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Structural and microstructural transitions during phase separation and crystallization of Al_2O_3–SiO_2–P_2O_5–Y_2O_3 glass

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A highly refractory glass in the system Al_2O_3–SiO_2–P_2O_5–Y_2O_3 has been designed and produced such that, upon heating, an essentially fully crystalline glass–ceramic evolves containing mullite (nominally $3Al_2O_3 \cdot 2SiO_2$) and xenotime (YPO_4) as the final principal phases. Phase separation in this glass occurred during cooling from the melt and continued during annealing. XPS of the Al 2p, P 2p and the Y 3d electrons revealed that the average chemical environment of each of these elements is measurably different in the annealed glass and in the completely crystallized material. This indicates that the compositions of the separated glass phases are very different from those of the crystal phases which form from them. Additional rearrangement of the glass structure was observed at 1173 K. Extensive formation of mullite was initially detected at 1223 K and was followed by the crystallization of xenotime and the transient compounds of $Y_4Al_2O_9$, $Y_2Si_2O_7$, $AlPO_4$ and YP_5O_{14}. The optimum crystal nucleation and crystallization temperatures of 1173 and 1473 K, respectively, were determined from DTA, XRD, SEM and TEM studies.

1. Introduction

A glass–ceramic is produced by the process of controlled nucleation and crystallization of a previously prepared glass. In most glass–ceramics the compositional formulation, in concert with a well-defined multi-step heat treatment process, induces several phase transformations. The initial transformations such as liquid–liquid immiscibility, provide important precursor phases which promote the eventual formation and growth of the desired crystalline phases.

The objectives of the research described below were the studies of glass formation, the resulting atomic structure of the annealed glass and the nucleation and progressive cyrstallization in the system Al_2O_3–SiO_2–P_2O_5–Y_2O_3. The driving force for this research programme was the need for high melting point structural ceramic materials which could be formed easily in the variety of complex shapes found in glass products. The particular composition shown in Table I[†] was selected from the system noted above, because it contained ratios of the components such that a completely crystallized glass containing the refractory phase of mullite (melting point, m.p. = 2101 K [1]) and xenotime (YPO_4, m.p. > 2073 K [2, 3]) could be formed. The decision to conduct structural studies of the uncrystallized glass was made after it became evident that the solubility of Al_2O_3 was far greater in this material than had been anticipated. This solubility also exceeded considerably the maximum concentrations possible in other SiO_2-based glasses. The mechanism(s) of underlying the incorporation of these high Al_2O_3 concentrations were believed to be structurally controlled. Thus, the specific objective of the X-ray photoelectron spectroscopy (XPS) research was to determine whether the changes in the tetra-

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[†] All the compositions in this paper are given in mol % unless otherwise stated.

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TABLE I The glass composition* of interest in terms of the mole percentages of the constituent oxides

Oxide	(mol %)
Al_2O_3	49.2
SiO_2	32.8
P_2O_5	9.0
Y_2O_3	9.0

*The above composition will frequently be referred to as AlSiPYO-glass.

hedral $[AlO_4]$ to octahedral $[AlO_6]$ arrangement of aluminium in the glass structure could be detected through differences in the qualitative character of the Al 2p core state. As implied above, the results of this research have technological ramifications in that they have demonstrated how and why one may substantially increase the Al_2O_3 concentration in a SiO_2-based glass to produce a very refractory glass–ceramic superior to any currently available.

2. Experimental procedure

Batch materials composed of A-14 Al_2O_3,[‡] CS-200 Supersil sand,[§] $Al(PO_3)_3$[¶] and Y_2O_3[1] were tumble mixed for 10.8 x 10^3 sec (3 h) in the percentages given in Table I, melted in 70% Pt–30%Rh crucibles at 2123 K for 14.4 x 10^3 sec (4 h), formed into bubble free glass plates in covered 12 x 10^{-2} m x 12 x 10^{-2} m x 0.6 x 10^{-2} m mild steel moulds, annealed at 923 K for 14.4 x 10^3 sec (4 h) and allowed to cool in the furnace.

