Crystallization of CaO-Al$_2$O$_3$-SiO$_2$ and CaO-MO-Al$_2$O$_3$-SiO$_2$ (M = Mg, Zn) glasses

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A range of CaO-Al$_2$O$_3$-SiO$_2$ glasses have been prepared by fusion of pure starting materials in platinum crucibles. Compositions containing large amounts on network formers, Al$_2$O$_3$ and SiO$_2$, are difficult to crystallize. If the amount of network former is reduced, glasses will self-nucleate and crystallize more readily, but the products of crystallization tend to react with water. This conflict has been partly resolved by adding MgO and ZnO and tailoring compositions so as to produce a phase, variously designated "Q" or "pleochroite", ideally Ca$_{20}$Al$_{32-2v}$MgvSivO$_{68}$, with v close to 4. Pleochroite crystallizes with a typically fibrous morphology. Preliminary experiments on fragments and melt-cast glass rods indicate that these compositions can be heat treated without deformation to yield highly crystalline, transparent ceramics.

1. Introduction

Although the system CaO-Al$_2$O$_3$-SiO$_2$ has a wide range of glass-forming compositions, and contains inexpensive components, it has not shown promise for the development of glass ceramics, although addition of nucleating agents has promoted crystallization. Stookey [1] studied compositions in the range (wt %) 5-20 CaO, 14-40 Al$_2$O$_3$, 50-80 SiO$_2$ which were nucleated with 11 wt % TiO$_2$. Toropov and Tigonen [2] studied nucleated anorthite-rich compositions along the anorthite-wollastonite binary join and found that Cr$_2$O$_3$ was a better nucleating agent than CaF$_2$, Fe$_2$O$_3$ or TiO$_2$. Topping [3, 4] studied nine compositions in the range (wt %) 24-48 CaO, 0-42 Al$_2$O$_3$, 54-62 SiO$_2$, and found that by using 18 wt % TiO$_2$ as a nucleating agent, the composition range in which good glass ceramic materials could be made was extended significantly.

The present study had two objectives. One was to re-investigate crystallization of CaO-Al$_2$O$_3$-SiO$_2$ compositions without nucleating agents and the second was to chemically modify these compositions, tailoring them so that the added components would either appear in solid solution, or as essential components of single-phase ceramics. The crystallization products of certain CaO-Al$_2$O$_3$-SiO$_2$ glasses are much affected by the presence of MgO as a fourth component. In particular, only low MgO contents are required to stabilize a quaternary phase, Ca$_{20}$Al$_{32-2v}$ · Mg$_v$Si$_v$O$_{68}$, (0 < v < 4) which is designated "Q".

2. Experimental procedure

Glass compositions in the system CaO-Al$_2$O$_3$-SiO$_2$, shown in Fig. 1 were prepared using as starting materials AnalaR grade CaCO$_3$, a very pure (99.9%) Cera alumina (Baco Chemicals) and SiO$_2$ as a very pure ($\leq$ 0.06 insoluble residue in HF) crushed quartz crystal (minus 160 mesh), supplied by Thermal Syndicate Ltd. Glass compositions in the system CaO-(MgO, ZnO)-Al$_2$O$_3$-SiO$_2$ (Table I) were prepared using the same starting materials, with MgO and ZnO as AnalaR grade reagents.

Each glass composition was prepared by weighing out sufficient reagents for $\sim$ 15 g of glass, mixing and blending with acetone slurry and drying under a heat lamp. The batches were pre-reacted for 8-12 h at 1000° C, and melted in uncovered platinum crucibles in an electrically heated furnace with SiC elements at 1500-1530° C. The total duration of the high-temperature melting period was typically 6 h, but every 2 h the melts were water quenched, removed from the crucible, and the crushed glass remelted. The homogeneity of the glass was verified by visual inspection, X-ray diffraction (XRD) and optical microscopy.

