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CURRENT UNDERSTANDING OF STABLE AND METASTABLE PHASE EQUILIBRIA AND REACTIONS IN THE SiO<sub>2</sub>-a-Al<sub>2</sub>O<sub>3</sub> SYSTEM

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IN THE  $\text{SiO}_2$ - $\alpha$ - $\text{Al}_2\text{O}_3$  SYSTEM

Joseph A. Pask

December 1982

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AND REACTIONS IN THE  $\text{SiO}_2$ - $\alpha$ - $\text{Al}_2\text{O}_3$  SYSTEM

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ABSTRACT

Procedures in the preparation of specimens in this system are critical due to the difficulty of nucleating  $\alpha\text{Al}_2\text{O}_3$  when the silicate liquid is not saturated with  $\text{Al}_2\text{O}_3$  even though it may be supersaturated relative to  $\alpha\text{Al}_2\text{O}_3$ , and the capability of mullite growing from an alumino-silicate melt during cooling with an accommodation of larger amounts of  $\text{Al}_2\text{O}_3$ . Metastable phase compositions and structures thus occur commonly. As a result, misinterpretations of experimental data have occurred in published reports. Stable and metastable phase equilibria diagrams in the  $\alpha\text{Al}_2\text{O}_3\text{-SiO}_2$  system are presented.

## INTRODUCTION

The  $\text{SiO}_2$ - $\alpha\text{Al}_2\text{O}_3$  system is one of the most important systems in ceramics, including both the traditional and modern industrial ceramics, both on a scientific basis as well as on a practical or processing basis. Understanding the phase assemblages and morphologies that develop provides a basis for the understanding of the microstructural development of a material with a fixed chemical composition. The properties and behavior of a material are in turn dependent on its microstructure, or character. This topic thus requires and is entitled to a great deal of research attention.

The system appeared, at one time, to be simple, but it does present problems in two respects. These can be posed as questions:

- a) Does mullite melt congruently or incongruently; and, if the latter what is the range of the  $\alpha\text{Al}_2\text{O}_3$  primary phase field?
- b) What is the nature and extent of the solid solution range of mullite?

## HISTORICAL REVIEW

It is of interest to provide a brief chronological review of studies in this system.\*

- 1) Sainte-Claire Deville and Caron (1) identified a compound in 1865 with a composition of  $\sim 70.5$  w/o  $\text{Al}_2\text{O}_3$  and  $29.5$  w/o  $\text{SiO}_2$ .
- 2) Vernadsky identified a similar compound in 1865 with a composition of  $\sim 70.3$  w/o  $\text{Al}_2\text{O}_3$ , and proposed the formula  $11\text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$ .

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\* No effort is made here to provide a complete literature review; a few articles in the literature have been selected to provide a significant historical perspective.

- 3) Shepherd, Rankin and Wright (3) published the first phase equilibrium diagram in this system in 1909; they believed sillimanite ( $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ) to be the binary compound: it was said to have a congruent melting point at  $1816^\circ\text{C}$  and form an eutectic with  $\alpha\text{Al}_2\text{O}_3$  at  $1810^\circ\text{C}$ .
- 4) Bowen and Greig (4) questioned the congruency and found the binary compound to be  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  (71.8 w/o  $\text{Al}_2\text{O}_3$ ) and to melt incongruently. The binary compound was essentially identical with a natural mineral designated mullite from its occurrence on the Island of Mull in Scotland.
- 5) Aramaki and Roy (5) questioned the reported incongruency and showed mullite to have a congruent melting point; they established a solid solution range for mullite of  $\sim 71.8$  to  $74.0$  w/o  $\text{Al}_2\text{O}_3$ .
- 6) Davis and Pask (6) reported diffusion studies of  $\text{Al}_2\text{O}_3$  in fused  $\text{SiO}_2$  up to  $1800^\circ\text{C}$  using  $\alpha\text{Al}_2\text{O}_3$ -fused  $\text{SiO}_2$  diffusion couples; the mullite solid solution range was determined to be  $71.0$  to  $74.0$  w/o  $\text{Al}_2\text{O}_3$  by microprobe analysis of mullite layers grown at the interfaces of the couples.
- 7) Aksay and Pask reported diffusion studies above  $1800^\circ\text{C}$ ; they found that the  $\alpha\text{Al}_2\text{O}_3$  liquidus profile essentially matched that of Bowen and Greig, indicating that mullite melts incongruently.

#### ILLUSTRATION OF PROBLEMS

Let us superimpose the two most widely accepted phase equilibrium diagrams in (4) and (5), as is done in Fig. 1. It can be seen that the principal disagreements exist in the high  $\text{Al}_2\text{O}_3$  region at temperatures above  $1800^\circ\text{C}$ . Now, let us examine some experimental results that contribute to this disagreement. If an overall chemical composition of

71.8 w/o  $\text{Al}_2\text{O}_3$  ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) is heated to  $1900^\circ\text{C}$  by a number of different paths and quenched to room temperature, the following results have been reported:

- a) Starting with polycrystalline or single crystal mullite, melting occurs at  $\sim 1880^\circ\text{C}$  and complete liquid is present at  $\sim 1900^\circ\text{C}$ , indicating congruent melting.
- b) Starting with a mixture of fine-grained  $\alpha\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  and heating slowly so that the reaction to form mullite is completed before  $1880^\circ\text{C}$  is reached, similar melting behavior as (a) is observed.
- c) Starting with a mixture of coarse-grained  $\alpha\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  powders and heating at a rate so that the reaction to form mullite is incomplete before the melt forming temperature is reached,  $\alpha\text{Al}_2\text{O}_3$  is still present with the liquid after an additional 36 hours at  $1900^\circ\text{C}$ . If  $\alpha\text{Al}_2\text{O}_3$  was a non-equilibrium phase, diffusion experiments (7) indicate that its dissolution to become part of the liquid would have occurred within an hour. This behavior indicates incongruent melting of mullite, since  $\alpha\text{Al}_2\text{O}_3$  could not be present if mullite melted congruently.
- d) Starting with a mixture of powders of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  of any structure, homogenizing it by melting at  $2000^\circ\text{C}$  and then cooling it to  $1900^\circ\text{C}$ , it remains as a liquid but on continued cooling to temperatures below  $\sim 1350^\circ\text{C}$ , mullite with  $\sim 78$  w/o  $\text{Al}_2\text{O}_3$  precipitates (8). If the sample is now raised to  $\sim 1700^\circ\text{C}$  and held, some exsolution of  $\text{Al}_2\text{O}_3$  occurs which enters the liquid phase and the mullite composition changes to  $\sim 73$  w/o  $\text{Al}_2\text{O}_3$  (9).  $\alpha\text{Al}_2\text{O}_3$  does not appear.



