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Evaluation of processing methods for a calcia–yttria–alumina–silica glass–ceramic

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A glass–ceramic in the calcia–yttria–alumina–silica system was prepared through the melt, sinter, sol–gel and solution routes. The development of a calcium yttrium silicate phase was found to depend significantly on the method of processing the glass. This is attributed to the strong influence of the surface/interface on reactivity. X-ray diffraction and Fourier transform infrared techniques were used for identification. The processing methods were also evaluated and compared for product quality and economy in cost.

1. Introduction

The conventional method for processing a glass–ceramic is by melting a batch composition, casting into a glass form and introducing crystallinity through controlled heating. Such a method ensures full density and reasonable control over properties [1], though in general it is not applicable to all systems wherein the batch components vary widely in their melting points. Though the melt is a good solvent at high temperatures, inhomogeneity sets in while casting because the ingredients differ in solubility at lower temperatures. The sol–gel process for glass and glass–ceramics through alkoxides has provided a convenient method for producing homogeneous, reactive, amorphous powders at comparatively low temperatures [2], but the raw materials cost more and are not always readily available. We have made a relative evaluation of these processing techniques for product quality, cost and time for a glass–ceramic in the calcia–yttria–alumina–silica system.

The properties of glass–ceramics are controlled by the nature, morphology and volume fraction of the crystallites present. Using just one composition in the calcia–yttria–alumina–silica system, we find that processing methods exert a strong influence on crystal growth. This can be linked to the surface reactivity. As the end-use of a material depends on properties controlled by the crystalline phase, this information is significant.

In the chemical processing of a multicomponent system, inert organic media are used for controlling reaction and precipitation rates. We have studied the influence of glycerol in this system.

2. Experimental procedure

The batch composition of the glass–ceramic was, in wt %, calcia 13.6, alumina 13.9, yttria 30.7 and silica 41.8. The glass–ceramic was processed via three routes using oxides, alkoxides or inorganic salts as batch ingredients. Table I describes the starting materials, processes and nomenclature of samples for subsequent discussion. Hot pressing of the commercial oxide batch and sol–gel powders was done at 20 to 22 MPa at 1200 °C.

2.1. Sinter/melt route

Batch oxides and carbonates were roller-milled, calcined at 900 °C, then either sintered after cold compaction or melted. Melting was done in platinum crucibles at 1600 °C for 1 h and casting on steel or graphite plates. A transparent glass was obtained. On heating the glass, crystal phases develop as shown in Table II.

2.2. Sol–gel route

The starting materials were calcium acetate, yttria and alkoxides of aluminium and silicon. They were dissolved in their respective solvents, mixed, aged and gelled for sample SG1. For SG2, after ageing the sol, the pH was increased with ammonia until precipitation was completed. SG3 was also gelled as for SG1 but the source of alumina was aluminium nitrate.

Glycerol was used in some batches of SG3 to study its influence, if any, on the gelation product. As the addition of glycerol affects the pH, it was maintained by adding ammonia. SG3a, b, c and d in Table I refer to these variations. They all formed a solid gel, b and b′ being very transparent.

2.3. Solution processing

To confer good mixing of the components, solutions of inorganic salts were used except for silica, which was added either as fused silica (C1) or as the alkoxide (TEOS for C2 and C3). The dehydrated powder was calcined at 600 °C, pelletized and sintered at 900, 1150 and 1400 °C to study the evolution and growth of the crystal phase. C2 and C3 contained glycerol. While dehydrating on a hotplate an exothermic reaction

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TABLE I Process and nomenclature of samples

Sample No.	Starting materials	Process
H1	Oxides	Sintered at 1400 °C for 0.5 h
H2	Oxides	Fused at 1450 °C, heated at 1000 °C for 4 h
H3	SG2 powder	Melted at 1600 °C for 1 h, cast and heat-treated
H4	Oxides	Melted at 1600 °C for 1 h, cast and heat-treated
SG1	Al secondary butoxide, TEOS, Ca acetate, yttria	Dissolved in respective solvents, mixed, aged, gelled.
SG2	As for SG1	Dissolved in respective solvents, aged for 24 h, ammonia added, ppt dehydrated
SG3	Aluminum nitrate, TEOS, Ca acetate, yttria	Dissolved in solvents, batch variation as follows: (a) glycerol added, pH 3.5; (b) no glycerol, pH 2.5; (c) with glycerol, pH 3.5; (d) NH_4OH added to make pH 3.5 in (b)
C1	Fused silica, others the same	Silica added to solution of other salts, dehydrated
C2	TEOS replaces silica; others the same, glycerol added	Solution-aged for 2 weeks, dehydrated on hotplate, exothermic reaction; black-coloured foam
C3	As for C2.	Aged, dehydrated
HP1	Oxide batch	Hot-pressed at 1200 °C, 20 Mpa
HP2	SG2 powder	Hot-pressed at 1200 °C, 20 Mpa

