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Synthesis of lithium aluminosilicate glass and glass-ceramics from spodumene material

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Abstract

The synthesis of lithium aluminosilicate glasses and glass-ceramics from spodumene material was investigated. Basing on the general formula $Li_{2-2(x+y)}Mg_xZn_yAl_{2-m}B_mSi_zO_{2z+4}$, 40 mol% of the Li_2O was replaced with 20 mol% of MgO and 20 mol% of ZnO, and 40 mol% of Al_2O_3 with B_2O_3. BaO was also introduced for improving glass melting behaviour. 2 and 5 wt.% TiO_2 was used as nucleation agent. In the TiO_2-containing glasses, virgilite was primarily crystallized. The degree of crystallinity was considerably improved at 900 °C. Virgilite was transformed into crystals of spodumene solid solutions embedded in a glass matrix, while Zn-gahnite formed a second crystalline phase. Rutile was crystallized in the glasses containing 5 wt.% TiO_2. The thermal expansion coefficient for the 2% and the 5 wt.% TiO_2-containing glass-ceramics was 6.39×10^{-7} and $17.1 \times 10^{-7}\,K^{-1}$, respectively (70–300 °C).

Keywords: B. Microstructure-final; C. Thermal expansion; D. Glass; D. Glass-ceramics; Lithium aluminosilicates

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1. Introduction

Lithium aluminosilicates have been widely used in glass and ceramic industry as lithia-bearing fluxes and low-expansion fillers in whiteware bodies [1–5]. At the early 1960s, the patent of Stookey [6], pointing out the efficiency of TiO_2 as nucleating agent, put the cornerstone for developing rapidly thorough studies in the $Li_2O–Al_2O_3–SiO_2$ (LAS) system and broaden applications of novel glass-ceramic compositions [7–9]. LAS glass-ceramics attract considerable commercial interest because they mainly feature low thermal expansion, together with remarkable chemical resistance and mechanical strength. LAS glass-ceramics with superior thermal properties are based on crystals of lithium aluminosilicates solid solution (high-quartz, keatite, β-eucriptite, or β-spodumene), and used at precision parts of optical observation systems, cooktop panels, stove windows, fire doors, cookware, and other technical devices [8–10].

The family of lithium aluminosilicates comprises compounds with the general formula $LiAlSi_xO_{2x+2}$. Cations, such as Mg and Zn, can substitute for Li, while x can vary considerably [11–13]. $AlPO_4$ can also partially replace SiO_2. Moreover, small trivalent and even divalent ions can partially substitute for Al [14–17].

The manufacturing process of LAS glass-ceramics comprises melting and forming of parent glass by conventional techniques, such as pressing, blowing, rolling or tube drawing. After annealing, the parent glass transforms itself into fine crystalline homogeneous glass-ceramic, depending on the amount of nucleating agents added in glass batch. TiO_2 and ZrO_2 have been widely considered and used as the most efficient nucleating agents for this type of glass-ceramics [7]. Nevertheless, the production of LAS glass-ceramics is relatively expensive due to the high cost of the raw materials used which are mostly reagents of analytical grade and the high melting (i.e. refining) temperature of the parent glass (>1600 °C) [7].

Therefore, this work presents the synthesis of glass and the crystallization to glass-ceramic from a spodumene natural rock material at relatively lower temperatures than those used in the preparation of conventional LAS glasses. The next section provides an insight on the design of the investigated formulations and the substitutions whether purposefully attempted or inevitably occurred due to the use of the natural material. The experiments aimed to determine the

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Table 1
Chemical compositions of some conventional Li-containing glass-ceramics (wt.%) [12]

Oxide	Pyroceram 9622	Pyroceram 9608	Shott glass-ceram 8562
SiO_2	65	69.5	62
Al_2O_3	23	17.8	21.2
Li_2O	3.8	2.5	2.8
MgO	1.8	2.8	1.0
ZnO	1.5	1.0	6.1
TiO_2	2.0	4.75	1.75
ZrO_2	2.0	0.25	1.75
P_2O_5	–	–	–
Na_2O	–	0.4	–
K_2O	–	–	0.4
As_2O_3	0.9	–	–
CaO	–	–	0.6
BaO	–	–	1.6