All of this experimental evidence plus other examples, none of which can be rejected, thus supports the existence of both congruent and incongruent melting of mullite. Thermodynamically, it must be assumed that one behavior represents stable equilibrium and others, metastable equilibrium conditions. Unfortunately, sufficient thermodynamic data for calculation of the assemblages which would have the lowest free energy are not available. Careful evaluation of the phase equilibria data always indicates the association of  $\alpha\text{Al}_2\text{O}_3$  with the examples which indicate incongruent melting of mullite. Experiments therefore can be devised whose interpretation would enable a resolution of this problem.

#### PHASE COMPOSITION EXPERIMENTS

A number of significant experiments can be identified. Their evaluation indicates that they can be divided into three groupings. In the first group  $\alpha\text{Al}_2\text{O}_3$  is a participant and the reaction products are obtained at constant temperatures. In the second group the reaction products are also obtained at constant temperatures but in the absence of  $\alpha\text{Al}_2\text{O}_3$ . In the third group  $\alpha\text{Al}_2\text{O}_3$  is not a reactant and the reaction products form during cooling.

Since it will be seen that  $\alpha\text{Al}_2\text{O}_3$  does not readily nucleate and grow from a saturated solution, it is worthwhile at this point to discuss the physical chemistry of solutions for subsequent interpretation of experimental results.

On cooling a solution it can become saturated with the solute; on further cooling it may retain its liquid state without separation of the excess dissolved solute when every trace of the solid solute is excluded, i.e. no crystal nuclei are present or form. Such a solution is said to

be supersaturated; it could also be referred to as being supercooled. It can be deduced that at saturation a balance exists between the bond energies of the solvent and the solute crystal for the solute molecules in the solution; at supersaturation, the solvent liquid has the capability of having more solute molecules in solution because of the absence of solute crystals or nuclei. If the concentration of the solute is increased in the starting solution so that on cooling, the solution becomes saturated relative to a given solute structure which is the maximum amount of solute molecules that the solution can dissolve, then nucleation and growth of solute occurs easily and supersaturation is not maintained.

Likewise, if a compound which on equilibrium heating would undergo a peritectic reaction to form another solid and a liquid does not undergo this reaction because of nucleation difficulties of the solid product, the compound experiences superheating. If, on further heating, a temperature is reached at which melting occurs without nucleation of the solid reaction product, the compound then experiences metastable congruent melting; the resulting liquid may retain its supersaturated condition.

#### In Presence of $\alpha\text{Al}_2\text{O}_3$ at Constant Temperatures

A stable phase equilibrium diagram should be developed by performing experiments in the presence of  $\alpha\text{Al}_2\text{O}_3$  at constant temperatures for a sufficient time to achieve a relaxed steady state. Diffusion couples fulfill these requirements. Typical cross-sections of couples of single crystal sapphire ( $\alpha\text{Al}_2\text{O}_3$ ) and fused silica are shown in Fig. 2: (A) at 1803°C for 167 hrs, and (B) at 1853°C for 2 hrs (7). Only specimen (A) shows a mullite layer at the interface, grown at temperature

by interdiffusion of  $Al^{3+}$  and  $Si^{4+}$  ions, through the layer, which has a concentration gradient from 71 w/o  $Al_2O_3$  at the silicate-mullite interface to 74 w/o  $Al_2O_3$  at the mullite- $\alpha Al_2O_3$  interface; observed by transmission electron microscopy (TEM) this mullite is clear of line defects. The prismatic precipitates in the silicate diffusion zone starting at the interface in both (A) and (B) are also mullite crystallized in a relatively few minutes during cooling, by short range diffusion of  $SiO_2$  away from nucleation sites in the liquid. The  $Al_2O_3$  content of this mullite was always higher than the host liquid and varied from 73 to 79 w/o depending on the  $Al_2O_3$  content of the adjoining host liquid, being higher in the grains closer to the interface, i.e. grains precipitating from a liquid with a higher  $Al_2O_3$  content. The rapidly grown precipitates near the mullite layer which was grown slowly by solid state reaction (Fig. 2A) thus have a higher  $Al_2O_3$  content, 79 w/o vs 71 w/o. Observed by TEM, the prismatic crystals contain many line defects.

Concentration profiles perpendicular to the interface of  $\alpha Al_2O_3$ -fused  $SiO_2$  couples were obtained with the use of an electron microprobe. The beam was oscillated over a distance of 100  $\mu m$  parallel to and at a given distance from the interface, and counts were integrated for a fixed time. Then the beam was moved a fixed distance, and the process repeated. Smooth curves of  $Al$  concentration were obtained because the procedure gave average liquid compositions at temperature since the precipitates were formed by short range diffusion of species through the liquid (7,10): Fig. 3 shows typical results.

Figure 4 shows schematically the relationship of the Al diffusion profile to the phase diagram at 1750°C; its profile is similar to that for Fig. 2A. Experimentally, the thickness of the mullite layer and the extent of the diffusion zone into the fused SiO<sub>2</sub> from the interface depended on the length of time allowed for reaction at a given temperature, but the interface compositions always remained constant and the transport of Al from the interface was diffusion-controlled indicating that the rates of reaction were faster than the diffusion rates. The interface compositions then represent stable equilibria and provide information for the stable phase equilibrium diagram. Figure 5 shows a similar schematic relationship at 1950°C; the profile is similar to that for Fig. 2B. Mullite does not grow at the interface because the temperature is above the melting point: the prismatic mullite which is observed forms on cooling. The average composition of the liquid with the precipitates at the interface, determined by microprobe as above, is ~ 71 w/o Al<sub>2</sub>O<sub>3</sub>, and is equivalent to the αAl<sub>2</sub>O<sub>3</sub> liquidus at 1950°C. Mullite must melt incongruently in the presence of αAl<sub>2</sub>O<sub>3</sub> under stable phase equilibrium conditions, as indicated in Fig. 5.

These experiments support the general features of the Bowen and Greig diagram shown in Fig. 1. The more recent experimentally determined stable phase equilibrium diagram (7) is drawn in solid lines in Fig. 6. It applies to phase equilibria for this system in the presence of αAl<sub>2</sub>O<sub>3</sub> nucleation sites in the higher Al<sub>2</sub>O<sub>3</sub> compositions.

