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Synthesis of glasses by hot-pressing of gels

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The synthesis of glasses by hot-pressing of gels was studied for pure SiO_2, as well as for La_2O_3–SiO_2 and B_2O_3–SiO_2 systems. It was recognized that gels prepared by hydrolysis and polycondensation of organometallic compounds crystallize less quickly than those obtained from hydrosols, and are, therefore, particularly suited for hot-pressing. Different methods of pressing were investigated; they influence the residual OH^- content of resultant glasses. Murray *et al.*'s densification model based on viscous flow was found to apply in the case of the gels under study and a dynamic viscosity evaluation is proposed to determine rapidly the pressing parameters for a given gel–glass conversion.

The method was used, in particular, for the refractory system La_2O_3–SiO_2 and the devitrification behaviour of hot-pressed glasses was studied quantitatively. It was found that the residual OH^- groups catalyse the conversion to a glass-ceramic material. The influence of pressure was also studied in some cases, and it was found to favour the precipitation of dense phases.

1. Introduction

The gel method of preparing refractory glasses enables them to be obtained with a degree of homogeneity difficult to attain by direct fusion from constituent oxides [1, 2]. It has already been shown that it is possible to obtain starting materials for the synthesis of glass-ceramics in this way [2]. However, even with this method it may still be difficult to prepare satisfactory glasses when the materials lead to very viscous systems and to avoid losses of more volatile components. Temperatures required for melting such gels may be quite high and the fining remains a difficult problem.

A few works mention the possibility of using hot-pressing to convert gels into glasses [3, 4]. The chief advantage of this method is that it is possible to obtain the conversion at relatively moderate temperatures, far below the melting point, when the viscosity of the glass is still very high.

Hot-pressing of gels thus seems ideally suited to the synthesis of glasses difficult to obtain in the classic way and suppresses the necessity of fining procedures.

2. Experimental

2.1. Preparation of gels

Pure silica glass as well as glasses of the SiO_2–La_2O_3 and SiO_2–B_2O_3 systems were investigated. The starting gels were prepared in two distinct ways which have already been described in detail elsewhere [2]:

(a) Destabilization of a silica gel, pure or containing other metal ions added in the form of aqueous solutions of salts (Method 1).

(b) Hydrolysis and polycondensation of alkoxysilane with other metal alkoxides or with suitable metal salts in the presence of a limited amount of water (Method 2).

Gels prepared by one of these methods shall be designated as "Gel 1" or "Gel 2".

Pure silica gels were prepared by both methods. For the SiO_2–La_2O_3 system, Method 2 was used, lanthanum being added as nitrate.

The compositions investigated ranged from 5 to 40 wt% of La_2O_3; they shall be labelled L*x* S when *x* is the wt% of La_2O_3.

Gels of the SiO_2–B_2O_3 system were prepared by Method 2. $Si(OCH_3)_4$ and $B(OCH_3)_3$ were used as starting materials which were mixed in fixed proportions with 1/2 volume of ethyl alcohol and left under stirring conditions for 4 hours at 60° C to ensure copolymerization. The amount of water theoretically required to ensure complete hydrolysis was added and stirring maintained for 4 hours. The solution was then left to gel, which took from 6 to 36 hours according to the proportion of B_2O_3.

These gels will be labelled B x S where x is wt% of B_2O_3.

2.2. Dehydration of gels

The gels were then dehydrated in several stages: first being dried for 2 days at 40° C then treated at 150° C with an infra-red heater, and finally heated from 150 to 800° C in an electrical furnace. It is necessary for the increase of temperature to be very slow to allow the rupture of alkoxy-bonds in Gel 2. If the temperature increase is too rapid the gel particles take on a brownish tint and further calcination results in a completely useless product. More than two weeks were necessary to bring the temperature of the gel up to 500° C. After 12 hours treatment at this temperature, the gel was finally fired for 2 hours at 800° C.

For the SiO_2–B_2O_3 system, the tendency of the gel to carbonize increases with its B_2O_3 content. The length of the dehydration cycle must therefore be adjusted for each composition. It is about 10 days for B 5 S and may be as much as one month for B 30 S. For a composition richer in B_2O_3 the occurrence of localized carbon residues seems inevitable but it is possible to eliminate these manually after complete dehydration of the gel.

2.3. Hot-pressing

2.3.1. The press

The press used operates under a primary vacuum with a graphite resistor as heating element. The power used (10 kV A) enables a rapid temperature increase (1400° in 20 min). The pressing set-up is shown schematically in Fig. 1.

The sample (A) is placed between two pressing pistons in a cylindrical die of 25 mm internal diameter, 55 mm external diameter and 40 mm height. A fine-grained graphite was used to constitute these elements.

A 0.05 mm play between the pistons and the die enables residual water vapour to escape during pressing; it is sufficiently small to prevent extrusion.

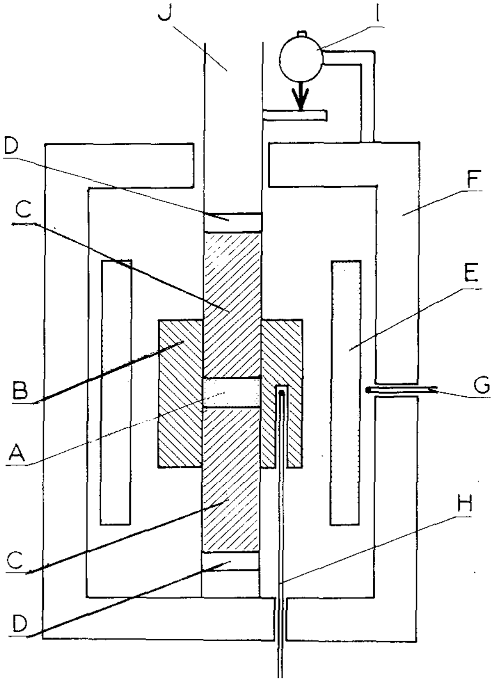


Figure 1 Hot-pressing cell (schematic). A, sample; B, die; C, pistons; D, thermal insulation; E, heating resistor; F, wall; G, regulating thermocouple; H, measuring thermocouple; I, displacement sensor; J, hydraulic ram.

Maximum pressure was limited to $6.10\,\mathrm{N\,m^{-2}}$ to avoid deterioration of the dies; 0.1 mm thick molybdenum foils were inserted between the pistons and the sample to prevent contamination by graphite.

Pyrolitic graphite discs (D) were inserted to minimize thermal leaks through the pistons. The temperature was measured using a 5%W–26%Rh thermocouple inserted into the die about 5 mm from the sample.

A micrometer (I) fixed to the body of the press was used to measure the displacement of the hydraulic ram.