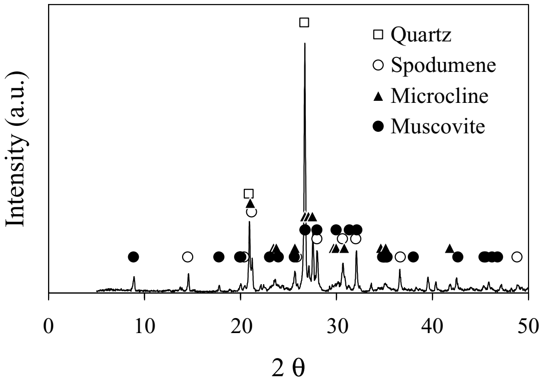


Fig. 1. XRD spectrum of the spodumene raw material (JCPDS cards: α-quartz (SiO_2): 88-2302; α-spodumene ($LiAlSi_2O_6$): 75-1091; microcline ($K(Si_{0.75}Al_{0.25})_4O_8$): 77-0135; muscovite ($KAl_3Si_3O_{10}(OH)_2$): 84-1304).

influence of these substitutions on the behaviour of these materials over heating at several temperatures and some properties of the resulting glass-ceramics.

2. Glass formulation

The design of the investigated glass composition was made in the light of thorough analysis of literature data which are available on LAS glass-ceramics. Table 1 presents the chemical composition of some conventional glass-ceramics [12]. If we neglect the nucleation and the refining oxides, then the chemical formulae of the parent glasses should be as shown in Table 2. Taking into account the Mg and Zn substituted for Li, these formulae resemble the formula of the pseudo-binary $LiAlO_2$–SiO_2 system [18]. As a matter of fact, these conventional LAS glass-ceramics are located between $Li_2O{\cdot}Al_2O_3{\cdot}7SiO_2$ and $Li_2O{\cdot}Al_2O_3{\cdot}5.4SiO_2$ with an excess of Al_2O_3.

As it was earlier mentioned, a spodumene natural rock material aimed to replace the expensive precursor in the production of the glass-ceramics. The chemical analysis (X-ray fluorescence) of the natural material was (wt.%) 72.76 SiO_2, 16.88 Al_2O_3, 0.23 Fe_2O_3, 0.03 MnO, 0.10 CaO, 0.09 MgO, 2.35 Li_2O, 1.15 Na_2O, 4.73 K_2O, 0.04 TiO_2, 0.24 P_2O_5, and 1.24 LOI. The crystalline structure (X-ray diffraction) comprised α-spodumene, potassium feldspar, quartz, and muscovite (Fig. 1).

The formulation of the designing glass-ceramics had to take into account the aforementioned theoretical approach and the features of the raw material. Therefore, the interest was centred at compositions around the stoichiometric spodumene, as defined at the $LiAlO_2$–SiO_2 phase diagram [18]. The range of these compositions was according to the general formula $Li_{2-2(x+y)}Mg_xZn_yAl_{2-m}B_mSi_zO_{2z+4}$, where $x = 0.2$–0.5, $y = 0$–0.2, $m = 0.8$–0.9, and $z = 4$–4.35. In this particular investigation, the parent glass was selected to have a formula of $Li_{1.2}Mg_{0.2}Zn_{0.2}Al_{1.2}B_{0.8}Si_{4.35}O_{12.7}$ (i.e. $x = 0.2$, $y = 0.2$, $m = 0.8$, and $z = 4.35$).

Evidently, this formula attempts to test the effect of substitution of Li (i.e. 20 mol% of MgO and 20 mol% of ZnO for 40 mol% of Li_2O) and Al (i.e. B_2O_3 for the 40 mol% of Al_2O_3) in $LiAlSi_zO_{2z+2}$, while it ensures the same SiO_2/Al_2O_3 ratio with the as-received spodumene material.

However, the natural material inevitably introduced other oxides in the investigated formulation, especially alkaline oxides, whose content in commercial LAS glass-ceramics do not usually exceed 1 wt.% [7,12]. BaO, introduced via $BaCO_3$ in the glass batch, aimed to improve glass melting behaviour. Thus, the calculated chemical composition of the parent glass, denoted hereafter as L, is shown in Table 3. According to Table 3, the chemical formula of the parent glass L is shown in Table 2.

TiO_2 was used as nucleating agent, whose influence was investigated by preparing two new formulations. The first one comprised (in wt.%) 2% TiO_2 and 98% L, and the second 5% TiO_2 and 95% L, denoted as L-2 and L-5, respectively.

