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Crystallization of gels in the SiO_2–Al_2O_3–ZrO_2 system

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The preparation of glasses and ceramics from gels in the ternary system of SiO_2–Al_2O_3–ZrO_2 has been investigated. The phase relations in this system suggest the existence of a stable joint between mullite and ZrO_2 in addition to the joint between mullite and zircon. The gel technique allows metastable ZrO_2 particles to be readily dispersed in alumino-silicate matrices.

1. Introduction

The phase relations in the silica–alumina–zirconia system have been the subject of interesting and controversial studies. There exist two subsolidus compatibility configurations, with a stable joint between zircon and mullite as well as a stable joint between mullite and zirconia. Consequently, only two binary compounds, zircon and mullite are formed and there are no ternary compounds in the system.

Zirconia and alumina have been well established by Sun [1] to be both glass formers and intermediates in relation to their bond strengths and glass formation capabilities. These oxides are expected to incorporate in the structure of silica networks to form a multicomponent glass. Glass formation in the silica–alumina–zirconia system deserves intensive study because of its importance in the refractory industries. The glass in this system can be chemically durable, refractory, of high modulus and excellent toughness. However, it is rather difficult to prepare by conventional melting techniques because of its high melting temperature and the presence of an extensive miscibility gap. Subsequently, recent attempts have been concentrated on the preparation of this glass by the calcination of gels and encouraging results have been reported [2, 3].

In this paper, results of glass preparation in the SiO_2–Al_2O_3–ZrO_2 system via the chemical polymerization of metal alkoxides are reported. The structural and microstructural changes associated with the crystallization of gels in the system were investigated in detail. The overall view of the phase relations in the silica–alumina–zirconia system will also be presented.

2. Experimental procedures

Commercial purity silicon tetraethoxide, sodium acetate and laboratory prepared zirconium tetraethoxide and aluminium isopropoxide were used as starting raw materials for the preparation of gels. The latter were prepared according to the experimental recipes of Bradley *et al.* [4] and Whitaker [5], respectively.

The preparation of gels involved mixing the metal alkoxides in a plastic cup containing carbon tetrachloride as a common solvent. The resultant mixture was then diluted with some dry ethanol and hydrolysed dropwise with water under vigorous stirring. Upon completion of hydrolysis, a plastic film with several holes was used to seal the cup and the solution was allowed to gel over a period of several days in a constant-humidity oven in which the temperature was increased in steps from 40 to 80° C.

Gel samples were formulated to correspond to the points (a–l, p and q) shown in Fig. 1. The complete details of gel compositions are enumerated in Table I.

Differential thermal analysis (DTA) of the gel samples was performed using a Rigaku Micro DTA apparatus at a heating rate of $10^\circ\,C\,min^{-1}$. When the gel sample was heat treated in an argon atmosphere, a flow rate of 0.05 l/min was used.

A Philips X-ray diffractometer (PW 1050/25 wide angle goniometer) was used to identify the crystalline phases present in the heat-treated gels. Finely ground gel powder was placed on an aluminium disc as a substrate and nickel-filtered Cu*Kα* radiation was employed.

The specimens for the infrared analysis were prepared by the pellet method. The gel powder was mixed with KBr and pressed into a thin disc. A sample to KBr ratio of 1 : 250 was used, with a reference pellet of KBr. Infrared spectra of gels were recorded on a Pye-Unicam SP3-200 Spectrometer. The carbon con-

TABLE I Compositions of gel samples

Sample	Calculated composition (wt %)
a	SiO_2 + 10% ZrO_2
b	SiO_2 + 20% ZrO_2
c	SiO_2 + 10% ZrO_2 + 3% Al_2O_3
d	SiO_2 + 20% ZrO_2 + 3% Al_2O_3
e	SiO_2 + 59% ZrO_2 + 4% Al_2O_3
f	SiO_2 + 56% ZrO_2 + 7% Al_2O_3
g	SiO_2 + 48% ZrO_2 + 29% Al_2O_3
h	SiO_2 + 30% ZrO_2 + 32% Al_2O_3
i	SiO_2 + 37% ZrO_2 + 44% Al_2O_3 + 2% Na_2O
j	SiO_2 + 24% ZrO_2 + 64% Al_2O_3
k	SiO_2 + 63% Al_2O_3
l	SiO_2 + 80% Al_2O_3
Mullite-ZrO_2 (p)	$3AlO_3 2SiO_2$ + (0–20% ZrO_2)
Alumina-ZrO_2 (q)	Al_2O_3 + (0–20% ZrO_2)

