

# Effect of ion exchange on the sinter–crystallisation of low expansion $\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ glass-ceramics

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Manuscript received 13 September 2010

Revised version received 27 October 2010

Accepted 11 November 2010

*In this work we propose an ion exchange (IE) treatment to minimize surface crystallization and thus improve the sintering of compacts made of glass particles. This concept was tested by subjecting glass powders of the  $\text{Li}_2\text{O}\text{--}\text{Al}_2\text{O}_3\text{--}\text{SiO}_2$  (LAS) system to molten  $\text{KNO}_3$  IE treatment aimed at developing a low thermal expansion glass-ceramic via sinter–crystallisation. The relative densities of treated and untreated glass powder compacts sintered at different temperatures were compared and suitable IE and sintering temperatures were selected. Optical microscopy, x-ray diffraction, dilatometry and scanning electron microscopy were used to characterise the sintered samples. The proposed IE decreased the optimum sintering temperature from 1100 to 1000°C and yet allowed the formation of virgilite, a desirable  $\beta$ -quartz solid solution having a negative thermal expansion coefficient. The compositional changes in surface of the glass particles caused by IE diminished the crystallisation tendency, which resulted in a smaller volume fraction of virgilite, thus increasing the overall thermal expansion coefficient of the resulting glass-ceramic. However, by mixing IE-treated with untreated powder this effect has been controlled leading to a glass-ceramic with low residual porosity (<1.5%) and a relatively low thermal expansion coefficient ( $1.6\times 10^{-6}\text{ }^\circ\text{C}^{-1}$ , between 40 and 500°C).*

## 1. Introduction

$\text{Li}_2\text{O}\text{--}\text{Al}_2\text{O}_3\text{--}\text{SiO}_2$  (LAS) glass-ceramics have high commercial value due to their low thermal expansion, combined with refractoriness up to 600°C and great thermal shock resistance.<sup>(1)</sup> They are commonly used as cooker top panels, telescope mirrors and high temperature windows.<sup>(2–4)</sup> The low thermal expansion coefficient of these materials is due to the presence of crystalline phases with highly anisotropic thermal expansion coefficients (TEC), such as  $\beta$ -quartz solid solutions.<sup>(5)</sup> The slightly positive TEC of the residual glassy phase combined with the negative TEC of the crystalline phase results in ultra low thermal expansion glass-ceramics.

Commercial LAS glass-ceramics are produced by a regular glass melting–forming technique using compositions containing one or more nucleating agents, such as  $\text{TiO}_2$  and  $\text{ZrO}_2$ , followed by (internal) nucleation and crystal growth heat treatments.<sup>(6)</sup> An alternative route is to form glass powder compacts of nucleant free compositions, followed by a thermal treatment for viscous flow sintering and crystallisation.<sup>(7)</sup> The interplay between the densification and surface crystallisation kinetics may result in a variety of microstructures with different porosities and crystallised fractions.<sup>(8)</sup> For instance, if surface crystallisation takes place in the early stages of sintering, viscous flow is hindered and a highly porous body is obtained.<sup>(9,10)</sup> Therefore, glasses that easily crystallise

are not suitable for achieving high densification (low porosity) by this method.<sup>(11)</sup> Heterogeneous nucleation is often favoured by flaws or impurities existing on the surface of glass particles.<sup>(12)</sup> Although surface crystallisation is required to obtain a glass-ceramics, it is not desirable until densification is in an advanced stage. On the other hand, excellent glass forming compositions may lead to a sintered vitreous body, which is not desirable for obtaining a glass-ceramic.