Table 2
Molecular formulae of the parent glasses of the conventional glass-ceramics listed in Table 1 and the investigated composition L

Parent glass	Molecular formulae
Pyroceram 9622	$0.67Li_2O{\cdot}0.23MgO{\cdot}0.10ZnO{\cdot}1.19Al_2O_3{\cdot}5.70SiO_2$
Pyroceram 9608	$0.51Li_2O{\cdot}0.42MgO{\cdot}0.07ZnO{\cdot}1.05Al_2O_3{\cdot}7.00SiO_2{\cdot}0.04Na_2O$
Shott glass-ceram 8562	$0.49Li_2O{\cdot}0.13MgO{\cdot}0.38ZnO{\cdot}1.08Al_2O_3{\cdot}5.37SiO_2{\cdot}0.02K_2O{\cdot}0.05CaO{\cdot}0.05BaO$
L	$0.59Li_2O{\cdot}0.21MgO{\cdot}0.20ZnO{\cdot}0.61Al_2O_3{\cdot}0.40B_2O_3{\cdot}4.44SiO_2{\cdot}0.08BaO{\cdot}0.27K_2\ O{\cdot}0.07Na_2O$

Table 3
Composition of the investigated parent glass, L

Oxide	Weight percent
SiO_2	61.44
Al_2O_3	14.25
B_2O_3	6.40
Li_2O	4.11
MgO	1.90
ZnO	3.71
TiO_2	0.03
P_2O_5	0.20
Na_2O	0.97
K_2O	4.00
CaO	0.08
BaO	2.70
MgO	1.90
MnO	0.02
Fe_2O_3	0.19

3. Materials and experimental procedure

The principal raw material of the synthesis of the glass was a spodumene natural rock obtained from Li-rich aplite-pegmatite dykes (Covas de Barroso district, northern Portugal). The results from mineralogical and purification studies of this type of dykes have been published elsewhere [19,20]. The as-received samples, comprising coarse grains, were planetary milled in absolute ethanol media with Al_2O_3 milling balls in Al_2O_3 jar for 6 h at 150–180 rpm. After milling, the mean grain size of the powder was ∼6 microns. Pure (reagent grade) powders of Li_2CO_3, H_3BO_3, $4MgCO_3$ $Mg(OH)_2$ $5H_2O$, ZnO, $BaCO_3$, and TiO_2 were also used.

Blends of powders were dry milled in porcelain jars for 45 min. Batches of 70–100 g, melted in corundum crucibles between 1500 and 1550 °C, for 2 h, in air, were cast in preheated bronze moulds. Annealing was carried out close to the transformation temperatures. The conditions for the crystallization were decided in accordance to the thermal analysis results, density measurements, and visual observation of the samples.

The samples were characterized using the following techniques and apparatus. Differential thermal analysis (DTA, Labsys Setaram TG-DTA/DSC, France, heating rate 5 °/min, air atmosphere). Dilatometer thermal analysis (Bahr Thermo Analyse DIL 801 L, Germany, heating rate 3 °/min). X-ray diffraction (XRD, Philips X'Pert MPD, the Netherlands, using Cu Kα radiation, equipped with high temperature attachment Anton Paar HTK 16). X-ray fluorescence analysis (XRF, Model XRF-1700, Shimadzu Corp., Tokyo, Japan). Microstructure observation at polished and etched surfaces (immersion in 5 vol.% HF for 30 s) by scanning electron microscopy (SEM, Hitachi S-4100, Japan, 25 kV acceleration voltage), and elemental analysis by energy dispersion spectroscopy (EDS) under point analysis mode. The apparent density of the glass and glass-ceramic blocks was determined using the Archimedes method (immersion in ethylenoglycol).

4. Results

In all the investigated cases, the melts of the glasses had suitable viscosity and flow properties. It has been reported that addition of refining agents in the batch, such as As_2O_3 or Sb_2O_3, and mechanical homogenization of the melt by stirring can have beneficial effect to the working characteristics of the glasses [21,22]. The addition of TiO_2 seemingly increased the melting temperature. The melting of the parent glass L occurred at ∼1500 °C in 2 h, whereas both L-2 and L-5 were completely melted at 1550 °C after 2 h. The colour of the solidified glasses was light blue for L, yellow for L-2 and black for L-5. All glasses were transparent and there was no evidence for bubbles, cloudiness, or crystallization.

After heat treatment at ∼600 °C for 2 h, the blocks of glass L exhibited a slightly homogeneous opalescence, the L-2 turned into light black with an inhomogeneous aspect, whereas there was no evidence of any change for the L-5. After 2 h at 800 °C, L was transformed to a homogeneous light blue opaque material, while both L-2 and L-5 turned into inhomogeneous partially crystallized materials comprising black vitreous and white–grey devitrified zones. Heat treatment at 900 °C for 2 h resulted in inhomogeneous crystallization of L, featuring an opaque vitreous light blue bulk encapsulated with a superficial grey crystalline layer. On the other hand, both L-2 and L-5 considerably improved the degree of crystallinity resulting in homogeneous and well-crystallized materials throughout their entire bulk. Hence, only the L-2 and L-5 glasses were selected for further investigation.