2.3.2. Pressing schedules

About 4 g of finely ground gel (average grain size 10 μm) are introduced into the die and compacted at ordinary temperature under pressure P. The temperature is then increased to T, either directly, without any pressure (Mode 1); with pressure during the heating stage (Mode 2), or with a supplementary thermal treatment at a temperature T_1, without pressure (Mode 3) or with pressure (Mode 4).

As soon as the chosen temperature T is reached, a pressure P is applied (or maintained) during the

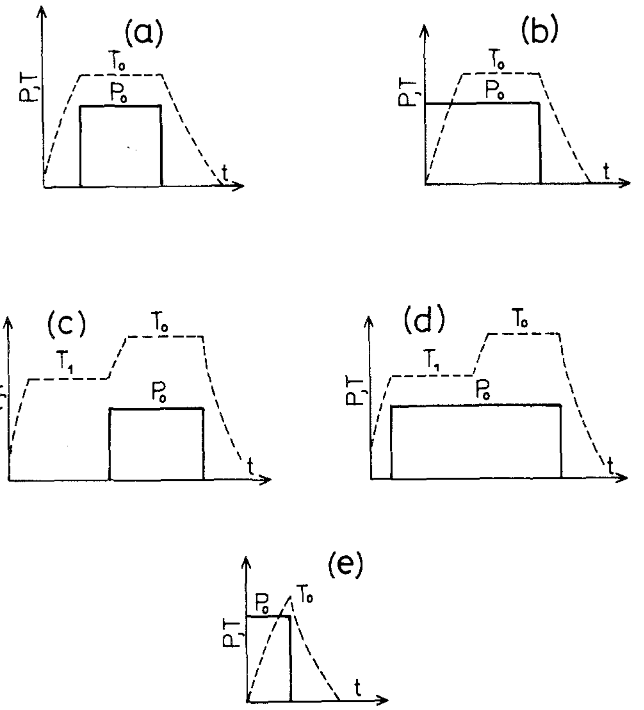


Figure 2 Different pressing modes: (a) Mode 1; (b) Mode 2; (c) Mode 3; (d) Mode 4; (e) "Flash pressing".

time t to allow densification. These different pressing schedules are shown in Fig. 2.

A particular variant of Mode 2 called "flash pressing" (Fig. 2e) was used with no isothermal hold at temperature T, the power being switched off as soon as this maximal temperature is reached.

2.3.3. Monitoring of the densification

The micrometer readings are the only data directly accessible during the pressing procedure.

The displacements of the upper mobile piston are measured during pressing at temperatures T and after cooling at ambient temperature, whence the final thickness e_f of the sample may be obtained. Because of very small expansion coefficients of the pressed samples, e_f may be considered as the final thickness reached by the sample at the pressing temperature.

At any given instant the thickness of the sample is given by the displacement x of the upper piston corrected for the expansion Δ of the pistons. In the case of pressing at thermal equilibrium, the expansion of the pistons is practically constant and equal to Δ_0 so that the sample thickness e may be deduced from its final value e_f by a translation of the curve relative to the displacement of the piston (Fig. 3a).

When pressing is carried out during a rise in temperature the expansion Δ of the pistons increases with time; it is necessary to perform an additional experiment without the sample to determine the variations of Δ. As the heating schedule is known it is possible to follow the thickness evolution as a function of temperature (Fig. 3b). It must be mentioned, however, that the temperature given by the thermocouple located 5 mm from the sample is about 20° C higher than the real temperature of the sample during the temperature increase. The pressure is suppressed when the sample's thickness reaches a constant value.

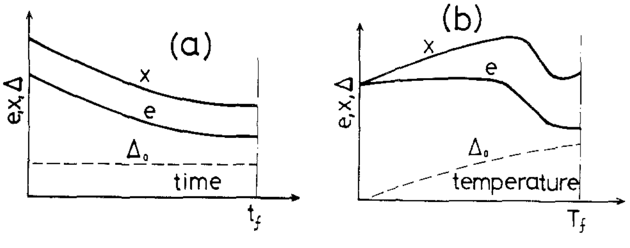


Figure 3 Determination of the thickness of the sample during: (a) Isothermal pressing; (b) "flash" pressing, where x is the piston displacement, Δ piston expansion and e sample thickness.

3. Characterization of products

The density of the samples was measured using Archimedes' method.

Microstructure was studied by scanning electron microscopy (SEM), direct transmission electron microscopy (TEM) on finely crushed samples or using Pt-shadowed carbon replicas.

The extent of possible crystallization and the nature of crystalline phases were determined by conventional X-ray diffraction methods.

Infra-red spectrometry in the 4000 to 400 cm^{-1} range was applied using pressed KBr pellets and quantitative evaluation of water content was made on the 2.73 μm band.

4. Results

4.1. Pure silica

4.1.1. Evolution of the structure of SiO_2 gel during dehydration treatment

Samples of gel taken during dehydration at different temperatures were studied by infra-red spectroscopy. Figs. 4 and 5 show i.r. spectra of Gel 1 and Gel 2, respectively. The assignment of chief absorption bands, deduced from earlier studies [5, 11] is shown in Table I.

All the gels studied showed characteristic absorption bands of vitreous silica at 1100, 800 and 470 cm^{-1}. The large band at 1100 cm^{-1} was attributed to the stretching vibration of the Si–O

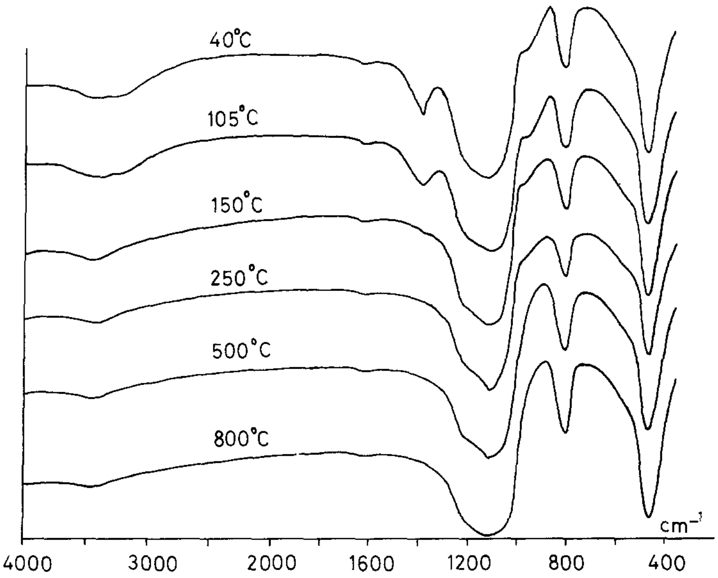


Figure 4 Infra-red absorption spectra of silica Gel 1 during dehydration treatment between 40 and 800° C.

