

Stable and Metastable Equilibria in the System $\text{SiO}_2\text{-Al}_2\text{O}_3$

I. A. AKSAY* and J. A. PASK*

Inorganic Materials Research Division, Lawrence Berkeley Laboratory and Department of Materials Science and Engineering, College of Engineering, University of California, Berkeley, California 94720

Concentration profiles of Al_2O_3 in diffusion couples made from sapphire and fused silica were used to determine the stable equilibrium phase diagram of the system $\text{SiO}_2\text{-Al}_2\text{O}_3$. The intermediate compound mullite, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, melts incongruently at $1828 \pm 10^\circ\text{C}$; its stable solid-solution region ranges from 70.5 to 74.0 wt% Al_2O_3 below 1753°C and from 71.6 to 74.0 wt% at 1813°C . The microstructures of diffusion zones and heat-treated specimens also indicate the incongruity of mullite. Additional information is given for 3 metastable systems: $\text{SiO}_2\text{-Al}_2\text{O}_3$ in the absence of mullite, SiO_2 -“ordered”-mullite in the absence of alumina, and SiO_2 -“disordered”-mullite in the absence of alumina. Under metastable conditions, ordered mullite melts congruently at $\approx 1880^\circ\text{C}$ and its solid-solution range extends up to ≈ 77 wt% Al_2O_3 . The solid-solution range of disordered mullite extends to ≈ 83 wt% Al_2O_3 with an estimated congruent melting temperature of $\approx 1900^\circ\text{C}$. The existence of metastable systems is associated with superheating of mullite above the incongruent melting temperature and with nucleation of alumina and mullite in supercooled aluminum-silicate liquids.

I. Introduction

THE first systematic phase equilibrium study in the $\text{SiO}_2\text{-Al}_2\text{O}_3$ system¹ showed mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) as the only stable compound of this system and reported that it melted incongruently at 1828°C . Since then, numerous conflicting investigations²⁻⁵ have been conducted. The findings of Troemel *et al.*³ generally agree with those in Ref. 1; Aramaki and Roy,⁵ however, indicate a congruent melting point for mullite. Mullite phase equilibria have been the subject of several reviews.⁶

The solid-solution range of mullite has been reported to extend from 71.8 to ≈ 74.3 wt% Al_2O_3 .⁵ This range, however, is realized only when mullite is prepared by solid-state reactions in the presence of alumina. The composition of mullite solidified from a melt may extend up to 82.6 wt% Al_2O_3 ,⁷ thus raising the question of metastability and the possible existence of a disordered form of mullite with the nominal composition $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$.⁵

Most phase-equilibrium studies on the system $\text{SiO}_2\text{-Al}_2\text{O}_3$ have been conducted by either the static method of quenching⁸ or by differential thermal analysis. These techniques, especially in silicate systems with an incongruently melting compound, can lead to misinterpretation because of nucleation and growth problems.^{9,10} In a diffusion study by Davis and Pask¹¹ semi-infinite couples of SiO_2 and Al_2O_3 and the electron microprobe were used for determining composition profiles; this technique was effective for obtaining stable and metastable phase-equilibrium data. The objectives of the present study (which used the same technique) were to determine (1) the phase equilibria of mullite above 1800°C and, thus, its stable melting behavior, and (2) the solid-solution range of mullite. Experiments using the static method of quenching provided additional data on stable and metastable equilibrium conditions. Diffusion-kinetics data obtained in the present experiments will be presented elsewhere.^{12,13}

II. Experimental Procedure

Much of the present experimental technique has been described by Davis and Pask¹¹ and, unless otherwise specified, the same materials and equipment were used.

(1) Diffusion-Couple Experiments

Diffusion couples were prepared with sapphire and fused silica or sapphire and aluminum-silicate glasses of 10.9, 22.8, and 42.2 wt% Al_2O_3 . These binary glasses are in equilibrium with mullite at

1678° , 1753° , and 1813°C .¹¹ Thus, sapphire-glass diffusion couples of these compositions at the corresponding annealing temperatures could be used to study the growth kinetics of mullite as an intermediate phase without solution of mullite in the liquid phase.

The diffusion cell consisted of Mo or Al_2O_3 crucibles containing a fused-silica or aluminum-silicate glass disk on a sapphire substrate. The runs at 1678°C were done in air with covered alumina crucibles. All anneals above 1700°C were done in a Ta resistance furnace with Mo crucibles which were sealed around the lid by electron-beam welding and He leak-checked in order to eliminate SiO_2 losses by evaporation during annealing. The amount of Mo in the melts was below the microprobe detection limit.