A large variety of methods were employed to characterize the as-formed AlSiPYO-glass and the physical and chemical changes which occur in this glass as a result of heat treatment at progressively higher temperatures. X-ray photoelectron spectroscopy (XPS) has provided unique information concerning the atomic arrangement of the annealed and the crystallized glasses. These analyses were conducted[2] using a Physical Electronics Model PHI 550 spectrometer[3] with monochromatic Mg$K\alpha$ X-rays. Samples of the primary glass as well as standards of sapphire,[4] fused cast mullite[5] (nominally $2Al_2O_3 \cdot SiO_2$), berlinite[6] (single crystal $AlPO_4$), and $57Al_2O_3$–$28SiO_2$–$15P_2O_5$ glasses[7] were prepared by diamond cutting small blocks having the dimensions of 1 x 10^{-2} m x 1 x 2^{-2} m x 0.07 x 10^{-2} m which were subsequently ground[8] and polished[9] on both sides. From the recorded electron spectra the binding energies of the core electrons of the different elements were determined. For the high resolution scans, the relative position of a spectral peak could be determined within ± 0.1 eV. All of the materials studied were highly insulating and therefore charged under the strong X-ray irradiation. The amount of charging was determined from the position of an Ar 2p peak (at 241.50 ± 0.1 eV); argon was present on all sample surfaces as a result of the surface sputter-etch cleaning procedure employed. For the high resolution measurements, all core state binding energies were adjusted by the difference between the measured value of the Ar 2p in that sample and an assumed value of 241.5 eV. The different values of the binding energies of the core electrons of the different elements provided important information on the formation of the glass in that selected system of oxides. A detailed description of the experimental procedures and the methods employed in the evaluation of results can be found in [4].

Differential thermal analyses (DTA) were used as one indicator of the range of temperatures necessary to produce crystallization within the bulk of the glass.[10] A powdered sample[11] of the

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[‡] Alcoa, Inc., Pittsburgh, PA, USA.

[§] Cabot Corporation, Boston, MA, USA.

[¶] Stauffer, Inc., Westport, CN, USA.

[1] Molycorp, Inc., White Plains, NY, USA.

[2] The XPS research was conducted at Energy Conversion Devices, Inc., Troy, MI, USA.

[3] Perkin Elmer Corporation, Eden Prairie, MN, USA.

[4] Linde, Division of Union Carbide, Torrance, CA, USA.

[5] Carborundum Company, Niagara Falls, NY, USA.

[6] Allied Chemicals Corp., Morristown, NJ (courtesy of Dr B. H. T. Chai).

[7] Corning Glass Works, Corning NY. This glass composition will be referred to as AlSiPO-glass. It was used by Dr B. S. Lee in research described in [17].

[8] 63.5 X 10^6 m (400 grit) and 42.3 X 10^{-6} m (600 grit) SiC paper was employed.

[9] A water suspension of 1 X 10^{-6} m and 0.3 X 10^{-6} m α-Al_2O_3, and 0.05 X 10^{-6} m γ-Al_2O_3 was employed.

[10] This aspect of the research was conducted by the Thermal Analysis Department of Harrop Laboratories, Columbus, OH.

[11] The amount of 0.2 X 10^{-3} kg of 425 X 10^{-6} m to 635 X 10^{-6} m material was selectively screened from the crushed product.

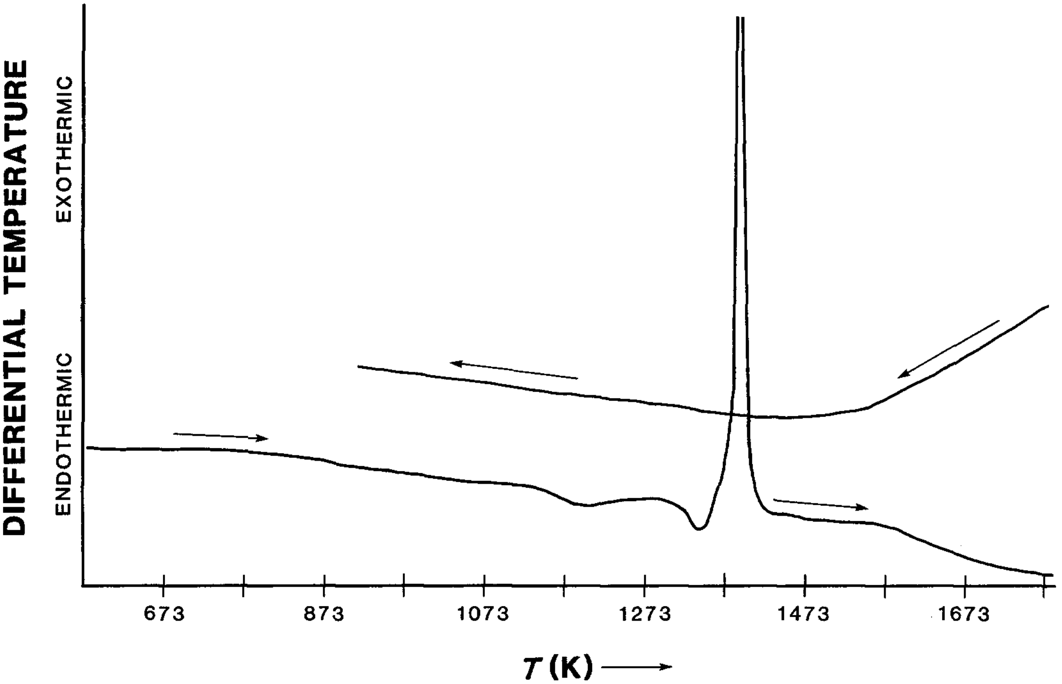

Figure 1 Heating and cooling DTA curves of the annealed AlSiPYO glass.

