

Section 17. Prospects

The formation of unusual glasses by sol–gel processing

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It has been claimed that one of the main advantages of the sol–gel technique relates to its potential to produce new glasses from compositions which would normally crystallize if processed by quenching a melt. This article shows that, due to the intrinsic nature of gels (high OH-content, residual carbon, high fictive state), sol–gel glasses crystallize faster than melt-derived glasses at any temperature. Additionally, gels must be (in general) slowly heated from room temperature to approximately half the liquidus temperature to densify to a glass. That is a riskier path than quenching from the liquid state because the nucleation region is crossed on heating, allowing crystal growth from a plethora of nuclei. Finally, there has been no report on a dense gel-derived glass made from systems prone to crystallize. It is concluded that the gel route is not as good as conventional processing to reach the vitreous state and is unlikely to lead to dense glasses of reluctant vitrifying compositions.

1. Introduction

The sol–gel route has been a subject of intensive research in recent years due to its advantages over conventional melting and quenching of glass. It is often claimed that one of the main advantages of the sol–gel technique is its potential to obtain exotic glasses, having unusual properties, from reluctant glass-forming systems [1–3]. Such compositions would normally crystallize in the cooling path if processed by the melting route. It is commonly argued that most gels could be densified to a glass through heat treatments at low temperatures, thus avoiding crystallization.

A contrary view to the above argument was first presented by Mackenzie [4], in an attempt to classify gel-derived oxides according to Zachariassen's rules. Mackenzie [4] observed that oxide gels with experimentally determined crystallization temperature on heating, T_{ch} , in a typical DTA or DSC run, such that T_{ch} is larger than half the melting point of the crystal, $T_{ch} > T_m/2$, easily vitrify, whereas those with $T_{ch} < T_m/2$ tend to crystallize. That correlation was observed for five reluctant glass formers ($BaTiO_3$, TiO_2 , Al_2O_3 , ZrO_2 and Ta_2O_5) and two good glass formers (SiO_2 and GeO_2). Although his findings

were quite interesting, they needed to be generalized via a theoretical justification.

Mackenzie's empirical observations were recently treated by Meyer et al. [5] by rationalizing in terms of the adiabatic nucleation theory (ANT) [6]. It was demonstrated that for reluctant glass forming compositions, T_{ch} is systematically lower than T_{14} whereas for good glass formers T_{ch} is larger than T_{14} , as shown in table 1. T_{14} is the most probable (thermodynamic) nucleation temperature predicted by ANT. Therefore, gels of hesitant glass forming systems tend to nucleate and crystallize at much lower (reduced) temperatures than good glass formers.

2. The problem

Thus, in at least two publications [4,5] the idea that the gel route can lead to (dense) glasses of reluctant vitrifying compositions is contested. The first is based upon an empirical correlation for the crystallization of seven oxides [4] and the second is based upon a theoretical analysis [5]. Zachariassen's rules provide only some qualitative insight for the glass formation tendencies of oxides and the present nucleation theories, adia-

Table 1
Reduced crystallization temperatures during non-isothermal heating of gels [5]

System	T_{ch}/T_m	T_{14}/T_m
<i>Good glass formers ($T_{ch} > T_{14}$)</i>		
$\text{Li}_2\text{O} \cdot 2\text{SiO}_2$	0.61	0.58
$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	0.71	0.57
SiO_2	0.75	0.64
GeO_2	0.78	0.61
<i>Reluctant glass formers ($T_{ch} < T_{14}$)</i>		
TiO_2	0.22	0.58
ZrO_2	0.26	0.54
Ta_2O_5	0.29	0.51
Y_2O_3	0.31	0.55
Al_2O_3	0.32	0.54

T_{ch} , crystallization temperature of the gel in non-isothermal experiments with DTA or DSC (10°C/min).

T_m , Melting point of the crystalline oxide.

T_{14} , Adiabatic nucleation temperature.

batic nucleation theory (ANT) and classical nucleation theory (CNT), are not fully satisfactory; for instance, ANT predicts only the most probable nucleation temperature but not the actual nucleation rates. CNT has an unknown parameter (the microscopic surface energy) and the theoretical crystal nucleation rates are many orders of magnitude smaller than the experimental values, for all glasses for which reliable measurements exist [7,8]. Therefore, these theories cannot be used reliably. In this communication, I use more accepted arguments to address the crystallization

behaviour as well as the issue of glass formation from gels.

3. The intrinsic crystallization behaviour of gels

The first important point regarding the present problem is related to the intrinsic nature of gels. The crystallization behaviour of specific gels, glasses obtained by melting gel precursors (MGP) and conventionally processed glasses (CG) has been reported by some authors and were reviewed by Uhlmann et al. [9]. Table 2 summarizes the non-isothermal crystallization temperatures for several glass-forming systems.

A first conclusion from the analysis of literature is that there is a total lack of detailed kinetic studies of the crystallization behaviour of gels of good glass forming compositions. Despite that, table 2 clearly shows that these materials crystallize at lower temperatures on heating, and thus have higher nucleation and growth rates at a given temperature than conventional glasses. That behaviour has been attributed to the elevated OH-content, residual carbon and high fictive state of gels. Therefore it is fair to expect that gels of any composition crystallize faster than its glass analogue for a given heat treatment. However, it should be emphasized that the glass transition temperatures of gels are (surprisingly) very *similar* to those of melt-derived glasses! Therefore,

Table 2
Crystallization temperatures (10°C/min) of several glasses and gels

System	T_{ch} (°C)			Observations
	Gel	MGP	CG	
$\text{La}_2\text{O}_5\text{-SiO}_2$	–	<	>	Higher crystallinity and smaller grains in MGP [10]
$\text{Li}_2\text{O-2SiO}_2$	550	–	650	Faster nucleation in Gel than CG [11]
PbO-GeO_2	539	647	655	[12]
$\text{Na}_2\text{O-2SiO}_2$	580	–	620	[13]
$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	1030	–	1040	[14]
NaAlCaTiSiO_x	900	–	1050	[15]
BaO-2SiO_2	853	–	900	Faster nucleation in Gel [16]

Gel, dried gel; MGP, melted gel precursors; CG, conventional glass.

additional effects must play an important role and should be studied.