TABLE I Quaternary glass compositions and properties

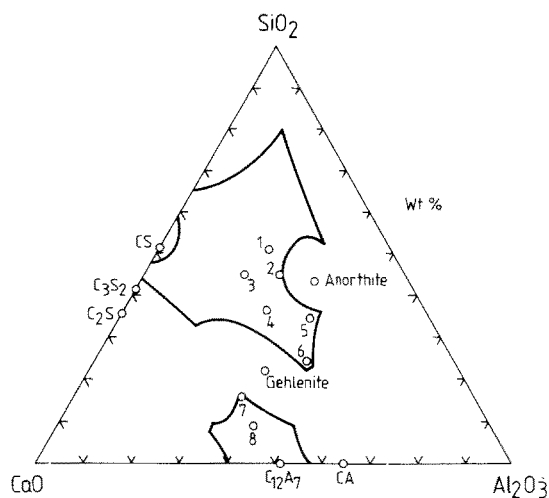| Designation	Oxide composition					Properties	
	CaO	MgO	ZnO	Al$_2$O$_3$	SiO$_2$	n^*	d (kgm^{-3})
I (wt %)	40.81	4.40	0.0	48.23	6.56	1.655	2870
(mol %)	51.28	7.70	0.0	33.32	7.70		
II (wt %)	40.36	3.26	2.19	47.70	6.49	> 1.655	2900
(mol %)	51.28	5.78	1.93	33.32	7.70	< 1.675	
III (wt %)	39.92	2.15	4.34	47.17	6.42	> 1.655	2920
(mol %)	51.28	3.85	3.85	33.32	7.70	< 1.675	
IV (wt %)	39.06	–	8.50	96.16	6.28	> 1.655	2990
(mol %)	51.28	–	7.70	33.32	7.70	< 1.675	

*Refractive index in white light.

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Figure 1 CaO–Al₂O₃–SiO₂ compositions prepared in the course of this study. The position of the 1500° C liquid isotherm is shown.
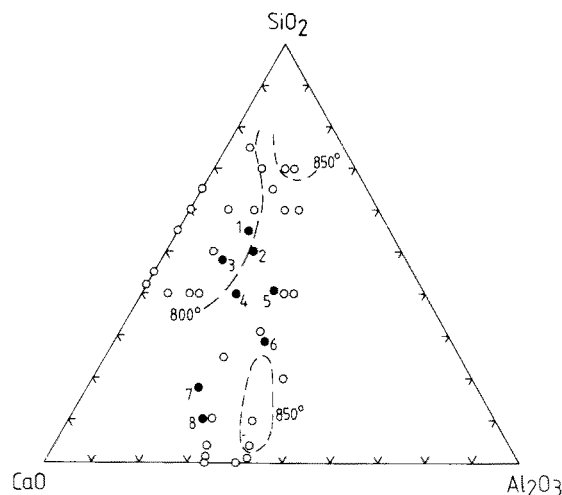

Figure 2 Glass transformation temperatures in the system CaO–Al₂O₃–SiO₂ system. Light open circles are taken from the literature [5]. Darker circles indicate compositions prepared in this study. The positions of the 800° C and 850° C transformation isotherms are suggested by dashed lines. Diagram in (mol %).

To crystallize the glasses, irregular fragments, ~ 5 mm, were annealed in platinum foil envelopes by heating isothermally in an electrical furnace for a selected time usually 2–48 h. A two-step heat treatment was applied to some specimens: a low-temperature primary nucleation treatment was followed by an anneal at somewhat higher temperatures. Crystallization of the heat-treated glasses was investigated by X-ray powder diffraction patterns, obtained on a Hägg–Guinier focusing camera. The microstructural features were examined by optical microscopy and fractured surfaces of selected glass ceramics were also observed by scanning electron microscopy, using a JEOL 2000 EX Temscan. These specimens were lightly etched with HF, washed, dried and coated with gold in an Ion Tech Microsputter ion beam coater. Cross sections of crystallized rods were cut with a diamond wheel, polished with silicon carbide, and etched in 2% HF for 1 min. They were finally carbon coated and examined at 200 kV.

3. Results

3.1. Crystallization of CaO–Al₂O₃–SiO₂ glasses

The glass compositions were chosen to have liquidus temperatures < 1500° C (Fig. 1) and all gave homogeneous glasses after melting. Compositions 1 to 6 gave colourless glasses but those with the highest CaO contents, nos 7 and 8 with 58.9 (mol %) and 61.8 (mol %) respectively, were pale yellow. This characteristic coloration was observed by Shelby [5] who found that glasses containing > 48 mol % CaO were yellow, whereas those containing less CaO were colourless. The colour was attributed to an increase in adsorption over the entire visible region which gradually decreased with increasing wavelength. Glass compositions prepared for the present investigation are shown in Fig. 2, together with those studied by Shelby, and the inferred glass transformation isotherms. In the title study, the glass transition temperature (Tg) was determined by DTA at a heating rate of 10° C min⁻¹.

