Si₂O₅ by Li₃PO₄ crystals, grown during an advanced temperature treatment at 1000 °C, as described by Headley and Loehman [16], could not be observed within conventional heat treatment in the scope of this study. Separate room-temperature X-ray measurements of the glass-ceramics containing P₂O₅ showed that Li₃PO₄ precipitated in minor quantities during ceramming treatment above approximately 650 °C.

For the majority of the samples volume crystallization and a resulting fine-grained microstructure was observed. The morphology of the main crystal phase lithium disilicate was lath-shaped. The determined $Li_2Si_2O_5$ crystal lengths were about 0.5 to 10 μ m while the aspect ratios (length : diameter) ranged between 2 and 7. Homogeneous precipitation of the fine-grained interlocking microstructure of the lithium disilicate crystal phase was responsible for the high mechanical strengths of the glass-ceramics. Within the scope of these investigations flexural strengths between 224 and 675 MPa were determined following EN 843-1 [11].

The variation of the composition of the initial glasses mainly influenced the translucency of the corresponding hot-pressed glass-ceramics. Contrast ratios between 0.3 and 0.8 = at method limits of 0 and 1 – were measured. Sample 2.0 P₂O₅ was the most translucent material after hot-pressing which is indicated by the lowest contrast ratio value 0.3. The glass-ceramic with the highest K₂O content (6.0 mol%) and Li₂SiO₃ as main crystal phase showed the lowest light transmittance.

5. Conclusions

The different compositions of the initial glasses in the SiO₂-Li₂O-ZnO-K₂O-P₂O₅ multicomponent system affected the phase formations during heating and therefore the microstructure of glass-ceramics after ceramming treatment as well as the mechanical and optical properties of the corresponding hot-pressed glass-ceramics. We concluded that for the desired mechanical and optical properties of the multi-component lithium disilicate glass-ceramics for dental applications a finegrained microstructure with lath-shaped Li₂Si₂O₅ crystals $< 10 \,\mu\text{m}$ in length was necessary. To obtain these properties the nucleation agent (P_2O_5) concentration of initial glasses had to be $\geq 1.0 \text{ mol}\%$, the K₂O content between 1.5 and 3.0 mol% while the ZnO content and the SiO₂/Li₂O molar ratio could be chosen over a broader range.

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