Most studies on the sinterability of LAS glasses have focused on the sintering of spodumene-like ( $\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2$ ) glass powders.<sup>(13–15)</sup> However, it has been shown that stoichiometric spodumene glass does not completely densify during sintering.<sup>(16)</sup> For non-stoichiometric compositions, densities greater than 90% of the theoretical density have been achieved by hot pressing (93%),<sup>(17)</sup> and for powders prepared by sol-gel (96%),<sup>(18)</sup> or by introducing sintering aids (99.8%).<sup>(19)</sup>

Ion exchange treatments have been so far employed mostly to strengthen glasses and glass-ceramics.<sup>(20–24)</sup> This method induces compressive stresses on the surface of the material by substituting small ions in the glass or glass-ceramic by larger ions supplied from an appropriate molten salt bath.<sup>(25,26)</sup>

In the present study we show that ion exchange treatments can be designed to modify the surface properties of LAS glass powder to enhance its sinterability. To the best of our knowledge IE treatments have not yet been used to decrease the surface crystallisation tendency of glass particles. Here we report on

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the development of a low expansion glass-ceramic via preparation of glass powder followed by IE, pressing, plus heat treatment for sinter-crystallisation. We have used a  $\text{KNO}_3$ -based IE treatment to partially replace lithium in the surfaces of the glass particles by potassium, aiming to induce a slight decrease of the surface crystallisation rate, which might help to achieve high densification during sintering. This is a new approach for obtaining high density sintered glass-ceramics, i.e. by a combination of IE and sinter-crystallisation.

## 2. Experimental procedure

A multicomponent glass based on the LAS system was designed and prepared by homogenizing a mixture of analytical grade oxides and carbonates, melting in a platinum crucible at  $1600^\circ\text{C}$  for 3 h, and subsequently pouring the melt on a stainless steel plate at room temperature. The chemical compositions of the parent glasses lie within the following range (mol%):  $60\text{--}70\text{SiO}_2$ ;  $10\text{--}20\text{Al}_2\text{O}_3$ ;  $5\text{--}10\text{Li}_2\text{O}$ ;  $0.5\text{--}3\text{P}_2\text{O}_5$ ;  $0.3\text{--}2\text{B}_2\text{O}_3$ ;  $0.5\text{--}3\text{Na}_2\text{O}$ ;  $0.2\text{--}1\text{K}_2\text{O}$ ;  $0.5\text{--}2\text{CaO}$ ;  $1\text{--}4\text{MgO}$ . It should be stressed that this composition does not contain any nucleating agent, such as  $\text{TiO}_2$  and  $\text{ZrO}_2$ , thus catalysts have been replaced by the crystallisation potential of glass particle surfaces (broken bonds, sharp edges, solid contaminants, etc<sup>(12)</sup>). The glass composition was specially designed to obtain a residual glass phase having a slightly positive TEC combined with the negative TEC of the desired crystalline phase, resulting in a glass-ceramic with a very small TEC.

The glass was milled in a planetary ball mill (Pulverisette 7) at 450 rpm for 60 or 90 min, using an agate jar. Two powders with different average particle sizes were obtained, 5  $\mu\text{m}$  and 2  $\mu\text{m}$ , respectively. Simulations using the Alfred model for particle packing<sup>(27,28)</sup> demonstrated that the maximum green density is achieved by mixing these two powders at the volume ratio of 40/60.<sup>(29)</sup>

In order to investigate in detail the effect of IE on the sintering of LAS glass powders, three different sets of experiments were designed, as summarized in Table 1. The experiments were carried out to find a suitable IE treatment time and, subsequently, to identify the optimum sintering temperature for this particular glass powder and size distribution. The IE was carried out using molten  $\text{KNO}_3$  for 6 or 30 min at  $350^\circ\text{C}$  (please note that these times and temperatures are much lower than those typically used for IE strengthening). The main reason to use a relative low temperature and short times was to promote only a very thin layer of potassium at the particle surfaces in order to preserve the glass composition inside the glass particles. The powder was mixed with the molten  $\text{KNO}_3$  in a stainless steel crucible, using a metallic rod passing through an external aperture on the top of the furnace. The  $\text{KNO}_3$ /glass weight

Table 1. Percentage volume of different particle sizes, IE-treatment and sintering temperatures of the investigated samples

Sample Group	Vol% (5 $\mu\text{m}$ powder)	Vol% (2 $\mu\text{m}$ powder)	IE time (min)	Sintering temperature ( $^\circ\text{C}$ )
1	40%	60%	0	1100
2-A	40% IE	60% IE	6	1100
2-B	40% IE	60% IE	30	1100
2-C	40% IE	60% IE	6	1100
3	40% IE	60% (without IE)	6	985–1100

ratio was 2.5, which corresponds approximately to 20 moles of potassium for each mole of lithium in the glass composition. The glass powder was subsequently washed in distilled water to remove the residual  $\text{KNO}_3$  and then filtered under vacuum using a 0.22 mm aperture polymeric sieve.