The diffusion anneals ranged from 15 min to one month, depending on the length desired for the diffusion zone. The temperature of the Ta chamber was monitored and electronically controlled using a W5Re-W26Re thermocouple (accuracy $\pm 7^\circ$ at 1800°C). The specimen temperature, however, was measured separately using 2 optical pyrometers (accuracy $\pm 10^\circ$ at 2000°C) which were focused on a blackbody cavity placed atop the crucibles. The pyrometers were frequently calibrated against an NBS secondary standard pyrometer and at the melting point of Pt (1772°C)¹⁴ and Al_2O_3 (2054°C).¹⁵ The pyrometers themselves were frequently checked against each other to detect any malfunction. All temperatures reported herein are based on the 1968 International Practical Temperature Scale (IPTS-68).¹⁴

The diffusion anneals were completed by rapidly cooling the furnaces down to 1500°C (≈ 1 min) in order to “freeze-in” the diffusion profile by preventing long-range diffusion. Continued cooling to room temperature, however, was very slow (≤ 4 days) to avoid loss of integrity at the interface as a result of the difference in thermal expansion. Couples were subsequently sectioned in halves parallel to the direction of diffusion, mounted in polyester resin, and polished.

(2) Phase Equilibrium Studies by Quenching

Quench experiments were performed to supplement diffusion experiments. Fused- SiO_2 and $\alpha\text{-Al}_2\text{O}_3$ mixtures of 42.2, 60.0, 71.8, and 80.0 wt% Al_2O_3 were melted at 1953° to 2003°C for 15 to 30 min. The composition of a representative section was analyzed by electron microprobe. Crucibles were then sealed and heat-treated in the Ta furnace in the range 1753° to 1953°C after a homogenization treatment above the corresponding liquidus temperature. Specimens were cooled by turning off the furnace and allowing He to flow rapidly through it. Microscopic examination of a 78.3-wt% Al_2O_3 specimen[†] showed that the mullite grains were surrounded by a continuous glassy phase.¹⁶

(3) Electron Microprobe Analysis

All the measurements were made with an accelerating voltage of 15 kV and a specimen current of $0.03 \mu\text{A}$. The diameter of the electron beam was $1 \mu\text{m}$, although the volume affected by it was probably in the order of 5 to $10 \mu\text{m}^3$.¹⁷ Two spectrometers recorded the intensities of the $\text{AlK}\alpha$ and $\text{SiK}\alpha$ peaks simultaneously. Concentration profiles were obtained by traversing the electron beam

Presented at the 75th Annual Meeting, The American Ceramic Society, Cincinnati, OH, May 1, 1973 (Basic Science Division, No. 45-B-73). Received July 20, 1974; revised copy received July 14, 1975.

Supported by the United States Atomic Energy Commission under Contract No. W-7405-eng-48.

*Member, the American Ceramic Society.

†Now with Department of Metallurgical Engineering, Middle East Technical University, Ankara, Turkey.

‡Commercial-grade fused cast aluminum-silicate, Carborundum Corp., Niagara Falls, NY. Wet chemical analysis performed by Coors Spectro Chemical Laboratory, Golden, CO. Spectrographic analysis (American Spectrographic Laboratory, San Francisco, CA) showed (in wt% as oxides) 0.12 Na, 0.02 Fe, 0.01 Mg, 0.01 Zr, 0.006 Ca, 0.005 Ti, 0.003 Cr, <0.005 Cu, and <0.001 Mn.

Table I. Experimental Conditions and Data for Sapphire–Fused-Silica Runs

Temp. (°C)	Time (min)	C_1^* Al ₂ O ₃ content	
		(mol%)	(wt%)
1803	60, 240, 360,† 480,† 10,035	29.0	40.9
1853	15, 30, 60, 120, 1095, 1525	40.9	54.0
1903	15, 30, 60	49.6	62.5
1913	15, 30	51.2	64.0
1953	15	59.6	71.5
2003	15	78.2	85.9

*Interfacial composition of the melt; see Fig. 1. †From Ref. 11.

along a desired path perpendicular to the diffusion-couple interfaces. Because alumina and/or mullite generally crystallize in the liquid portion of the sapphire–fused-silica diffusion couples during cooling, concentration profiles obtained by the point-beam technique were extremely difficult to analyze. A scanning technique¹¹ provided average compositions at any distance from an interface over an area affected by localized crystallization. A computer program written by Frazier *et al.*¹⁸ was used to correct the electron microprobe data for dead time, drift, background, absorption, and fluorescence. Atomic number correction was not necessary since the difference between the atomic number of Al and Si is small.