Thermal analysis showed only one weak exothermic peak for both the L-2 and the L-5 glasses at 720 and 710 °C, respectively (Fig. 2), which apparently evidences a single crystalline phase precipitation during heat treatment. Increasing TiO_2 reduces the intensity and narrows this exothermic peak, which is also slightly shifted to lower temperatures. These results agree fairly well with an earlier work on the crystallization of glasses in the CaO–MgO–Al_2O_3–SiO_2 system with the incorporation 5 and 7 wt.% TiO_2 as nucleating agent [23].

XRD spectra, obtained in situ between 700 and 1000 °C, verified the formation of spodumene solid solutions (Fig. 3),

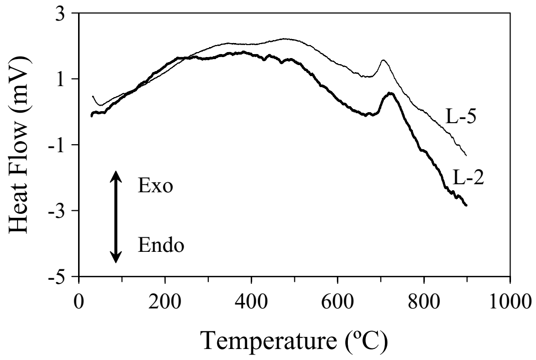
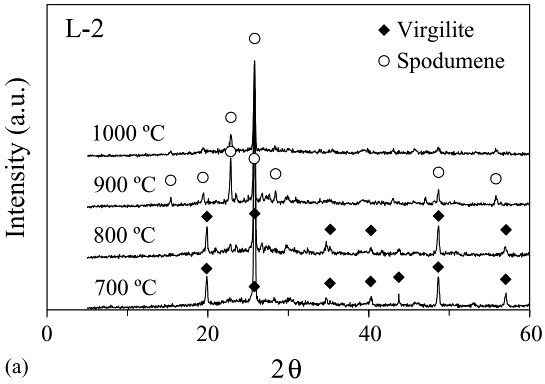


Fig. 2. DTA of the glasses L-2 and L-5.



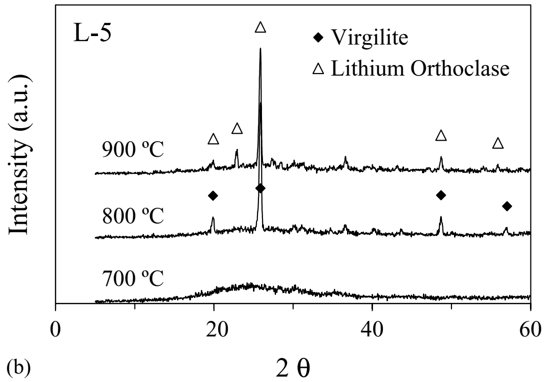


Fig. 3. High-temperature XRD spectra obtained in situ at several temperatures (heating rate 10 °/min, holding time at each temperature 60 min) for the L-2 and the L-5 formulations (samples in powder form) (JCPDS cards: virgilite ($Li_xAl_xSi_{3-x}O_6$): 31-0707; β-spodumene: 74-1106; Li-orthoclase ($LiAlSi_3O_8$): 35-0794).

in accordance with DTA. L-2 shows stronger tendency for devitrification than L-5 at the beginning of the process, since at 700 °C, virgilite ($Li_xAl_xSi_{3-x}O_6$) was detected in L-2, whereas there was no effect in L-5. At 800 °C, virgilite was the only phase detected in both L-2 and L-5. At 900 °C, the degree of crystallinity was considerably improved, while virgilite was transformed into another lithium aluminosilicate, $LiAlSi_3O_8$.

Fig. 4 plots the thermal expansion of the glasses L-2 and L-5. For the L-2, the characteristic glass-transition temperature (T_g) was ~575 °C and the dilatometric softening point (T_s) ~620 °C. The glass L-5 had slightly lower T_g and T_s values.