X-ray diffraction results for glasses heat treated at several temperatures in the range 750–1100° C are summarized in Table I. At 900° C, for up to 48 h,

compositions 1, 3, 5, 6 and 7 did not develop sufficient crystalline material to permit its identification by XRD, while compositions 2, 4 and 8 showed only partial crystallization. Composition 5 was the only one not to show crystallization after treatment at 950° C for 18 h.

Compositions 1, 2 and 6 appeared slightly opaque after treatment at 950° C while glass 8, similarly-treated, showed a pale yellow colour on the surface, but the bulk of the glass consisted of irregular transparent fragments which remained fairly transparent. Compositions 3 and 4 were totally opaque and white after treatment at 950° C, and the particles had undergone deformation indicating that they had been above their softening temperature prior to crystallization. In fact, within the composition range studied, compositions 3 and 4 have the lowest liquidus temperatures [6], and it is also likely that they have the lowest glass transformation and softening temperatures.

After treatment at 1000° C, white-opaque particles of the glass composition 1 were obtained, while compositions 2, 6, 7 and 8 did not soften, 2 and 6 appeared white-opaque and 7 and 8 were pale yellow. After treatment at 1100° C, compositions 2, 6, 7 and 8 did not show apparent deformation, but glasses 7 and 8 deformed and presented a whiter colour.

Examination of powdered samples under polarized light showed that glasses 1 and 2 had developed a crystalline fibrous microstructure at ~ 950° C. However, glass 2 appeared to crystallize slightly better than glass 1 under the same conditions. Compositions no. 3, 4 and 6 developed small needle-like crystals with dendritic structures.

The X-ray powder diffraction patterns of crystallized glasses 1, 2 and 3 were identical with that of a mixture of anorthite, CaAl₂Si₂O₈, and 5CaO–3Al₂O₃; d spacings of the latter phase, after subtraction of reflections due to anorthite, are compared with those reported in the literature in Table II. We refer specifically to the orthorhombic "5 : 3" phase, not to the cubic 12:7 mole ratio calcium aluminate phase, (which was incorrectly characterized in older literature

as also having the 5:3 ratio). The fibrous microstructure is believed to be due to the presence of the orthorhombic $5CaO \cdot 3Al_2O_3$ phase.

Optical microscopy indicated that glass 5 was the most difficult to crystallize but no special microstructural features were noted. In X-ray powder diffraction patterns of crystallized glasses 5 and 6, a considerable number of reflections due to $CaO \cdot Al_2O_3 \cdot SiO_2$, were encountered, and it was the predominant crystalline phase in glass 5 after treatment at 1000° C; a comparison of d-spacings values is shown in Table III.

Microscopic examination of heat treated glass 7 showed that bulk nucleation and crystallization had occurred; spherulitic crystals of $CaO \cdot Al_2O_3$ and $2CaO \cdot SiO_2$, with fibres radiating from a common centre, were present after a two-stage treatment: 850° C (15 h) + 1000° C (5 h). The amount of glassy phase in specimens from composition 8 appeared to be less than in specimens from composition 7, in which fibrous crystals of $12CaO \cdot 7Al_2O_3$ and $CaO \cdot Al_2O_3$ were developed at temperatures $\geqslant 950°$ C.

None of these glass compositions showed sufficient promise to warrant further investigation, for example, of their mechanical properties. However, the fibrous nature of the 5:3 aluminate suggested that a desirable microstructure could be conditioned. This particular crystalline product is, however, of uncertain thermodynamic stability, and its synthesis is not reliably reproducible. But it did initiate a systematic survey of candidate fibrous crystalline phases which could be induced to form with minimal changes to the CaO–Al_2O_3–SiO_2 base compositions.

3.2. Crystallization of CaO–(MgO, ZnO)–Al₂O₃–SiO₂ glasses

All compositions listed in Table I were easily melted at 1500° C, giving pale yellow glasses, similar in colour to comparable $CaO \cdot Al_2O_3 \cdot SiO_2$ glasses.