TABLE II Crystalline phases in melt/sintered materials[a]

Sample	Melt/sintered	950 °C	1100 °C	1380 °C
H1, H2		No reaction	No reaction	CYSO
H3	G	G	YS2	CYSO
H4	G	G	YS2 + CYSO	CYSO
HP2				CYSO

[a] CYSO = $Ca_4Y_6(SiO_4)_6O$, YS2 = yttrium disilicate.

TABLE III Development of crystalline phases with heat treatment in SG materials

Sample	600 °C	900 °C	> 1000 °C
SG1 (gelled)	Amorphous	Broad peaks of YS2	CYSO
SG2 (alkaline ppt.)	Amorphous	Broad peaks of YS2	CYSO
SG3 a–d (gelled)	Amorphous	Amorphous + weak CYSO	CYSO

took place in C2. A dark foamy material resulted. It became white on calcination. C3 did not foam on dehydration.

3. Results

Powder X-ray diffraction (XRD) with CuK_α radiation was used to identify the phases after various heat treatments. Infrared transmittance was recorded in the 400–4000 cm^{-1} range for samples in KBr discs or in the DRIFT mode using a Michelson-100 Fourier transform infrared (FTIR) spectrometer. The microstructure of the fractured surface was analysed after etching and carbon-coating in a scanning electron microscope, for morphology and composition of crystallites.

3.1. X-ray diffraction

The results of XRD are shown in Tables II, III and IV. Amorphous phases were seen in sol–gel and solution-processed powders calcined at 600 °C. The broad bands had peaks at $d = 0.298$ nm similar to those in melt-quenched glass specimens. Further heating resulted in the growth of a calcium yttrium silicate phase, $Ca_4Y_6(SiO_4)_6O(OH)_2$ (CYSO), above 900 °C (Fig. 1) in sol–gel powders. Most of the peaks agree in intensity and position with the hydroxyl form (JCPDS 31-315), but did not change even after heating to 1400 °C. Because of similar spacings it is difficult to distinguish the hydroxyl from the oxysilicate (JCPDS 20-73). In sol–gel powders a few broad peaks of an intermediate phase, yttrium disilicate (YS2) appeared at 800 °C before the onset of CYSO. The evolution of crystallinity varied in other materials.

In the solution-processed glass–ceramics C1, C2 and C3, CYSO phase was seen only around 1400 °C. C1 had segregated yttria up to 1200 °C. C2 and C3 were amorphous at 600 °C. At 800 °C yttria and YS2 separated. On increasing the temperature YS2 grew at the expense of yttria. YS2 phase was dominant at 1200 °C in all C samples.

Sintered pellets of oxides had no reacted phase until 1200 °C. Needle-shaped CYSO formed at 1400 °C.

The mixed oxide batch and sol–gel prepared SG2 powders did not differ much in melting characteristics. Crystallization was retarded in the melt-glass. It remained as glass (XRD-amorphous) on heating at 950 °C for 6 h. CYSO phase developed above 1100 °C. Nucleation was accelerated with iron oxide as additive.

Hot-pressed powders of the oxide batch and SG2 yielded a glass–ceramic with CYSO phase.