annealed AlSiPYO-glass was heated in 99.8% Al_2O_3 crucibles to a maximum temperature of 1723 K at a programmed rate of 12.5 K min^{-1} in static air. Al_2O_3 was employed as a reference material. From the DTA curve shown in Fig. 1, the temperature of 1473 K was chosen as an approximate crystallization temperature. The progression of crystallization in the heat-treated glass was also monitored by the change in densities as measured in the Archimedes method.

The crystalline phases present in the as-cooled, annealed and systematically heat-treated samples were identified by using both a high resolution X-ray powder diffraction technique[12] [5] and the selected area diffraction (SAD) method.[13] Thin sections for the latter technique were obtained by using argon ion milling.[14] In addition the etched and unetched fractured surfaces of the as-formed, annealed and the progressively crystallized glasses were investigated using SEM.[15] In addition, carbon replicas of the surface features of the polished and the etched samples were prepared by the double stage technique and examined at higher magnifications by transmission electron microscopy (TEM).

3. Results and discussion

3.1. Structural considerations of glass formation

In the initial formulation of the glass composition used in this research, theoretical consideration was given to the structural roles within the glass of the cations of each oxide according to their size and resulting field strength, as well as, their electronegativities and bond energies. The maintenance of electroneutrality in the glass was also considered. Based on classical structural theories of glass formation [6–14], it was initially assumed that Si^{4+} and P^{5+} would act as network formers, Y^{3+} as a network modifier and Al^{3+} as a network former and/or modifier depending on the composition. The presence of P_2O_5 allows an equal amount of Al_2O_3 to become stabilized in tetrahedral positions in the glass. Furthermore, each Y^{3+} in its modifying position may neutralize 3 $(AlO_4)^-$ groups and thus allow additional Al_2O_3

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[12] Ni-filtered Cu$K\alpha$ radiation was employed at 40 × 10^3 V and 10 × 10^{-3} A.

[13] A JEM Model 120 (Jeol Inc., Japan) TEM was employed at 80 kV.

[14] Commonwealth Scientific Corp., Alexandria, VA. This mill was operated at 4 × 10^3 V and an ion current of 9 × 10^{-5} A.

[15] An Autoscan, (ETEC Corp., Hayward, CA) was used at an acceleration voltage of 20 × 10^3 V.

to be added to the glass. The remaining 13.2 mol % Al_2O_3 must be distributed in the SiO_2 network, and one-fourth of that amount must act as a modifier to compensate for the excess negative charge on these last $(AlO_4)^-$ groups.[16]

3.2. Spectroscopic and microscopic analyses of glass formation and phase transformation

The foregoing theoretical discussion is based on the assumption that the assumed structural roles of the various cations are maintained in that glass at all temperatures. However, it is a basic tenet of crystal chemistry that the coordination number of the cationic species tends to decrease as temperature is increased. It is reasonable to assume that at the 2123 K temperature of melting, most of the Al^{3+} occupies quasi-tetrahedral positions [15–17]. However, it is strongly believed that if given sufficient time at much lower temperatures, a portion of Al^{3+} will tend to revert to the octahedral coordination and, in turn, promote phase separation in the glass. In addition, the composition of the Al_2O_3–SiO_2 subsystem in this glass, as calculated from the above composition of the complex system Al_2O_3–SiO_2–P_2O_5–Y_2O_3 (see footnote 16), is in the reported region of spinodal decomposition [15, 18]. Furthermore, in the competition for oxygen, P^{5+} is also believed to promote phase separation, as described below. As a result of these phenomena, liquid immiscibility on a very fine scale was expected and is revealed in the electron micrograph of the heavily etched (23.0% HF for 30 sec) unannealed glass shown in Fig. 2a. Coalescence of these phase-separated droplets also occurred during annealing, as shown in the micrographs of Figs. 2b and c.

