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Liquid immiscibility and crystallization in refractory phosphate glasses

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The nature and evolution of liquid immiscibility and essentially complete crystallization in an optimized glass composition containing Al_2O_3, SiO_2 and P_2O_5 are examined from the results of electron microscopy, X-ray diffraction and density changes. Phase separation occurs during cooling from the melt; subsequent reheating to 850° C causes crystal nucleation followed by growth of the refractory phases of mullite (nominally $3Al_2O_3$–$2SiO_2$) and $AlPO_4$ at approximately 1050 and 1160° C, respectively. Additional crystallization of these phases also occurs at 1400° C. Similar materials containing additions of ZrO_2 and Y_2O_3 are also discussed.

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1. Introduction

The production of commercial glass-ceramics involves the initial formation of a glass of the desired composition and the heat treatment of this glass at various temperatures to induce or enhance liquid immiscibility and to promote the additional nucleation and growth of the desired crystalline phase(s). The advantages of these materials are that they can be formed in any shape which can be made with glass, with the subsequent crystalline microstructure being uniform and free from porosity, with crystals normally $\leqslant 1\,\mu m$ average diameter in size. Furthermore, glass-ceramics possess the potential for compositional tailoring to produce many different types of crystal phases in varying amounts having a variety of properties, either separately or in combination with each other, which may be utilized to meet the requirements of applications requiring extremes in different properties.

The purpose of the research described below has been to develop compositions and characterize the microstructural and related property changes which occur during the formation of glass-ceramics containing a very high percentage of refractory crystalline phases. A combination of oxide components were used such that mullite (nominally $3Al_2O_3$–$2SiO_2$) m.p. 1828° C [1] and aluminium orthophosphate ($AlPO_4$; m.p. > 2000° C) or YPO_4 or $ZrPO_4$ crystallized from the glass upon reheating. To date, the $Al_2O_3 \cdot SiO_2 \cdot P_2O_5$ system has been the most extensively studied and will be the principal focal point of discussion in this paper.

2. Experimental procedure

Batch materials composed of A-14 Al_2O_3†, CS-200 Supersil Sand‡ and $Al(PO_3)_3$§ were tumble mixed for 3 h in the experimentally optimized ratios given in Table I, melted in 70% Pt–30% Rh crucibles at 1850° C for 4 h, formed

TABLE I Glass composition in terms of the oxide components.

Oxide	wt %	mol %
Al_2O_3	60.4	57.0
SiO_2	17.5	28.0
P_2O_5	22.1	15.0

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*When this work was conducted, the writers were Graduate Research Assistant and Associate Professor of Materials Engineering, respectively. Mr Lee is currently at Ohio State University.

†Alcoa, Inc., Pittsburgh, Pennsylvania.

‡Cabot Corporation, Boston, Massachusetts.

§Stauffer, Inc., Westport, Connecticut.

into bubble-free glass plates in covered 12 cm × 12 cm × 0.64 cm steel moulds, annealed at 650° C for 4 h and allowed to furnace cool.

A 200 mesh powdered sample of the annealed glass was heated in a DTA unit* using Al_2O_3 as a reference material at a programmed rate of $10° C/min^{-1}$ to a maximum temperature of 1200° C to determine the approximate temperatures of crystallization. This data was used to design additional heat treatment programmes in Kanthal or SiC element furnaces controlled within ± 3° C using 2 cm × 1 cm × 0.5 cm bulk glass pieces in conjunction with subsequent X-ray diffraction (CuKα radiation) for identification and quantitative analysis, density measurements (Archimedes method using distilled H_2O of a known (accuracy = ±0.1° C) temperature) and double stage replicate TEM and SEM of ground and polished† surfaces to elucidate the optimum nucleation and crystallization temperatures, as discussed in detail below.

The quantitative X-ray analysis of the resulting crystal phases was conducted on samples having the maximum crystallinity (obtained at 1400° C using the 21.8° (2θ) peak of the cristobalite form of $AlPO_4$, as it was not overlapped by other peaks occurring during the crystallization process. This peak was counted 6 times for 32 sec each time on both samples and standards. The latter were composed of 100 mesh powders of fused mullite and the cristobalite form of $AlPO_4$ (produced by heat treatment at 1400° C for two days to remove traces of other polymorphic forms) mixed in integer ratios of 4/6 to 8/2 in single steps. The needle-like shape of the fused mullite unfortunately caused considerable preferred orientation when placed in the X-ray powder holder; thus, the amount of mullite was obtained by difference, assuming no glass phase. This assumption very closely approximates reality as no indication of amorphous regions was found in the X-ray or other characterization studies.

