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Sintering of β.q.$_{SS}$ and Gahnite Glass Ceramics

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Abstract

The sinterability of β.*quartz solid solution,* β.*q*.$_{ss}$, *and* $ZnAl_2O_4$ *glass ceramics was studied. It was found that the sinterability of glass powders with mean particle sizes greater than a threshold value rapidly decreases. Quantitative measurement of the crystalline phases and the shift of the dilatometric softening point of the residual glasses as determined by DTA, indicate that in addition to the amount of crystalline phases, the composition and viscosity of the residual glass influence the maximum densification temperature. © 1999 Published by Elsevier Science Ltd. All rights reserved*

Keywords: $ZnAl_2O_4$, sintering, glass ceramics, SiO_2.

1 Introduction

Heat treatment at appropriate temperatures after the casting of a molten glass is the traditional method for manufacturing glass ceramics; alternatively, the sintering and crystallisation of compacted glassy powder have been the subject of many studies, owing to the possibility of making complex shapes as well as glass–ceramic composites.

Nucleation and growth of crystalline phases on the one hand, and densification of compacted glassy body due to the viscous flow on the other, compete with each other, during sintering. It is known that if extensive crystallisation occurs during sintering before complete densification, the viscosity of the material increases and thus the maximum degree of densification may not be achieved.[1–6]

The effects of composition,[5,7,8] particle size of the glass powder[4,5,9–11] and the heating rate[4,6] on the sintering behaviour of various glasses and glass ceramics have been investigated. It seems that the positive effect of the higher heating rate on densification is common to nearly all glass ceramics but the effect of the other factors usually differs from composition to composition.

In this work, the sinterability and crystallization kinetics of β.quartz solid solution, β.q.$_{ss}$, and gahnite glass ceramics were investigated with respect to the particle size of the glassy powders, the sintering temperatures and soaking times. The chosen compositions were located in the SiO_2–Al_2O_3–ZnO system to which 17·5 wt% PbO was added in order to facilitate the sintering process. Ale SiO_2–Al_2O_3–ZnO system has the capability of showing thermal expansion coefficient, above and below that of silicon carbide. Hence, this system was chosen to study the effect of compressive or tensile residual stress of the matrix on the mechanical properties of glass ceramic/silicon carbide composites. ZrO_2 and TiO_2 were used as suitable nucleants for precipitation of the βq.$_{ss}$ and gahnite phases, respectively.

2 Experimental Procedure

2.1 Glass preparation

Glasses were prepared by fusing reagent-grade chemicals in a platinum crucible. The glasses were melted and maintained for 2 h at 1480°C in an electric furnace. The molten glasses were then quenched in cold distilled water. The chemical compositions of the glasses are displayed in Table 1.

Glass A was prepared by the addition of 2 wt% Li_2O to the original glass adopted from Ref. 12 in which 17·5 wt% ZnO was also replaced by PbO. The glass B was prepared by replacing ZrO_2 with TiO_2 and adding 17·5 wt% PbO to the original glass.

2.2 Methods of analysis

The frits obtained were milled for 2, 5, 9, 14, 18 and 22 h, respectively, in aqueous media. The particle size measurements of A and B glasses were

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Table 1. Chemical composition (wt%) of glasses

Glass	SiO_2	Al_2O_3	ZnO	PbO	ZrO_2	TiO_2	Li_2O	As_2O_3
A	45·57	22·78	5·28	17·5	6·37	—	2·00	0·49
B	38·36	19·18	19·18	17·5	—	5·36	—	0·41

Table 2. DTA characteristic temperatures of glasses

Glass sample	T_g	T_s	T_o	T_c
A	660	705	825	875
B	665	690	690	845

carried out by a laser particle size analyser (Fritsch, analysette 22). The powders were pressed in two steps using a laboratory uniaxial hydraulic press into 57×15×4 mm rectangular bars at initial and final pressures of 10 and 40 MPa, respectively. Carboxy methyl cellulose (0·45 wt%) was used as a binder. The crystallization temperature of the glasses was determined by Simultaneous Thermal Analysis (STA) (Polymer Laboratories model 1640) at a rate of 20°C min^{-1}. Sintering was carried out at a rate of 40°C min^{-1} between the glass transformation and the end of crystallisation peak temperatures for various times, in an electric tube furnace. Our experiments with different heating rates showed that higher rates cause deformation of the body while lower rates prevent its complete densification during sintering. The holding temperatures were 750, 800, 820 and 835°C and 800, 835, 850, 870 and 900°C for glasses A and B, respectively.

