

Heterogeneous Nucleation of Alkaline Earth Feldspars in Glasses

DOV BAHAT

Research and Development Laboratories, Corning Glass Works, Corning, New York, USA

Received 31 March 1969

Though suitable conditions of structural geometry favouring epitaxy were demonstrated, yet it was observed that epitaxy was not a dominant and, possibly, not even an important factor in the nucleation processes studied. Indeed, the mere presence of close structural geometrical fit between the catalyst and the nucleus does not necessarily lead to epitaxy. Other factors such as the concentration of the nucleating agent in the glass and variations in the chemical composition of the glass, and their effects on the nucleation are discussed. Also the effect of the feldspar structure on the kinetic barrier for its nucleation, and several specific liquid phase separation phenomena, are evaluated.

1. Introduction

Alkaline earth feldspars may be readily nucleated from glasses of the $\text{BaO-Al}_2\text{O}_3\text{-SiO}_2$, $\text{SrO-Al}_2\text{O}_3\text{-SiO}_2$, and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ systems by a wide variety of nucleating agents. This fact enables one to observe different aspects of heterogeneous nucleation in these systems, due to the different miscibility and interface relationships that exist between the glasses and the various nucleating agents. Some observations made on this subject are presented below.

2. Experimental Techniques

2.1. Preparation of Glasses

The glasses were prepared mostly from Morgan Sand ($\text{SiO}_2 = 99.8\%$), T-61 aluminium oxide ($\text{Al}_2\text{O}_3 = 99.7\%$), and calcium, strontium, and barium reagent carbonates. Some glasses were prepared from kaolins and alkaline earth sulphates. The latter glasses had impurities up to about 2% of combined K_2O , Na_2O , FeO , Fe_2O_3 and TiO_2 . Glasses were prepared to the stoichiometric compositions of the three alkaline earth feldspars, as well as to compositions with deviations from the stoichiometry. Impurities of various metals such as Pt and Rh in the form of chlorides, and oxides such as WO_3 and NiO were added for nucleation purposes [1]. These impurities were generally up to 1 or 2% excess. The batch materials were weighed to an accuracy of 0.1 g and dry-mixed. Standard batch mixtures

of 600 g were melted at 1800°C in a gas-oxygen furnace generally for 4 h in 20% Rh-80% Pt crucibles. Quenched patties were made from melts and annealed at 800°C for 1 h. Portions of these patties were subjected to various heat treatments.

2.2. Heat-Treatment and Nucleation

A standard-heat treatment was applied to all glasses containing nucleating agents for the purpose of nucleation and formation of glass-ceramics. This treatment was at 1000°C for 1 h. Under such conditions most glasses were fully crystallised (90 to 100%). Glasses nucleated by certain metals, however, require a longer heat-treatment or a higher temperature for a complete crystallisation. Apart from the standard heat-treatment, various other treatments were applied as well. These were carried out under an air pressure of 1 atm. Generally, in the glass-ceramics formed, crystals of 1 to $10\ \mu\text{m}$ were randomly oriented.

2.3. Analytical Techniques

Most new glass-ceramics were routinely examined by X-ray diffraction. Colours and textures of glasses and glass-ceramics were studied. Selected glasses and glass-ceramics were investigated by the scanning electron microscope and the transmission electron microscope techniques.

For the scanning electron microscope investi-

gation, samples were prepared by fracturing a section of the glasses and glass-ceramics, mounting on a specimen holder, and evaporating a conductive film of approximately 400 Å aluminium on to the surface to be examined. Observations were made perpendicular and at 45° to the samples.

For the transmission electron microscope investigation, replicas were prepared from fractured and from fractured-and-etched surfaces.

Wet chemical analyses on selected samples were carried out as well.