The two powders with different particle sizes were dried, mixed and pressed in a stainless steel mould at room temperature at 130 MPa, with a holding time of 20 s. Cylindrical samples of 10 mm in diameter and 4 mm thick were prepared. The sintering treatments were carried out in an electric furnace using a heating rate of  $30^\circ\text{C}/\text{min}$ , from room temperature up to the sintering temperature without any holding time. The samples were cooled down with the furnace.

Differential scanning calorimetry (DSC) analyses were performed at a heating rate of  $10^\circ\text{C}/\text{min}$  using precursor powders of samples 1, 2-B and 3 to investigate the crystallisation behaviour of IE-treated and untreated specimens. The porosity of the sintered samples and the crystallised volume fraction for samples 2-B and 2-C were determined by optical microscopy (Leica DM-RX with a CCD camera DFC 490) and image analysis using the software Image-J. The evolution of the crystalline phases in samples sintered at different temperatures was followed by x-ray diffraction (XRD, Siemens-D5005, Cu  $\text{K}_\alpha$  radiation) and the crystallised volume fraction was measured by the matrix fluxing method.<sup>(30)</sup> Scanning electron microscopy (SEM) with a secondary electron (SE) detector (SEM, Phillips TMP) was employed to observe the microstructure of polished and etched (by immersion in 2 vol% HF for 15 s) gold coated, transverse sections of the samples. Measurements of the change in length,  $\Delta L$ , with temperature were carried out in a push rod dilatometer (Netzsch DIL 402 PC) using a heating rate of  $5^\circ\text{C}/\text{min}$  and the mean TEC was then calculated for sintered samples  $4\text{ mm}\times 4\text{ mm}\times 50\text{ mm}$  in size from  $40^\circ\text{C}$  up to  $500^\circ\text{C}$ .

## 3. Results and Discussion

An example of the microstructure of a sample of group 1 is shown in Figure 1(a). A considerable crystallised fraction can be observed. The resulting porosity was  $4.0\pm 0.1\text{ vol}\%$ . Such a relatively high degree of densification indicates that viscous flow sintering occurred to a significant extent before being hindered

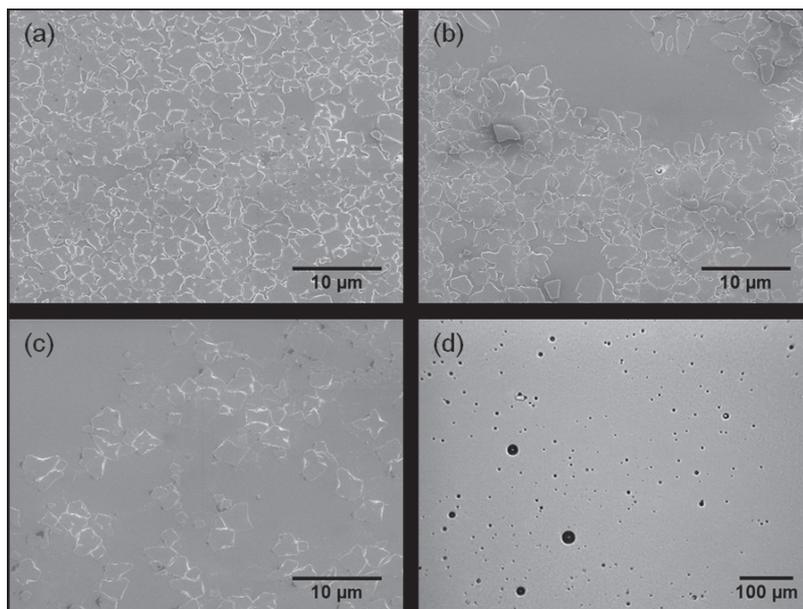


Figure 1. SEM images of polished and etched cross sections of LAS glass-ceramics sintered at 1100°C. (a) sample 1 (untreated); (b) sample 2-A, submitted to IE for 6 min; (c) sample 2-B, submitted to IE for 30 min; (d) optical micrograph of polished sample 2-B

by surface crystallisation. The sintering condition used here resulted in maximum densification for this particular composition, as determined previously.<sup>(29)</sup>