The identification of crystalline phases precipitated during sintering and their quantitative analyses were performed by XRD (Siemens, model D-500). The internal standard method was used for estimating the amounts of β.q.$_{ss}$ and gahnite phases. The reference materials for β.q.$_{ss}$ and gahnite glass-ceramics were pure low quartz and synthetic gahnite powder, respectively. High grade pure silicon and alumina were also used as the standard materials in the, β.q.$_{ss}$ and the gahnite glass ceramics, respectively.

3 Results and Discussion

Figure 1(a) and (b) depicts the particle size distribution of series A and B glasses, respectively. Figure 2(a) and (b) depicts the DTA traces of these two series and Table 2 summarises these results. T_g, T_s, T_o and T_c show the glass transformation, dilatometric softening point, crystallisation onset and maximum rate of crystallisation temperatures, respectively. According to XRD results of these two glass series, heated at their crystallisation onset temperatures, the first exothermic peak in glass A belongs to the crystallisation of β.q.$_{ss}$ and the second broad peak belongs to the crystallisation of lead aluminosilicate (Fig. 3). Gahnite, $ZnAl_2O_4$, and cristobalite are the crystalline phases precipitated in glass B fired at the first and second peak temperatures, respectively (Fig. 4). Because the aim of the present work was to obtain monophase glass ceramics, the sintering was done between T_s and up to the temperature at which complete densification occurs. According to the Fig. 2(a) and (b) by decreasing particle sizes in

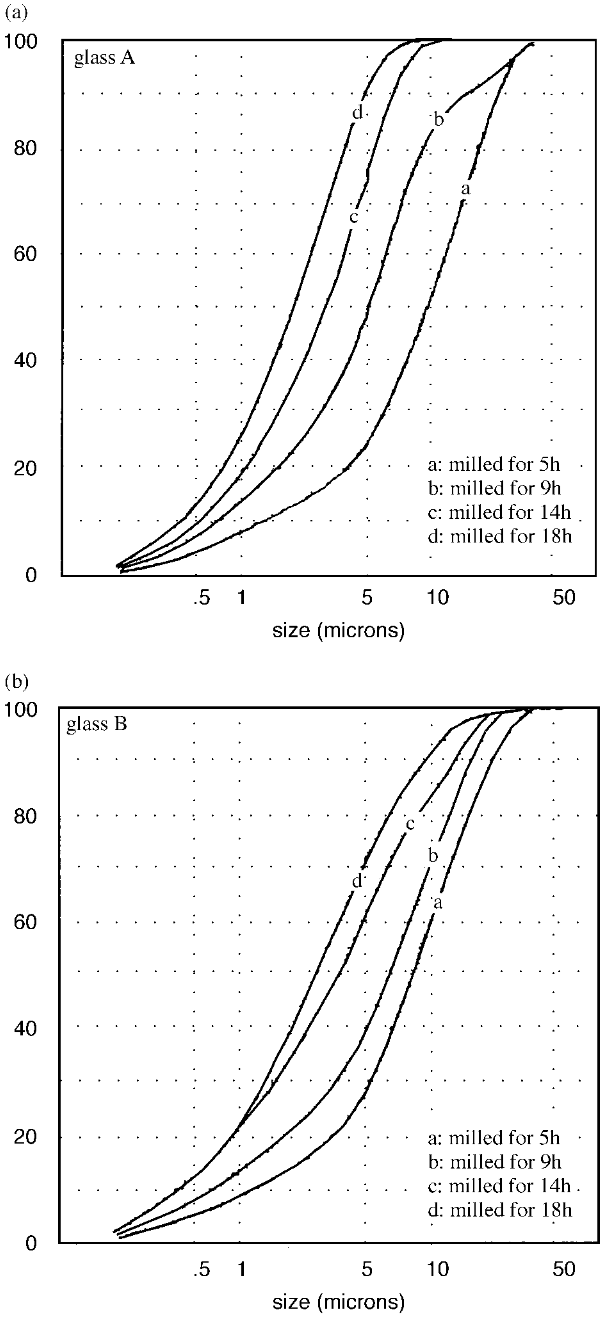

Fig. 1. (a) Particle size distribution of glass A powders milled for different times; (b) particle size distribution of glass B powders milled for different times.