The measured binding energies for the P 2p, Si 2p, Al 2p, O 1s, and Y 3d core electrons of the standards and the investigated glass are presented

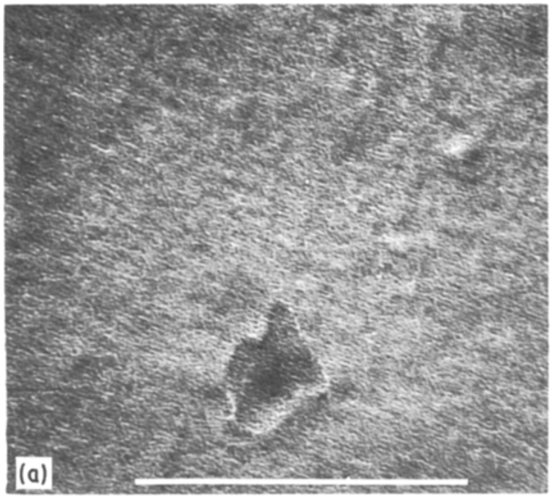
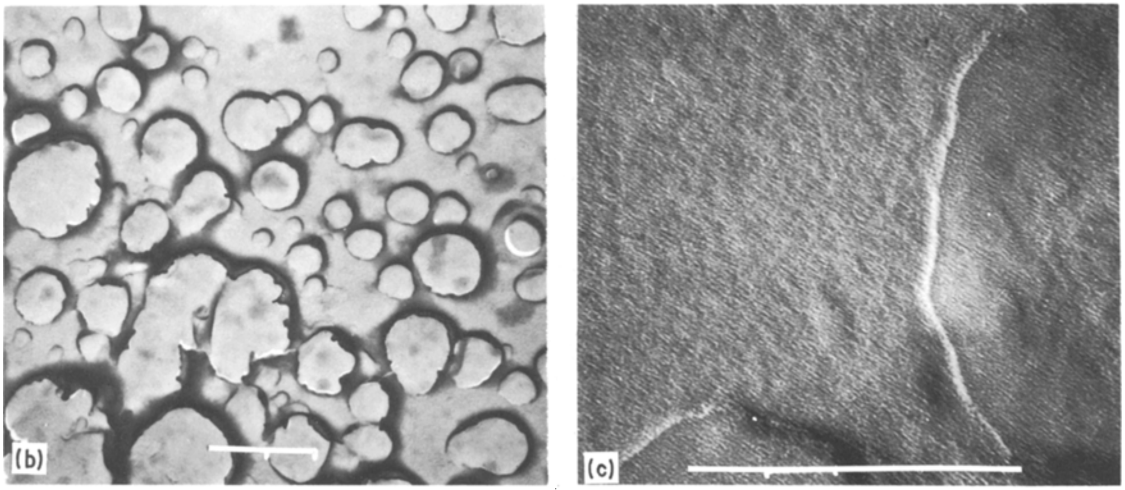


Figure 2 TEM replicas of heavily etched (23% HF for 30 sec) (a) unannealed and (b), (c) annealed (923 K for 14.4×10^3 sec) AlSiPYO glass showing initial phase separation and subsequent coalescence of the droplet phase (bar = 0.5×10^{-6} m in Figs. 2a and c; bar = 1.0×10^{-6} m in Fig. 2b).



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[16] This binary mixture of 13.2 mol % Al_2O_3 and 32.8 mol % SiO_2 (the amount of SiO_2 in the original composition) has the normalized composition of 28.7 mol % Al_2O_3 and 61.3 mol % SiO_2. This will be referred to as the "Al_2O_3–SiO_2 subsystem" in the remainder of this paper.

TABLE II The measured binding energies (in eV) for standards and AlSiPYO-glass

Compound	P 2p	Si 2p	Al 2p	O 1s	Y 3d*
Al_2O_3	–	–	74.1	531.1	–
SiO_2	–	103.0	–	532.4	–
$2Al_2O_3$–SiO_2†	–	102.0	74.6	531.5	–
AlSiPO glass	134.2	102.3	74.7	531.8	–
AlSiPYO glass	133.9	102.0	74.3	531.2	158.2
$AlPO_4$	134.3	–	75.0	532.3	–
AlSiPYO glass cryst‡	131.3	102.5	74.5	531.2	157.4
AlSiPYO glass cryst§	131.3	102.5	74.5	531.5	157.6

*The reported value is the lower binding energy of the Y 3d doublet.

†Although the composition of the mullite which crystallizes from the glass is $3Al_2O_3 \cdot 2SiO_2$, the calculated difference in binding energies for the Al 2p core electrons between the 3 : 2 and the 2 : 1 composition is only 0.05 eV which is outside the resolution of the spectrometer.

‡Glass with the heat treatment for 14.4×10^3 sec (4 h) at each 1173 and 1473 K.