In the electron microscopy experiments, the etching of the samples was most crucial to visualizing the microstructure. Different etching times and etching solutions were used depending on the amount of crystallization in the samples; a 15% HF solution for 3 min was used to reveal the glass structure, a 1% HF solution for 1 sec was employed on the highly crystallized samples to reveal $AlPO_4$ and 48% HF for 10 sec at 0° C was necessary to reveal both mullite and $AlPO_4$ simultaneously.

Complete descriptions of all the procedures outlined above may be found in [2].

3. Results and discussion

3.1. Liquid immiscibility

Transmission micrographs of the annealed glass (Figs. 1a and b) show a bimodal distribution: small 60 Å droplets distributed uniformly throughout a matrix glass and larger, much less prevalent and randomly distributed 300 to 600 Å diameter droplets. The latter phase is descernible only occasionally in the glass, indicating a small amount of inhomogeneity. This is reasonable as the melting arrangement did not permit stirring prior to pouring. Additional evidence for this inhomogenity is derived from the inconstancy in the densities of the annealed glass (ρ = 2.600 to 2.610 g cm^{-3}) from different sections of the large plate.

This microstructure noted above is retained

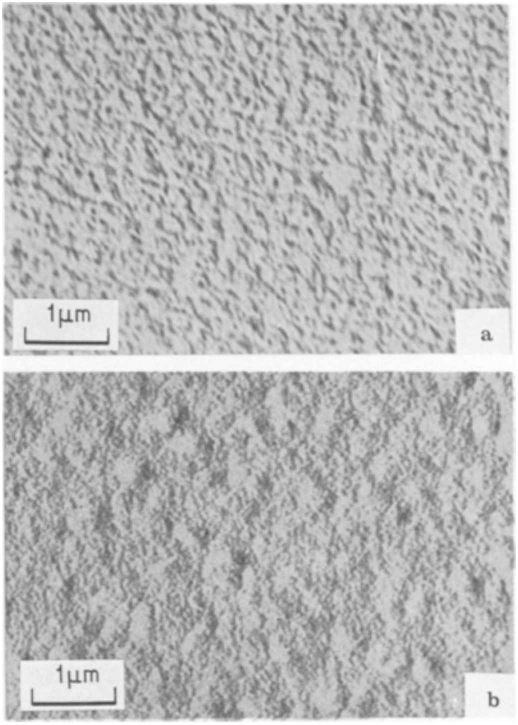

Figure 1 (a) and (b). Annealed glass microstructure showing both small 60 Å microspheres and less common 300 to 600 Å droplets. Etched with 15% HF for 3 min at 23° C.

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*Model DTA-12, Robert L. Stone Co., Austin, Texas.

†Grinding: 60, 120, 240, 320, 400 and 600 grit emery paper, 3 min each. Polishing: 3 µm and 0.25 µm Al_2O_3 powder, 2 min each.

indefinitely after heating at 800, 850 or 900° C for 4 h (up to 250° C above the annealing temperature). This pictorial evidence strongly indicates that the glass melt undergoes atomic and/or molecular rearrangement and classical homogeneous nucleation of separate amorphous phases, each rich in particular components drawn from the overall composition, which is essentially completed during cooling.

To understand why liquid immiscibility should occur in this system, it is instructive to consider how this immiscibility may be eliminated or produced through judicious compositional control in this and other silicate systems. When Al_2O_3 and P_2O_5 are added in combination to fused SiO_2 or to alkali and alkaline earth binary and ternary glasses, the effect on immiscibility of one compound is offset by the presence of the other according to how closely they approach equality in concentration. The reasons for this have been suggested by McMillan [3] in terms of the structural roles of each constituent in SiO_2 glass and the present authors agree with this reasoning. It is postulated that both the Al^{3+} and P^{5+} ions can substitute rather easily for Si^{4+} in the glass. Each tetrahedrally coordinated Al^{3+} ion creates an excess unit negative charge which must be satisfied by a portion of these ions occupying modifying positions; the presence of P^{5+} ions, however, can also alleviate this initial electrical imbalance by becoming linked to an AlO_4 group. This, in turn, also eliminates the doubly bonded oxygen formerly attached to the P^{5+} ion, since the excess charge of the PO_4 group is neutralized by the single negative charge associated with the AlO_4 group. In terms of the important ionic size effects the radii of Al^{3+} and P^{5+} in four-fold coordination (0.39 and 0.33 Å, respectively) [4] are such that when these ions occupy adjacent tetrahedral positions, the total atomic spacing for the two groups closely approximates that of an adjacent pair of SiO_4 groups. Finally, additional evidence that the joining of AlO_4 and PO_4 groups should promote a stabilizing effect on the SiO_4 glass network is derived from the fact that crystalline $AlPO_4$ has polymorphic forms which closely resemble the crystalline forms of SiO_2 [5, 6].