3.2. FTIR spectra

I.r. spectra were recorded for all samples at various stages of heat treatment. These support the transformations inferred from XRD. Some spectra are shown in Fig. 2 and Table V lists the assignments. Vibrations from nitrate groups were present in the gel-

TABLE IV Crystalline phases in chemically processed materials

Sample	600 °C	900 °C	1150 °C	1400 °C
C1 (sol + silica mixed, dehyrated)	Y (strong)[a] + YS2 (weak)		Y (weak) + YS2 (strong)	CYSO
C2 (foamed on dehydration)	Amorphous	Y + YS2	YS2	CYSO
C3 (dehydration of solution)	Amorphous	YS2	YS2	CYSO

[a]Y = yttria.

processed samples whereas absorption from carbonate groups at 1430 and 850 cm^{-1} were additional in the glycerol-mixed samples. Vibrations from these groups were absent in the melt-cast and sintered oxide materials. Hence the glass phase and crystal phase vibrations could be identified and compared.

Fig. 3 shows the variation in FTIR peak position of the Si–O stretch mode with heat treatment temperature for samples SG1–3.

3.3. Microstructure

Fig. 4 shows the morphology of crystallites. In pellets of oxides sintered at 1400 °C needle-shaped crystallites averaging 10 μm in length and submicrometre width were observed, whereas in SG1 sintered at 1200 °C they were spherical and submicrometre-sized. In SG2 precipitated under alkaline conditions some needles were seen. The process seems to be responsible for morphology differences. Needle-shaped crystallites were seen above 1380 °C. Dendritic growth of crystallites was observed in melt-cast glass. Fe$_2$O$_3$ as additive accelerated the growth.

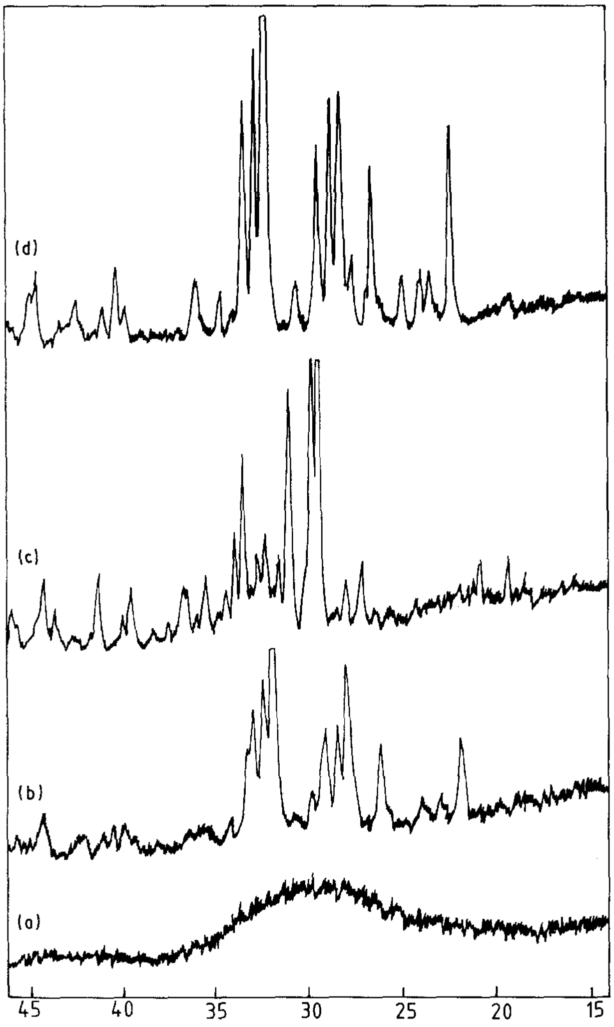

Figure 1 XRD of glass–ceramics: (a) from sol–gel process treated at 600 °C (G); (b) from sol–gel process treated at 1000 °C (CYSO); (c) from inorganic solutions treated at 1150 °C (Y, YS2); (d) sintered at 1400 °C (CYSO).