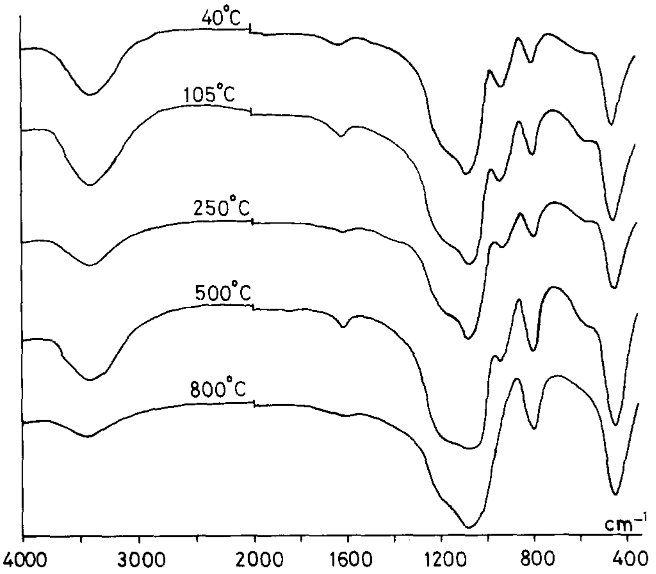
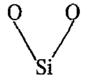
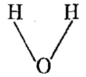
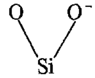


Figure 5 Infra-red absorption spectra of silica Gel 2 during dehydration treatment between 40 and 800° C.

TABLE I Infra-red absorption frequencies (in cm^{-1}) for Gels 1 and 2 dehydrated at 800° C and in vitreous silica

Vibration	Gel 1	Gel 2	Vitreous silica	Reference no.
ν Si–O	1104	1080	1100	5, 6
δ 	467	456	468	5, 6, 7
Ring groups	800	800	800	8
ν H–O–H ν Si–OH	3450	3450	–	9
δ 	1620	1620	–	9
ν Si–O^-	950	940	–	10, 11
δ 	550	550	–	10, 11

bond [5, 6]. The 467 cm^{-1} band corresponds to the deformation vibration of O–Si–O [5–7] and the 800 cm^{-1} band to the ring structure of SiO_4 tetrahedra [8]. In addition to the characteristic bands of vitreous silica there are also bands due to water: a very large band around 3450 cm^{-1} results from a superposition of vibration bands of hydroxyl groups [9] and stretching vibrations of adsorbed water molecules. The deformation band H–O–H of water occurs near 1620 cm^{-1}.

Two additional bands at 940 and 550 cm^{-1} were seen particularly in the case of Gel 2.

In the case of alkali silicates a band is present at 950 cm^{-1}; it is independent of the cation's mass [10] and is generally attributed to the vibration Si–$\bar{O}$. Associated with this band also appears a band at 540 cm^{-1} due to the deformation vibration of Si–$\bar{O}$ groups.

It is therefore probable that in the case of gels these two bands are associated with the presence of non-bridging oxygens.

Other authors [11] proposed this explanation in the case of SiO_2–TiO_2 gels prepared from organometallic compounds.

Finally a band at 1380 cm^{-1} and a shoulder at 3200 cm^{-1} in the spectra of Gels 1 slightly dehydrated are attributable to the presence of an unstable compound which decomposes towards 150° C; this is probably ammonium nitrate formed during synthesis of Gel 1.

The dehydration treatment leads to the departure of water included in the structure of the gel; the absorption bands due to water and hydroxyl groups show a progressive decrease. The unstable products are decomposed e.g. NH_4NO_3 bands in Gel 1 disappear.

Finally the non-bridging oxygens disappear. They are particularly numerous in gels before dehydration and their presence is linked with the hydroxyl groups [11]. They disappear only at 800° C. In the case of Gel 1 the non-bridging oxygens may be due to the presence of residual ammonium ions originating in the silica sol.

During dehydration treatment the structure of the gels tends progressively towards the structure of glass. Water and unstable products are slowly eliminated and non-bridging oxygens disappear. After dehydration both types of gel are very similar and their structure is close to the vitreous silica.

A shift of the vibration frequencies was, however, visible in the case of Gel 2 where the frequency of the 1100 cm^{-1} band was about 20 cm^{-1} lower than that of the vitreous silica; similarly the 470 cm^{-1} band was about 10 cm^{-1} lower. This would mean that the Si–O bond is less strong in the gel and that the SiO_4 tetrahedra are more expanded [7]. On the other hand the spectrum of Gel 1 is almost identical to that of vitreous silica, differing only by the presence of bands attributable to the water content of the structure. This is to be expected as this gel was prepared from a sol, a colloidal aqueous dispersion of high-purity silica particles with a hydroxylated surface [12]. It would thus seem that the *size* of elementary tetrahedra is a reminder of the history of gel preparation even after the dehydration treatments, Gel 2 having a more open structure than Gel 1.

4.1.2. Characterization of dehydrated silica gels

The dehydrated gels have an aspect of irregular solid particles of about 1 mm^3 in volume. The dried gel is hard and fragile; its fracture is conchoidal. It is a material very close to glass this is particularly true for Gel 2 which is highly transparent while Gel 1 is rather translucent or opalescent.

The porosity, determined by Archimedes' method, was totally open and amounted respectively to 48% and 55% in the case of Gels 1 and 2.

The texture revealed by SEM showed Gel 1 to be an aggregate of spherules of 500 Å diameter (Fig. 6a). This texture, originating from the sol, was not modified by dehydration. On the other hand, Gel 2 appeared as a spongy solid (Fig. 6b);

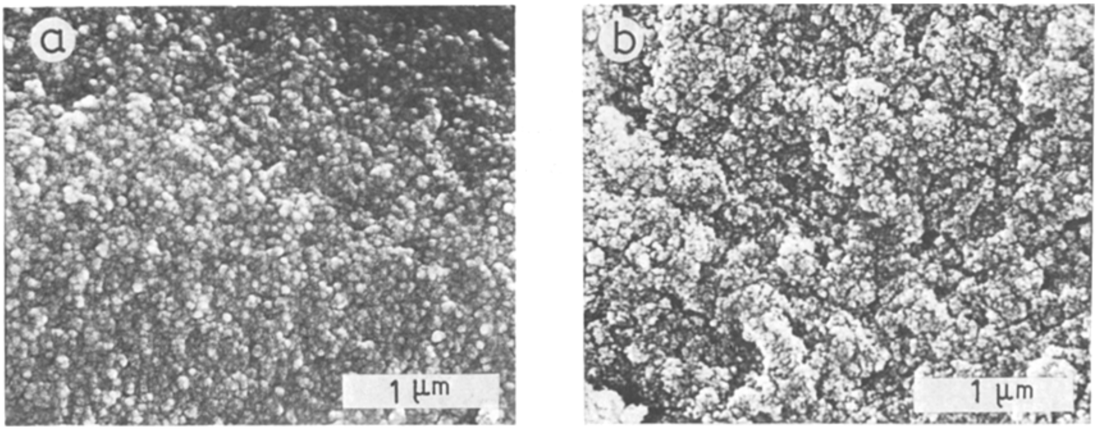


Figure 6 Scanning electron micrographs of silica gel after dehydration at 800° C: (a) Gel 1; (b) Gel 2.

its texture is less regular and its porosity higher.