3. Results and Discussion

3.1. General

The present investigation shows heterogeneous nucleation of various feldspar modifications by a variety of nucleating agents in the systems BaO–Al₂O₃–SiO₂, SrO–Al₂O₃–SiO₂, and CaO–Al₂O₃–SiO₂. Heterogeneous nucleation is more highly developed in the BaO–Al₂O₃–SiO₂ system than in the other two, i.e. in the former system intensive nucleation of good quality glass-ceramics is produced by the various nucleating agents specified below, whereas in the other two systems some nucleating agents are not as effective as others; this is manifested in various cases by lack of uniformity in crystal size, zoning, and variations in colours (which are not ascribed to sample preparation). In the BaO–Al₂O₃–SiO₂ system, nucleation is mostly confined to the metastable form hexacelsian (BaAl₂Si₂O₈), whereas in the other two systems both metastable forms (hexagonal and orthorhombic) and stable forms (triclinic SrAl₂Si₂O₈ and CaAl₂Si₂O₈) may be formed (with a stronger emphasis still placed on the metastable forms). Hexacelsian may probably be nucleated by more nucleating agents than any other crystal known so far in the glass-ceramic field. These include: (a) metals – Au, Pt, Ir, Rh, Pl; (b) oxides – Fe_xO_y, V_xO_y, Mo_xO_y, BaWO₄, NiO; (c) sulphides – ZnS; (d) fluorides – CaF₂. Most of these, nucleating agents are effective in small amounts generally below 1%.

It is generally considered that an important factor in determining the effectiveness of heterogeneous nucleation is a close correlation between the lattice parameters of the catalyst and the nucleated crystal product [2, 1]. Accordingly, two-dimensional low disregistries between the atomic arrangements on the 111 plane of the noble metals and on the 0001 plane of the

various hexagonal feldspars, are obvious (fig. 1), thus suggesting close epitaxial relationships. It was, however, found in the present study that nucleation promoted by other nucleating agents (such as iron oxide or fluorite, see below) appears to be unrelated to the crystal structure of the nucleating agent, thus questioning the importance of epitaxy in the nucleation process of the feldspars. Following this finding, further detailed observations on nucleation and crystal growth in the various feldspar systems brought into focus some additional factors that had important effects on the processes. These observations are described below in relation to the individual catalysts.

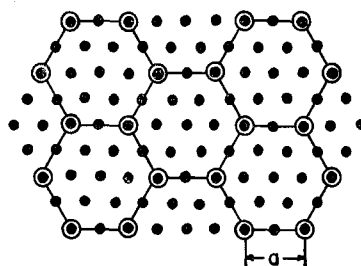


Figure 1 Two dimensional low disregistry between the 111 plane of a noble metal and the 0001 plane of a hexagonal feldspar. The noble metal is marked by dots, and oxygen is shown as open circles forming a sheet of hexagons. All the oxygens in the figure are of the same level, each represents a tetrahedron from which the other oxygens, silicon, and aluminium are omitted. The distance between neighbouring oxygens is given by the a parameter of the feldspar which approximates the $a\sqrt{2}$ of the noble metal.

3.2. Platinum, Iridium, and Gold

Platinum was added to BaAl₂Si₂O₈ glasses in various quantities from 0.003 to 0.333% in excess of the major oxide constituents computed as 100%. It was found that on heating the glasses, the rate of crystal growth was a function of the decrease of platinum content in the glasses (see below similar results related to the nucleation by rhodium).

Rindone [3] described variations in rates of crystallisation (he presumably meant crystal growth rate) of a Li₂O.4SiO₂ glass as a function of platinum concentration. Rindone, however, concluded that nucleation was effective when the concentration of platinum was low enough to produce a small enough average nucleus to fit within the structure of lithium-rich clusters

surrounded by silica-rich regions. Since a glass of the stoichiometric composition of barium feldspar shows no indications of phase separation when examined by the transmission electron microscope after being exposed to various heat-treatments, the explanation relating concentration and crystal size of platinum nuclei to a segregated structure of the glass, cannot be adopted.

On heating a glass with a low concentration of platinum (excess of 0.166%), nucleation due to platinum catalysis starts from relatively few, large centres (fig. 2). The initial crystal growth is very rapid, even at the lowest temperatures where crystallisation occurs. As a result of this the crystalline glass-ceramic is relatively coarse (approximately 12 μm , fig. 3).