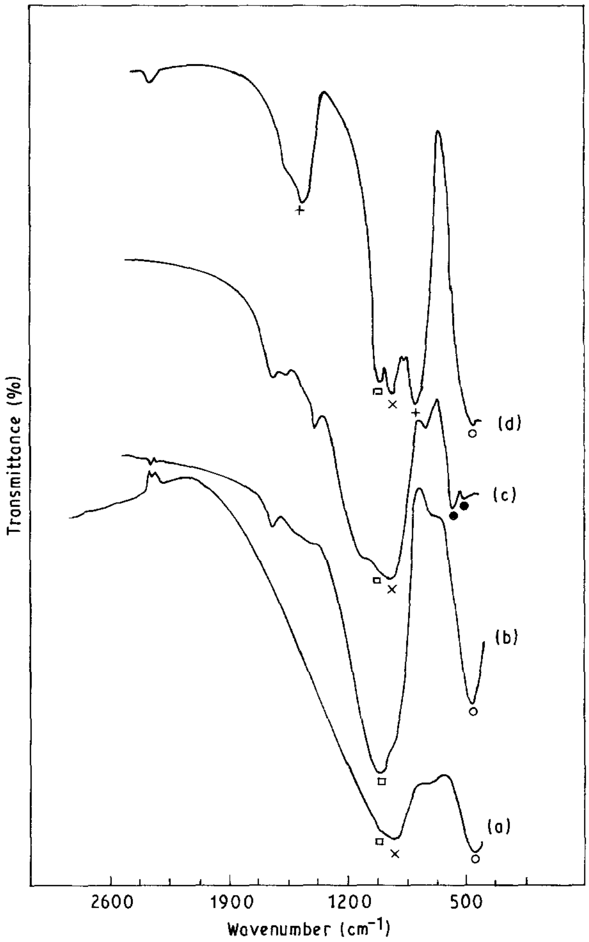

Figure 2 FTIR spectra in (a) glass H4 heat-treated at 950 °C (G, YS2);, (b) SG3 treated at 600 °C (G); (c) SG2 treated at 1000 °C (CYSO); (d) C2 treated at 900 °C (YS2). (+) 1430, 850 cm^{-1} CO$_3$; (□) 1025 cm^{-1} Si–O; (×) 948 cm^{-1} Si–O–Y; (o) 465 cm^{-1} O–Si–O; (•) 570, 506 cm^{-1} Y–O.

The observations can be summarized as follows:

(i) All sol–gel powders are amorphous below 800 °C and form CYSO above 900 °C. The intermediate YS2 phase is transient, between 800 and 900 °C in sol–gel powders. The i.r. data confirm the evolution of CYSO as a sharp shift in Si–O stretch number due to changes in the chemical bonds.

TABLE V I.r. transmittance peaks ($cm^{-1} \pm 4\ cm^{-1}$) and assignments

	H4 (950 °C)	SG2 (600 °C)	C3 (600 °C)	C2 (900 °C)	SG2 (1000 °C)	H1 (1400 °C)
Modes						
CO_3 stretch		1430	1430	1430		
NO_3		1390	1390	1390		
Si–O	1025	1032		1007		
Si–O–Y	948		960	945	948	950
CO_3 deform			850	850		
Si–O stretch	710	716	720	790	720	
Y–O stretch					570, 506	570, 502
O–Si–O deform	465	473	465	465	430	432
XRD phase	Amorphous	Amorphous	Amorphous	Y + YS2	CYSO	CYSO
Identical spectrum in:		SG1, SG3 (600 °C)	C2 (600 °C)	C3 (900 °C)	SG3 (900 °C) all SG (1000 °C)	SG1 (1000 °C) all C (1400 °C)

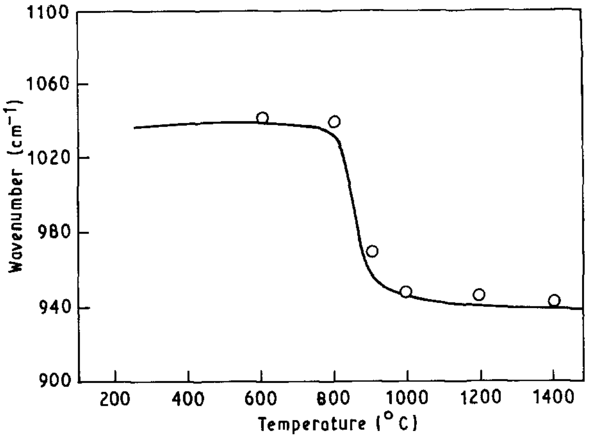

Figure 3 FTIR peak position of Si–O stretch mode versus heat treatment temperature in SG1–3 samples.

(ii) Gelation results when nitrate replaces aluminium secondary butoxide. The gel powders are similar in all respects.

(iii) Gelation and evolution of crystalline phases are similar in SG3a to d, in spite of several variations in pH.