X-ray diffraction shows that both gels were totally amorphous.

Measurement of weight loss after calcination of gels at 1100° C showed that dehydrated Gel 1 contained twice the amount of water contained in Gel 2 (2 and 1 wt%, respectively). These structural and textural characteristics influence the crystallization behaviour of both types of gel.

4.1.3. Characterization of products of pressing

Pressing is stopped when the thickness of the sample reaches a constant value due to the disappearance of porosity. The time necessary to obtain a dense material by pressing in isothermal conditions (Mode 1) was determined for both Gels 1 and 2. The densification behaviour is strikingly different: Gel 1 densified at much lower temperatures than Gel 2 (Fig. 7) but crystallized during pressing.

It is thus impossible to synthesize a glass by hot-pressing a gel obtained from a sol; Gel 2 obtained from organometallics allows the synthesis of glasses free of crystallization. Materials obtained by hot-pressing of Gels 2 were transparent and compact (Fig. 8). Their density was 2.21 which is that of vitreous silica; no porosity was revealed by electron microscopy. X-ray diffraction spectra showed absence of crystallinity. Infra-red spectra of the gel before pressing and after a "flash" pressing are shown in Fig. 9. It can be seen that the pressing operation has shifted the bands due to the vibration of SiO_4 tetrahedra towards higher frequencies: from $1080\,cm^{-1}$ to $1100\,cm^{-1}$ for stretching Si–O and from $458\,cm^{-1}$ to $468\,cm^{-1}$ for deformation Si–O–Si. Bands due to structural and adsorbed water (3450 and $1620\,cm^{-1}$) have totally disappeared. The final water content was determined by infra-red spectroscopy on massive samples and was found to vary from 50 to 400 ppm according to the mode of pressing used (cf. Table II). This shows that the dehydration during the pressing cycle plays an important role, as the gels contained about 1% of water before pressing.

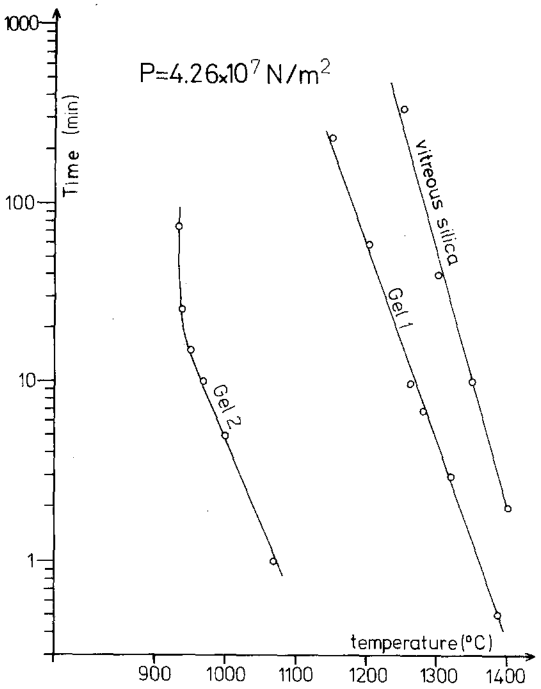


Figure 7 Pressing time to reach dense sample as a function of temperature for silica Gel 1, silica Gel 2 and powdered vitreous silica.

Two effects are observed according to the pressing mode:

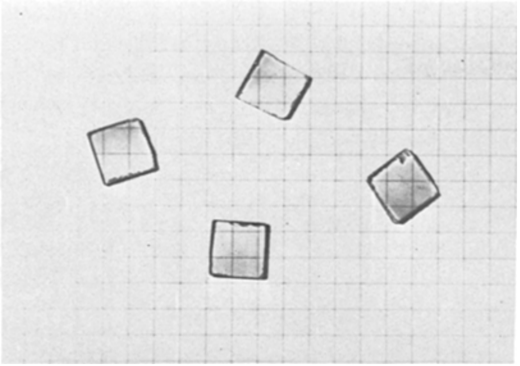


Figure 8 Silica glass obtained by hot-pressing of Gel 2. I.r. spectra of flash pressed dehydrated Gel 2 and vitreous silica.

(a) In general, the water content is higher for Mode 2 than for Mode 1. This phenomenon is especially noticeable for the highest pressing temperatures. The pressure applied during the temperature rise favours a premature closing of the pores; water from the deshydroxylation reaction is thus imprisoned in them.

(b) The water content increases with the temperature of pressing. The deshydroxylation reaction continues during the isothermal hold, even when the pressure is applied. This reaction is more pronounced at lower temperatures where the porosity decreases more slowly.

Mode 3 results in a notable reduction of OH content, down to about 10 ppm thanks to an additional thermal treatment which precedes the pressing and helps deshydroxylation.

The results of pressing by Mode 4 show that the pressure applied during the thermal treatment at the temperature T_1 slows down deshydroxylation considerably.

In conclusion, apart from a slightly higher hydroxyl content, silica obtained by hot-pressing of Gel 2 is essentially identical to vitreous silica obtained by fusion of quartz.

4.2. SiO_2–La_2O_3 system

4.2.1. Compositions containing 5 wt% of La_2O_3

The parameters of hot-pressing of this material were very close to those of pure silica gels previously examined. The pressing times were identical to those of Fig. 7. The materials obtained were translucent or opalescent. Their density was 2.295 ± 0.005.

The crystallinity of the materials was always very slight. In the diffraction spectra, only two faint maxima corresponding to $d = 3.13$ and 2.94 Å can be detected.

Exceptionally quartz α was identified in samples pressed at the lowest temperatures (between 1150 and 1200° C). "Flash" pressing was most satisfactory; it leads to dense materials without any trace of crystallinity. This mode of pressing thus seemed to be the best for the gel–glass conversion. To evaluate the hydroxyl concentration in the L 5 S materials by i.r. spectroscopy, extinction coefficients of OH^- in pure SiO_2 were used; it was assumed that small La_2O_3 content did not affect the results. Under these conditions the water content was seen to be identical to that of pure SiO_2 (Table II). For Modes 3 and 4 water content can be further reduced (Table III).