An explanation for the structural placement of the Al^{3+} and P^{5+} ions in the glass composition of the present research is now in order. The assumption is formulated that all the P^{5+} ions (equivalent to 6.3 mol% of the total ion concentration) are substituted directly for the Si in the tetrahedral position. Using the argument presented above, an equal amount of tetrahedrally coordinated Al^{3+} would be utilized for structural and electrical balance. Taking the 5.9 mol% Si^{4+} and the necessary oxygen into account, this would produce a SiO_2-type material composed of 67.5 mol% of the above oxide constituents with a residual 32.5 mol% Al_2O_3 to be partitioned among the tetrahedral and octahedral positions in the glass.

It has been noted by MacDowell and Beall [7], Aramaki and Roy [8], Davis and Pask [9] and Aksay [10] that in the Al_2O_3–SiO_2 system, the higher the temperature the more easily the Al^{3+} is accommodated in the tetrahedral position. At the very high melting temperature (1850° C) used in this research, it is plausible that a high percentage of the residual Al^{3+} ions become situated in the tetrahedral position. On cooling, a portion of these tetrahedral ions remain in this coordination. The fact that a SiO_2-type glass containing this large amount of Al_2O_3 can be formed in such large bulk pieces is noteworthy. MacDowell and Beall [7], in their study of the Al_2O_3–SiO_2 binary, found that above 30 mol% Al_2O_3, only extremely rapid quenching through water-cooled rollers produced amorphous samples. The presence of the P_2O_5 obviously allows a greater accommodation of Al^{3+} in the glass structure than a simple 1 : 1 ratio of Al^{3+} to P^{5+}. This is in addition to that allowed by the Al_2O_3–SiO_2 binary coupled with the condition of high temperature. A somewhat related effect has been reported by Sakaino [11] and Tashiro and Wada [12] who found that the presence of P_2O_5 noticeably enhances the solubility of ZrO_2 in alkali-aluminosilicate glasses even though the Zr^{4+} carries a charge of four – equal to that of the Si^{4+} ion.

In contrast, it is also reasoned by the present authors that a large fraction of the Al^{3+} ions in tetrahedral positions at 1850° C become unstable in this coordination during cooling and migrate toward the more stable octahedral arrangement. This structural adjustment influences the positions of other cations and oxygen and causes the Al_2O_3-rich silicate glass to separate from the P_2O_5-rich glass with the latter apparently forming in droplets, as noted below.

3.2. Nucleation and crystallization

The results of the DTA experiment, Fig. 2, reveal a broad exothermic plateau in the range of 800 to

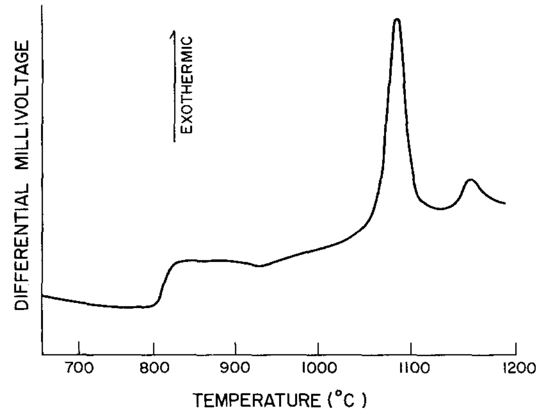

Figure 2 DTA curve for the Al_2O_3–SiO_2–P_2O_5 glass. Heating rate, 10° C min^{-1}.

930° C, a more rapid reaction at approximately 1090° C, and a small additional peak around 1160° C. The broad plateau was assumed to be indicative (but not proof) of the range of crystal nucleation.