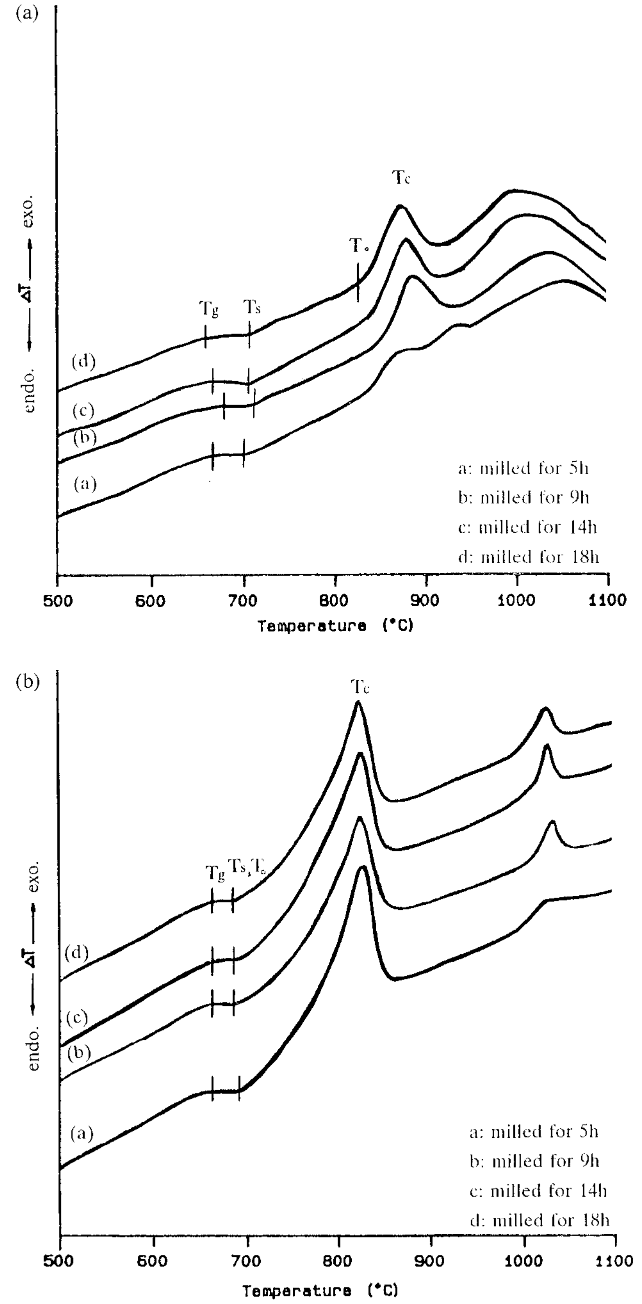

Fig. 2. (a) DTA traces of glass A powders milled for different times, (heating rate = 20°C min^{-1}). 2(b) DTA traces of glass B powders milled for different times, (heating rate = 20°C min^{-1}).

these glass ceramics no changes in the crystallisation peak temperatures were observed. This means that bulk crystallisation is the dominant mechanism of crystallisation in these two glasses. Therefore the powder with the finest particle size, was adopted for investigation of sinterability of these glasses with soaking temperature and time [(Fig. 5(a) and (b)].

The comparison of the β.q.$_{ss}$ and gahnite glass ceramics indicates that the latter reaches its final density at 900°C which is higher than its DTA crystallisation peak whereas the former reaches its final density almost at the onset of the DTA crystallization peak temperature (820°C).

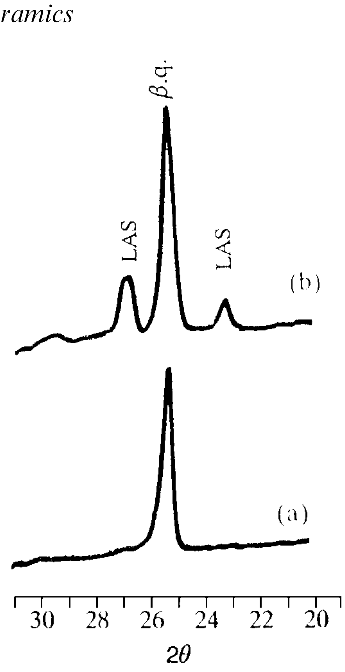

Fig. 3. XRD analysis of glass A fired at (a) the first and (b) second DTA peak temperatures of Fig. 2(a) (LAS = lead aluminosilicate)