(iv) The presence or absence of glycerol does not affect the crystalline phase except that additionally carbonate groups contribute to i.r. vibrations.

(v) CYSO phase evolves in melt-glass at higher temperatures.

(vi) Amorphous bands seen in melt-glass, sol–gel powder and solution-processed powder occur at the same *d* spacing.

(vii) In solution-processed batches C1 to C3, YS2 phase persists up to 1200 °C and CYSO forms at 1400 °C.

(viii) The FTIR spectrum in melt-glass is similar to SG powder spectra.

4. Discussion

4.1. FTIR spectra

I.r. transmission spectra are essentially determined by the molecular units and do not depend upon crystallinity or the nature of the structure, as long as the electron density distribution in the vibrating group remains the same. The i.r. peaks at about 1030, 710 and 470 $\pm$ 4 cm^{-1} could be ascribed to SiO_4 groups of the glassy network. The strong peak of Si–O stretch mode at 1030 cm^{-1} shifts and intensifies with crystallization. There is a steep change in the shift as shown in Fig. 3 and it coincides with the crystallization temperature. The i.r. peak at 1030 cm^{-1} shifts to 946 $\pm$ 4 cm^{-1} when CYSO phase is formed. Observations in different silicates and glass systems [3–5] show this peak to arise from the stretch mode of Si–O–M bonds (M = Al, B, Ti or OH). Here we attribute this to the formation of Si–O–Y with consequent change in the covalency of the bond. Saksena *et al.* [6] considered this absorption to be from ring-like structure. CYSO has a structure similar to hydroxylapatite with ring-like linkage of silicon tetrahedra [7]. Crystallization to CYSO has brought in evident changes in the i.r. peaks, mainly because of the formation of Si–O–Y bonds with altered covalency. On crystallization, Y–O stretch from octahedrally bonded yttrium (YO_6) occurs at 570 and 505 cm^{-1}. The assignment of modes has been confirmed by comparing with Y_2O_3, $Y_2Si_2O_7$ and $Y(NO3)_3$ [8].

4.2. Process and precursor phase

Usually sol–gel processed powders are considered to be amorphous due to microcrystallinity. However, no component oxide phase was observed from 800 to 1400 °C. Furthermore, i.r. vibrations in all SG samples heat treated at 600 °C are similar to those of melted glass. The vibrations could be ascribed to stretch and bend modes of SiO_4 units of the glass network (Table V). The precursor phase appears to be a multi-ion glass.

Replacement of aluminium alkoxide by inorganic aluminium nitrate in SG3 does not inhibit gelation because TEOS forms the polymeric network and aluminium ions can take up either network or moderator positions.

In the acid-catalysed hydrolysis of mixed alkoxides and other component salts, proper ageing yields a polymeric gel. The chemical polymerization is akin to thermal polymerization of batch oxide silicates at high temperatures [9]. A glass can form at temperatures below T_g if certain rules of packing are satisfied [10]. As crystallites nucleate at 800 °C in sol–gel powders the glass temperature T_g must be below this. In