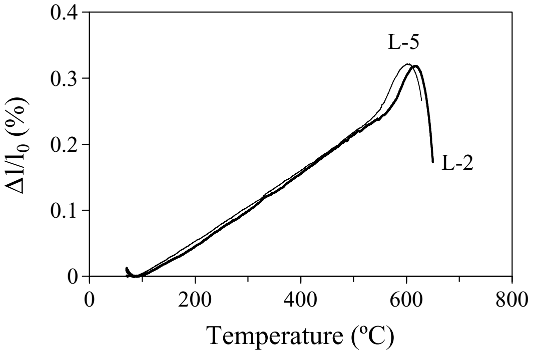


Fig. 4. Thermal expansion of the glasses L-2 and L-5.

In the preparation of glass-ceramics, the experimental determination of nucleation and crystallization temperatures are key technological points. A suitable method for determining the development of nuclei in LAS glasses has been already reported [24]. Time–temperature-transformation (TTT) diagrams can also provide guide lines for the conditions of nucleation [25]. In the present work, the first stage of heat treatment for starting the nucleation was set up at 600 °C, i.e. slightly higher than T_g, but lower than T_s for preventing possible deformation during heat treatment [26].

Fig. 5 shows characteristic SEM micrographs of the cast and the heat treated (600 °C for 2 h) glasses. In the cast samples of both L-2 and L-5 glasses, there are cloud-like droplets of segregated liquid phase (Fig. 5a and b, respectively). This large droplet-containing area strongly resembles the droplet silicate phase enriched in Li, Mg, Zn, Al, and Ti, which was observed in Pyroceram 9608 glass [27]. In the L-5, there were also observed secondary droplet areas which comprised nanosize particles, probably rich in TiO_2 (Fig. 5b, inset). Phase separation was advanced after heat treatment at 600 °C for 2 h (Fig. 5c and d). The droplets of the segregated liquid phase were transformed into agglomerates, whose homogeneous distribution in the matrix likely corresponds to a pre-crystalline state. Prolonged heating at 600 °C until 14 h had negligible influence on either the microstructure or the density of the materials.

Evidently, heat treatment at higher temperatures had to be carried out in order to reach the maximum crystal growth regime. Thus, the glasses already heated at 600 °C for 2 h were progressively heated at several temperatures from 700 to 1000 °C. After heat treatment at each particular temperature, the degree of crystallinity was swiftly evaluated by density measurements and visual observation. The maximum apparent density of the glass-ceramic L-2 was achieved at 900 °C for 3 h (2.49 g/cm^3). Although density did not change until to 1000 °C, L-2 showed evidences of degradation over heating beyond 900 °C, in terms of the formation of different coloured layers in the bulk of the material. For the glass-ceramic L-5, the maximum density (2.55 g/cm^3) was achieved after heat treatment at 925 °C for 6 h. The resulting glass-ceramic was a well-crystallized monolith of ivory colour. Further heat treatment until 1000 °C resulted in an increasing yellowish shade, but density was almost unchanged.

Fig. 6 presents the XRD patterns of glass-ceramics prepared via bulk crystallization process with different heat treatments. For the L-2, at 900 °C and short soaking (1 h), lithium orthoclase $LiAlSi_3O_8$, which is a spodumene solid solution (s.s.), was the only crystalline phase, while in prolonged heating (3 h) precipitation of Zn-gahnite ($ZnAl_2O_4$) also occurred, forming a second crystalline phase (Fig. 6a). However, the experimental results cannot ascertain if Zn-gahnite was precipitated from the glass reservoir or from the decomposition of the spodumene s.s. The same