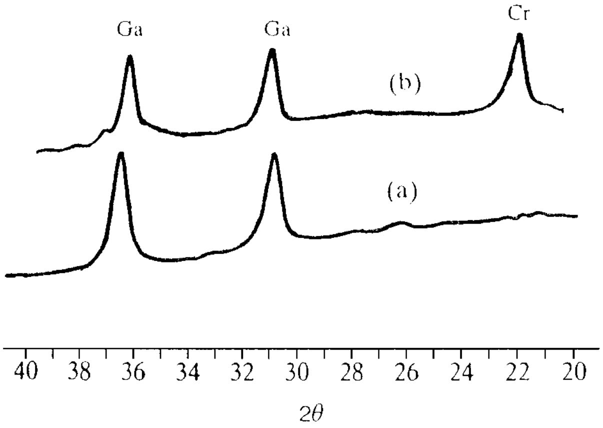

Fig. 4. XRD analysis of glass B fired at (a) the first and (b) second DTA peak temperatures of Fig. 2(b) (Ga = gahnite, Cr = cristobalite)

As Sung[8] noted, the temperature interval between T_g (glass transformation temperature) and T_o (crystallisation onset temperature) is a criterion for the sinterability of glasses. According to this criterion if a glass has a T_g and T_o which are close to one another, then the glass cannot be fully densified by sintering below T_o since it is highly probable that crystallisation would occur before sintering is completed.

The temperature interval [Fig. 2(a) and (b)] and sinterability of the two glasses [Fig. 5(a) and (b)] conform to this criterion. With attention to the crystallisation results reported in Tables 3 and 4 it can be concluded that glass A which is more sinterable has also developed higher crystalline phases in T_o–T_s interval compared to glass B. Therefore it can be concluded that besides the amount of crystalline