The materials obtained by flash pressing were examined by electron microscopy; a phase separation was seen (Fig. 10a). The droplets of about 500 Å correspond to the La_2O_3-rich phase as

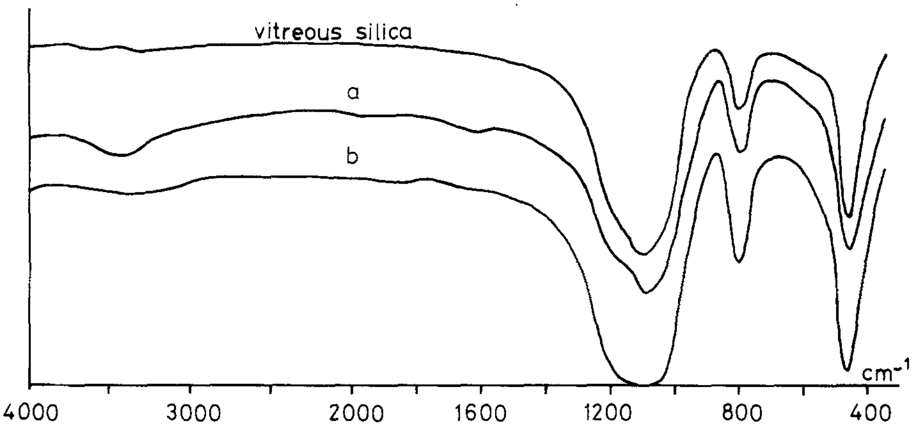


Figure 9 Infra-red spectra of silica Gel 2 (a) before and (b) after "flash" hot-pressing compared to vitreous silica.

TABLE II Water content (in ppm OH^-) of silica glass obtained by hot-pressing of Gel 2

Hot-pressing temperature (° C)	Mode 1	Mode 2	Flash pressing
1150	60	50	
1200	100	150	
1260	150	300	
1320	210	360	
1360	200	400	
1365			400

TABLE III Water content (in ppm OH^-) of 5% La_2O_3–95% SiO_2 glasses hot-pressed at 1360° C and previously dehydrated for 30 min at different dehydration temperatures T_1

Dehydration temperature T_1 (° C)	Mode 3	Mode 4
1020	150	280
1060	120	140
1100	50	70
1160	13	60

shown by TEM (Fig. 10b) which explains their opalescence. Electron diffraction revealed no trace of crystallinity. L 5 S glasses obtained by hot-pressing are then similar to those previously obtained by fusion methods [2].

4.2.2. Compositions richer in La_2O_3

The "flash" pressing mode which has given the best results on the gel L 5 S was successively applied for gels richer in La_2O_3.

From gel L 10 S a translucent glass was obtained; its density was 2.39 and no traces of crystallinity could be detected by X-ray diffraction. In the case of gels richer in La_2O_3 (L 15 S and L 20 S) it was no longer possible to obtain a glass even with "flash" pressing. The material was opaque and partially crystallized (intense peaks corresponding to $d = 2.94$ and 3.13 Å).

When the La_2O_3 content was higher (L 40 S) the product of pressing was fully crystallized showing the presence of cristobalite.

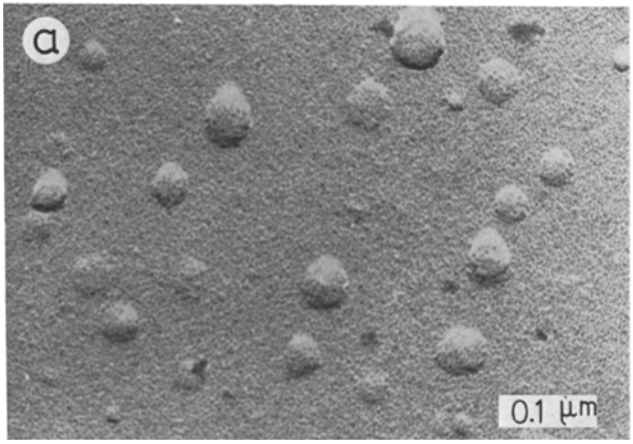
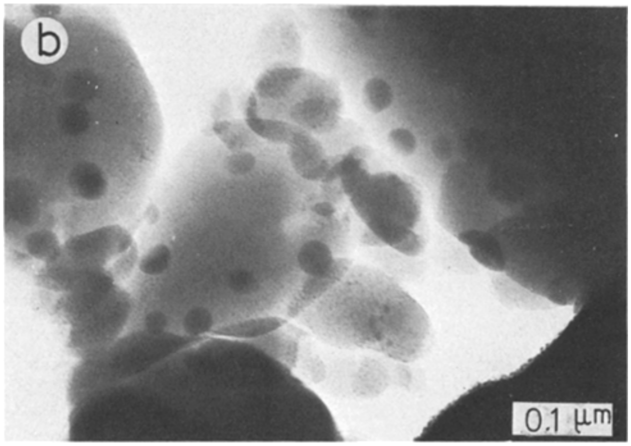


Figure 10 Phase separation in a 5% La_2O_3–95% SiO_2 glass observed by electron microscopy. (a) Carbon–Pt replica; (b) direct transmission.



The interval of glass formation by hot-pressing of gels extended up to 10 wt% La_2O_3 for this system.

The characteristics of glasses obtained by hot-pressing (density, microhardness, OH content) are very close to those obtained by fusion of gels in a solar furnace [2]. However the conditions of elaboration are better controlled in the pressing, namely the OH^- ion content.

5. Densification model

5.1. Isothermal pressing

The isothermal densification curves of the gel are deduced from the thickness variations of the sample during pressing. The densification state of the gel is characterized by the relative density D, ratio of the density ρ of the material and the theoretical density ρ_0 of the material devoid of porosity.

$$D = \frac{\rho}{\rho_0} = \frac{e_0}{e}$$

where e is the thickness of the sample and e_0 the thickness of the sample completely densified.

The theoretical model of densification under load of Murray *et al.* [13] based on a viscous flow mechanism was successfully applied to describe the densification of vitreous silica [14].

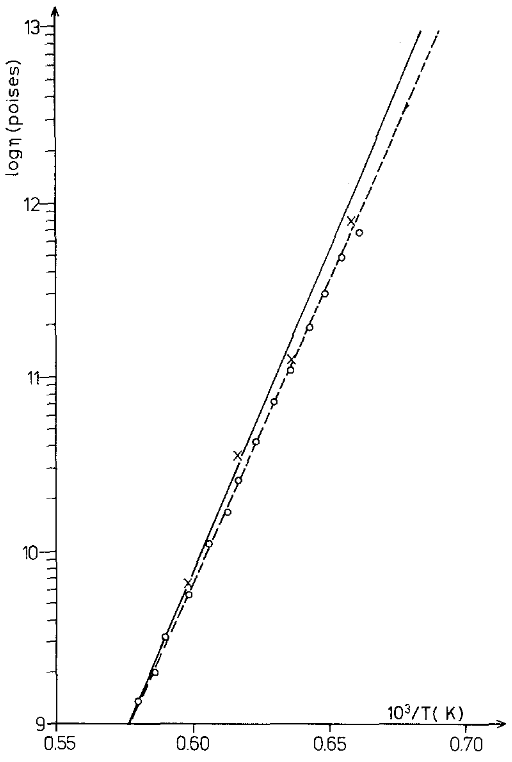


Figure 12 Viscosity of vitreous silica calculated from Murray *et al.* model X—X—X isothermal o—o—o dynamic study; – data after [15].