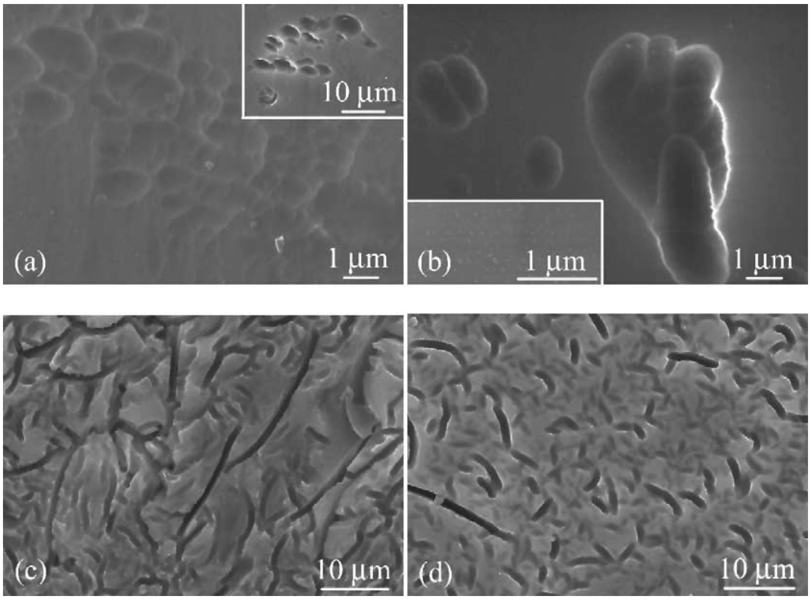


Fig. 5. Characteristic SEM micrographs of the glasses L-2 and L-5 (after HF-etching): (a) as-cast L-2, (b) as cast L-5 (inset: secondary segregation), (c) L-2, 600 °C for 2 h, (d) L-5, 600 °C for 2 h.

crystalline phases, i.e. lithium orthoclase and Zn-gahnite, together with rutile (TiO_2), were precipitated during heat treatment of the monolithic glass L-5 at 925 °C for 6 h and 1000 °C for 2 h (Fig. 6b).

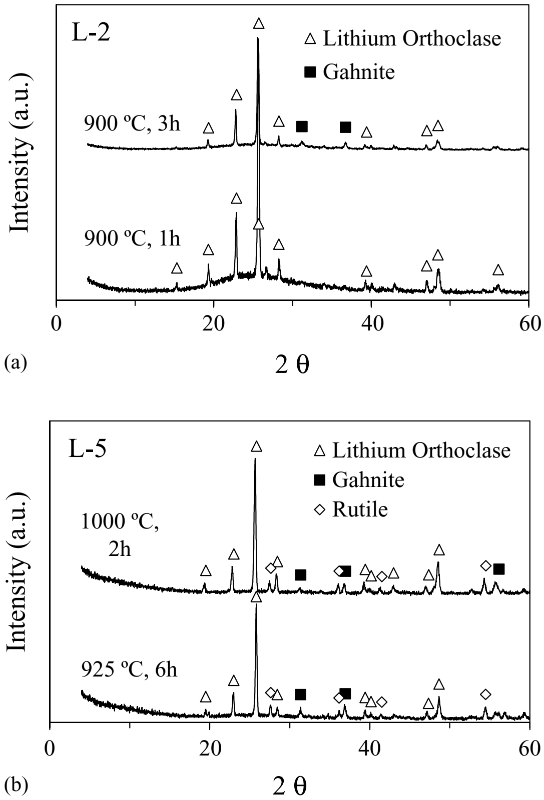


Fig. 6. XRD spectra of bulk crystallized glass-ceramics (a) L-2 and (b) L-5, obtained after different heat treatments of the corresponding glasses (JCPDS cards: Li-orthoclase ($LiAlSi_3O_8$): 35-0794; Zn-gahnite ($ZnAl_2O_4$): 74-1136; rutile (TiO_2): 99-0090).

Fig. 7 plots the thermal expansion of the bulk crystallized glass-ceramics L-2 (900 °C for 3 h) and L-5 (925 °C for 6 h). From these plots, the linear thermal expansion coefficient (CTE) of the resulting glass-ceramics was calculated as $6.39 \times 10^{-7}\,K^{-1}$ for L-2 and $17.1 \times 10^{-7}\,K^{-1}$ for L-5 (70–300 °C).

The microstructure of the L-2 and L-5 glass-ceramics prepared after different heat treatments generally comprised crystals of spodumene s.s. embedded in a glass matrix (Fig. 8). Increasing TiO_2 (L-5) seemingly resulted in higher homogeneity of the distribution of the spodumene s.s. crystals (Fig. 8b). The microstructure of L-5 shown in Fig. 8c implies that the growth of spodumene s.s. crystals should have almost completed after heat treatment at 1000 °C for 2 h. Meanwhile, fine crystalline particles have been precipitated on spodumene s.s. crystals. This phenomenon is probably related to the crystallization of rutile from the secondary droplet areas, rich in TiO_2 (Fig. 5b) [28].

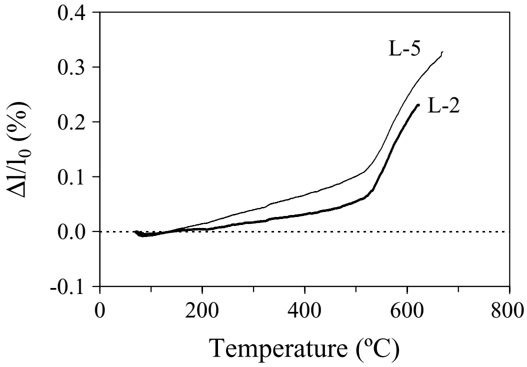


Fig. 7. Thermal expansion of the bulk crystallized glass-ceramics L-2 (900 °C for 3 h) and L-5 (925 °C for 6 h).