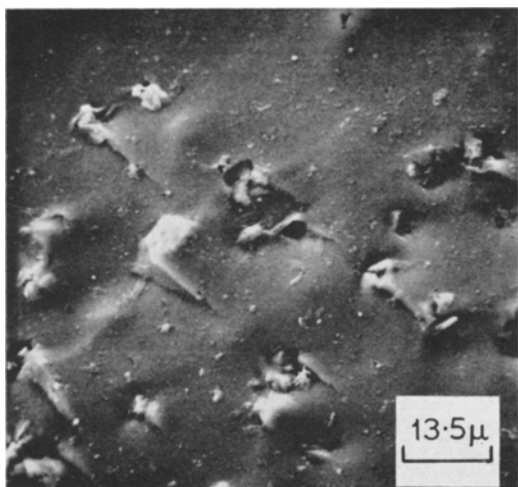


Figure 2 A $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ glass nucleated by an excess of 0.166% platinum after being heated at 1080° C for 12 min. Crystal growth starts from large centres. Numbers in the centre of squares in figs. 2 to 5 indicate micron scales (scanning electron microscope).

The effect of iridium on the nucleation of hexacelsian glass-ceramics is similar to that of platinum, as observed both in macrospecimens and microstructures. The nucleation of hexacelsian by gold is less effective. Variations in colours and crystal size in the glass-ceramic nucleated by gold indicate heterogeneous dispersion of the gold nuclei in the glass. The rate of crystal growth of hexacelsian following nucleation by these three metals is, however, similar. Crystal growth is slow at 1000° C; less than 10% crystallisation occurs after a heat-treatment for

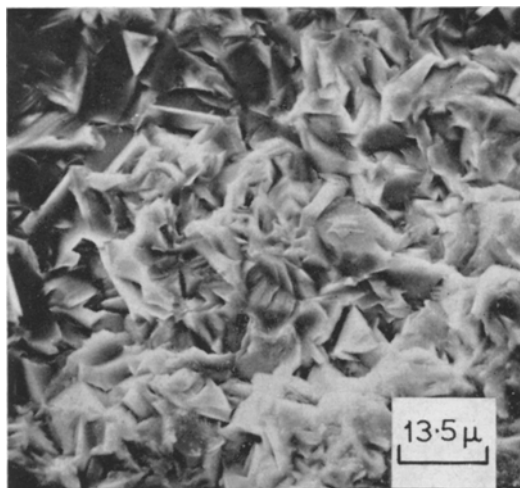


Figure 3 A $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ glass nucleated by an excess of 0.166% platinum after being heated at 1010° C for 45 min and then at 1170° C for 60 min. Crystals are large (sem).

2 h; it is rapid at 1100 and 1200° C, and takes several minutes to complete crystallisation at 1200° C.

3.3. Rhodium and Palladium

Rhodium was added in two levels of concentration to glasses of the $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ stoichiometry, at a high concentration (0.66%) and a low concentration (0.10%). On heating, these glasses were readily nucleated to hexacelsian glass-ceramics. Significant differences in the nucleation of the two glasses were observed. When treated at 1000° C, the glass with the high concentration of rhodium was crystallised to a translucent brown-grey glass-ceramic. The crystals produced were fine (0.5 μm or less) and undefined in shape (fig. 4), and as was indicated by X-ray analyses, crystal growth was relatively slow (crystallisation was completed within 2 h). The glass with the low concentration of rhodium, on the other hand, was crystallised to an opaque white glass-ceramic. Crystal growth was rapid (crystallisation was completed in 1 h), and the crystals produced were relatively large (3 to 4 μm) and had rectangular well-defined boundaries (fig. 5).