In order to obtain even higher densification, the glass powder was submitted to IE. Hence the lithium ions that were near the surfaces of the glass particles were exchanged with potassium ions. The IE was performed at 350°C (well below  $T_g$ ) for two different short times: 6 and 30 min. The samples were sintered at a heating rate of 30°C/min up to 1100°C. The residual porosity was  $2.3\pm 0.1$  vol% after 6 min IE and  $1.9\pm 0.1$  vol% after 30 min, and thus was significantly decreased in comparison to the samples produced from the powder without IE. The similar residual porosity of samples in the groups 2-A and 2-B indicates that increasing the IE time does not lead to significant further densification and that the residual porosity is probably caused by degassing (the new

“pores” observed in a polished surface of sample 2-B are like spherical bubbles, as shown in Figure 1(d)). The microstructures of samples 2-A and 2-B after 6 min and 30 min of IE, respectively, are shown in Figure 1(b) and (c). It is evident that the amount of crystals after 6 min IE is larger than after 30 min, which suggests that the increase of the potassium concentration drastically reduces crystallisation. Thus, an IE time of 6 min was used in the following experiments, since it promotes a high densification and sufficient crystallisation. Sample 2-C was sintered at 1000°C with the same heating rate (30°C/min) and its residual porosity was  $2.1\pm 0.1$  vol%, a value similar to that observed for samples of groups 2-A and 2-B. This result shows that IE enables a reduction of 100°C in the sintering temperature without affecting the final degree of densification.

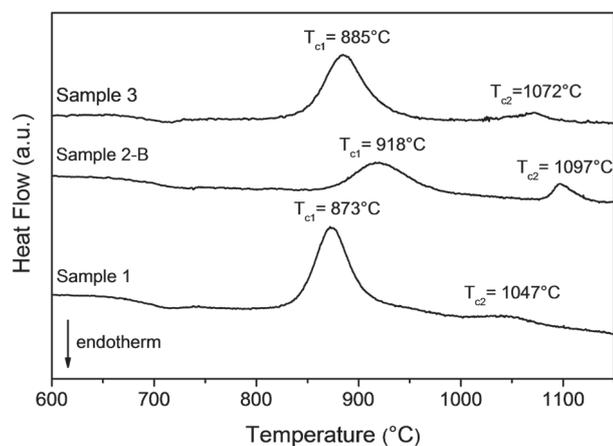


Figure 2. DSC curves of the samples 1, 2B and 3 obtained with a heating rate of 10°C/min

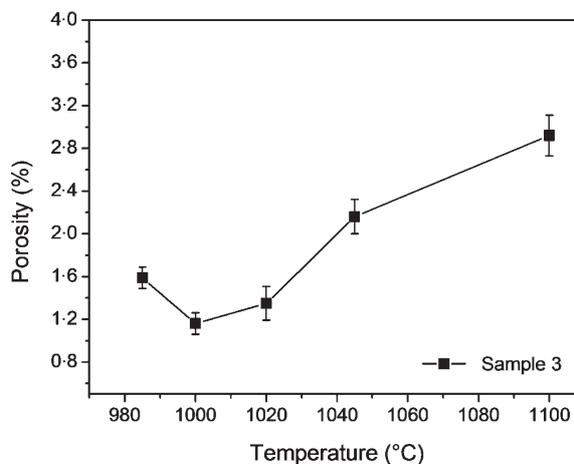


Figure 3. Porosity versus sintering temperature for samples of group 3. The error bars correspond to the standard deviation for ten images analysed