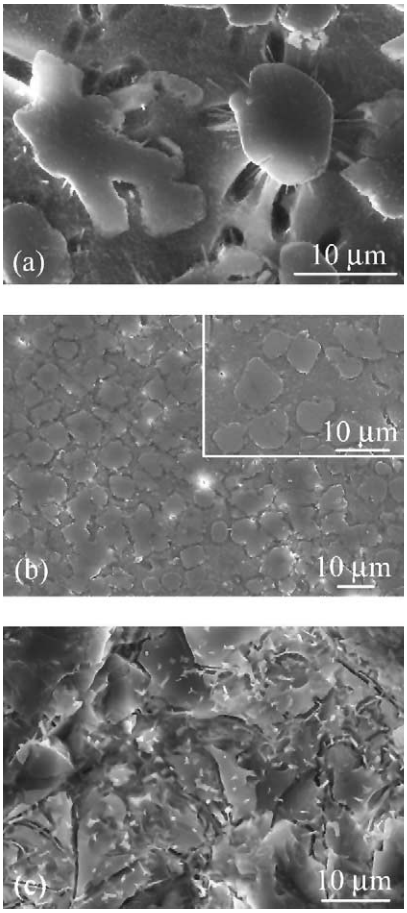


Fig. 8. Characteristic SEM micrographs of bulk crystallized glass-ceramics (after HF-etching) (a) L-2, 900 °C for 3 h, (b) L-5, 900 °C for 4 h, and (c) L-5, 1000 °C for 2 h.

The composition of the spodumene s.s. crystals was not determined because very light elements, such as Li and B, can not be detected by EDS. However, EDS analysis showed that the weight ratio of SiO_2/Al_2O_3 in these crystals was exactly the same in both L-2 and L-5 (2.96). Moreover, it was found that the glass matrix was rich in alkaline (K_2O, Na_2O) and divalent cation oxides (MgO, ZnO, BaO). The total amount (in wt.%) of these oxides was 17.2 and 18.8% in the glass matrix of the L-2 and the L-5, respectively.

Table 4 summarizes some properties of the obtained glasses and glass-ceramics and the schedule of the heat treatment for the crystallization process.

Table 4
Properties of glasses and glass-ceramics and the schedule of crystallization

Properties	Formulation	
	L-2	L-5
Glass		
Melting temperature (°C)	1550	1550
Colour	Yellow	Black
Density (g/cm^3)	2.47	2.49
Thermal expansion coefficient ($\times 10^{-7}$ K^{-1})		
70–300 °C	43.3	50.1
70–500 °C	45.6	50.6
T_g (°C)	575	550
T_s (°C)	620	610
glass-ceramic		
Colour	Dark grey	Ivory
Density (g/cm^3)	2.49	2.55
Thermal expansion coefficient ($\times 10^{-7}$ K^{-1})		
70–300 °C	6.39	17.1
70–500 °C	12.3	23.4
Schedule of the heat treatment during crystallization (°C–h)		
Annealing	550–0.5	
Nucleation	600–1	
Crystallization: first stage	730–2	
Second stage	900–3	925–6

5. Discussion

In the pseudo-binary $LiAlO_2$–SiO_2 system [18], the composition of the parent glass L (Table 2) is located between spodumene ($LiAlSi_2O_6$) and lithium orthoclase ($LiAlSi_3O_8$), closer to the spodumene border. In this type of melts, high-quartz solid solution readily crystallizes from supercooled liquids. The partial replacement of Li and Al ions with other divalent or trivalent cations usually reduces the thermodynamic stability of the high-quartz and keatite aluminosilicates [13,16].

In the L-2 and L-5 glasses, the single weak exothermic peak at ~710–720 °C (Fig. 2) should be assigned to lithium aluminosilicate virgilite ($Li_xAl_xSi_{3-x}O_6$), whose composition corresponds to a stuffed disordered β-quartz structure. The threefold substitution of Mg and Zn for Li, and B for Al, caused a relatively rapid transformation of virgilite into spodumene s.s. crystals following by the precipitation of Zn-gahnite over prolonged heating (Fig. 6).