This indicates that the glass with the higher concentration of rhodium was nucleated simultaneously in many more sites than the glass with the low concentration of rhodium. In the glass with the higher rate of nucleation, crystal

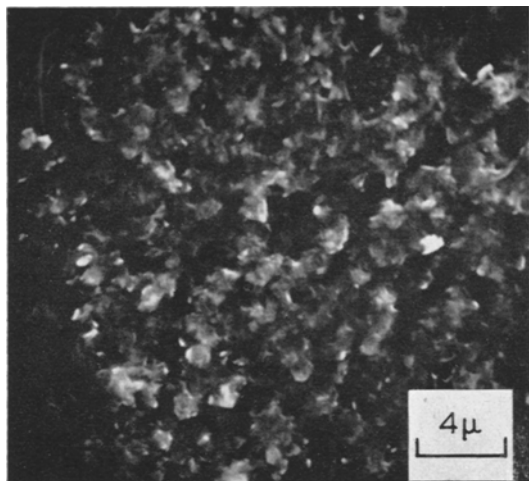


Figure 4 A $\text{BaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ glass nucleated by an excess of 0.66% rhodium after being heated at 1000°C for 60 min. Fine crystals of undefined shapes are observed (sem).

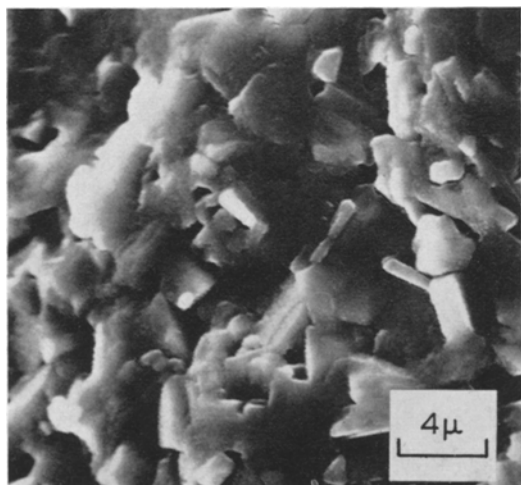


Figure 5 A $\text{BaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ glass nucleated by an excess of 0.10% rhodium after being heated at 1000°C for 60 min. Large rectangular crystals are observed (sem).

growth was lower, and hence the crystals produced were finer.

A $\text{BaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ glass containing 0.116% palladium appears a dark reddish-brown colour. It could be rapidly transformed into a grey opaque glass-ceramic at 1000°C . As far as rates of nucleation and crystal growth of $\text{BaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ at 1000°C are concerned, the catalysing effect of palladium is similar to that of rhodium and dissimilar from those of iridium, platinum, and gold. Hexacelsian nucleated by palladium and rhodium completes its crystallisa-

tion in less than 2 h at 1000°C , whereas when nucleated by iridium, platinum, and gold at the same temperature, crystallisation is very slow; after 2 h it is only slightly noticeable.

It is difficult to speculate on the significance of this division into two groups of noble metals, but it is clear that it is not based on differences in lattice parameters (rhodium has a closer lattice parameter to iridium than to palladium). This division, however, can be correlated with the position of the noble metals in the periodic table. The atomic weights of rhodium, palladium, iridium, platinum, and gold are 102.9, 106.7, 193.1, 195.2, and 197.2, respectively.

3.4. The Three $\text{RO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ Systems

The above difference in the effects of the noble metals on hexacelsian nucleation at 1000°C is not so significant in the analogous strontium and calcium glasses.

It was observed in about 100 glasses that generally the effectiveness of the noble metals in nucleating $\text{SrO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ and $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ glasses is considerably poorer than in $\text{BaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ glasses, although the discrepancy between the lattice parameters of the noble metals and the strontium and calcium hexagonal feldspars is still relatively low. For instance, the discrepancies between the 111 plane of rhodium and the 0001 plane of hexagonal barium, strontium, and calcium feldspars are 1.22%, 2.39%, and 4.99%, respectively. It is obvious that other parameters than low discrepancy have inhibiting effects on the nucleation of strontium and calcium high-symmetry (hexagonal) feldspars. It is possible that the homogeneous nucleation rates of strontium and calcium feldspars are somewhat lower than that of hexacelsian.