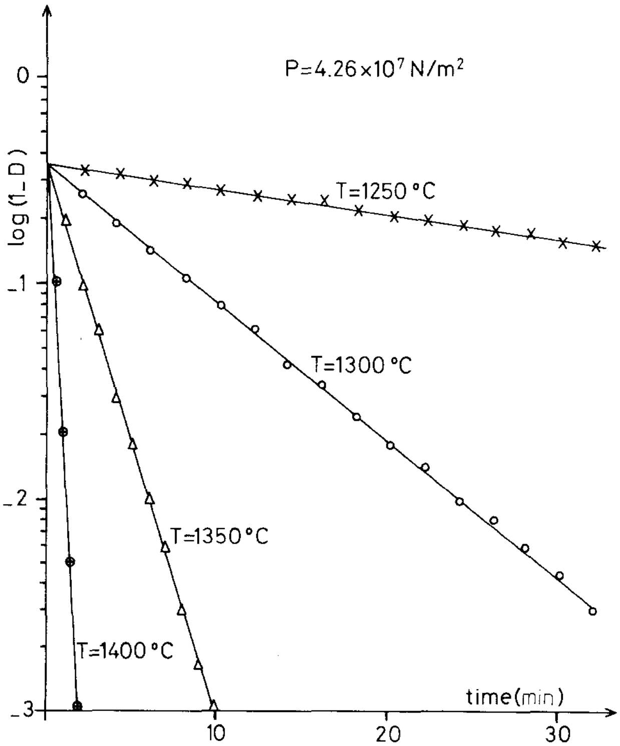


Figure 11 Densification of powdered vitreous silica during hot-pressing.

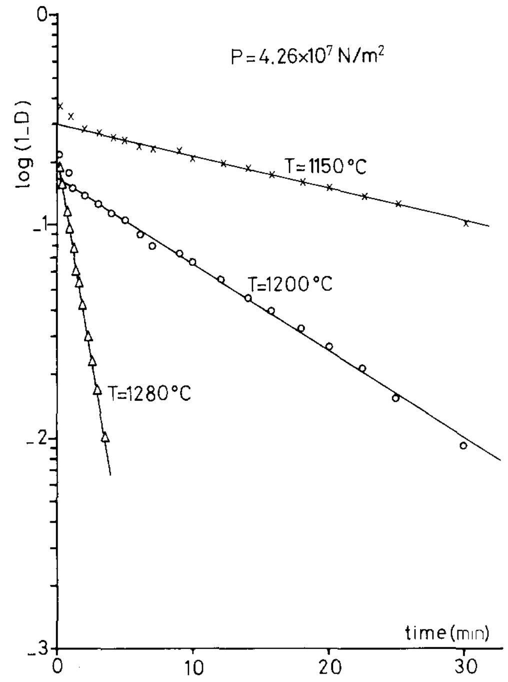


Figure 13 Densification of silica gel during hot-pressing in the temperature range 1150° C to 1280° C.

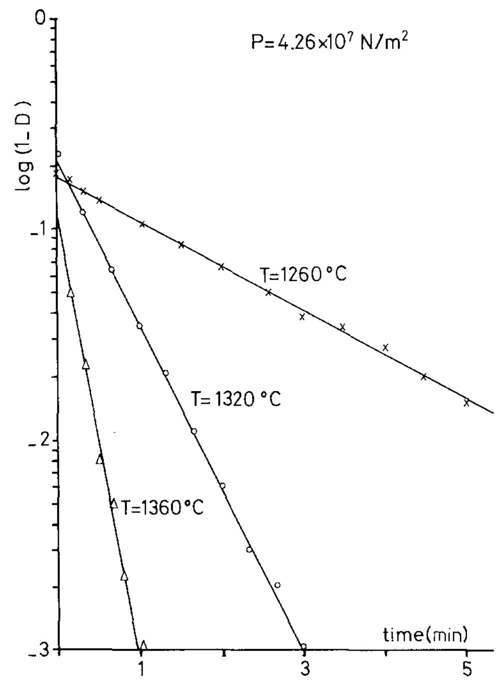


Figure 14 Densification of silica gel during hot-pressing in the temperature range 1260° C to 1360° C.

Given the structural analogy between the dehydrated silica gel and vitreous silica this model was tentatively applied to our hot-pressing experiments.

The theoretical relationship

$$\log(1-D) = -\frac{3}{2.3 \times 4}\frac{P}{\eta}t + \log(1-D_\mathrm{i})$$

where D_i is the initial relative density, P the applied pressure, η the viscosity and t the time of pressing was first tested on samples of powdered vitreous silica.

Fig. 11 shows the plots of experimental data obtained for different temperatures at a pressure $P_0 = 4.26 \times 10^7 \mathrm{N\,m^{-2}}$. A linear relationship exists between $\log(1-D)$ and t, which shows that the system agrees with the theoretical model. The viscosity values obtained from the slopes of the graphs are plotted in Fig. 12. In the temperature interval considered these values follow Andrade's law

$$\eta = \eta_0 \exp(E^*/RT)$$

where E^* is the apparent activation energy for viscosity. These values are in excellent agreement with the viscosity data for vitreous silica with low $\mathrm{OH^-}$ content as determined by a fibre elongation method [15]. Murray *et al.*'s relation is thus well adapted to the study of densification of silica glass in the temperature interval studied.

The same procedure applied to the study of silica gel gives the results shown in Figs. 13 and 14. With the exception of the very first stages of densification $\log(1-D)$ varies linearly with time as required by the model of Murray *et al.* However, several phenomena specific to gels may be detected:

(a) a notable increase in the initial relative density D_i with the temperature of pressing. This means that the gel densifies during the rise in temperature even in the absence of pressure.

(b) a very rapid increase in the relative density D during the very first moments of pressing. This phase which corresponds to a high porosity cannot be described by the equation of Murray *et al.*

The viscosity deduced from the slope of the graphs at different temperatures is shown in Fig. 15. It can be seen that it is lower than that for vitreous silica, probably because of the presence of hydroxyl groups in the gel [16]. The corresponding activation energy ($111\,\mathrm{kcal\,mol^{-1}}$), is inferior to that of vitreous silica (170 to $120\,\mathrm{kcal\,mol^{-1}}$) depending on the water content of the glass [15].