§Glass with the heat treatment for 14.4×10^3 sec (4 h) at each 1173 and 1623 K.

in Table II. These binding energies depend on the chemical enivornment of the particular ion, as described in more detail in [4], and are, therefore, affected by the local atomic arrangement in the investigated material. As expected, the measured binding energies of the Si 2p core electrons in the annealed and progressively crystallized glass did not vary significantly from the values obtained from the standards (see Table II). However, the changes in the measured binding energies of the P 2p, Al 2p and Y 3d core electrons indicate that extensive structural rearrangement in the chemical environment of these elements occurred during crystallization of the glass.

Roy [19] has suggested that one or more of the liquids in a phase separated glass has a composition close to that of particular crystalline compounds or solid solutions. Although this may be true in some cases, the necessity for compositional similarity in order that crystalline phases may evolve has been earlier questioned by Hillig [20]. It is also brought into question by some of the results of this research. It might be expected that the position of the Al 2p peak in the AlSiPYO-glass after cooling and annealing be near to that for mullite, which is the predominant compound in the set of crystallized materials. However, its position was found to be slightly closer to that of aluminium in Al_2O_3. Since the binding energy depends on the chemical environment of a particular element rather than the prevailing structure, the observed chemical shift of this peak suggests an average environment around the Al^{3+} which is different from that which exists in both mullite and Al_2O_3. After nearly complete crystallization of this glass, the position of Al 2p peak was nearly the same as the value measured in mullite (see Table II). Similarly, the shift in the binding energies of the P 2p and the Y 3d electrons from the annealed glass to the crystalline compound YPO_4 in the fully crystallized material indicates an environment around these ions which is also notably different in the two materials.

Mullite is also the major compound which crystallizes (along with $AlPO_4$) in the AlSiPO glass. However, in this annealed material, the binding energies of both the Al 2p and the P 2p are very similar to the analogous values found in mullite and $AlPO_4$, respectively. This suggests that, in this case, the environments of these ions and the compositions of the separated glass phases are indeed similar to the phases in the fully crystallized glass.

From a microstructural viewpoint, Figs. 2b and c reveal that the droplet phase in the annealed glass etched more readily in HF than the matrix. This suggests that the droplet phase is a P_2O_5-rich glass. It is also believed to contain both Al_2O_3 and Y_2O_3. Because of its high field strength, P^{5+} competes strongly for O^{2-} with Si^{4+} and Al^{3+} and will, therefore, phase separate from a silicate network during cooling, together with Al^{3+} and Y^{3+} to maintain the charge balance. As noted in Table II, the binding energy of the P 2p electrons in the annealed AlSiPYO glass is lower than for pure $AlPO_4$ which is indicative of the presence of an element with a lower electronegativity than that of Al^{3+} [4]. This would be Y^{3+} in this particular glass. The matrix phase remains rich in Al_2O_3 and SiO_2 with some Y_2O_3 also present which enables a portion of the Al^{3+} to remain in tetrahedral coordination.

The characteristic droplets-in-matrix microstructure of the annealed glass shown in Figs. 2b and c was not retained during heat treatments at 1173 K and higher temperatures. In the following discussion it will be shown that during the heat treatment of the glass at these higher temperatures, extensive rearrangement occurred which enabled the subsequent formation and growth of the major crystalline phases of mullite and xenotime.

3.3. Nucleation and growth of the crystalline phases

X-ray data of Table III show that a small amount of mullite crystallized from the glass during cooling. Similar crystallization has also been reported by other investigators [15, 18]. The microstructure of the samples heat-treated at 1173 K shown in Fig. 3 indicates the occurrence of an extensive structural rearrangement. The X-ray diffraction (XRD) results (Table III) reveal that the intensity of the mullite lines increased with increasing time at 1223 K. The growth of mullite crystallites at this temperature was observed by scanning electron microscopy (SEM) as very small white areas near the boundaries, as shown in Fig. 4. However, the range of densities of these specimens reported in Table IV remained essentially unchanged as a function of time. In addition to the phases of mullite, YPO_4, $Y_2Si_2O_7$ and $AlPO_4$ detected by XRD, the results of electron diffraction on thin sections of the glasses, heated only at 1273 K for 68.4×10^3 sec (19 h), detected the compound with the composition YP_5O_{14}. The diffraction pattern of this ultraphosphate phase corresponds to the orthorhombic form reported by Bargieu-Beucher and Tranquil [21] and Durif [22]. According to the results of these and other investigators [21–23], this compound melts incongruently at 1133 ± 10 K; however, it was stable in the investigated system to 1273 K. This phase was not detected following heat treatments at higher temperatures. Prolonged heat treatment at 1273 K caused the YPO_4 crystals to grow rapidly, as shown in Fig. 5.