To determine the optimum crystal nucleation temperature, the 2 cm × 1 cm × 0.5 cm pieces previously heated treated at 800, 850 and 900° C for 4 h and used for electron microscopy were reheated slowly to 1200° C and held for 4 h – above any exothermic temperature shown on the DTA curve – in order to ensure the crystallization of all phases. The intensities of the peaks of the X-ray diffraction pattern were identical for both the principal crystalline phases of ($AlPO_4$) and mullite regardless of the lower temperature. Therefore, 850° C was chosen as an optimum nucleation temperature (a slab heated directly to 1200° C for 4 h produced very poor crystallization; thus, the low temperature anneal is necessary for producing viable glass-ceramics). To discern the necessary nucleation time, another set of glasses was heated to 850° C for 1, 2 and 4 h, respectively, and 1200° C for 4 h. X-ray diffraction results and density measurements reveal that times exceeding two hours do not significantly affect the quantity of the two crystalline phases in the samples; although, somewhat longer times were employed in later experiments to insure complete nucleation.

To determine the optimum crystallization temperature and time, densities and X-ray diffraction data were compared on glass pieces nucleated at 850° C for 2 h and heated to one of the four temperatures of 1000, 1050, 1100 and 1150° C for times of 0.5, 1, 2 and 4 h for each temperature.

TABLE II Densities (g cm^{-3}) of progressively crystallized glasses heated to 850° C for 4 h and at the temperatures and times noted below.

Time (h)	Temperature (° C)			
	1000	1050	1100	1150
0	2.606	2.607	2.608	2.609
$\frac{1}{2}$	2.610	2.670	2.718	2.718
1	2.603	2.718	2.722	2.720
2	2.658	2.722	2.723	2.719
4	2.704	2.719	2.721	2.723

The X-ray diffraction patterns show that mullite and $AlPO_4$ are increasing as a function of time in this range; however, their initial occurrence is not simultaneous as detailed below. This is complimented by the values of Table II, which show the densities of the samples to be increasing up to an essentially constant value of = 2.721 ± 0.002 g cm^{-3} as a function of increasing temperature and time at temperature.

Based on these results, a crystallization scheme of 1150° C for 4 h was selected for use in the remainder of the experiments where the maximum possible crystallization in this temperature region was desired. The chronological and microstructural evolution of the various phases which causes the gradual changes in densities shown in Table II may also be followed by X-ray diffraction and electron microscopy, respectively.

If one heats the glass initially at 850° C for 2 h followed by 950° C for at least 4 h or 1000° C for 0.5 h, the microstructures of Fig. 1 change to one composed of large quasi-spherically-shaped droplets (depressions in the actual sample) having different etching rates, as shown in Fig. 3a. Micrographs taken from samples heated for shorter times at these temperatures show only a sudden change rather than a gradual movement from one microstructure to the other. The larger droplet microstructure appears only after the mullite phase has begun to crystallize on the droplet surfaces, thereby producing etch resistant boundaries. The mullite is believed to be manifest in the small crystallites occurring on all surfaces, as shown in Fig. 3b. The occurrence of mullite at the boundaries is logical as the latter provide energetic sites for nucleation of a new phase, i.e., the energy barrier to create the new surface of the nuclei is lessened by the presence of the interface.

Although no crystallinity is detected by X-ray diffraction in the heat treatments noted above, prolonged heating at 950° C for 16 h or 1000° C