### In Absence of $\alpha\text{Al}_2\text{O}_3$ at Constant Temperature

A single crystal of mullite was successfully grown by the Czochralski technique (11) even though it was shown that it should melt incongruently under stable equilibria conditions. The crystal had  $\sim 77$  w/o  $\text{Al}_2\text{O}_3$ , nominally  $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ , even though the starting liquid composition was  $\sim 71.8$  w/o  $\text{Al}_2\text{O}_3$  (i.e.,  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ); mass balance was achieved by the presence of silica-rich liquid inclusions in the crystal. TEM did not show any line defects. The starting liquid was homogenized above the  $\alpha\text{Al}_2\text{O}_3$  liquidus temperature (Fig. 6) and supercooled because of absence of nuclei and difficulty of nucleation of  $\alpha\text{Al}_2\text{O}_3$ . On supercooling, the liquid becomes saturated with mullite and a mullite single crystal is grown at constant temperature; the liquid was also supersaturated with  $\alpha\text{Al}_2\text{O}_3$  whose nucleation and growth from the melt was less favorable.

The intersection of the extensions of the mullite liquidus and solidus curves of the stable phase equilibrium diagram, shown in Fig. 6, corresponds to the experimentally grown mullite single crystal composition of  $\sim 77$  w/o  $\text{Al}_2\text{O}_3$ . Polycrystalline mullite has been superheated above the peritectic temperature, because of the difficulty of nucleating  $\alpha\text{Al}_2\text{O}_3$ , until it melted at  $\sim 1880^\circ\text{C}$ . These phase relationships are the basis for a metastable phase diagram for  $\text{SiO}_2$ -mullite in the absence of  $\alpha\text{Al}_2\text{O}_3$  nucleation sites. Under these conditions, the mullite that is grown at a constant temperature close to the melting temperature has a maximum  $\text{Al}_2\text{O}_3$  content of  $\sim 77$  w/o.

### In Absence of $\alpha\text{Al}_2\text{O}_3$ with Rapid Cooling

Melts of several composition series with high  $\text{Al}_2\text{O}_3$  contents were homogenized at a temperature above the stable equilibrium  $\alpha\text{Al}_2\text{O}_3$  liquidus, to eliminate any  $\alpha\text{Al}_2\text{O}_3$  nuclei. Crystallization was examined after cooling with no constant temperature periods maintained at any time after homogenization.

Members of an initial series with  $\text{Al}_2\text{O}_3$  contents from 60 to  $\sim 83$  w/o on rapid cooling were supersaturated with  $\alpha\text{Al}_2\text{O}_3$  and became saturated with mullite resulting in precipitation of mullite but no  $\alpha\text{Al}_2\text{O}_3$  (12). Mullite compositions were always higher in  $\text{Al}_2\text{O}_3$  content than the liquid from which they nucleated and grew except that the  $\text{Al}_2\text{O}_3$  contents of both phases appeared to converge at  $\sim 83$  w/o  $\text{Al}_2\text{O}_3$ , nominally  $3\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ .

A second series was extended to 88 w/o  $\text{Al}_2\text{O}_3$ . Compositions with higher than 83 w/o  $\text{Al}_2\text{O}_3$ , after similar homogenization and then furnace quenching or cooling slowly, spontaneously nucleated  $\alpha\text{Al}_2\text{O}_3$  followed by mullite. The series was examined by TEM and optical microscopy using the Nomarski technique (13). Three typical microstructures were observed up to  $\sim 77$  w/o, from  $\sim 77$  to  $\sim 83$  w/o, and from  $\sim 84$  w/o to higher  $\text{Al}_2\text{O}_3$  contents. The first group showed feathery or rod-like crystals of mullite with many line defects as observed by TEM. The second group showed more unusual and complex microstructures. Figure 7 is a transmitted polarized light micrograph of a specimen showing lamellae with subtexture of oriented exsolution of  $\alpha\text{Al}_2\text{O}_3$  precipitates formed on slow cooling of the melt. Figure 8 shows TEM micrographs of complementary dark field images from superlattice reflections indicating twinning in a specimen with 83.5 w/o  $\text{Al}_2\text{O}_3$ . The third group showed primary precipitates of  $\alpha\text{Al}_2\text{O}_3$  with mullite. Figure 9 shows the lattice

parameters for this series on slow cooling (13). Since the mullite crystals precipitate from the melts on cooling, essentially in a few minutes, the trends in the parameter changes are not distinct. However, changes are indicated at about 78 w/o  $Al_2O_3$  and about 84 w/o  $Al_2O_3$  in the liquids which correlate with significant values discussed above. The lattice parameters for the third group of specimens have become essentially the same as those for a standard specimen and for mullite formed by solid state reaction.

Another study (8) which dealt with the application of various cooling cycles to a melt with 60%  $Al_2O_3$ , homogenized above its liquidus temperature, indicated that the melts undercooled to  $\sim 1325^\circ C$ , which corresponds approximately to the miscibility gap temperature for this composition (9), before mullite precipitated, as interpreted from Fig. 6. At the experimental cooling rate, the precipitated mullite had  $\sim 78$  w/o  $Al_2O_3$  but on continued heating at  $1700^\circ C$  its  $Al_2O_3$  content was decreased to  $\sim 73$  w/o, by exsolution. Figure 10 shows the mullite morphology; no  $Al_2O_3$  was nucleated and grown on cooling through the primary phase field of  $\alpha Al_2O_3$  (Fig. 6).

## DISCUSSION

Extensive metastability occurs in this system because of the difficulty of nucleating  $\alpha Al_2O_3$  both from an appropriate liquid and mullite, and the capability of mullites precipitating from a cooling melt to accommodate additional amounts of  $Al_2O_3$  in their structure in the absence of  $\alpha Al_2O_3$ . Each of these factors will be discussed.