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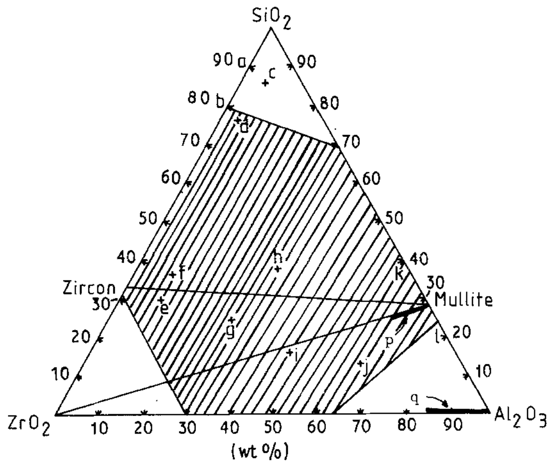

Figure 1 Topological compositions of gel samples. The estimated region of metastable immiscibility in the Al_2O_3–SiO_2–ZrO_2 system at the ambient temperature is hatched. Points a–l, p and q indicate the points of composition of the formulated gel samples.

tent present in the treated gels was analysed at the Melbourne Research Laboratory of BHP using a Leco CS044 carbon analyser.

3. Results

3.1. Stability of gel-derived zirconia

The stability and persistence of tetragonal zirconia in the absence or presence of a matrix constraint was investigated by calcination of hydrated zirconium ethoxide and gels, respectively, at various temperatures. Calcined samples were analysed for tetragonal and monoclinic zirconia by X-ray diffraction (XRD). The data are plotted as the amount of tetragonal zirconia, expressed as a percentage of the total crystalline zirconia, against temperature (Fig. 2). During the calcination of zirconium ethoxide, the results indicated a sharp reduction in the proportion of tetragonal zirconia left at between 600 and 800° C, and less than 3% remained at 1300° C. In contrast to this, 100% tetragonal zirconia persisted up to 1000° C in the silica–zirconia and silica–alumina–zirconia gels.

Figures 3 and 4 show the growth of metastable zirconia crystallites in the silica–zirconia and silica–alumina–zirconia systems, respectively. The crystallites appeared to grow at a faster rate in the alumina–silica matrix than in the silica matrix. The proportion of zirconia in both matrices was about 20 wt %. The results also indicates that the isothermal growth rates of these crystallites were very slow.

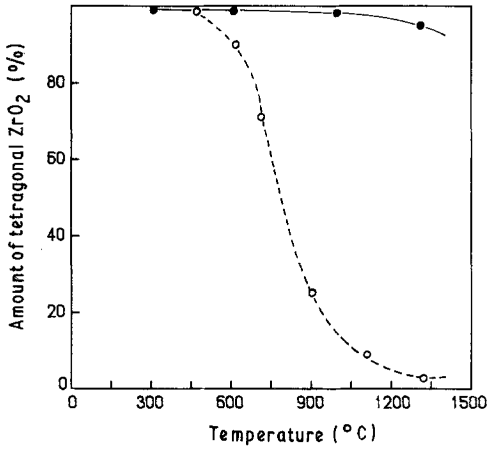

Figure 2 Variation of the amount of tetragonal ZrO_2 present in hydrated zirconium ethoxide (○) and prepared gels (●) as a function of temperature.

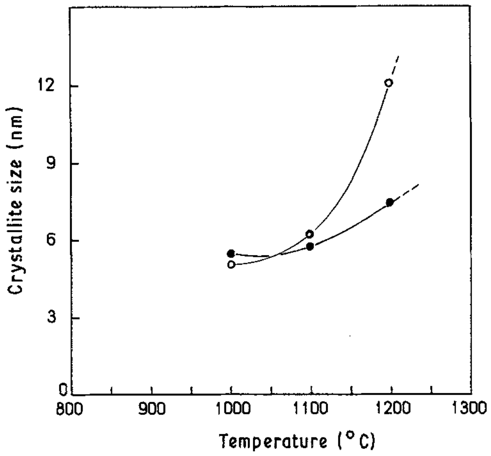

Figure 3 Growth of metastable ZrO_2 particles in silica (●) and alumina–silica (○) matrices.

3.2. Crystallization characteristics of gels

The dessicated gels, as obtained by heating up to 600° C, remained glassy or amorphous as confirmed by the complete absence of crystalline phases in the XRD results. The crystallization temperatures of the various phases, in particular the zirconia phase, were sensitively dependent on the composition of the gels. The first crystalline phase to appear was always the metastable zirconia. At higher temperatures, monoclinic zirconia, zircon, mullite or cristobalite phases were detected.