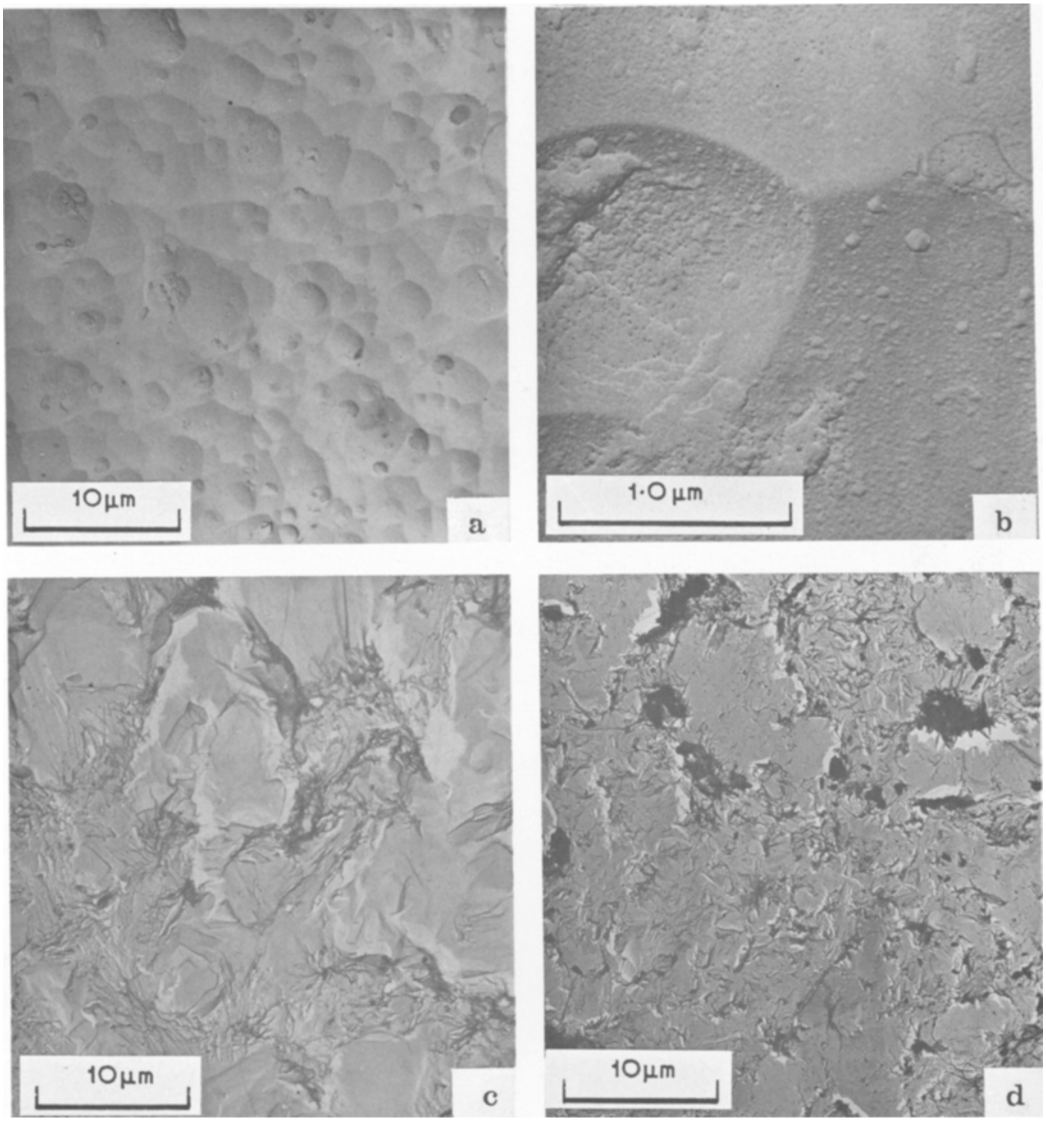

Figure 3 Microstructural evolution in the Al_2O_3–SiO_2–P_2O_5 glass showing (a) the increasing size of the immiscible P_2O_5-rich droplet phase after 850° C for 2 h and 1000° C for 0.5 h with (b) mullite crystallites visible at higher magnification on the surfaces of the droplets shown in (a). (c) shows the mullite crystals beginning to form around the droplet phase (850° C for 2 h and 1000° C for 2 h) and to a greater extent in (d) after 850° C for 2 h and 1000° C for 4 h. All samples etched with 15% HF for 2 min at 23° C.

for 4 h, Table III and Fig. 3d, does produce detectable amounts of crystallization of the initial phase of mullite. Fig. 3c is particularly informative in that it shows apparent traces of crystallinity (assumed to be mullite) surrounding some of the residual droplet phase. A moderate density change also occurs, Table II, indicating that crystallization has begun. In other words, the areas where the disappearance of a portion of the droplet phase occurs and an increasing amount of matrix phase results are strongly believed to transform to mullite.

TABLE III The crystal phases detected at different crystallizing temperatures. All samples were nucleated at 850° C for 4 h. M: mullite, A: $AlPO_4$.