Traces of the Q phase were noted by X-ray diffraction in the powder pattern of a glass of the Q composition after annealing at 900° C for 16 h: the others were largely glassy. Crystallization was improved in all four compositions when a two-stage treatment, 850° C (24 h) followed by 900° C (16 h), was used, and two-stage treatments were generally used in subsequent crystallizations.

The yellow colour of the MgO-containing glasses (I, II and III) turned paler upon heating for long periods (> 48 h) at 900° C, while at higher temperatures they became more opaque, eventually becoming grey after annealing at 1200° C. The appearance of opacity in glass (IV), in which MgO had been totally substituted by ZnO, occurred only after heating at 1100° C and the glasses became grey-white at 1200° C. A striking feature of glass IV was that, when crystallized at somewhat lower temperatures, typically 1000° C, it yielded much Q phase but still remained transparent in 1–2 mm fragments. Figures 3–6 shows the microstructure of some of these crystalline but optically-transparent materials. Figure 3 shows the cellular–fibrous morphology of glasses which devitrified Q phase. Plate-like aggregates of radiating fibres develop. Etching, which is most severe along plate boundaries, reveals

TABLE II Comparison between X-ray data for the minor phase in compositions 1, 2 and 3 and $5CaO \cdot 3Al_2O_3$

Extra phase		$5CaO \cdot 3Al_2O_3$	
d (nm)	I	d^* (nm)	I^*
0.77	vvw	0.790	12
0.385	w	0.394	20
0.352	mw	0.356	20
0.331	m	0.337	50
0.305	mw	0.315	40
0.298	s	0.293	100
0.284	m	0.289	90

v = very, w = weak, m = medium, s = strong.
*X-ray data from [9].

TABLE III Comparison of X-ray data for the minor phase in composition 5 and $CaO \cdot Al_2O_3$–SiO_2

d (nm)	I	$CaO \cdot Al_2O_3 \cdot SiO_2$	
		d (nm)	I^*
0.858	mw	0.860	17
0.302	ms	0.303	30
0.297	vs	0.298	100
0.285	ms	0.287	30

v = very, m = medium, w = weak, s = strong.
*X-ray data from [10].
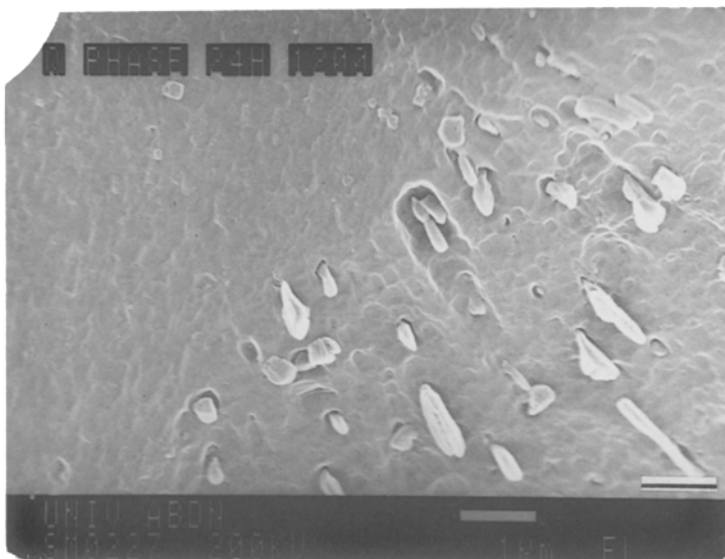
the fibre structure. At 1200° C, the fibrous structure alters completely (Fig. 4). A few fibres persist, well-dispersed in a fine-grained matrix which is largely crystalline but relatively featureless. Cross sections at two magnifications show the radiating fibrous morphologies favoured by ZnO-containing compositions. The outer surface of a fragment is shown at the top left corner, Fig. 5; spherulitic crystallites radiate inwards. Fig. 6 shows the complex crystallite morphology at higher magnifications. However, particles from glass IV (the highest in ZnO) adhere to each other at 1100° C, while the other compositions sintered appreciably only after heating at 1200° C, suggesting greater fluidity of the high ZnO compositions.

The X-ray powder diffraction of all the zinc-containing glass compositions were identical to the indexed X-ray powder diffraction pattern of the Q phase; XRD results and optical microscopy examination indicated that glass I completely crystallized at 1250° C for 48 h, in agreement with previous results [7].