TABLE III The results of XRD of the unannealed, annealed and progressively heat-treated AlSiPYO glass

Heat treatment temperature (K) – Time (h)	Crystalline phase detected
Unannealed	M (t)
Annealed	M (t)
1173–2	M (t)
1173–4	M (t)
1223–1	M (t)
1223–2	M, Y (t)
1223–4	M, Y (t), YS (t), AP (t)
1273–2	M, Y (t), YS (t), AP (t)
1273–6	M, Y (t), YS (t), AP (t)
1273–19	M, Y, YS (t), YA (t), AP (t)
1323–3	$\underline{\text{M}}$, $\underline{\text{Y}}$, YS (t), YA (t), AP (t)
1323–19	$\underline{\text{M}}$, $\underline{\text{Y}}$, YS, YA (t), AP (t)
1673–16	$\underline{\text{M}}$, $\underline{\text{Y}}$, YA (t), AP (t)
1173–3 + 1473–3	$\underline{\text{M}}$, $\underline{\text{Y}}$, YA (t)
1223–3 + 1473–3	$\underline{\text{M}}$, $\underline{\text{Y}}$, YA (t)
1473–15 + 1673–16	$\underline{\text{M}}$, $\underline{\text{Y}}$
1173–4 + 1473–4	$\underline{\text{M}}$, $\underline{\text{Y}}$, YA, YS, AP
1173–4 + 1523–4	$\underline{\text{M}}$, $\underline{\text{Y}}$, YA YS (t), AP (t)
1173–4 + 1573–4	$\underline{\text{M}}$, $\underline{\text{Y}}$, YA (t), YS (t), AP (t)
1173–4 + 1623–4	$\underline{\text{M}}$, $\underline{\text{Y}}$, AP (t)
1173–2 + 1473–4 + 1673–16	$\underline{\text{M}}$, $\underline{\text{Y}}$, AP (t)

M: Mullite $2Al_2O_3 \cdot SiO_2$, ASTM no. 15-776.
Y: Xenotime YPO_4, ASTM no. 9-377.
YS: Yttrium Silicate $Y_2Si_2O_7$, ASTM no. 21-1459.
YA: Yttrium Aluminate $Y_4Al_2O_9$, ASTM no. 22-987.
AP: Aluminum Phosphate $AlPO_4$, ASTM no. 15-254.
(t): trace.
—: very strong lines.

TABLE IV The results of density measurements of annealed, unannealed, and progressively crystallized AlSiPYO glass

Sample heat treatment: Temperature (K) – Time (h)	Density $\times 10^{-3}$ (kg m^{-3})
Unannealed	3.000
Annealed	2.998–3.011*
1173–2	3.000
1223–8	3.005†
1273–2	3.028
1273–4	3.095
1323–2	3.114
1473–4	3.030
1173–4 + 1473–4	3.213
1173–4 + 1523–4	3.225
1173–4 + 1573–4	3.223
1173–4 + 1623–4	3.231
1173–2 + 1473–4 + 1673–16	3.231
Sapphire‡	3.986

*The densities of the annealed glass varied depending on the portion of the large annealed glass piece from which they were cut.

†The differences in the densities of the samples separately heat-treated for 2, 3 or 4 h in the temperature range between 1173 and 1223 K were statistically insignificant.

‡The density of the sapphire was measured in order to check the accuracy of the procedure. The value determined by the Archimedes method equals the theoretical density reported in [21]. The accuracy of the density measurements is estimated to be $\pm 0.003 \times 10^{-3}$ kg m^{-3}.

At 1223 K and higher temperatures relatively rapid crystallization of mullite was observed, and the grain size of the mullite crystallites was non-uniform, as observed by TEM and SEM. In order to avoid rapid and excessive growth of a few nuclei and to obtain the largest possible number

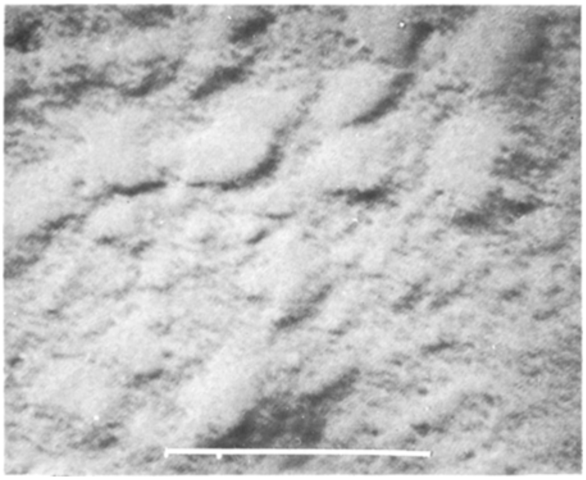

Figure 3 TEM replicas of heavily etched (23% HF for 30 sec) AlSiPYO glass heat treated for 7.2×10^3 sec at 1173 K. (bar = 1.0×10^{-6} m in Fig. 3a).