3.5. Molybdenum

Molybdenum oxide (MoO_3) was introduced in various levels to a $\text{BaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ glass. On heating, hexacelsian glass-ceramics were obtained quite rapidly, within 45 min, at 1000°C . The colours of the glass-ceramics varied with the concentration of the molybdenum oxide in the initial glass. This was paralleled by changes in the rate of crystal growth.

Glasses 1 and 2 in table I have the same composition (off the $\text{SrO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ stoichiometry). Glass 1 has an excess of 0.04% rhodium, and glass 2 has an excess of 2% molybdenum oxide and 2% tungsten oxide.

When these two glasses were exposed to an identical heat-treatment, glass 1 crystallised to hexagonal strontium feldspar glass-ceramic, and glass 2 was crystallised to triclinic strontium feldspar glass-ceramic (the nucleation is essentially achieved by the molybdenum oxide and improved by the tungsten oxide). Glasses 3 and 4 in table I have the same composition (bytownite). The former has an excess of 0.3% nickel oxide, and the latter has an excess of 2% molybdenum oxide. When exposed to the same heat-treatment, the glass with the nickel oxide was crystallised to a glass-ceramic with a feldspar mixture dominated by the hexagonal modification, and the glass with the molybdenum oxide was crystallised to orthorhombic calcium feldspar glass-ceramic [4]. For the above experiment, a deviation from an anorthite end member ($\text{CaAl}_2\text{Si}_2\text{O}_8$) to a bytownite composition (2.3% Na_2O , 16.1% CaO , 33.3% Al_2O_3 , 48.3% SiO_2) was selected, since in the presence of sodium the reaction approach to equilibrium is more complete. These two examples clearly illustrate different paths of nucleation, followed by different nucleation agents for a glass of a given composition.

It was mentioned above that the metastable (hexagonal and orthorhombic) modifications of the alkaline earth feldspars nucleate more readily from their respective glasses than the stable (monoclinic and triclinic) modifications do. This is attributed to the fact that the high symmetry modifications have simple structures. The hex-

agonal modifications are built roughly of alternative double sheets of tetrahedra and a single layer of R^{2+} cations perpendicular to the c axis [5]. The low symmetry modifications, on the other hand, are more complicated; they are made of three-dimensional networks in which the aluminium and silicon are at least partially ordered in a special distribution [6]. Owing to this difference in structure, the high symmetry modifications have lower kinetic barriers for nucleation. For some reason, the difference in the kinetic barriers for nucleation between the low and high symmetry modifications in the $\text{SrAl}_2\text{Si}_2\text{O}_8$ and $\text{CaAl}_2\text{Si}_2\text{O}_8$ compositions appear to be lower than in the $\text{BaAl}_2\text{Si}_2\text{O}_8$ composition (as is shown by occasional nucleation of triclinic strontium and calcium feldspars and the conspicuous lack of nucleation of barium monoclinic feldspar from their respective glasses).

Ambero [7] studied the effects of nine oxides on the surface tension of a molten soda lime silicate glass, a glaze, and an enamel. His measurements showed molybdenum oxide to be an outstanding surface tension reducer or wetting agent, and tungsten oxide to be second best. It is suggested that some proportion of the molybdenum and tungsten oxides did not separate from the glass and their outstanding properties in reducing surface tension managed to overcome the kinetic barrier of nucleation of the triclinic feldspar (glass no 2, table I). Also, due to the difference in wetting properties of molybdenum and nickel oxides, different nucleation results in

TABLE I Selected compositions of feldspar glass-ceramics (in wt %)

	1	2	3	4	5	6
SiO_2	27.8	27.8	48.3	48.3	32.4	34.82
Al_2O_3	37.1	37.1	33.3	33.3	25.9	24.7 ± 0.1
BaO	—	—	—	—	40.0	38.3 ± 0.06
SrO	34.9	34.9	—	—	—	0.08
CaO	—	—	16.1	16.1	—	0.13
Na_2O	tr	tr	2.3	2.3	0.2	0.28
K_2O	tra	tra	tra	tra	0.7	0.80
FeO	—	—	—	—	—	0.22
Fe_2O_3	tr	tr	tr	tr	0.7	0.48
TiO_2	tra	tra	tra	tra	0.1	0.047
MoO_3	—	2.0	—	2.0	—	—
WO_3	—	2.0	—	—	—	—
NiO	—	—	0.3	—	—	—
Rh	0.04	—	—	—	—	—
Cl	0.04	—	tra	tra	—	—
SO_3	—	—	—	—	—	0.005