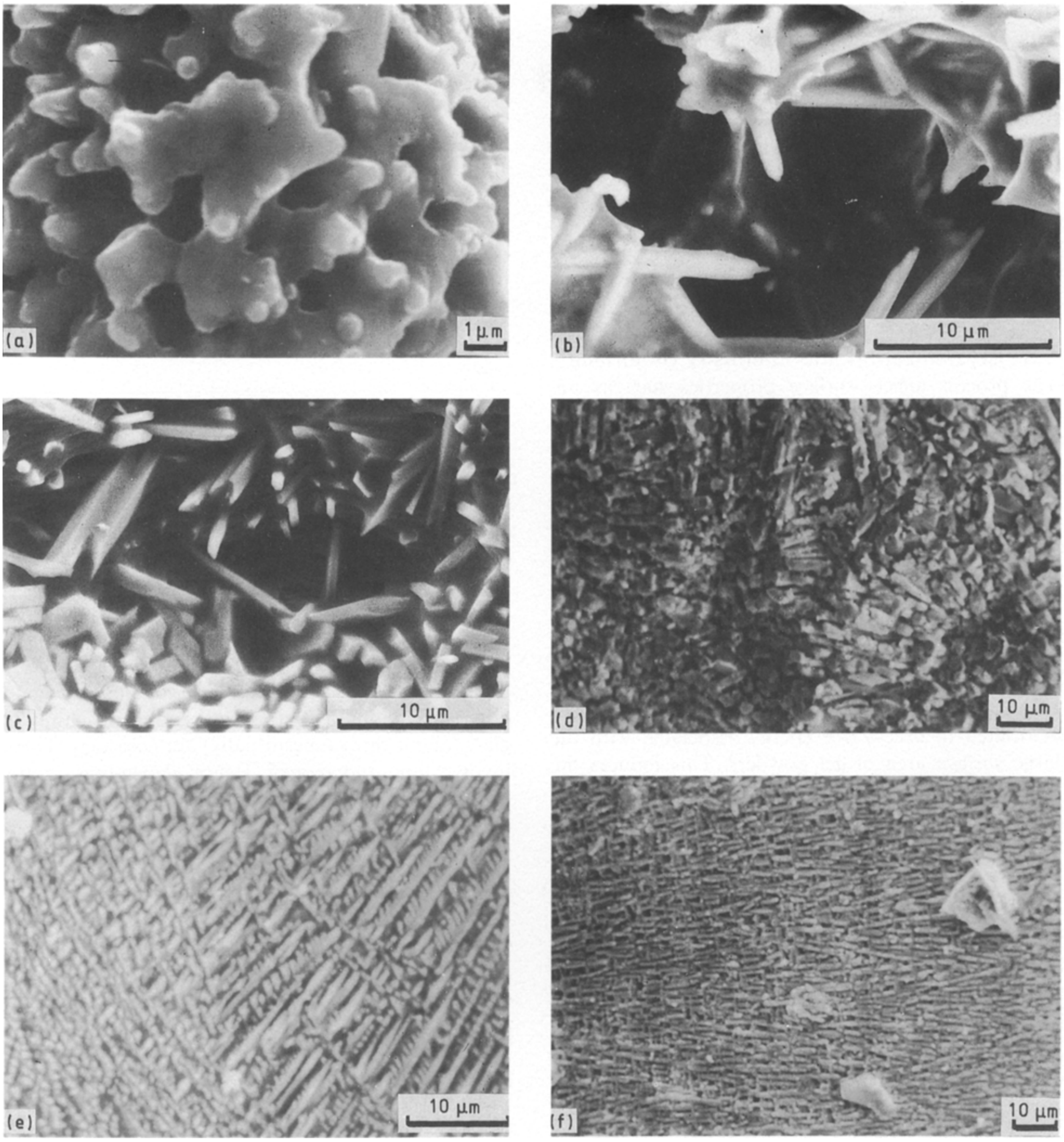

Figure 4 Microstructure of fractured surface in (a) SG1 (1200 °C), (b) SG2 (1200 °C), (c) H1 (1400 °C), (d) H4 (1380 °C), (e) H4 (1100 °C), (f) H3 + Fe_2O_3 (1380 °C).

yttria–alumina–silica glass systems (through melt) T_g ranges between 880 and 895 °C [11] for some compositions with density between 2.86 and 3.81 $g\,cm^{-3}$. Our composition has density 3.21 $g\,cm^{-3}$ for melt-glass and peaks in XRD start appearing above 800 °C. This could be considered as reasonable agreement, though low, for two reasons – the presence of some hydroxyl groups in sol–gel powders is known to reduce the annealing point, and secondly calcia in our sample could act as a flux.

In a multicomponent material the amount of intermixing of components determines the precursor phase and its transformation with heating. The evolution of crystallinity in solution-processed samples was different. The electrostatic interactions that occur in suspension are influenced by solvent pH and ionic strength. The zero point charge varies in oxides, e.g. in alumina it is at pH ~ 6 and in silica at pH ~ 2. In a sol containing both these oxides there is Coulombic attraction between negatively charged silica and positively charged alumina at pH = 2–9. At molecular-level contact, aluminosilicate glass and its solid solution with other ingredients could form. In the C series, an amorphous phase in the absence of gelation is plausible. I.r. spectra of SG(600 °C) and melt-glass are similar, supporting the glassy nature of the precursor. Though C2 and C3 are XRD-amorphous at 600 °C it is likely that some yttria is segregated. From i.r. data the precursor appears to be a mixed phase. This difference could be ascribed to the process. When the zero point charge differs widely amongst components, segregation and coagulation are possible. Clustering can take place either due to electrostatic attraction or van der Waals forces. This results in heterogeneity.