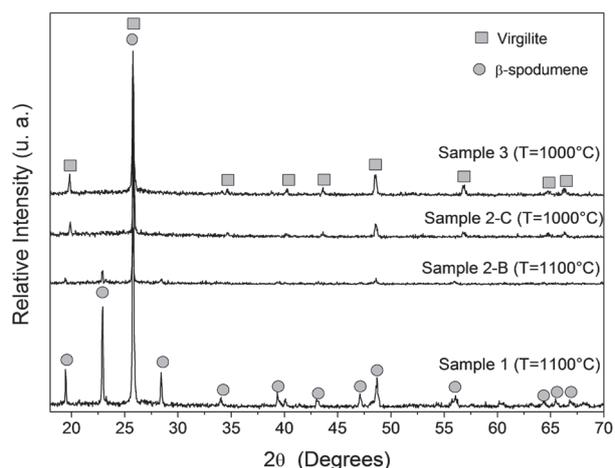


Figure 4. XRD patterns of LAS glass-ceramics sintered at 1100 and 1000°C. Circles: tetragonal  $\beta$ -spodumene ( $\text{LiAlSi}_2\text{O}_6$ ) JCPDS 35-0794; square: hexagonal virgillite ( $\text{Li}_x\text{Al}_x\text{Si}_{3-x}\text{O}_6$ ) JCPDS 31-0707

The decrease of crystallisation after IE is confirmed by the DSC results shown in Figure 2. A smaller crystallisation peak is observed for the precursor powder of sample 2-B (which had all particles submitted to IE) than for sample 1. Although it is desirable to avoid early crystallisation to reach high densification, it is necessary to keep a high crystalline fraction in the glass-ceramic. Considering the TEC of the glass ( $4.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ) and virgillite ( $-1.3 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ )<sup>(34)</sup> a crystallinity equal or larger than 70 vol% is necessary to ensure a glass-ceramic TEC equal or below  $0.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ . Hence to ensure sufficient crystallisation only part of the powder was submitted to IE in samples of group 3. As shown in Figure 2, an intermediate crystallisation peak is observed. The most desired property for commercial purposes, near zero TEC, can be achieved with a combination of a crystalline phase of very low or negative TEC and a residual glass with slightly positive TEC.

In order to determine a suitable sintering temperature, specimens from group 3 were treated at different temperatures and the resulting porosity was analysed. Figure 3 shows that 1000°C is the sintering temperature that results in the lowest residual porosity. Porosity increases with further increases of the sintering temperature, which is probably due to

Table 2. TEC, crystalline phase, residual porosity and crystallised fraction of samples 1, 2-B, 2-C and group 3

Sample	Sintering T (°C)	TEC ( $10^{-6} \text{ }^\circ\text{C}^{-1}$ ) 40–500°C	Main crystalline phase	Residual porosity (%)	Crystallised fraction (%)
1	1100	1.2	$\beta$ -spodumene	4.0±0.1	85±8
2-B	1100	-	$\beta$ -spodumene	2.3±0.1	50±10*
2-C	1000	3.4	Virgillite	2.1±0.1	50±10*
Group 3	1000	1.6	Virgillite	1.2±0.1	60±5*

\*Determined via image analysis

degassing during crystallisation, as observed in other glass systems.<sup>(31,32)</sup> Part of the expelled gas remains in the glass-ceramic microstructure forming new pores with a characteristic spherical shape.

For the sintering temperature 1000°C, the main crystalline phase is virgillite ( $\text{Li}_x\text{Al}_x\text{Si}_{3-x}\text{O}_6$ ;  $0.5 < x < 1$ ), whereas for 1100°C the only crystalline phase is  $\beta$ -spodumene ( $\text{LiAlSi}_2\text{O}_6$ ). Virgillite has a stuffed  $\beta$ -quartz type structure that converts into  $\beta$ -spodumene at higher temperatures,<sup>(33)</sup> the transition temperature corresponds to the second exothermic peak indicated in the DSC curves in the Figure 2.