The gel to glass conversion and its crystallization to various phases in samples (b), (d), (f), (h), (j), (p) and (q) are tabulated in Table II which serves to indicate that the crystalline phases formed are in good agreement with the phase relations in their respective phase diagrams. A close similarity between the gels and the oxide mixtures is clearly indicated. The phase relations in the gel-derived Al_2O_3–ZrO_2–SiO_2 system at 1400° C as obtained in this study can be summarized as in Table III.

The thermochemical reaction taking place and the progressive evolution of the gel with separation of

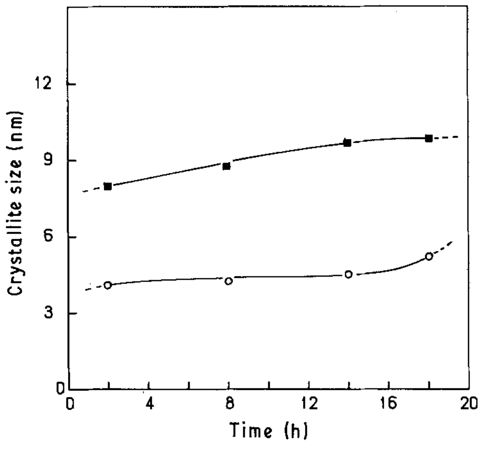

Figure 4 Isothermal growth of metastable ZrO_2 particles in the silica matrix at (○) 1000° C, and (■) 1200° C.

TABLE II Crystallization of some representative gels

Temperature (° C)	Samples						
	b	d	f	h	j	p	q
< 600	A	A	A	A	A	A	A
800	A	A	A	TZ_s	TZ_m, γ_m	γ'_m, TZ_t	γ_m, TZ_t
1000	TZ_w	A	TZ_s	TZ_m, M_s MZ_m	TZ_s, γ_s	γ'_s, TZ_w	γ_m, TZ_m
1200	TZ_m	TZ_s	TZ_m, MZ_m Z_m	TZ_m, MZ_s M_s	TZ_m, MZ_m γ_m	M_m, γ'_s TZ_m	α_s, θ_w TZ_m, MZ_m
1400	TZ_s, C_s	TZ_w, Z_s C_s, M_w	MZ_m, Z_s M_w	TZ_w, MZ_s M_s	MZ_s, M_s α_s	M_s, α_s TZ_w, MZ_s	α_s TZ_s, MZ_s

A = amorphous; γ-, θ-, α = γ-, θ-, α-Al_2O_3, γ' = Al–Si spinel; TZ, MZ = tetragonal and monoclinic ZrO_2, respectively; M = mullite; C = cristobalite; Z = zircon; t = traces; w = weak; m = medium; s = strong.

crystalline phases during heat treatment have been studied by the DTA and thermogravimetric analysis (TGA) techniques. The DTA and TGA curves for some gel samples are depicted in Fig. 5. The exotherms associated with respective crystalline phases in samples (b) and (d) were not significantly altered when these gels were fired in air or argon. On the contrary, the reverse was true for samples (f), (h) and (i). The prominent endothermic features of the DTA curves are attributed to the desorption of physically adsorbed water (100–150° C) and the carbonization of alkoxyl groups (200–300° C). The exothermic combustion of carbon occurs in the range of 300–400° C. The other exotherms are associated with devitrification to the respective crystalline phases. The substantial weight loss in the TGA curve is associated with a removal of large quantities of water or organic materials.

The carbon content of a few selected gels fired both in air and argon is shown in Table IV. The results indicate that argon-treated gels contained a much greater amount of carbon in the form of residual OR groups than gels treated in air (where R is an alkyl group).

A representative infrared spectrum of gels studied is depicted in Fig. 6. The broad absorption band ranging from 3600–3000 cm^{-1} arises from the stretching vibrations of hydroxyl groups. The band at around 1600 cm^{-1} is due to the deformation vibration of water [6]. Si–O stretching vibrations are reported to occur in 1172, 1100, 778, 647 and 608 cm^{-1}. Ring structures of Si–O–Si bonds vibrate at around 800 cm^{-1}. For comparison, a standard spectrum of a pure silica glass is also shown.