In the sintering of pellets with or without pressure the formation of CYSO glass–ceramic is through solid-state reaction of the crystalline components. In melt-cast samples (H series) the precursor could be glass or nucleated crystallites.

4.3. Crystallization and chemistry of surface

The process affects surface properties such as unbalanced charges, unsaturated bonds and surface area. The difference in crystallization in variedly processed samples could be attributed to surface chemistry. Crystallization involves movement and rearrangement of atoms and bonds. In reactive sol–gel powders a large surface area and defect volume results in a reduced diffusion barrier and lowered viscosity.

Nucleation and crystallization kinetics depend upon the diffusion distances involved and the thermodynamic barrier potential [12]. It has been noted [13] that in silica-gel powder the phase transformation rate is much faster than for vitreous glass, and this was attributed to excess free energy associated with the large surface area of gel powders. This reduces the diffusion barrier energy. Depending upon the level of contact between particles, the diffusion distances to be travelled differ. The homogeneity in mixing, particle sizes and surface chemistry decide these distances. Hence the temperature of crystallization, which depends on the transport distance and barrier potential, becomes dependent on the process. In gelled powders, crystallization to CYSO at 900 °C is due to mixing and contact at molecular level and a lower barrier for diffusion owing to the large surface area. When the intermixing is not so homogeneous due to segregation of components or when the particles are coarse as in the case of C and H series powders, longer diffusion distances are required. Hence a higher temperature is needed to form CYSO.

In a bulk glass prepared from the melt in the absence of additives, homogeneous nucleation is delayed. Development of CYSO phase in melt-glass is above 1100 °C and does not differ for SG2 and oxide melt-glass. Crystallization is at a temperature higher than for SG powder but lower than for the C series. This could arise because in a bulk glass surface defects are absent (the diffusion barrier is not low) compared to sol–gel powders, but transport distances are smaller compared to oxide or C series powders.

Production cost and time comparisons are shown in Table VI. The absolute cost varies with the purity of materials and place of purchase. Hence we show the relative differences in cost as units. Yttria being the most expensive item, the cost of alkoxides does not much influence the cost for batch lots. The costs of power and labour vary and have an influence more because of the duration involved in the heat treatments.

TABLE VI Cost and production comparison for 100 g batches

	Oxide batch heating	Chemical processing	Sol–gel
Raw material cost	1 unit	1.4 units	2 units
Batch produced at a time	100–200 g	Same as oxides	Limited in volume; 20–50 g batch
Time involved	3 days	5 days	7 days
Power cost (calcination + sinter/melt, hot press)	1 unit	2 units	2 units
Homogeneity, purity	Fair	Good	Excellent

In the sol–gel process solvents take up a large volume. Hence the processing could be done only for small batches, which affects manufacturing economy. The time involved for gelation, ageing and dehydration also add to the cost. These are disadvantages in the application of the sol–gel method for production. With commercial oxide powders in the conventional melt process, large quantities could be handled at a time. This reduces the production cost, but for good homogeneity milling of powders and remelting of glass (about three times usually) are necessary. These involve time and money. Hence, depending on the end-use, homogeneity and purity required, the cost effectiveness needs to be assessed for the different processes.

5. Conclusion

The process controls nucleation and crystallization of a glass–ceramic as it influences the surface chemistry, level of mixing of components and barrier potential for diffusion. So we find that

(i) in sol–gel processed powders, which have a large surface area and fine particle size, contact and mixing of particles is at a molecular level, resulting in the formation of glass at low temperatures and crystallization of CYSO phase at > 800 °C;

(ii) in all other powders, owing to segregation and coarser-level contact, YS2 continues up to 1200 °C while CYSO forms at 1400 °C; and

(iii) in melt-cast bulk glass, nucleation is retarded owing to lack of surface or defects; crystallites grow dendritically above 1100 °C and additives accelerate growth.

The above results also show that homogeneity is excellent in sol–gel powders. Cost effectiveness for a process is to be compared according to end-use quality requirements.

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