Numbers 1 to 5 show nominal compositions. Number 6 is a chemical analysis.
tr = traces below 0.025%; tra = traces below 0.01%.

the CaO–Na₂O–Al₂O₃–SiO₂ system were observed as well, as described above (glasses 3 and 4, table I).

It was found in this study that with a given combination of nucleating agents (excess of 2% MoO₃ + 2% WO₃) and heat-treatment, the path of nucleation of SrO–Al₂O₃–SiO₂ glasses depends upon variations in composition. Generally, fluid glasses of low silica content (30% SiO₂) in which the SrO/Al₂O₃ ratio does not deviate much from 1:1, are more readily nucleated than glasses of the SrO.Al₂O₃.2SiO₂ stoichiometry (37% SiO₂) or other SrO–Al₂O₃–SiO₂ compositions richer in silica. In addition, the former glasses crystallise more readily to triclinic strontium feldspar glass-ceramics (with excess SrO and Al₂O₃ in residual glass), whereas the silica-rich glasses crystallise more to hexagonal or a combination of hexagonal and triclinic feldspar glass-ceramics. This trend shows the dominant effects that variations in the chemical composition and the resultant changes in viscosity and other physical properties have on the path of nucleation.

3.6. Tungsten

Glass of the BaO.Al₂O₃.2SiO₂ stoichiometry can take about 9% nominal WO₃ (as opposed to hardly 1.5 to 2% nominal MoO₃) into solution without causing crystallisation on cooling. Such a glass is yellow and may readily be crystallised on heating into a white glass-ceramic with hexacelsian as the dominant phase. It was found that, due to the high content of tungsten oxide in the glass, a secondary phase (in volume, not chronologically) was formed on heating, and this was identified by X-rays as barium tungstate (BaWO₄). It is suggested that the nucleation of hexacelsian came about as a result of a large-scale (see below) phase separation on heating of a tungsten-rich phase. An epitaxial growth of hexacelsian upon the tetragonal lattice of BaWO₄ is unlikely. A comparison of the respective lattice parameters does not even show any significant similarity.

In the present study the term "large-scale phase separation" means that the glass is separated into two major oxide phases, where the smaller one comprises more than 4 wt % of the glass. One phase is silica-rich and the other contains the nucleating agent as the only component or a part of a compound. The latter compound may be alumina-rich and/or may have an alkaline earth as a modifier. This phase separation could start on cooling, but a fully

developed phase separation would normally require a heat-treatment.

A "small-scale phase separation" is characterised by a single major phase which comprises the bulk of the glass. A separation of a minor phase which does not much exceed 1 wt % (the nucleating agent) is essentially completed on cooling.

The phase separation of both scales is not restricted to definite compositions. It may vary in correspondence with changes in the composition of the original glass. This is in contrast to the separation of metals, sulphides and fluorides from glass which is confined to definite compositions, regardless of changes in the composition of the base glass.

3.7. Vanadium

Vanadium oxides may be dissolved to a limited extent (excess of about 3%) in a BaO.Al₂O₃.2SiO₂ glass after a quench from 1800° C, producing blue-grey colours. Hexacelsian glass-ceramic is readily obtainable on heating such a glass.

Hexagonal strontium feldspar glass-ceramics of good quality (homogeneous distribution of fine crystals) are not readily obtainable from stoichiometric SrO.Al₂O₃.2SiO₂ glasses when nucleated by vanadium oxide upon heating. In these materials, zones of different colours (grey, green, and purple) and crystal sizes are typical. However, a blue, excellent-quality hexagonal strontium feldspar glass-ceramic may readily be produced from an off-stoichiometry composition (SiO₂ = 30%; Al₂O₃ = 45%; SrO = 25%; and V₂O₅ = + 0.66%).