### Nucleation of $\alpha\text{Al}_2\text{O}_3$

Mixtures of fused  $\text{SiO}_2$  and increasing amounts of  $\alpha\text{Al}_2\text{O}_3$  have two thermodynamic driving forces just above the peritectic temperature: solution of  $\alpha\text{Al}_2\text{O}_3$  in the silicate melt, and the growth of  $\alpha\text{Al}_2\text{O}_3$ . When the solution driving force is greater,  $\alpha\text{Al}_2\text{O}_3$  dissolves; when it is equal to the driving force for growth of  $\alpha\text{Al}_2\text{O}_3$ , stable equilibrium is reached. This occurs when liquid has 50 w/o  $\text{Al}_2\text{O}_3$  (Fig. 6). Further additions of  $\alpha\text{Al}_2\text{O}_3$  cause no change in the liquid composition since the liquid is in equilibrium and saturated with respect to  $\alpha\text{Al}_2\text{O}_3$ , which corresponds to the  $\alpha\text{Al}_2\text{O}_3$  liquidus composition at the peritectic. Experimentally, the entire series from  $\text{SiO}_2$  to  $\alpha\text{Al}_2\text{O}_3$  can be converted to liquid by heating above the liquidus temperatures; on cooling the melts to just above the peritectic temperature, in the absence of  $\alpha\text{Al}_2\text{O}_3$  nucleating surfaces,  $\alpha\text{Al}_2\text{O}_3$  nucleates spontaneously only in the melts with  $> 83$  w/o  $\text{Al}_2\text{O}_3$ . Therefore, the liquid compositions with 50 to 83 w/o  $\text{Al}_2\text{O}_3$  are supersaturated relative to  $\alpha\text{Al}_2\text{O}_3$ , i.e., the liquid structure accommodates this additional amount of  $\text{Al}_2\text{O}_3$  in the absence of competition from the  $\alpha\text{Al}_2\text{O}_3$  growth surfaces. With precipitation of  $\alpha\text{Al}_2\text{O}_3$ , i.e. formation of  $\alpha\text{Al}_2\text{O}_3$  nuclei, they will grow until the liquid will decrease its  $\text{Al}_2\text{O}_3$  content to the  $\alpha\text{Al}_2\text{O}_3$  liquidus value of 50 w/o.

On cooling the indicated liquid compositions below the peritectic temperature, at some point the precipitation of mullite becomes more favorable than  $\alpha\text{Al}_2\text{O}_3$ . With primary nucleation of  $\alpha\text{Al}_2\text{O}_3$  as well as mullite with high  $\text{Al}_2\text{O}_3$  contents from mixtures with more than 83 w/o  $\text{Al}_2\text{O}_3$ , the mullite will exsolve  $\text{Al}_2\text{O}_3$  which will precipitate onto the  $\alpha\text{Al}_2\text{O}_3$  nuclei. It is expected that the  $\text{Al}_2\text{O}_3$  content of the mullite will decrease to  $\sim 77$  w/o and probably to  $\sim 74$  w/o.



When mullite is heated above its peritectic temperature of 1810°C, it does not melt incongruently because of the difficulty of nucleating  $\alpha\text{Al}_2\text{O}_3$  within the mullite; it can then be superheated to its metastable congruent melting point of  $\sim 1880^\circ\text{C}$ . The resulting liquid is supersaturated relative to  $\alpha\text{Al}_2\text{O}_3$  which does not appear because of nucleation difficulties of  $\alpha\text{Al}_2\text{O}_3$ . With the presence of a small amount of  $\alpha\text{Al}_2\text{O}_3$  grains, however, the mullite behaves similarly but the  $\alpha\text{Al}_2\text{O}_3$  remains up to the liquidus temperature of  $\sim 1920^\circ\text{C}$  and equilibrates with the liquid; this observation was reported by Bowen and Greig (4). A mixture of  $\text{SiO}_2$  and  $\alpha\text{Al}_2\text{O}_3$  does not form mullite above 1810°C as expected with a stable incongruent melting point; mullite does form below 1810°C as indicated by the diffusion couples (Fig. 2 and (6) and (7)).

#### Solid Solution Ranges Exhibited by Mullite

Mullite exhibits three solid solution ranges depending on the conditions of their formation. The range shown in the stable phase equilibrium diagram formed by solid state reaction of  $\text{SiO}_2$  and  $\alpha\text{Al}_2\text{O}_3$  at constant temperature is from 70.5 to 74 w/o  $\text{Al}_2\text{O}_3$ . The solid solution range in the metastable phase equilibrium diagram for  $\text{SiO}_2$  and mullite in the absence of  $\alpha\text{Al}_2\text{O}_3$  is extended to  $\sim 77$  w/o  $\text{Al}_2\text{O}_3$  (nominally  $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ). This composition has been achieved by growth of a single crystal of mullite by the Czochralski technique. It should also be reached by the sol-gel process because of the use of a source of  $\text{Al}_2\text{O}_3$  other than  $\alpha\text{Al}_2\text{O}_3$ . Since the mullite atomic structure is based on the sillimanite structure with substitutions of Al ions for Si ions and omission of oxygens to maintain charge balance, these experiments suggest that  $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  is the terminal composition of the substitutional series (13). This overall series, free of line defects, is considered to

have been formed by chemical interdiffusion of  $Al^{3+}$  and  $Si^{4+}$  through the growing mullite layer at constant temperature.

The third solid solution range of mullite with  $Al_2O_3$  from  $\sim 73$  to  $\sim 83$  w/o is formed by supercooling of homogenized liquids with  $Al_2O_3$  contents from  $\sim 60$  to  $\sim 83$  w/o. The mullites form on cooling in a relatively short time by short range diffusion of essentially molecules of  $SiO_2$  and  $Al_2O_3$ . As a result, it is expected that the liquid structure is related to that of mullite so that on cooling it is favorable to form mullite with entrapment of  $Al_2O_3$  to give compositions beyond the terminal substitutional composition without the nucleation of  $\alpha Al_2O_3$ ; this formation mechanism is probably responsible for the many line defects. Complex microstructures in the specimens with  $Al_2O_3$  above 77 w/o, e.g. one of lamellae with subtextures of  $\alpha Al_2O_3$  (Fig. 7) and one with transformation twinning (Fig. 8), can be the result of such entrapments. Furthermore, such entrapments can also be responsible for the exsolution of  $Al_2O_3$  from such mullites on annealing.

#### SUMMARY

The stable phase equilibrium diagram, as presently understood, is shown in Fig. 6 in solid lines. It is derived by reaching a steady state at constant temperature in the presence of  $\alpha Al_2O_3$  nuclei or nucleation surfaces. A metastable phase equilibrium diagram, obtained by a similar heating procedure but in the absence of  $\alpha Al_2O_3$ , is realized by extension of the stable mullite liquidus and solidus lines which intersect at an  $Al_2O_3$  content of 77 w/o corresponding to a nominal composition of  $2Al_2O_3 \cdot SiO_2$  (short dash lines in Fig. 6). In the presence of  $\alpha Al_2O_3$ ,

mullite exhibits incongruent melting behavior, and in the absence of  $\alpha\text{Al}_2\text{O}_3$ , congruent melting. The difficulty of nucleation of  $\alpha\text{Al}_2\text{O}_3$  is probably due to the fact that in this composition range the liquid is not saturated with  $\text{Al}_2\text{O}_3$  molecules even though it is supersaturated relative to  $\alpha\text{Al}_2\text{O}_3$ ; at  $\sim 84$  w/o  $\text{Al}_2\text{O}_3$  the liquid has the maximum amount of  $\text{Al}_2\text{O}_3$  in solution and  $\alpha\text{Al}_2\text{O}_3$  precipitates spontaneously on cooling.