The crystallized Zn-containing Q phases exhibited strong optical pleochroism, like their isostructural magnesium counterparts. However, while those from the Mg-Q composition showed a pleochroic variation from deep-purple-blue to grey or colourless, the Zn-Q products typically showed a variation from deep-purple-blue to yellowish-brown. Individual crystallites grew as needles with low optical birefringence and a mean refractive index of 1.70 ± 0.01. The mean refractive index is not very sensitive to variation in the Mg/Zn ratio, despite the greater molar refractivity of Zn presumably because of the low total cation content of M^{2+} ions.

3.3. Optical properties of crystallized glasses containing Q phase

Calcium aluminate glasses exhibit good transparency across a wide range of frequencies, and although silicon increases somewhat the absorbance, glasses close to the Q composition also exhibit generally good transmission. Figure 7 shows two representative spectra from glass IV: Fig. 7a is from a glass disc ∼ 2 mm thick in the range 4000–600 cm^{-1}; the spectra has been smoothed to eliminate sharp absorptions arising from traces of water, CO_2, etc. The broad dip in transmission in the vicinity of 3400 cm^{-1} is tentatively attributed to residual OH^- attached to Al. A sharp cutoff becomes apparent below ∼ 2200 cm^{-1}. The glass spectra may be contrasted with that of an equivalent thickness of crystalline Q from glass IV devitrified at 1000° C, and shown by X-ray diffraction to be highly crystalline (Fig. 7b). The transmittivity remains high
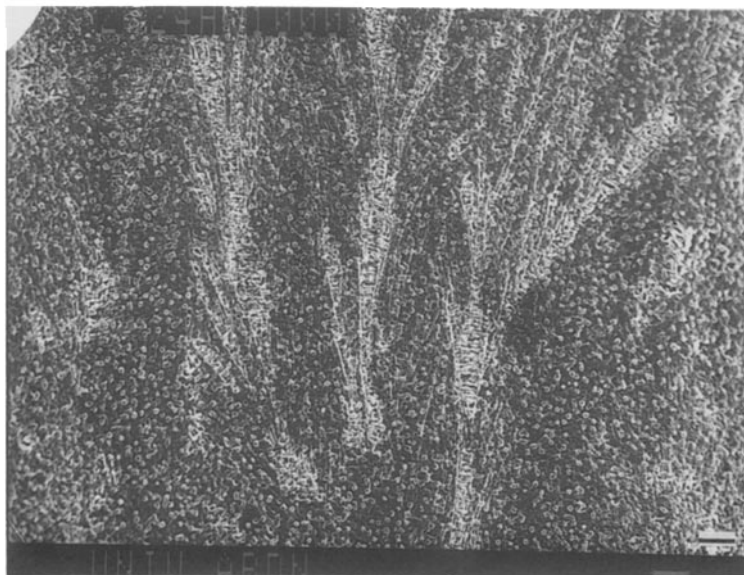
Figure 6 Scanning electron micrograph of a fractured surface of crystallized glass of composition (51.28 CaO, 7.70 ZnO, 33.32 Al_2O_3, 7.70 SiO_2 (mol%)) heat treated for 24 h at 1000°C. Same etching conditions. Scale bar = ?.

across a broad range of frequencies, a cutoff becoming apparent only below $\sim 1200 \, cm^{-1}$.

3.4. Mechanical properties of Q-phase glass–ceramics

Glass–ceramic rods $\sim 85 \, m \times 8 \, mm$ were prepared by casting glass into a heated cylindrical mould. The cooled glass rods were somewhat imperfect owing to difficulties in casting; small-scale melts cool quickly, and increase rapidly in viscosity before forming could be completed. The majority of the rods were oval in cross section, which ranged from 7 to 10 mm in diameter and their surfaces were somewhat lumpy. However, the as-fabricated rods were essentially completely glassy. Any conspicuous surface irregularities were first removed by grinding, and the smoothed rods heat treated for $\sim 24 \, h$ at 850°C followed by $\sim 16 \, h$ at 900°C. The modulus of rupture was obtained in 3-point

bending tests on an Instron Universal testing machine, operated at a cross-head speed of $1 \, mm \, min^{-1}$. Since only a few glass rods were available, the results can only be taken as indicative of the strengths. In general, the modulus of rupture of the glassy rods range between 117 and 275 MPa but for glasses I and III, crystallization produced a substantial enhancement in strength. Figure 8 shows the surface of the fractured rod, obtained at high tilt. At the top right, the exterior surface of the rod, bearing polishing scratches can be seen. The fracture surface consists of a series of stepped plates; each plate is composed of numerous sub parallel fibres. Little evidence of conchoidal fracture occurs, except perhaps at the circumference of the rod.