This clearly illustrates that the nucleation is greatly influenced by the glass properties as suggested above.

3.8. Iron

Glasses Nos. 5 and 6 in table I contain iron oxides, potassium and sodium oxides, and traces of other impurities. These glasses can be readily crystallised to fine-grained glass-ceramics on heating (figs. 6 and 7). An investigation of these glasses, which involved systematic variations in the glass compositions maintaining reproducible melting conditions, indicates that the iron oxides are the nucleating agent. The alkali oxides have an effect on the colour of the glass and glass-ceramic and an important influence on the quality of the nucleation. The other impurities do not have any significant effect on the nucleation.

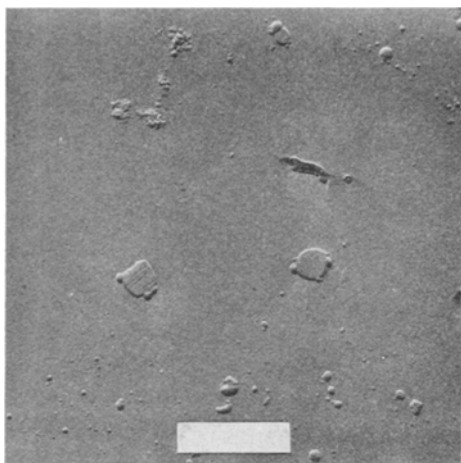


Figure 6 A $\text{BaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ glass formed from a kaolinite and BaSO_4 batch (No. 6, table I) shows initial crystal growth after being heated at 960°C for 5 min. A texture of round crystals and bumps resembling liquid phase separation is observed. White bar at bottom of the picture is $1\ \mu\text{m}$ (transmission electron microscope).

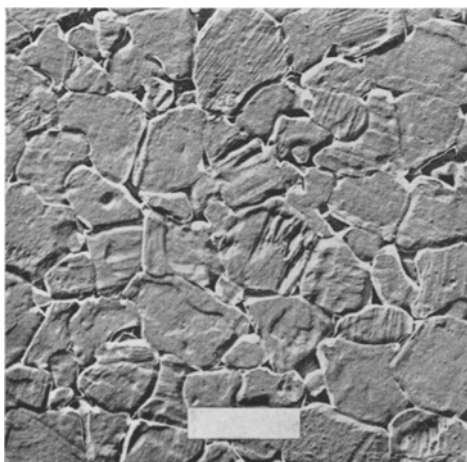


Figure 7 A $\text{BaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ glass formed from a kaolinite and BaSO_4 batch (No. 6, table I) is fully crystallised after being heated at 910°C for 40 min. Crystals are smaller than $1\ \mu\text{m}$. Fine unconnected islands of residual glass are observed around the crystals. White bar at the bottom of the picture is $1\ \mu\text{m}$ (tem).

Ten chemical analyses which were carried out on iron oxide-containing $\text{BaAl}_2\text{Si}_2\text{O}_8$ glasses and glass-ceramics in the attempt to determine the $\text{FeO}/\text{Fe}_2\text{O}_3$ ratios in them, show that this ratio varies a lot, suggesting that it is not essential as such for the nucleation of the glasses. This renders improbable the possibility of epitaxy due

to the presence of a specific mineral structure such as magnetite or hematite in the $\text{BaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system. The alternative to a separation of an iron oxide with a definite composition is a small-scale phase separation of a liquid (with a composition variable to a small extent). It is significant that in this glass on heating, crystal growth to a fine-grained glass-ceramic is fast (figs. 6 and 7), indicating a high rate of nucleation. This suggests that a phase separation of the iron oxide to minute droplets is already completed on cooling.