A metastable phase equilibrium diagram may be constructed from quench data obtained on alumino-silicate liquids in the absence of crystalline  $\alpha\text{Al}_2\text{O}_3$ . It is similar in appearance to the previous metastable diagram but with a maximum  $\text{Al}_2\text{O}_3$  content of  $\sim 83$  w/o in the precipitated mullite which is nominally  $3\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  (shown by long dash-dot lines in Fig. 6). Higher  $\text{Al}_2\text{O}_3$  contents cause a spontaneous precipitation of  $\alpha\text{Al}_2\text{O}_3$  and reversion of mullite to the stable phase equilibrium on annealing by exsolution of  $\text{Al}_2\text{O}_3$ .

Metastable phase equilibria are thus being identified phenomenologically which show a rational interrelationship of the extensive experimental data. A great deal more work, however, is needed to determine the kinetics and mechanisms of the various phase transformations and resulting microstructures.

#### ACKNOWLEDGMENT

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FIGURE CAPTIONS

- Fig. 1  $\text{SiO}_2\text{-Al}_2\text{O}_3$  phase equilibrium diagrams as determined by Bowen and Greig (ref. 4) and by Aramaki and Roy (ref. 5).
- Fig. 2 Interference-contrast micrographs of the diffusion zone between starting couples of sapphire and fused silica (A) at 1803°C for 167 hrs. and (B) at 1853°C for 2 hrs. Sapphire at bottom. Mullite layer at interface in (A) grew by solid state reaction at temperature. The prismatic mullite formed on cooling from the test temperature in both cases.
- Fig. 3 Typical computer plotted concentration profiles of sapphire-fused silica couples in the temperature range of 1803 to 2003°C arranged with a common Boltzmann-Matano interface.
- Fig. 4 The relationship between the concentration profile of a semi-infinite  $\text{SiO}_2\text{-Al}_2\text{O}_3$  diffusion couple and the phase diagram, at 1750°C. Boltzmann-Matano interface corresponds to the phase boundary at  $t = 0$ .
- Fig. 5 The relationship between the concentration profile of a semi-infinite  $\text{SiO}_2\text{-Al}_2\text{O}_3$  diffusion couple and the phase diagram at 1950°C.
- Fig. 6 Stable and metastable equilibrium phase diagrams within the  $\text{SiO}_2\text{-Al}_2\text{O}_3$  system. Identification in text.
- Fig. 7 Mullite lamellae with oriented exsolution of  $\text{Al}_2\text{O}_3$  precipitates in 81-83 wt.%  $\text{Al}_2\text{O}_3$  samples slowly crystallized from the melt, observed by transmitted polarized light.

- Fig. 8 TEM micrographs of complementary dark field images from twinned mullite superlattice type reflections in 83 wt.%  $\text{Al}_2\text{O}_3$  sample.
- Fig. 9 (a) EDAX composition analysis of mullite or mullite matrix alone vs. overall composition of melts; and (b) corresponding Guinier X-ray lattice parameters of slowly crystallized mullite vs. overall composition of melts, S - parameters for solid state sintered mullite, and A - parameters for ASTM mullite standard.  $\alpha\text{-Al}_2\text{O}_3$  precipitates were present in compositions with more than 81 w/o  $\text{Al}_2\text{O}_3$ .
- Fig. 10 Microstructure of 60 wt.%  $\text{Al}_2\text{O}_3$  melt cooled to room temperature after homogenization at 2090°C. 78 wt.%  $\text{Al}_2\text{O}_3$  in mullite precipitates and 19 wt.%  $\text{Al}_2\text{O}_3$  in glass.

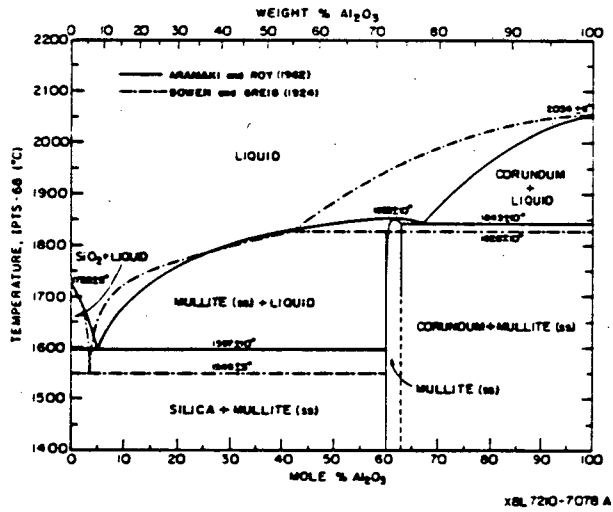
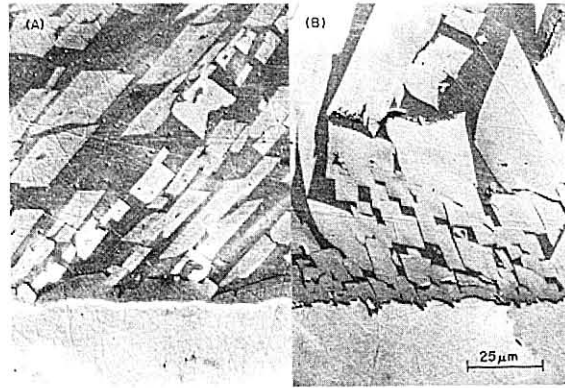