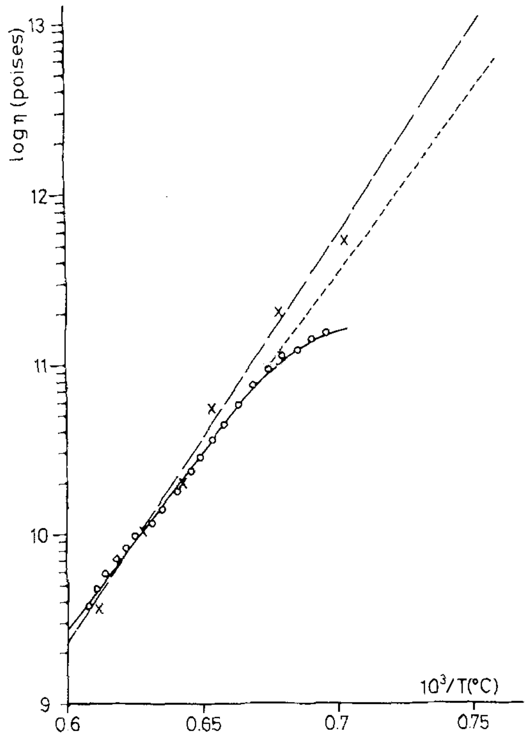


Figure 15 Viscosity of silica gel.

5.2. "Flash" pressing

In the case of "flash" pressing it is assumed that the temperature varies linearly with time in the small temperature interval where densification occurs. The basic equation can be written as follows:

$$\frac{\mathrm{d}\log(1-D)}{\mathrm{d}T} = \frac{3P}{4\eta \times 2.3\,v_0}\,\frac{1}{}$$

where v_0 is the rate of increase in temperature.

From the slope of the $\log(1-D) = f(T)$ curves it is possible to calculate the viscosity η of the glass within the temperature interval studied.

Values of η deduced in this way are sufficient to calculate the times of isothermal pressing to obtain a porosity-free silica glass.

In the case of silica gels (Fig. 15) it can be seen that below 1260° C the high porosity of the

TABLE IV Flash pressing temperature T_0 for the gels of B_2O_3–SiO_2 system

Glass	T_0 (° C)
B 5 S	1255
B 10 S	1150
B 15 S	1000
B 30 S	820

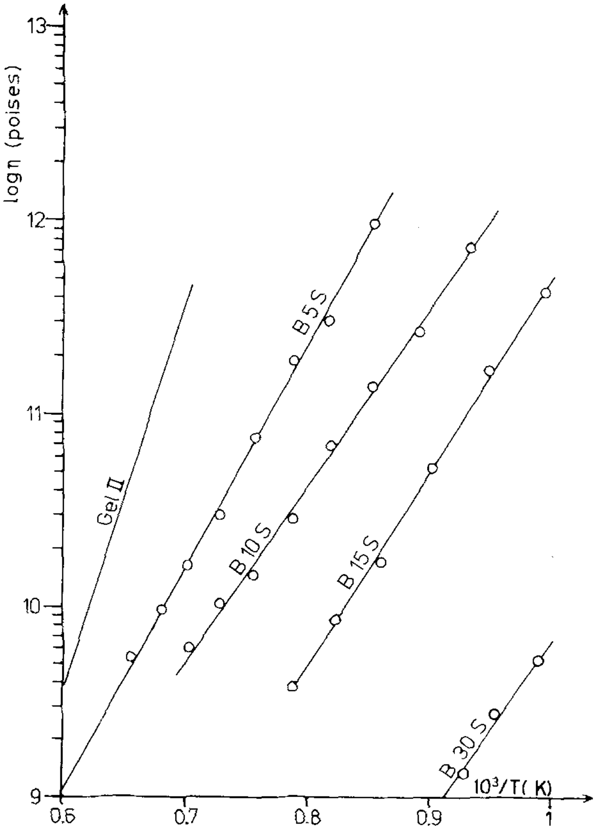


Figure 16 Viscosity of glasses in the system B_2O_3–SiO_2 obtained by the flash pressing method.

material does not allow the model of Murray *et al.* to be applied. For higher temperatures the viscosity values deduced from a "flash" pressing coincide with those obtained from isothermal pressing.

The model of Murray, Rodgers and Williams correctly describes the densification of gel into glass for porosities lower than 10%.

A single "flash" pressing run is enough to calculate the length of time needed for pressing a gel into a glass in an isothermal mode.

Flash pressing in the case of gels of the B_2O_3–SiO_2 system leads to perfectly transparent materials. The temperature of the hot-pressing decreases rapidly with the B_2O_3 content (Table IV). This is directly related to the decrease in the temperature of the liquidus. The viscosity data obtained from flash pressing run show that Andrade's law is obeyed (Fig. 16). The activation energy decreases very rapidly when the B_2O_3 increases and from about 10% tends to a value close to 45 kcal mol^{-1}.

6. Devitrification of glasses of the SiO_2–La_2O_3 system obtained by hot-pressing of gels

Refractory glasses of the SiO_2–La_2O_3 system may be converted into glass-ceramic materials. The fusion of gels is well adapted to synthesize the base-glasses for this system [2]; however, hot-pressing is a technique which permits the gel–glass conversion at a considerably lower temperature.

6.1. Experimental

A gel containing 5 wt% La_2O_3 was prepared by Method 2 and after dehydration at 800° hot-pressed under a pressure $P_0 = 4.26 \times 10^7 \mathrm{N\,m^{-2}}$. Two different pressing schedules were used:

(a) a glass labelled "A" was obtained by isothermal pressing at 1200° C for 1 hour; it contains about 100 ppm of OH^-.

(b) a glass labelled "B" was obtained by a "flash" pressing up to 1350° C; it contains about 400 ppm OH^-.

Both types of glasses immediately after their synthesis were subjected to a crystallization treatment at 1200 or at 1300° C inside the press.

In the case of Glass A pressure was either maintained or removed during devitrification treatment to evaluate the influence of pressure on crystallization.

After extraction from the die the crystallized specimens were subjected to X-ray diffraction analysis.

6.2. Results

X-ray diffraction showed that the crystalline phases present in the devitrified samples were α-quartz ($d = 3.34$ Å) and α-cristobalite ($d = 4.05$ Å). In addition, all the spectra showed two faint lines corresponding to $d = 3.13$ and 2.94 Å. They can probably be attributed to a silica–lanthana compound; they do not however correspond to the disilicate as could be foreseen from the equi-

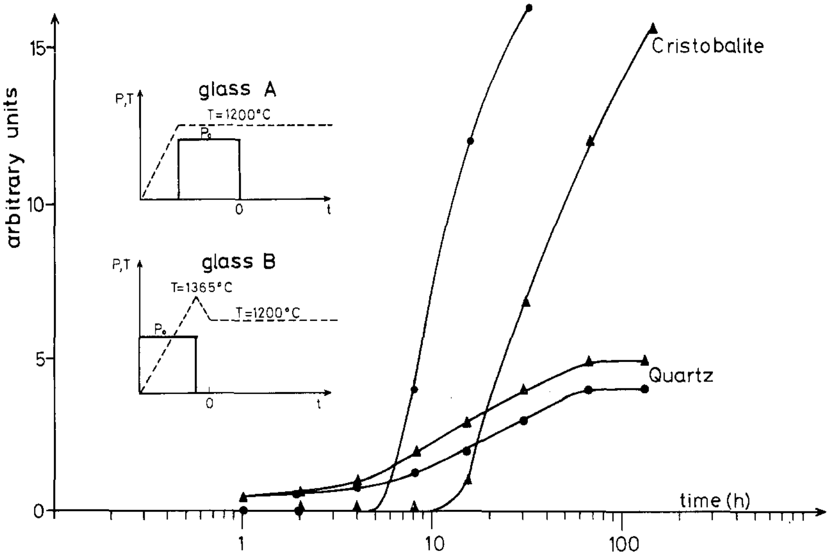


Figure 17 Crystallization of glasses 95% SiO_2–5% La_2O_3 at 1200° C; ▲ Glass A; ● Glass B. See insert for definition of treatments leading to glasses A and B.