Temperature	Time (h)					
(° C)	$\frac{1}{2}$	1	2	4	8	16
950	–	–	–	–	–	M
1000	–	–	–	M	M, A	
1050	M	M, A	M, A			

The droplet phase remains after the initial crystallization of mullite transforms into lath-shaped, highly soluble crystals of $AlPO_4$. The

Figure 4 The blocky microstructure of mullite crystals after rapid formation following heat treatment at 850° C for 4 h and 1090° C for 4 h. Etched with 15% HF for 4 min at 23° C.

cristobalite form is dominant; however, small amounts of the α-quartz and tridymite forms also occur. The mechanism by which this occurs may be either by homogeneous nucleation in the droplet phase or heterogeneous epitaxial growth on the surrounding mullite crystals. An examination of the lattice spacings of mullite and the cristobalite form of $AlPO_4$ show no atomic lattice spacings which are similar for the two materials; thus, the latter mechanism is somewhat doubtful.

The above droplet phase obviously contains some SiO_2 which is exsolved during crystallization, as all attempts to prepare a glass of the composition of $AlPO_4$ have failed [13–15]. The only amorphous region in the binary system occurs between 67 and 73 mol% P_2O_5 [16] which is unlikely to be the composition of the droplet phase. The exsolved SiO_2, in turns, reacts with any residual Al_2O_3 to produce more mullite at higher reaction temperatures. Increasing the temperature to 1090° C also causes the above crystallization process. Here mullite is seen to rapidly nucleate and grow in the form of blocky shapes, Fig. 4.

The above results, in general, coincide with the information derived from the DTA curve, i.e., the lower temperature peak at 1090° C coincides with the onset of crystallization of mullite, while the peak at 1160° C indicates the formation of $AlPO_4$. The higher DTA temperatures are caused by the rapid rate of heating employed.

In summary, the presence of P_2O_5 allows the accommodation of an abnormal amount of Al_2O_3 into the silica structure. On cooling, P_2O_5-containing microimmiscibility occurs, which evolves on reheating to 950° C or above into substantially larger droplets and a distinct Al_2O_3-rich matrix phase which are believed to approximate the compositions of $AlPO_4$ and mullite, respectively. Both amorphous phases contain sufficient SiO_2 to prevent crystallization, as the high Al_2O_3 contents of each phase would readily produce crystallization with a low concentration of SiO_2 present. The amorphous matrix transforms to produce X-ray detectable crystalline mullite after a period of heating which depends on the temperature. This is succeeded by the crystallization of $AlPO_4$ from

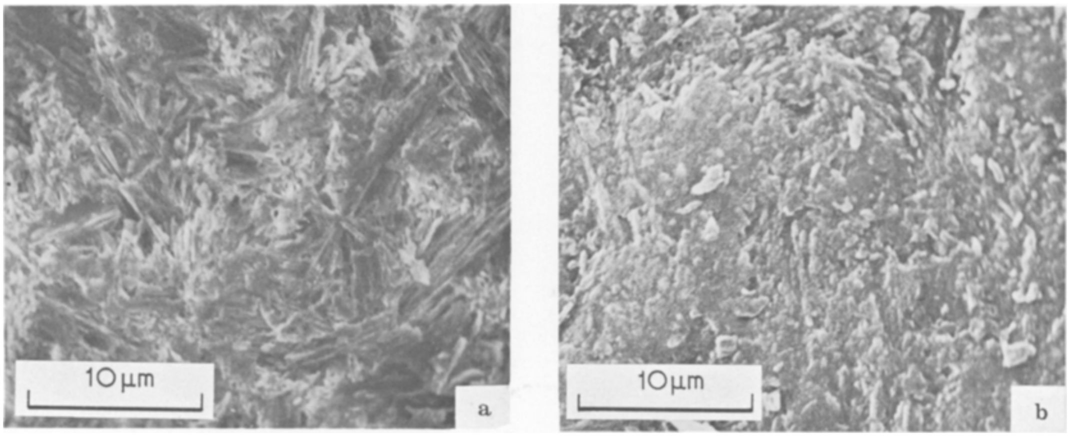

Figure 5 The microstructure of (a) the cristobalite form of $AlPO_4$ formed in the glass after heating at 850° C for 4 h, 1150° C for 4 h and 1400° C for 16 h, and (b) the mullite crystals of the same sample. The former were revealed by a 48% HF for 10 sec etch at 0° C while the latter was etched with 15% HF for 5 min at 23° C.

the droplet phase after an even longer time of heating or an increase in temperature.