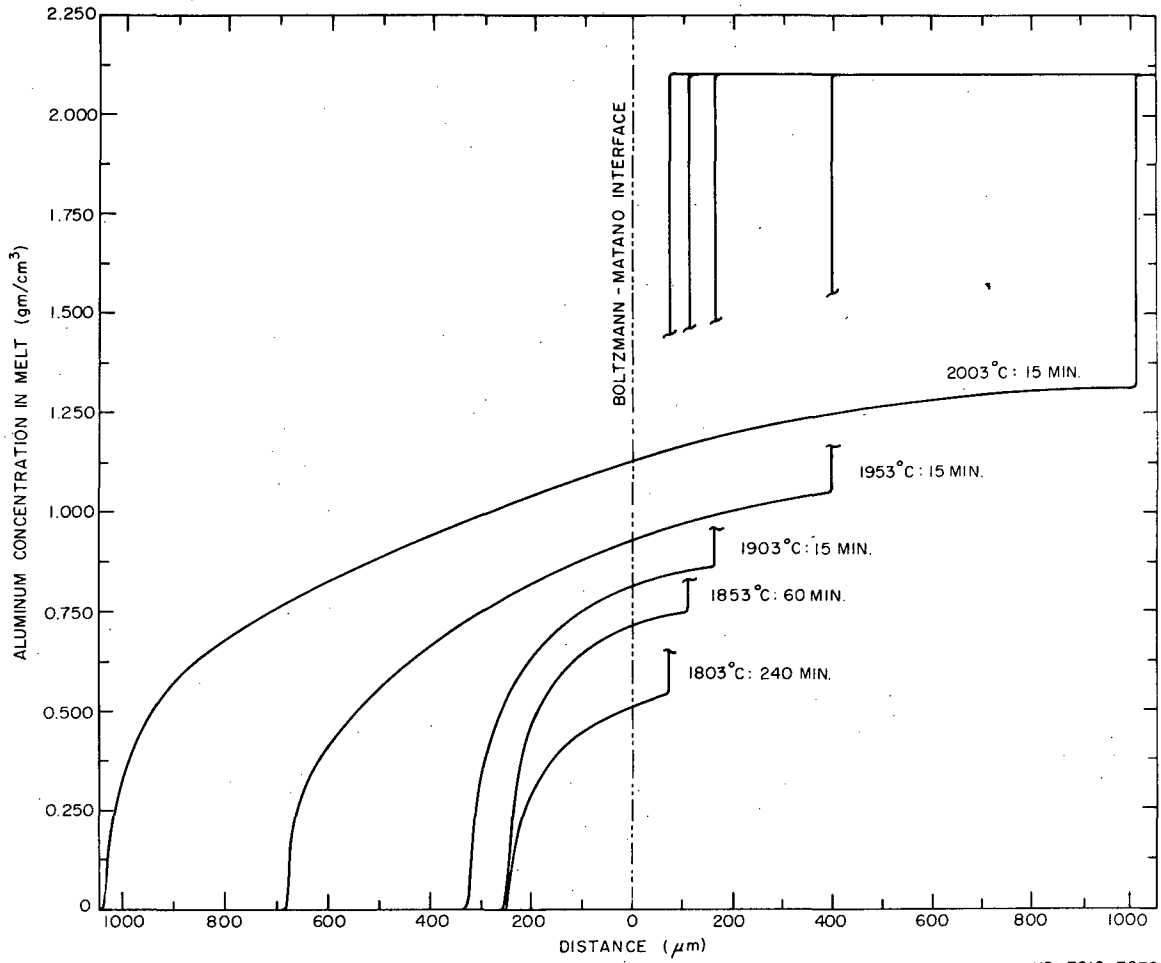
Fig. 1



XBB 720-5300

Fig.2





XBL7210-7070

Fig. 3