The absorption band due to hydroxyl groups were observed to reduce in intensity as the gels were heated to higher temperatures, indicating a continuous desorption of hydroxyl ions from the gel structure. The absorption bands due to Si–O and Si–O–Si bonds were also observed to shift to higher wave numbers with an increase of heating temperature, inferring the strengthening of these bonds in the gel structure. As would be expected, the concentration of Si–O and Si–O–Si groups decreased with an increase in zirconium and aluminium ions that were introduced into the silica network of the gel [7].

4. Discussions

4.1. Stability and persistence of gel-derived metastable zirconia

The results presented above clearly indicate that metastable zirconia particles can be stabilized in a gel-derived glass matrix. The stabilization of tetragonal zirconia particles obtained either by precipitation or calcination at various temperatures up to 1000° C was explained by Garvie [8] in terms of a higher surface energy for the stable monoclinic form

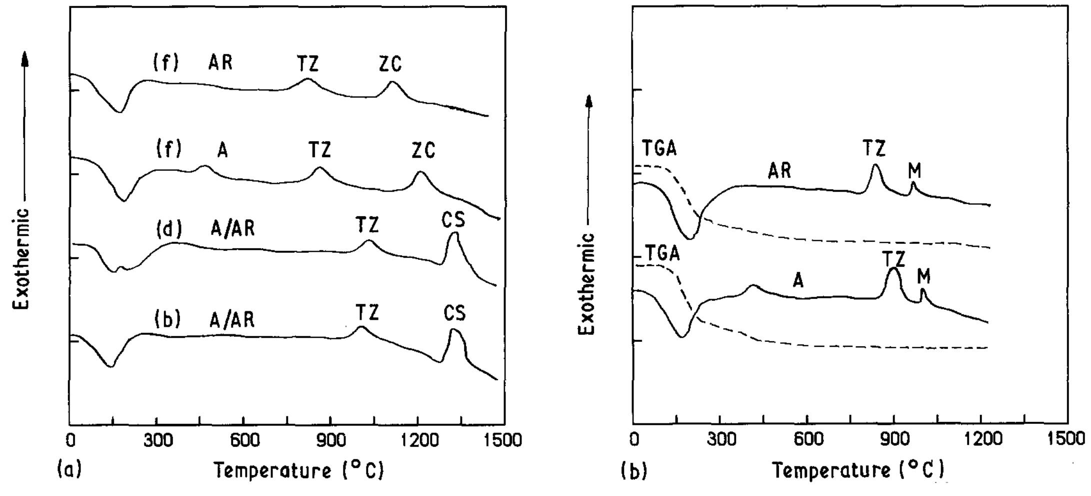

Figure 5 (a) DTA and TGA curves of some prepared gels samples (b), (d) and (f), and (b) DTA and TGA curves of sample (h). TZ = tetragonal zirconia crystallization; ZC = zircon crystallization; CS = cristobalite crystallization; M = mullite crystallization; A = air; AR = argon; A/AR = air and/or argon

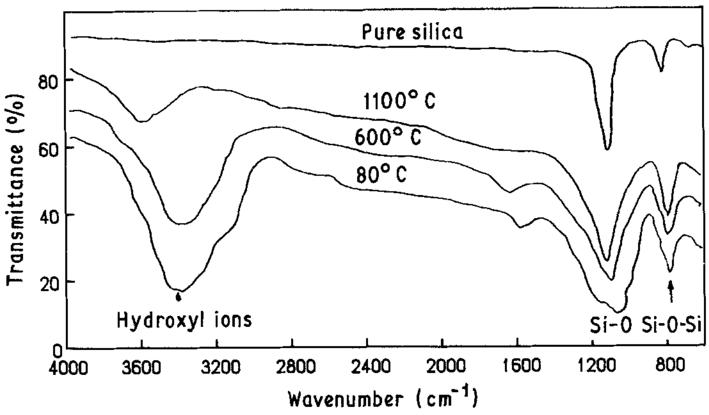

Figure 6 Infrared spectra of sample (b) composition.

with respect to that of the metastable, tetragonal one. According to Garvie, the tetragonal zirconia particles cannot exist, at room temperature, for a crystallite size larger than 30 nm.

The growth and coarsening of metastable zirconia crystallites as shown in Figs 2–4 infer that these processes occur very slowly, probably via a diffusion-controlled mechanism. Similar results were also reported by Fagherazzi and Enzo [9].