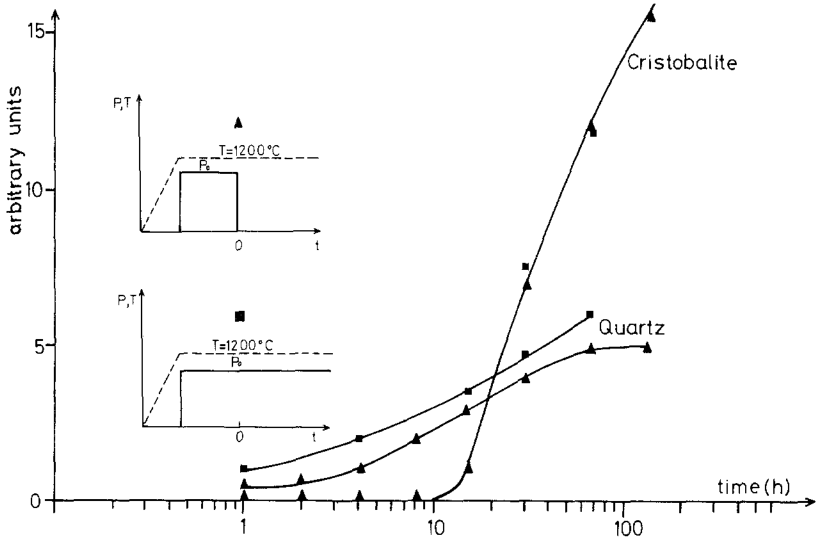


Figure 18 Effect of pressure on the crystallization of Glasses A 95% SiO_2–5% La_2O_3 at 1200° C; ■ with pressure; ▲ without pressure.

librium diagram [17] and earlier crystallization studies of gels and glasses in this system [2, 18]. The intensity of the peak corresponding to 2.94 Å remained constant for all devitrified specimens irrespective of the duration of thermal treatments. This line has been chosen as an internal standard to follow quantitatively the precipitation of quartz and cristobalite.

During thermal treatment at 1200° C (Fig. 17) quartz was the first crystalline phase to appear. The quantity precipitated reached a limit after about 100 hours; it was greater in Glass A than in Glass B. Cristobalite can be detected only after a few hours; it appeared and grew more rapidly in Glass B than in Glass A.

Pressure applied during thermal treatment favoured quartz formation (Fig. 18).

For thermal treatments at 1300° C the crystallization sequence was similar (Fig. 19).

Quartz appears first in Glass A although in lesser quantity than during a treatment at 1200° C; it is totally absent in Glass B. Cristobalite appears earlier and grows more quickly in Glass B.

No effect of pressure could be detected at 1300° C on the crystallization of Glass A.

6.3. Interpretation

The pressure–temperature diagram of silica [19] can be used to forecast the nature of crystalline phases which appear during the devitrification

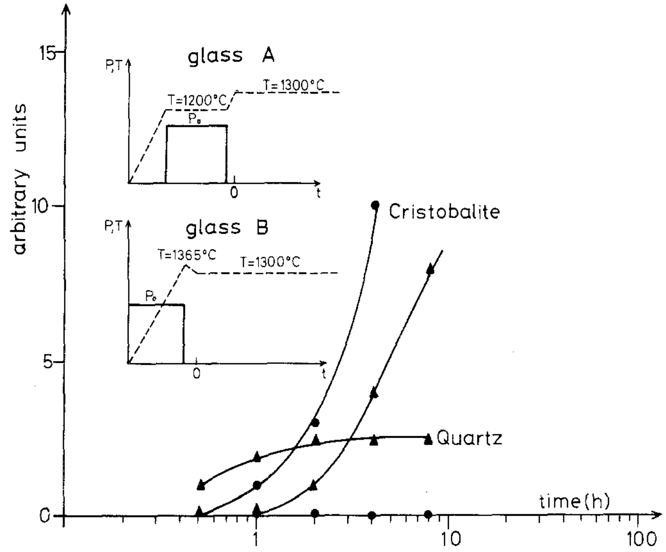


Figure 19 Crystallization of glasses 95% SiO_2–5% La_2O_3 at 1300° C; ▲ Glass A; ● Glass B.

procedure. At 1200 and 1300° C the most representative phase in an advanced crystallization stage is cristobalite which is the stable phase. The application of pressure P_0 during thermal treatment favours precipitation of quartz; this is in accordance with the increase with pressure of the transition temperature quartz β-cristobalite β(1050° C in the absence of pressure and 1200° C under pressure P_0).

The two modes of pressing lead to glasses which differ in their crystallization behaviour. Cristobalite was seen to appear more rapidly in Glass B than in Glass A. This effect is directly related to the hydroxyl content of the two glasses; OH^- ions, which act as mineralizers, favour the formation of the stable crystalline phase [18]. Finally crystallization seems to depend on the temperature of pressing used to convert the gel into glass. This effect is particularly evident at 1300° C (Fig. 19). Quartz, a phase stable at moderate temperatures appears in Glass A pressed at 1200° C but is totally absent in Glass B synthesized by a "flash" pressing below 1300° C. It is probable that quartz crystals initiated at 1200° C grow during thermal treatment at 1300° C.

7. Conclusion

Hot-pressing of gels enables glasses to be obtained without the necessity of going through the melting stage at temperatures well below the fusion temperatures. Infra-red and electron microscopy studies showed that the structure of the gel evolves progressively towards that of glass with loss of water and porosity. It has been shown that the densification of the gel during hot-pressing followed the model of Murray, Rodgers and Williams. Applied during a temperature rise, this model enables the viscosity of the gel to be calculated in the pressing temperature interval. By this method pressing conditions for obtaining a glass at a given temperature may be quickly determined. By thermal treatments these glasses may be converted into glass-ceramic materials. The catalyzing effect of OH^- groups and the effect of pressure have both been studied.

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