of small nuclei, the heat treatments were conducted at lower temperatures for various times. At the temperature of 1173 K extensive structural rearrangement occurred without a density change and no additional crystallization of mullite; therefore, this temperature was chosen as the optimum crystal nucleation temperature and was checked by analysing the XRD patterns and densities of samples heated at 1173 K for 14.4×10^3 sec (4 h) and subsequently heated to one of the temperatures of 1473, 1523, 1573 or 1623 K for 14.4×10^3 sec (4 h). The minimum temperature of 1473 K in the list was chosen on the basis of the DTA results, since the curve, shown in Fig. 1, does not indicate any major thermal events above this temperature. Therefore, it was assumed that crystallization was completed. The heat treatment at 1623 K caused substantial crystal growth in the glass samples while the samples heated at 1473 K still contained a moderate amount of glass, as indicated by their difference in densities (Table IV). Also, the XRD results indicated the presence of the minor crystal phases of $Y_4Al_2O_9$, $Y_2Si_2O_7$ and $AlPO_4$ at 1473 K, which dissolved at the higher heat treatment temperatures leaving only a trace of $AlPO_4$. Since there was some glass phase present even after crystallization at 1623 K, a much longer time of heat treatment (57.6×10^3

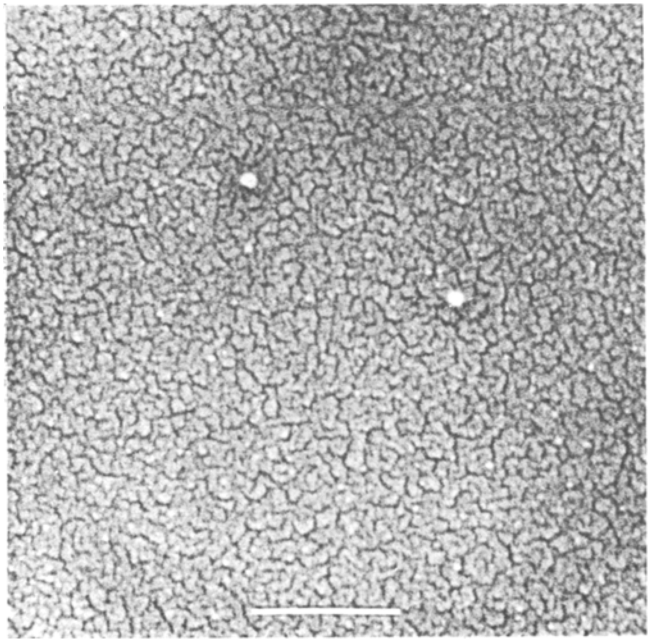

Figure 4 SEM fractograph of the unetched surface of the AlSiPYO glass heat treated at 1223 K for 7.2×10^3 sec showing mullite crystallites as small white areas (bar = 1.0×10^{-6} m).

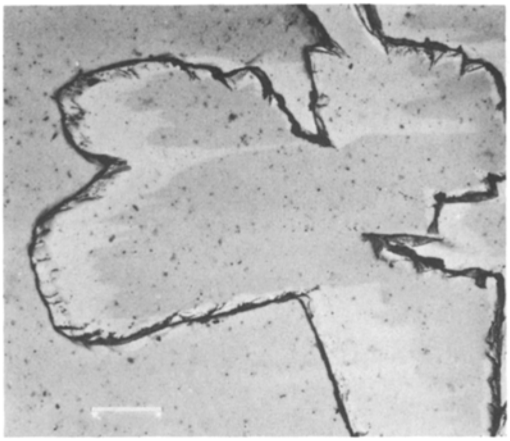

Figure 5 TEM replica of heavily etched (23% HF for 30 sec) AlSiPYO glass heat treated at 1273 K for 7.2×10^{-3} sec showing an extensive growth of YPO_4 crystallites. (Bar = 10.0×10^{-6} m).

sec (16 h)) and an additional higher temperature of 1673 K were employed. The lightly and heavily etched fractographs of a sample with the heat treatment scenario of 1173 K and 7.2×10^3 sec (2 h), 1473 K and 14.4×10^3 sec (4 h) and 1673 K and 57.6×10^3 sec (16 h) are shown on Figs. 6a and b. The XRD results of this material also indicated the presence of mullite and xenotime and a trace of $AlPO_4$, as in the material with the final heat treatment temperature of 1623 K.