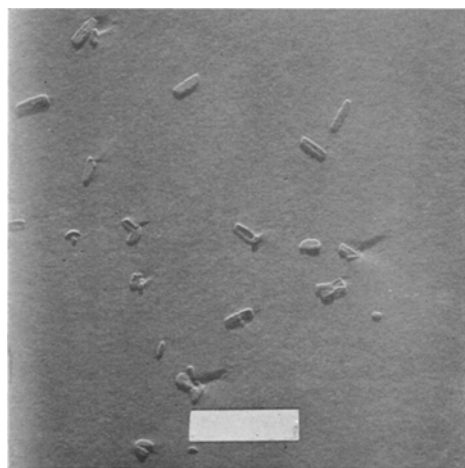


Figure 8 A $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ glass formed from a kaolinite and CaSO_4 batch shows initial crystal growth after being heated at 920°C for 20 min. Rectangular crystals are observed. White bar at the bottom of the picture is $1\ \mu\text{m}$ (tem).

Figs. 6 and 8 are micrographs showing early stages of crystal growth in glasses of $\text{BaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ and $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ compositions, respectively, synthesised from kaolin and sulphates, and given short heat-treatments. Fig. 6 shows round crystals adjacent to what appear to be small rounded bumps of liquid phase separation. Fig. 8, on the other hand, shows a few rectangular long crystals on a glass background. On further heating of these two glasses, many more small crystals are produced in the $\text{BaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ glass (fig. 7), whereas only a small number of coarse crystals grow in the $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ glass.

Heterogeneous nucleation of $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ glasses by molybdenum oxide produced glass-ceramics of mixed feldspars dominated by the hexagonal modification. However, in the $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ glass synthesised from kaolin

and sulphate, which deviates somewhat from the stoichiometry, an anorthite (fig. 8) was nucleated, as shown by X-ray analysis.

3.9. Fluorite and Sphalerite

Fluorite (CaF_2) and sphalerite (cubic ZnS) do not dissolve in the barium aluminosilicate melt, and hexacelsian is readily nucleated by both of these compounds on heating, even when their excess in the glass is below 1%. The nucleation of the analogue strontium and calcium feldspars by these nucleating agents, on the other hand, is relatively poor.

As opposed to the clear match in the lattice parameters of the noble metals and the feldspars discussed above, no such relationships are apparent between the fluorite, sphalerite, and the various high-symmetry feldspars. Although there is a close match between the a parameters of the two nucleating agents and the feldspars, there is no two-dimensional fit between low-index planes of a nucleating agent and a feldspar, and the significance of similarity of one-dimensional interatomic distance is doubtful [8]. Epitaxy then is not considered to be a factor in the nucleation of hexacelsian by fluorite or sphalerite. As mentioned above, this questions the importance of epitaxy in the nucleation process of the feldspars.

Acknowledgement

The writer is grateful to all the people who helped him carry out this study. Dr G. H. Beall offered useful discussions and critically read the manuscript. Dr T. P. Seward, III, critically read the manuscript. The scanning electron micrographs were taken by Mr E. Korda and Mr R. Fritz. The transmission electron micrographs were taken by Mr G. B. Carrier and Mr S. Irving. The valuable technical assistance of Mr W. F. Lynch is gratefully acknowledged.

References

1. S. D. STOOKEY, *Glastech. Ber.* **32** (1959) 1.
2. B. VONNEGUT, *J. Appl. Phys.* **18** (1947) 593.
3. G. E. RINDONE, *J. Amer. Ceram. Soc.* **45** (1962) 5.
4. G. L. DAVIS and O. F. TUTTLE, *Amer. J. Sci.* Bowen Vol. (1952) 107.
5. T. ITO, "X-ray Studies on Polymorphism" (Maruren Co Ltd, Tokyo, 1956).
6. R. E. NEWNHAM and H. D. MEGAW, *Acta Cryst.* **13** (1960) 303.
7. C. R. AMBERO, *J. Amer. Ceram. Soc.* **29** (1946) 87.
8. YU D. CHISTYAKOV and B. D. LAINER, "Growth of Crystals", Vol. 4 (Consultants Bureau, NY 1966) (translation from Russian).