In general, the presence and the amount of TiO_2 considerably affected the crystallization of the investigated compositions. TiO_2 apparently takes part at the earlier stages of segregation, where Li_2O, MgO, ZnO, and Al_2O_3 are accumulated in the larger droplet areas [27]. After heat treatment at 600 °C, this type of segregation was more pronounced. One should also take into account that the composition of the parent glass is overlapped with the metastable miscibility gap in the system Li_2O–Al_2O_3–SiO_2 [12]. This fact should further favour crystallization of virgilite, which was subsequently transformed into spodumene s.s. crystals. TiO_2 seemingly plays essential role in the secondary segregation and the formation of the smaller droplet areas, rich in TiO_2 (Fig. 5b). These nanosize droplet areas likely result from the precipitation of rutile, as observed in L-5 (Fig. 8c). At the same time, the large droplet areas from the early stages of segregation resulted in large spodumene s.s. crystals, (particularly ~12–15 µm for L-2 and slightly smaller (~10 µm) for L-5, Fig. 8a and b), which were coarser than those observed in Pyroceram [27].

With regards to the attempted substitutions, one should note that Mg, Zn and the alkaline oxides were found also in the glassy phase. Although the experimental techniques could not provide information about the distribution of light elements, such as Li and B, between the crystalline and the glassy phase due to the limitations of the EDS analysis, this finding indicates that there should be some limitations on the possible substitutions. In lithium aluminosilicates, there are generally limited possibilities for chemical substitution [16], although MgO has successfully replaced ~40 mol% of Li_2O in Pyroceram 9608. The substitution of ZnO for Li_2O is also rather limited. B_2O_3 can partially substitute for Al_2O_3 (up to 25 mol%) [16]. Therefore, in this work, the excess of B_2O_3 should be accommodated in the glassy phase which was also enriched in alkaline and divalent (MgO, ZnO, BaO) oxides. Evidently, the glassy phase caused the lowering of the transformation temperature (T_g) of the investigated glass-ceramics (Fig. 7), with respect to the conventional LAS glass-ceramics [29].

It is also very important to underline that due to the use of the spodumene natural rock materials, the investigated formulations contain almost one order of magnitude higher amount of Na_2O and K_2O than that Pyrceram 9608 or Shott glass-ceramic (Tables 1–3). However, the CTE (70–300 °C) of both glass-ceramics matches well the CTE of Pyroceram 9608 ($4–20 \times 10^{-7}\,K^{-1}$ for 20–320 °C) [12]. L-5 has significantly higher CTE than L-2 (Table 4), likely due to the precipitation of rutile (Fig. 6b) and the higher content of alkaline oxides in the glassy phase.

In the literature, the use of TiO_2 together with ZrO_2 as nucleating agents has been proposed for improving the quality of the resulting LAS glass-ceramics. The coupling of these two nucleation agents can lower the temperature of transformation of the glass into high-quartz s.s., lighten the yellowish colour of the LAS glass-ceramics and, therefore, transparency may be considerably increased [30–32]. Further studies are currently underway addressing themselves to the use of both TiO_2 and ZrO_2 as nucleating agents and choose the optimal concentration in the same threefold substitution. The main aim is to decrease the size of the crystals precipitated form the melt, since smaller crystals should improve the thermal and the mechanical properties of the resulting glass-ceramics.

6. Conclusions

This work aimed to produce lithium-aluminosilicates (LAS) glass-ceramics where considerable cation substitution (Mg and Zn for Li, and B for Al) was taken place, with the aid of 2 and 5 wt.% TiO_2 as nucleation agent. The goals of the study were to reduce the melting temperature of glasses (<1600 °C), and to produce homogeneous glass-ceramics with low thermal expansion. The experimental results showed that the threefold substitution resulted in successful production of glasses at 1500 °C. The presence of TiO_2 increased the melting temperature to 1550 °C but considerably promoted devitrification. The microstructure of the TiO_2-containing glasses comprised large droplets of segregated liquid phase. In the case of higher TiO_2-content, nanosized droplets were also formed. Heating at 600 °C made phase separation more evident. Virgilite was primarily crystallized, which was transformed into spodumene solid solution crystals at higher temperatures. Prolonged heating caused precipitation of Zn-gahnite. In the case of high TiO_2-content, the tiny droplets of the glass were seemingly crystallized into rutile. There are experimental evidences which indicate that there are limited possibilities for chemical substitution since the excess of the substituted elements was led to the glassy phase. The high content of the glassy phase in alkaline and divalent cation oxides resulted in lower T_g values than those found in conventional LAS glass-ceramics. The thermal expansion (70–300 °C) of the resulting glass-ceramics is comparable to Pyroceram 9608.

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