4. Discussion

The results demonstrate the influence of composition on the extent to which self-nucleation occurs, on the nature of the phases obtained, and of phase morphology. In the course of the title study, only a small range of compositions has been investigated but even within these limits a wide range of behaviour was encountered.

Glasses such as 3, 4 and 6 crystallized anorthite or gehlenite, or mixtures of the two. Anorthite is a particularly desirable target phase on account of its hardness, resistance to chemical attack and the
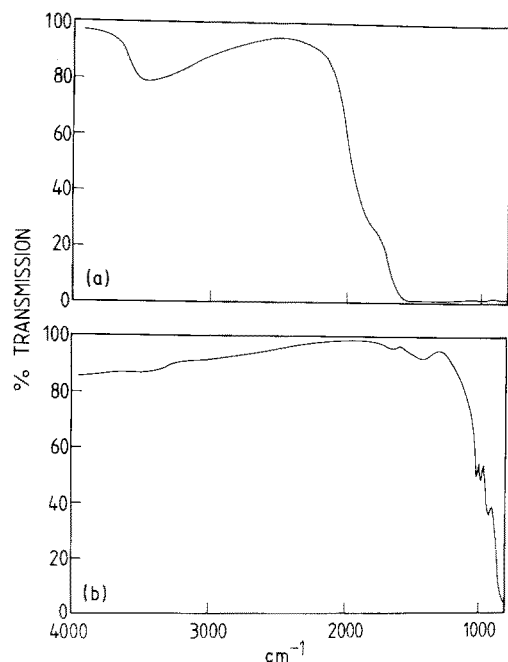

Figure 7 Infrared transmission of a 2 mm thickness of glass IV (a) as-prepared and (b) after crystallization for 24 h at 1000°C. Both were obtained in double beam mode against KBr blank.
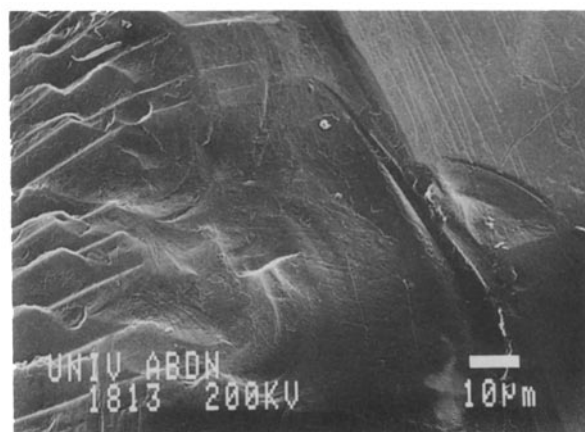

Figure 8 Scanning electron micrograph of the fracture surface of a transparent but crystalline rod broken in the course of strength measurement.

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favourable, fine-grained microstructures. However it is not a good subject for self-nucleation, and much residual glass is retained. Glasses 3 and 4 softened before much crystallization had occurred, although glass 6 remained fairly rigid with less sign of deformation.

Glasses containing less network former, such as 7 and 8, crystallized readily, but yielded phases known to be rather soluble in water, e.g. $12CaO \cdot 7Al_2O_3$, and on that account are unlikely to give rise to durable ceramics. Composition 3, and to a lesser extent 2, gave products which include orthorhombic $5CaO \cdot 3Al_2O_3$. This phase has a fibrous habit but its resistance to water, while greater than that of other calcium aluminates of similar mole ratios, e.g. 12:7 (from which it differs by only $\sim 0.7 \text{mol} \%$), is unlikely to be good. The occurrence of $5CaO \cdot 3Al_2O_3$ is noteworthy: it is difficult to obtain from relatively pure calcium aluminate compositions but is almost certainly stabilized in ternary compositions by crystallochemical incorporation of SiO_2. Another noteworthy feature of the devitrification of these low-SiO_2 compositions is the appearance of the $CaO \cdot Al_2O_3 \cdot SiO_2$ phase as in compositions 5 and 6; little is known about it properties. The present data are not sufficient to delineate the optimum crystallization conditions for each melt. But compositions giving high yields of $CaO \cdot Al_2O_3 \cdot SiO_2$, or of anorthite, are viewed as having the best potential for further investigation. Optimization is likely to have as its objective the production of fine grained, pore-free, bulk devitrifications, as these are known to favour good ceramics [8].