The X-ray pattern of these materials heated at 1150° C for 4h show that the cristobalite form of $AlPO_4$ is the principal polymorph which occurs; however, as noted above, a small amount of the berlinite (α-quartz) and the tridymite forms are also present. In an attempt to transform all the $AlPO_4$ to the cristobalite form, samples were heated to 1400° C for 16h. This objective was accomplished; however, the amount of crystallinity of both phases unexpectedly increased at this temperature and some microcracking was also induced in the samples. SEM of a very lightly etched sample of this 1400° C material, Fig. 5a, reveals the presence of lath-like crystals noted earlier, which are believed to be $AlPO_4$. This hypothesis is substantiated by a more severe etch, Fig. 5b, which removes the former phase and reveals an irregular, blocky-shaped material. An X-ray pattern of the residual powder scraped from the surface of a very heavily etched (10 h) material, reveals mullite as the only phase. Furthermore, additional micrographs of the surface etched for 10 h also show a picture similar to that of Fig. 5b. This demonstrates that the $AlPO_4$ grows in a needle-like form while mullite forms in blocky, irregular-shaped crystals. Heating directly from 850° C for 2 h to 1400° C lessens considerably the amount of crystals of each phase which form even after 16 h at the latter temperature.

3.3. Quantitative analysis

X-ray diffraction counting techniques and density determinations were used to ascertain the weight percentages of the $AlPO_4$ and mullite crystal phases in the sample heated to 850° C for 4h, 1150° C for 4 h and 1400° C for 16 h. The material was assumed to be completely crystalline – a condition which is indicated by the micrographs of Figs. 4 and 5a and b, and the X-ray pattern (it is likely that a small amount of glass remains at the grain boundaries and/or triple points, for unless the glass is extremely homogeneous, certain small portions of the glass will not have the correct proportion(s) of components in order to undergo crystallization).

If the crystallization is complete and no vaporization loss of components occurred during melting, the weight percent ratio of mullite to $AlPO_4$ is 62:38. Using the 21.8° 2θ peak of APO_4, it was determined by quantitative X-ray diffraction that this crystal phase ratio in the 1400° C glass-ceramic was 65:35. It is possible that some P_2O_5 was lost during the melting of the glass at 1850° C; however, the somewhat more accurate method of density measurements would suggest that very little, if any, of this oxide vaporized.

A maximum density of 2.75 g cm^{-3} in this glass-ceramic material was also achieved by the above same long term heat treatment. The densities of mullite and $AlPO_4$ (cristobalite form) are 3.166 and 2.304, respectively. Using the measured glass-ceramic density value noted above, a value of the wt % $AlPO_4$ content was calculated to be slightly higher than the theoretical amount.

Thus both techniques provide reasonable accuracy when the glass-ceramic can be assumed to be 100% crystalline or the amount of residual glass and its density are known.

3.4. Other systems

In addition to the system discussed in detail above, glass produced from compositions (in mol %) containing 49.2% Al_2O_3 32.8% SiO_2, 9% P_2O_5 and 9% ZrO_2 (or 9% Y_2O_3) were also discovered to be fabricated easily and to transform essentially completely to mullite and $ZrPO_4$ or YPO_4 within the same temperature range of the $AlPO_4$-containing glass. It is now believed that a large range of similar materials can be produced containing transition metal and lanthanide phosphates in various ratios with mullite as the principal second phase.

4. Conclusions

(1) The presence of 15 mol% P_2O_5 in an $Al_2O_3 \cdot SiO_2 \cdot P_2O_5$ glass allows more than 57 mol% Al_2O_3 to be accomodated in the structure; however, a change in coordination on cooling of a portion of the Al^{3+} ions not bonded to PO_4^{3-} groups causes liquid immiscibility.

(2) Reheating of the glass to 850° C causes crystal nucleation with subsequent and essentially complete crystallization of the refractory phases of mullite and aluminium orthophosphate at higher temperatures.

(3) Mullite crystallizes on the surfaces of an enlarged droplet phase but forms in the matrix glass as blocky crystals surrounding the droplets. Lath-shaped $AlPO_4$ crystals form at higher temperatures from the droplets, apparently homogeneously and independently of the mullite.

(4) The major portion of the crystallization

occurs in the temperature range of 1050 to 1190° C; however, additional crystallization, the complete transformation of all $AlPO_4$ forms to the cristobalite polymorph and some microcracking occur on heating to 1400° C. Also the resulting mullite/$AlPO_4$ wt% ratio is very close to the theoretical 62:38 value, assuming complete crystallization.

(5) A host of analogous refractory materials may also be prepared by the addition of transition metal and lanthanide series oxides to the basic ternary components noted above.

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