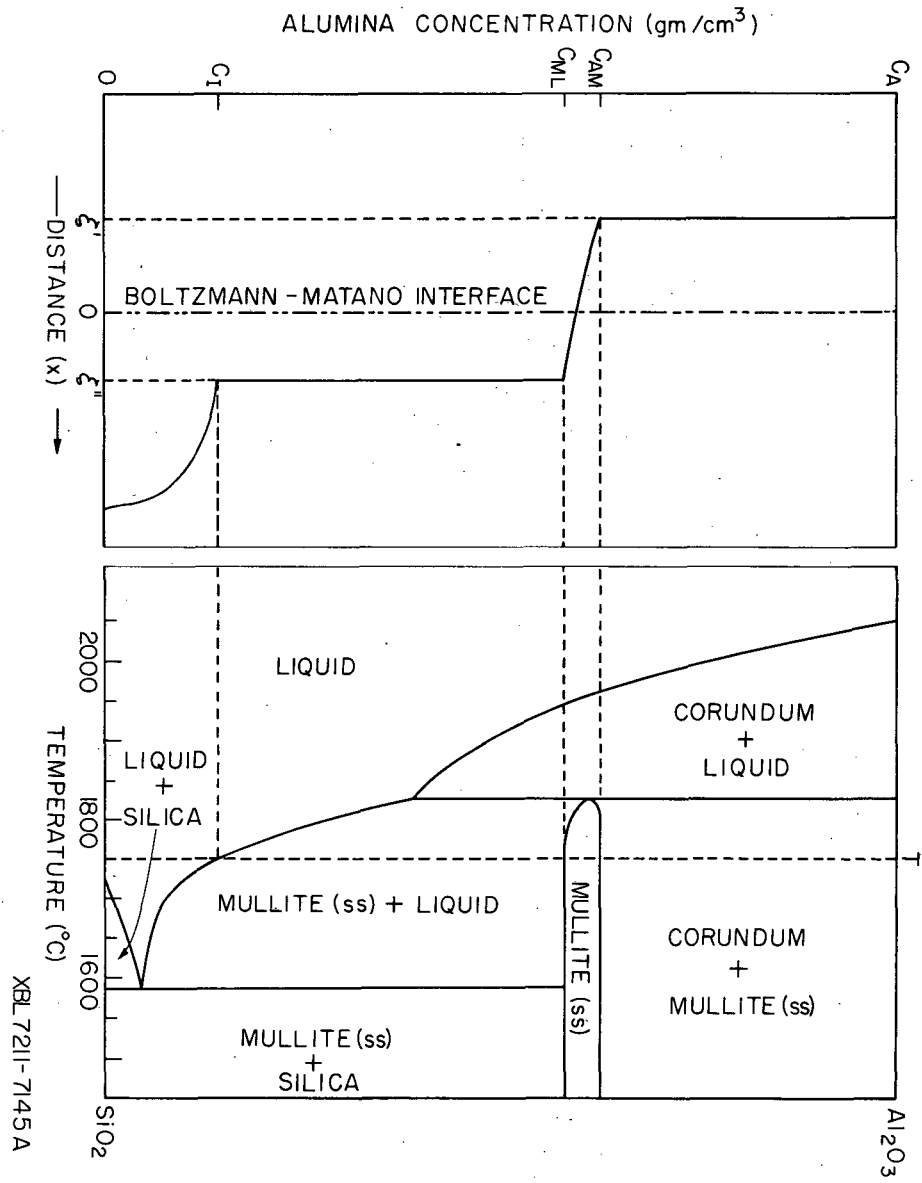


Fig. 4

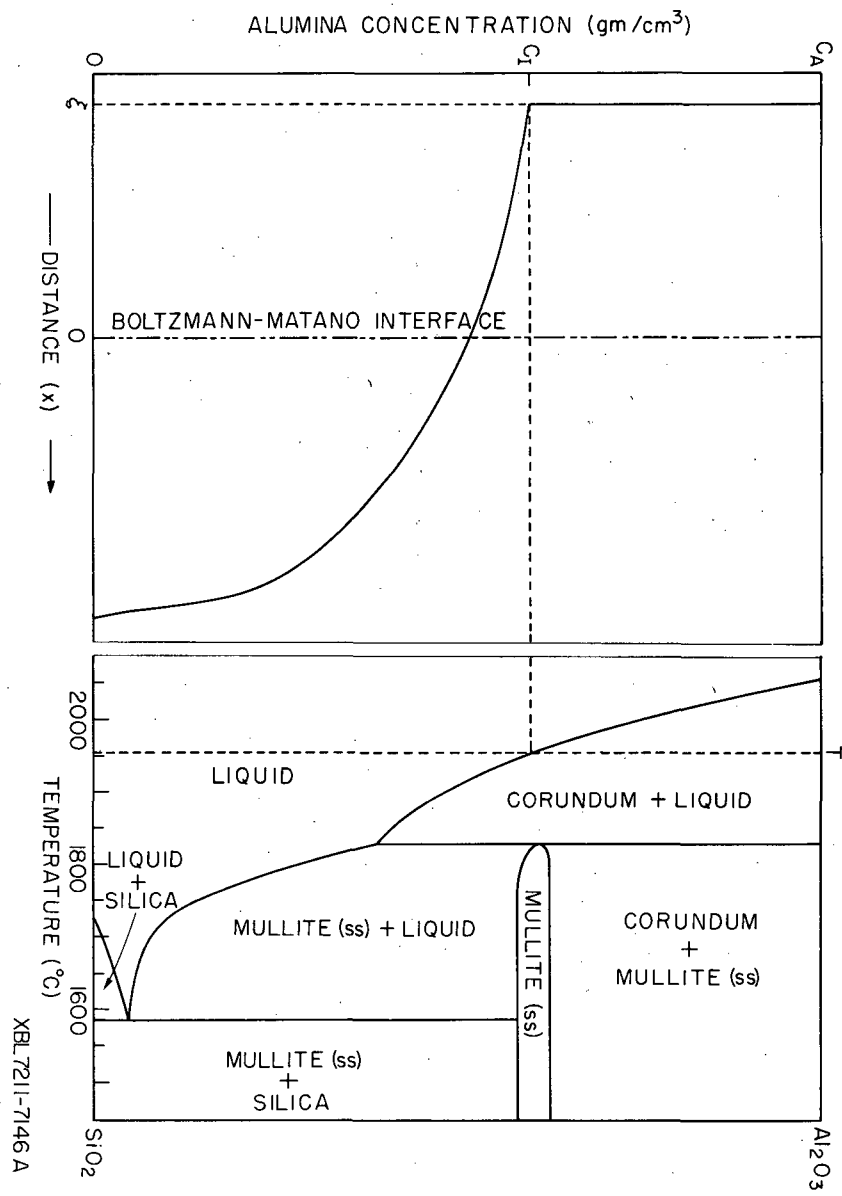
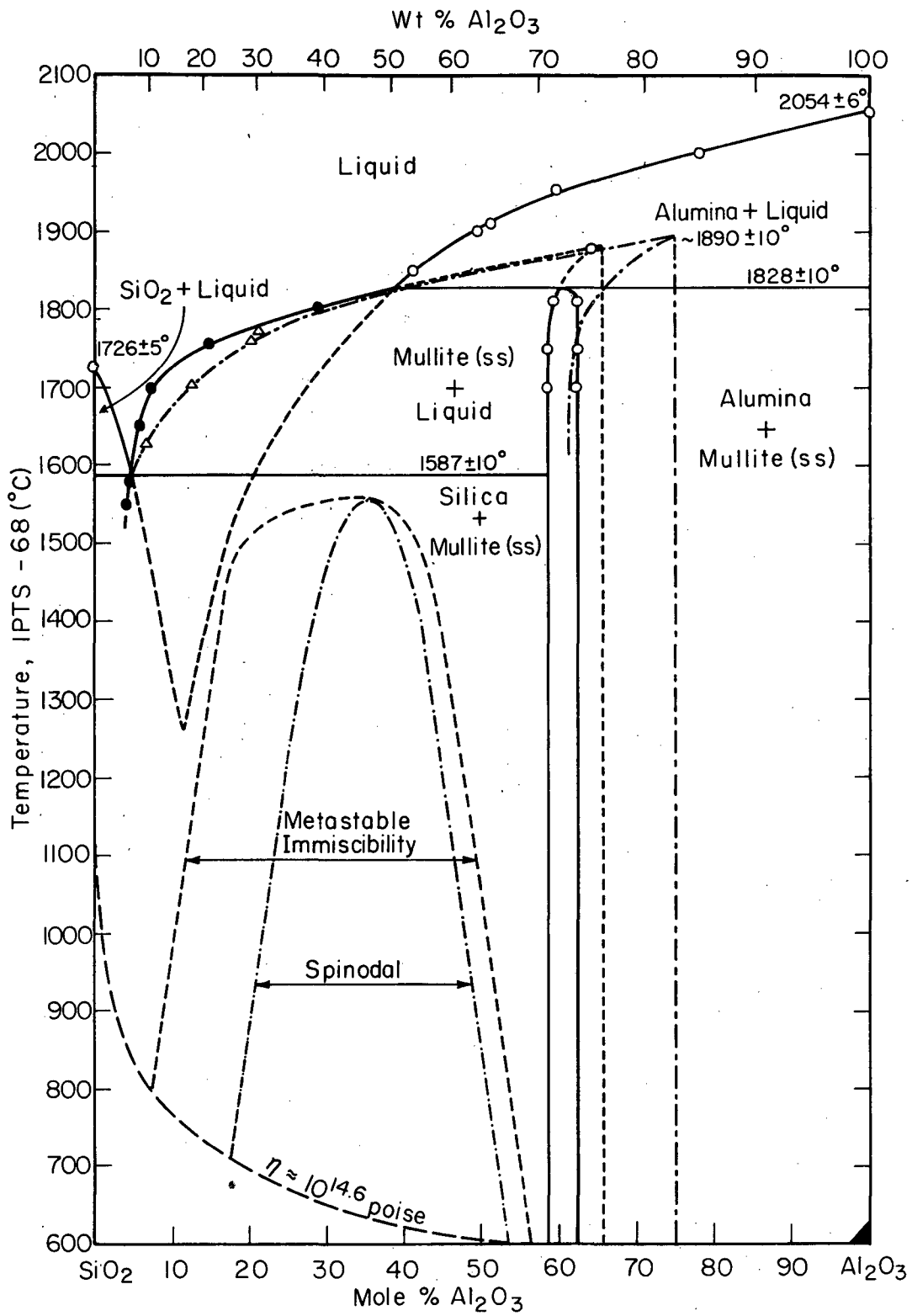