Chemically more-complex glasses, containing at least four oxide components, have also been studied: these include as components CaO, Al_2O_3 and Al_2O_3, together with either or both MgO and ZnO. The strategy adopted for ceramic development in these more complex compositions was to focus on selecting a particular target phase, in this instance Q, and optimizing its yield by adjusting both parent glass compositions and thermal treatment. Results indicate that translucency and good strengths can be maintained during crystallization. The rather fibrous nature of the crystalline product and the interlocking of fibres into radiating fan-shaped platy aggregates are considered advantageous for production of ceramic products with good moduli of rupture. Moreover, the Q phase is reasonably tolerant of chemical substitution; Mg, Al and Si can to a limited extent replace each other, and moreover, Mg can be partially or wholly replaced by Zn. This permits some flexibility in adjusting the glass bulk composition without at the same time, having a multiphase ceramic product.

The results obtained on the system CaO–(Mg, Zn)O–Al_2O_3–SiO_2 illustrate the importance of chemical composition and its relationship to phase composition and microstructures. The zinc analogue of pleochroite has been synthesized for the first time, and shown to form continuous solid solution with the magnesian phase. The total content of (Mg, Zn)O required to stabilise the Q phase is small, only a few weight percent, yet the microstructure of the resulting ceramic is completely transformed by their addition to CaO–Al_2O_3–SiO_2 compositions. Under favourable conditions, crystals of the Q phase grow as plates consisting of radiating, slightly sub-parallel needles. The plate structures form stacks or spherulitic aggregates, the exact form depending on crystallization temperature. These favourable microstructures cannot be dependably obtained in "base" CaO–Al_2O_3–SiO_2 compositions, demonstrating the importance of the MO oxide addition.

5. Conclusions

The results indicate that the morphology of the crystallized phases in both CaO–Al_2O_3–SiO_2 and CaO–MgO–ZnO–Al_2O_3–SiO_2 systems are strongly dependent on the glass composition and thermal treatment. Crystallization was enhanced if a two-stage treatment was applied relative to a single crystallization treatment at the highest temperature.

Glasses close in composition to the quaternary compound, Q, with or without substitution of ZnO for MgO, began to crystallize at lower temperatures than corresponding chemically simpler glasses in the system CaO–Al_2O_3–SiO_2.

Essentially identical X-ray powder diffraction patterns were obtained for the crystallized glasses resulting from phase composition Q in which part or all MgO had been substituted by ZnO. Glasses containing MgO at the highest level tended to give a coarse spherulitic structure which was destroyed upon heating at higher temperatures ultimately giving a fine grained, equiaxed microstructure. However the gradual substitution of MgO by ZnO also promoted the appearance of fine-grained structures but with persistent fibrous microstructures. Transparent but highly crystalline ceramics have been produced having good mechanical strengths.

References

1. S. D. STOOKEY, "Method of Making Ceramics and Product Thereof", US Patent 2,920,971, January, 1960.
2. N. A. TOROPOV and G. V. TIGONEN, *Inorg. Mater. (USSR)* **3** (11) (1967) 1789.
3. J. A. TOPPING, *J. Can. Ceram. Soc.* **45** (1976) 63.
4. *Idem*, *Amer. Ceram. Soc. Bull.* **56** (6) (1977) 574, 577.
5. J. L. SHELBY, *J. Amer. Ceram. Soc.* **68** (3) (1985) 155.
6. E. M. LEVIN, C. R. ROBBINS and H. F. McMURDIE, "Phase Diagrams for Ceramists", Vol. 1 (American Ceramic Society, Inc. 1964) Figure 630, p. 219.
7. I. KAPRALIK and F. HANIC, *ibid.* **79** (1980) 128.
8. P. W. McMILLAN, "Glass Ceramics", (Academic Press, London, 1969) 2nd edn.
9. J. ARUYA, *Acta Cryst.* **10** (1957) 337.
10. R. KIRKPATRICK and I. STEELE, *Am. Mineral.* **58** (1973) 545.