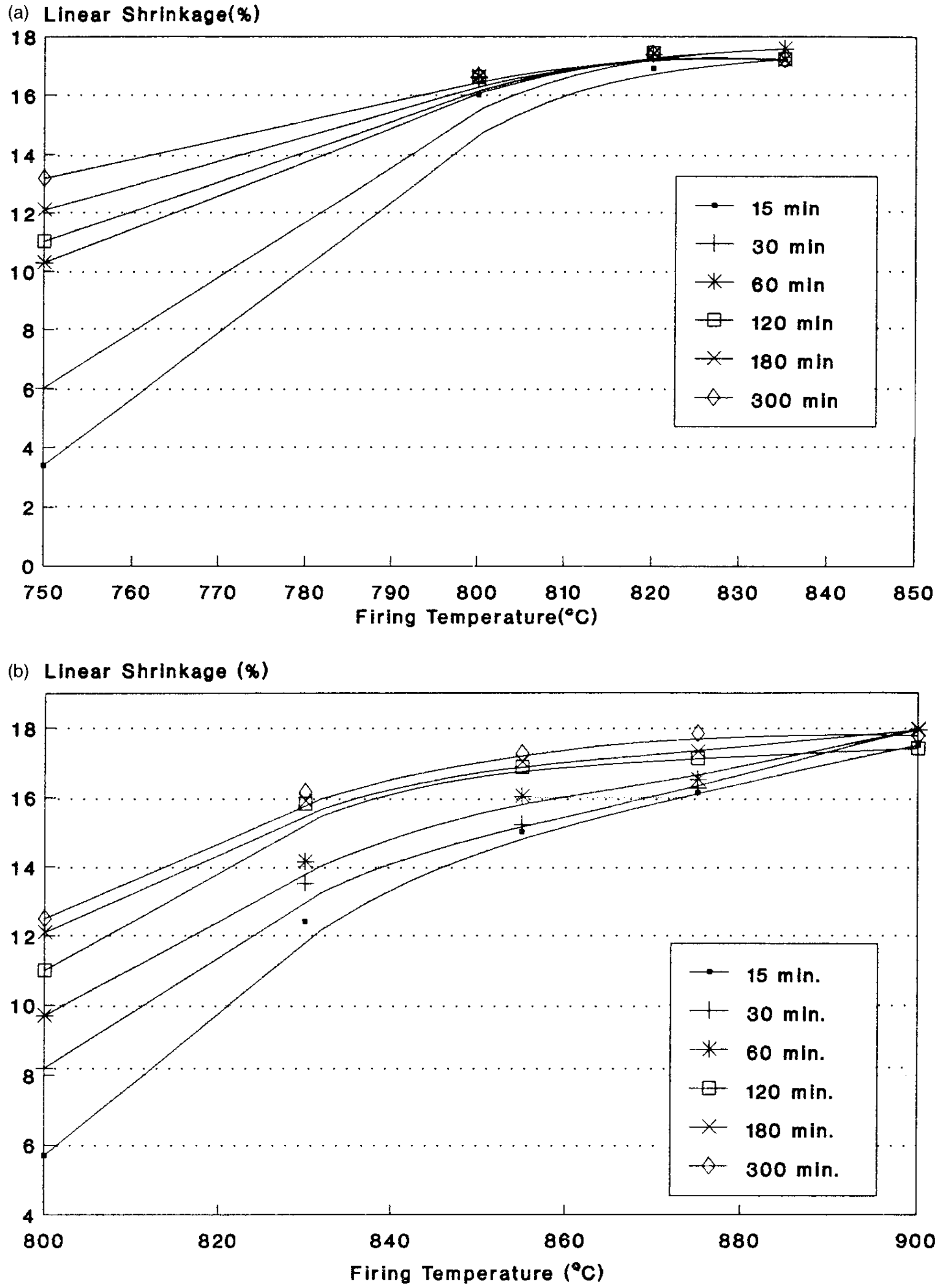

Fig. 5. (a) Linear shrinkage of glass A with firing temperature at different soaking times, (heating rate = 20°C min^{-1}); (b) linear shrinkage of glass B with firing temperature at different soaking times (heating rate = 20°C min^{-1}).

phase, other parameters might affect the sintering process.

McMillan[13] has discussed the influence of residual glass phase on a number of properties including viscous deformation. So the composition of residual glass phase can influence the sintering behaviour of glasses.

Determination of the dilatometric softening points of the residual glass phases of samples sintered at different temperatures between T_g and T_o can establish a correlation between composition of the residual glass phase and sinterability of glasses. Figure 6(a) and (b) depict the DTA traces of glass samples before and after heat treatment. It can be seen that there is a larger shift in dilatometic softening point temperature (T_s) of the residual glass in the sintered B sample in comparison to A, which

Table 3. Effect of sintering time and temperature on β.q.$_{ss}$ phase weight percent in composition A

Soaking temperature (°C)		*700*	*800*	*820*	*850*
Amount of	60 (min)	9	22	40	47 + LAS
crystalline phase	180 (min)	—	30	49	46 + LAS
(wt%) after	300 (min)	—	38	29 + LAS	30 + LAS

LAS = Lead Aluminosilicate.

means that the viscosity of the residual glass in sintered B composition is higher than that of A composition. It appears that in the case of glass A, the decrease of SiO_2 in the residual glass phase due to the precipitation of β.q.$_{ss}$ led to a decrease in its viscosity, while in glass B, crystallization of gahnite by consuming ZnO and Al_2O_3 increases the SiO_2 content of glass and its viscosity.

Table 4. Effect of sintering time and temperature on gahnite phase content in composition B

Soaking temperature (°C)		*700*	*830*	*860*	*900*
Amount of	60 (min)	7	14	17	25
crystalline phase	180 (min)	—	16	22·5	26
(wt%) after	300 (min)	—	18·3	23·0	23 Cristobalite