Fig. 5



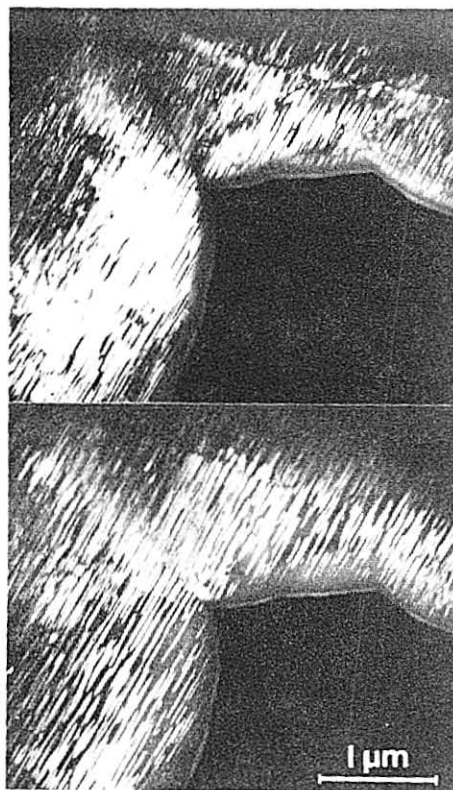
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Fig. 6



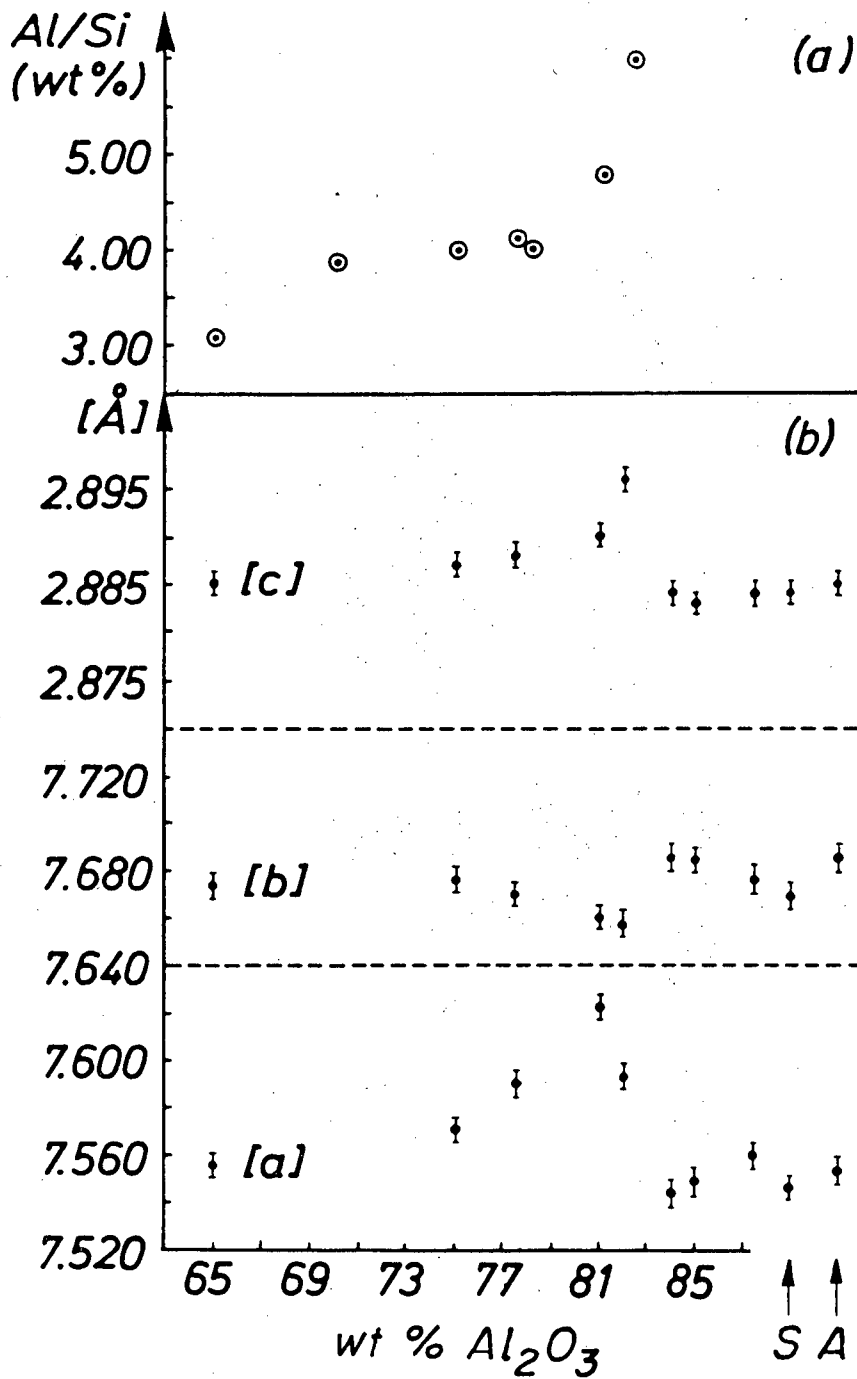
XBB 825-4748

Fig. 7



XBB 825-4749

Fig. 8



XBL 825-10193

Fig. 9

60 - 18



75  $\mu\text{m}$

MULLITE  $\approx$  78 WT. %  $\text{Al}_2\text{O}_3$   
GLASS  $\approx$  18.5 WT. %  $\text{Al}_2\text{O}_3$

XBB 766-5219

Fig. 10



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