Fig. 7 reveals the very large grains which form when the AlSiPYO glass is heat-treated at 1673 K for 14.4×10^3 sec (4 h) without any lower temperature anneals to allow composition adjustment and controlled crystal nucleation.

4. Summary

A glass with the composition 49.2 mol% Al_2O_3–32.8 mol% SiO_2–9.0 mol% P_2O_5–9.0 mol% Y_2O_3 has been designed with the objective of producing a highly refractory glass–ceramic. Phase separation in this glass occurred during cooling from the melt and more extensively during subsequent annealing. Traces of mullite were also detected in both instances. XPS of the annealed AlSiPYO glass revealed that the average chemical environment of the Al^{3+} is different from that present in either Al_2O_3 or mullite. Similarly, the environments of both Y^{3+} and P^{5+} in the glass were different from that noted for these ions in YPO_4. This was in contrast to that found in the annealed AlSiPO glass wherein the binding energies of the Al^{3+} and P^{5+} ions were similar in the glass and the crystal phases of mullite and $AlPO_4$. This indicates that the compositions of the separated phases were different from the crystal phases which subsequently formed in the former glass but similar in composition in the latter glass. An extensive rearrangement of the glass structure was observed on reheating to a temperature of 1173 K or higher. The crystallization of additional mullite was initially detected at 1223 K and 7.2×10^3 sec (2 h). By contrast, the crystallization of

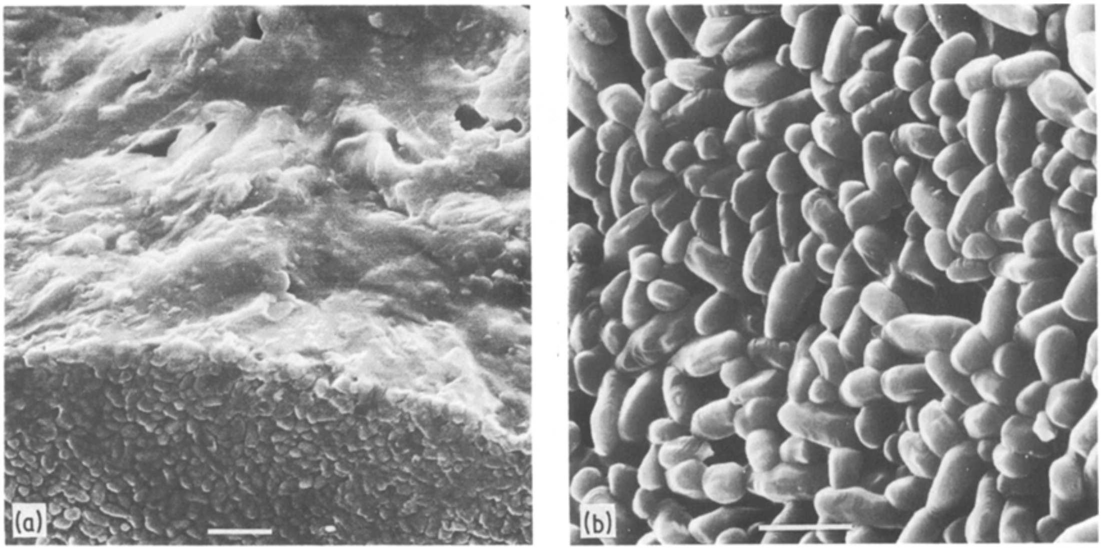

Figure 6 SEM fractographs of an AlSiPYO glass crystallized using a heat treatment schedule of 1173 K – 7.2×10^3 sec, 1473 K –14.4×10^3 sec, and 1673 K – 57.6×10^3 sec (a) lightly etched (9% HF for 5 sec) and (b) heavily etched (49% HF for 60 sec). (Bar = 10.0×10^{-6} m in Fig. 6a; bar = 1.0×10^{-6} m in Fig. 6b).

Figure 7 SEM micrograph of the fractured surface of a heavily etched (49% HF for 30 sec) AlSiPYO glass crystallized using a heat treatment of only 1673 K for 14.4×10^3 sec. (Bar $= 10.0 \times 10^{-6}$ m).

xenotime was not detected until the temperature was increased approximately 100 K. Trace amounts of additional transient crystalline phases with the compositions $Y_4Al_2O_9$, $Y_2Si_2O_7$, YP_4O_{14} and $AlPO_4$ were detected during crystallization; however, after heat treatment at 1673 K for 14.4×10^3 sec (4 h) only the $AlPO_4$ remained in trace amounts in the material.

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