4. The thermal path

Glass formation is feasible by the conventional route if the cooling rate is fast enough to avoid nucleation and crystal growth on cooling the liquid from the melting point to the transition region. In controlled laboratory conditions, i.e., in the absence of spurious contamination, which could lead to heterogeneous nucleation, quenching is a favourable path because the time interval at high temperatures is short and the homogeneous nucleation rates become significant only at high undercoolings ($T_n/T_m = 0.6-0.5$ for ordinary glasses, where T_n is the temperature range where nucleation is important). In that region, the crystal growth rates are reduced, since their maxima occur at a temperature, T_c , typically at $T_c/T_m = 0.9$, followed by a rapid decline. Thus crystallization can be arrested by fast quenching.

Glass formation by the sol-gel route, on the other hand, requires heating the gel, normally with a slow rate (an exception is flash heating of thin films) followed by holding the specimen for some time at a temperature, typically in the neighbourhood of T_g ($0.5-0.7T_m$). That is a much more risky path to follow because the nucleation region has to be crossed ($T_{ch}/T_m \approx 0.2-0.3$ for gels of reluctant vitrifiers and therefore T_n/T_m is even lower). It should also be stressed that both the nucleation and growth rates are higher for gels than for melt-derived glasses, at any temperature. Thus, vitrification is more difficult.

5. Sintering versus crystallization competition

It is possible that the sintering kinetics of some gels (of reluctant glass-forming compositions) are faster, in some temperature range, than crystallization kinetics; hence, a glass could be formed (as observed for good glass-forming compositions). To treat analytically (and reliably) the kinetics of both sintering and crystallization for a porous gel undergoing simultaneously structural rearrange-

ments and loss of organics and OH-groups would be a formidable task.

This problem has been discussed by Zarzycki [17], Uhlmann et al. [18] and Scherer [19]. An approximate analysis, where the activation energies for nucleation, crystal growth and viscous flow are equated ($\Delta G_n \cong \Delta G_g \cong \Delta G_\eta$), demonstrated that, for *isothermal* treatments, both sintering and crystallization (transport) rates are proportional to the time viscosity ratio, t/η . Thus, any factor (water, impurities, etc.) which affects η will change both phenomena equally. Scherer [19] pointed out that manipulation of pore size and green density, through control of chemical synthesis, may decouple the rates of densification and transformation. However, the effects of gel synthesis on crystallization are not yet known.

In *non-isothermal* sintering, the integral $\int dt/\eta$ should be evaluated. Since η can increase by as much as three orders of magnitude in one single isothermal hold and, therefore, η can change by different amounts at each temperature in a non-isothermal treatment, the above integral is not known, a priori. Crystal nucleation rates cannot be safely predicted by CNT [7,8] and consequently overall crystallization rates cannot be predicted. It should also be stressed that contamination by solid particles, which could trigger *heterogeneous* nucleation, may be more significant in gel preparation than in melting since most impurities dissolve at high temperatures. External surface contamination could also occur during sintering of a gel or quenching of a melt. Heterogeneous nucleation could occur in both gel and melt processing depending on specific processing conditions.

Viscous sintering models [19] neglect inhibiting densification factors such as entrapped gases of low solubility, rearrangement and distribution of pore sizes. As a result, the theoretically predicted sintering rates tend to be overestimated. Thus, at present, it is not safe to make conclusions on the sintering versus crystallization dispute based solely on theoretical predictions.

There is a plethora of experimental data on the sol-gel synthesis of several glasses. In spite of numerous researchers who produce more than 400 papers per year on sol-gel processing, as far

as I know, there is no report available in the international literature on a (fully dense) monolithic gel-derived glass made of a *reluctant vitrifying composition*. That indicates that crystallization prevails upon sintering, or at least that freshly sintered gel-derived glasses of that type rapidly crystallize before being cooled to room temperature. Despite that, metallic glasses and other hesitant glass formers, such as LiNbO_3 , are routinely produced by very fast quenching from the liquid state. As a matter of fact, virtually any glass can be made by extremely fast quenching!

6. Conclusions

From the above discussion, four observations are clear.

(i) Gels of hesitant glass-forming compositions fully crystallize at temperatures ($0.2 < T_{\text{ch}}/T_{\text{m}} < 0.3$) much lower than good glass formers ($0.6 < T_{\text{ch}}/T_{\text{m}} < 0.8$) under non-isothermal conditions.

(ii) Gels crystallize faster than melt-derived glasses at any temperature.

(iii) The typical thermal path of sol–gel processing (heating at a slow rate followed by a holding period) crosses the nucleation region and is riskier than fast cooling if crystallization is to be avoided.

(iv) There is a lack of reports on (dense) gel-derived glasses made from reluctant glass forming compositions.

Therefore, it is possible to conclude that, in spite of its several advantages over the traditional route, the sol–gel route is not as good as the quenching technique in achieving the vitreous state. Thus, it is unlikely to lead to unusual glasses of reluctant vitrifying compositions.

The author would appreciate hearing from any reader who has been able to produce a (fully

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