4.2. Phase relations in the gel-derived Al_2O_3-ZrO_2-SiO_2 system

The crystalline phases formed correspond correctly to the phase relations of the respective oxides system, thus indicating a striking similarity between ceramics derived from gels and those derived from oxides. The results in the silica–alumina–zirconia system clearly substantiate the subsolidus compatibility relations defined by Fowler [10] and Herold and Smothers [11], in that there exist stable joints between mullite–zircon and mullite–zirconia as well as a metastable joint between zircon and alumina. The latter can become stable if the composition of the sample is closer to the zircon phase field, such that oxides react to form zircon more rapidly than mullite and the reverse is probably true.

The crystallization behaviour of some gel-derived glasses depends on the heat-treatment atmosphere. Gels treated in air have a lower amount of hydroxyl ions and are white in colour because complete combustion of residual alkyl groups takes place, allowing hydroxyl groups to be removed without hindrance. Heat treatment in argon, results in the formation of polymeric carbon as a result of insufficient oxygen, which in turn effectively seals off the pores before the organic radicals and hydroxyl groups have the chance to burn off or escape. Consequently, the gel treated in argon turns black and saturates with excess hydroxyl ions which can significantly dictate or modify the crystallization characteristics of the gel [7]. These hydroxyl ions are effective mineralizers which tend to reduce the viscosity of the glass and cause enhancement of phase separation as well as devitrification.

The results also show that structures completely amorphous to XRD could be prepared over a wide range of compositions in the SiO_2–Al_2O_3–ZrO_2 system. This observation is in general agreement with similar studies by splat quenching [12], flame spherulization [13], plasma synthesis [14] and plasma spraying [15]. Transmission electron microscopy of thin, plasma-sprayed zircon coatings has shown the presence of a finely modulated structure, with a wavelength of about 10 nm [16], whose origin was attributed to the existence of a wide metastable miscibility gap in the ZrO_2–SiO_2 system. A similar observation was reported for Al_2O_3–SiO_2 powders prepared by plasma synthesis from the vapour [14] with one composition (37 wt % Al_2O_3) showing that the powders had separated into two amorphous phases by spinodal decomposition [17], in agreement with the position of a metastable miscibility gap in the Al_2O_3–SiO_2 system proposed by McDowell and Beall [18].

The presence of metastable miscibility gaps in the systems Al_2O_3–SiO_2 and ZrO_2–SiO_2 and observations of spinodal decomposition in rapidly cooled liquids in both systems, suggests that a metastable miscibility gap extends across the Al_2O_3–SiO_2–ZrO_2 ternary system, and that the spinodal decomposition of rapidly quenched liquids is probable over a wide range of compositions if primary crystallization is suppressed [19]. The ease and range of compositions over which glassy materials may be formed in the gel-derived Al_2O_3–SiO_2–ZrO_2 system (Table II) serve to indicate

TABLE III Phase relations of SiO_2–Al_2O_3–ZrO_2 gels at 1400° C

Composition triangle	Verified by sample	Phase formed
SiO_2–zircon–mullite	a, b, c, d, f, h, k	C, M, TZ, MZ, Z
Zircon–ZrO_2–mullite	e, g, i, p	MZ, M, Z
Mullite–ZrO_2–Al_2O_3	i, j, l, p, q	MZ, α, M

A = amorphous; γ-, θ-, α = γ-, θ-, α-Al_2O_3, γ′ = Al–Si spinel; TZ, MZ = tetragonal and monoclinic ZrO_2, respectively; M = mullite; C = cristobalite; Z = zircon; t = traces; w = weak; m = medium; s = strong.

TABLE IV Carbon content of selected gels

Sample	Heat treatment atmosphere at 600° C	Carbon content (wt %)
h	Air	0.19
	Argon	0.34
i	Air	0.60
	Argon	1.00
d	Air	0.10
	Argon	0.12

and establish the existence of a large metastable miscibility gap (the hatched area) which extends across this system (Fig. 1). This has been verified by transmission electron microscopic observations of spinodal decomposition in most of the gel samples studied [7].

5. Conclusion

The preparation of glasses and ceramics containing metastable ZrO_2 from gels in the ternary system of SiO_2–Al_2O_3–ZrO_2 was investigated. This technique offers the possibility of preparing glasses of very high purity and of compositions which the conventional melting technique could not give because of the large immiscibility, rapid crystallization and high melting temperatures. A large metastable miscibility gap in the SiO_2–Al_2O_3–ZrO_2 system was established.

The results of phase relations in this ternary system have unequivocally verified the existence of a stable joint between mullite and zirconia, in addition to the joint between mullite and zircon. The metastable joint between zircon and alumina cannot be ruled out.

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