The decrease of the sintering temperature leading to the formation of virgillite (Figure 4) is very important for technological applications since the average TEC of polycrystalline  $\beta$ -spodumene ( $0.9 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ) is considerably higher than that of polycrystalline virgillite, which has a negative TEC ( $-1.3 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ).<sup>(34)</sup> Furthermore, as shown in Figure 3, by decreasing the sintering temperature the porosity was reduced from 2.9% to 1.2% in the samples of group 3.

The calculated values of TEC, residual porosity and crystallised fraction are summarized in Table 2. The crystallised volume fraction was estimated for samples 2-B and 2-C by image analysis using the software Image-J. This method has inferior accuracy to the x-ray diffraction method used because one cannot precisely distinguish the crystals, but it does allow a comparison between different samples. The estimated crystallised fraction was  $0.5 \pm 0.1$  in both samples. Some pictures used for the estimates for each sample are shown in Figure 5. Table 2 shows that IE treated samples densify more than the untreated samples. The main reason for this improvement is the decrease in the crystallization rate on the particle surfaces (deduced from the smaller crystallized fraction shown in Table

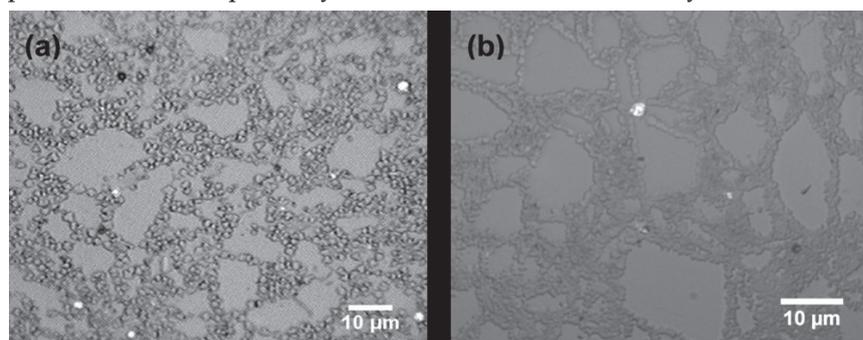


Figure 5. Optical micrograph of a polished surface chemically etched in HF 2 vol% for 15 s. (a) sample 2-B; (b) sample 2-C

2). The IE treatment allowed the reduction in  $100^\circ\text{C}$  in the sintering temperature and the formation of virgilite, which has a negative TEC and acts more effectively for the reduction of the overall TEC of the glass-ceramic. However, the overall TEC of sample 2-C was excessively increased as a result of the lower crystallinity ( $50\pm 10$  vol%) and the addition of a certain amount of potassium in the residual glass. This effect was minimized for samples of group 3 by substituting part of the starting glass powder (40 vol%) for an IE-treated powder. Therefore, in this way it was possible to obtain high densification without compromising the TEC, which reached a similar value than that of untreated samples. In this special case it was possible to produce a sintered glass-ceramic having both low porosity and low TEC.

#### 4. Conclusions

The ion exchange treatment proposed and tested in the present research was efficient in reducing surface crystallisation and the residual porosity of sintered LAS glass-ceramics. Moreover, this treatment allowed a reduction in the optimum sintering temperature from  $1100$  to  $1000^\circ\text{C}$ , and the formation of virgilite, the desirable crystal phase for applications that require low TEC. Although the IE treatment improved densification, it decreased the crystallised fraction and consequently increased the TEC of the resulting glass-ceramic. This effect was minimized by subjecting only a portion of the glass powder to IE.

The best sintered glass-ceramic obtained in this research has low residual porosity ( $<1.5\%$ ) and a relatively low TEC ( $1.6\times 10^{-6}\text{C}^{-1}$  between  $40$  and  $500^\circ\text{C}$ ).

Although we only tested one system (LAS), similar types of IE treatments could, perhaps, be useful in the development of sintered glass-ceramics for other systems.

#### Acknowledgements

We would like to thank FAPESP 2007/08179-9 for financial support and Thiana C. Berthier for interesting discussions.

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