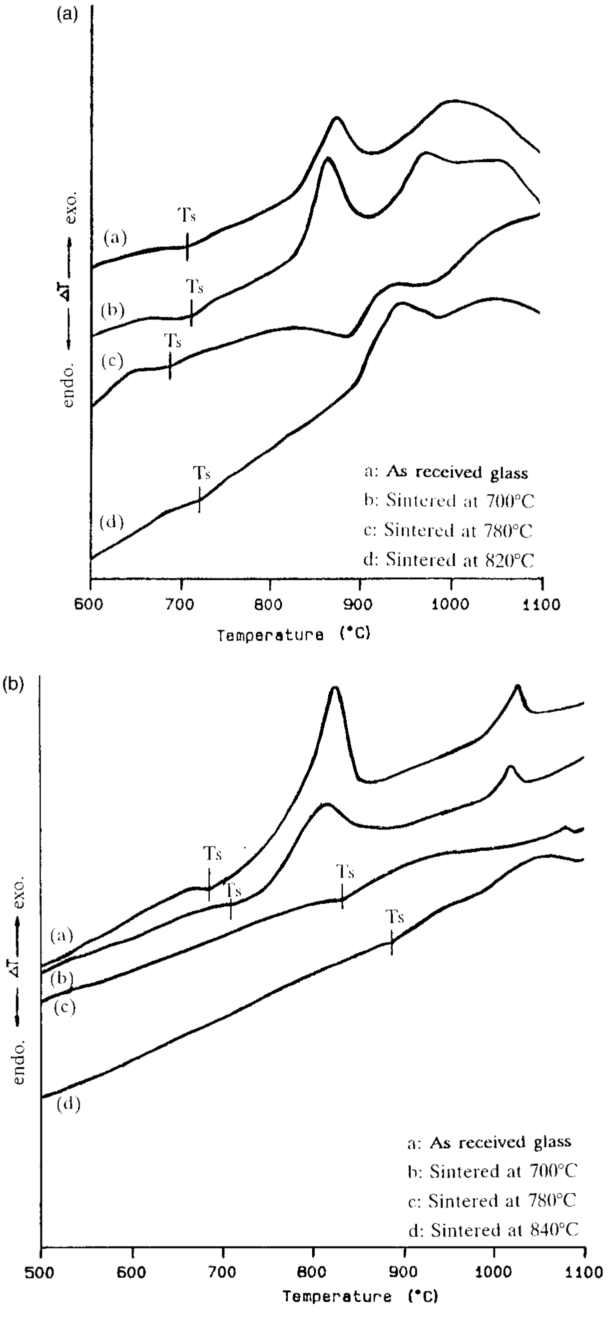

Fig. 6. (a) DTA traces of glass A before and after heat treatment (heating rate = 20°C min^{-1}); (b) DTA traces of glass B before and after heat treatment (heating CR rate = 20°C min^{-1}).

The effect of particle size on sinterability of the two glass powders was also investigated. Figure 7 represents the variations of firing shrinkages with the mean particle sizes of glasses A and B soaked for 60 min at 820 and 900°C, respectively. It can be seen that there is a threshold particle size for each composition after which sintering decreases rapidly. These threshold particle size for A and B compositions are about 7 μm. This is consistent with the findings of other investigators[4,5,9–11] which has shown the positive effect of smaller particle sizes on the densification of glasses and glass ceramics. On the other hand, it has been shown[14] that with decreasing particle sizes the amount of β.q.$_{ss}$ increases and its transformation rate to stable phases decreases. But consideration of Tables 5 and 6 leads to the conclusion that the particle size had no effect on the amount of metastable high quartz and stable gahnite phases. It seems the only additional effect of decreasing particle size is precipitation of a new crystalline phase named lead

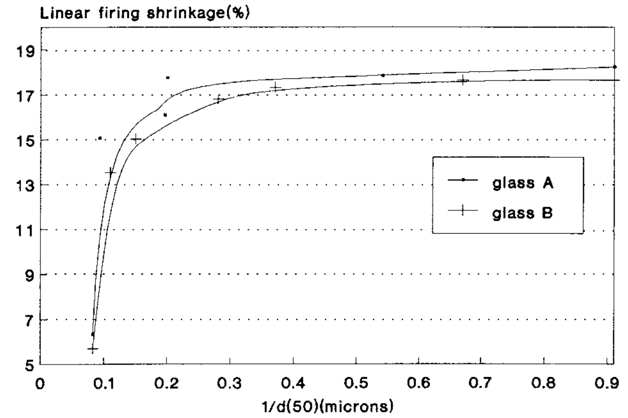

Fig. 7. Linear sintering shrinkage versus $\frac{1}{d(50)}$ of glass powders milled for different times: soaked for 60 min at 820 and 900°C for glass A and B, respectively.

Table 5. Effect of frit particle size on β.q.$_{ss}$ content in glass A fired at 820°C for 60 min

d_{50} (μm)	*12·01*	*5·10*	*1·82*
Crystalline phase (wt%)	40	40·37	38 + LAS

Table 6. Effect of frit particle size on gahnite content in glass B fired at 900°C for 60 min

d_{50} (μm)	*9·19*	*6·84*	*2·69*
Crystalline phase (wt%)	24·6	24·0	25·1

aluminosilicate in composition A. This shows that surface crystallisation is the dominant mechanism for crystallisation of lead aluminosilicate in this composition.

4 Conclusions

1. There was a threshold mean particle size (~7 μm) for the glass powders investigated herein above which the sinterability decreased rapidly.
2. Besides temperature interval (T_o–T_g), the composition and viscosity of residual glass influence the sinterability of glass ceramics.
3. Although the sinterability of β.q.$_{ss}$ glass ceramic possessing a higher (T_o–T_g) interval was better than gahnite, the amount of its final crystalline phase after sintering was also higher.

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