III. Results and Discussion

(I) Diffusion Profiles and Phase Equilibria

(A) *Diffusion Couples:* The experimental conditions of the diffusion anneals in the range 1803°C to 2003°C are outlined in Table I. At least 2 or 3 specimen runs were made at each set of annealing conditions. The interfacial compositions remained constant with time at a given temperature, indicating that diffusion in the liquid phase was slower than the intrinsic dissolution rate of sapphire.¹² This fact was further verified by ascertaining that, at a given temperature, the distance from the original (Boltzmann-Matano) interface for a given concentration is directly proportional to the square root of time.¹² Although no time studies were performed at 1953°C and 2003°C, it was assumed that diffusion in the liquid phase was still the rate-controlling step at these temperatures. Thus the average interfacial compositions listed in Table I correspond to liquidus compositions.¹² No Si was detected in the sapphire substrate by electron microprobe.

When the fused-silica portions of the couples described in Section II(1) were replaced by melts with compositions corresponding to the mullite liquidus,¹¹ an intermediate mullite layer could be grown to a thickness ($>10\ \mu\text{m}$) suitable for electron microprobe analysis.¹³ The results of these runs in the temperature range of 1678°C to 1813°C are outlined in Table II. The thickness of the mullite layer increased linearly with the square root of time,¹³ indicating that the growth mechanism is diffusion-controlled. The interfacial compositions of the mullite layer obtained from these profiles, then, correspond to the equilibrium limits of the mullite solid solution region.

Mullite growth at the diffusion couple interfaces was observed in specimens annealed at 1803°C and 1813°C but not at 1853°C (Section III(2)), indicating that mullite became stable at some temperature below 1853°C. Thus, C_1 values in Tables I and II correspond to the liquidus of Al₂O₃ at 1853°C to 2003°C whereas those at and below 1813°C correspond to the liquidus of mullite.

Table II. Experimental Conditions and Data for Sapphire–Equilibrium-Melt Runs

Temp. (°C)	Time (min)	Al ₂ O ₃ content (wt%)*		Mullite thickness (μm)
		Melt (C_1)	Mullite ($C_{ML} - C_{AM}$)	
1678	12,182	10.9	70.5–74.0	10
1678	47,380	10.9	70.5–74.0	18
1753	6,608	22.8	70.5–74.0	13
1813	10,025	42.2	71.6–74.0	36

*Interfacial compositions; see Fig. 1.

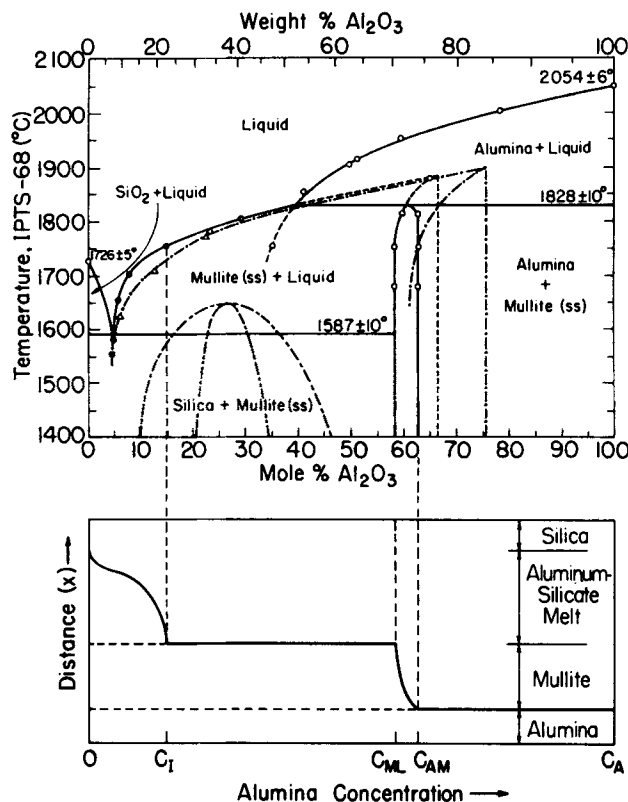


Fig. 1. Stable SiO₂-Al₂O₃ equilibrium phase diagram is shown by solid lines at top. Superimposed on stable equilibrium diagram are possible metastable phase diagrams for SiO₂-“ordered”-mullite and SiO₂-“disordered”-mullite systems. Data points for disordered mullite liquidus are from diagram of Ref. 5; immiscibility region is from Ref. 21. Relation between concentration profile of a semi-infinite fused-silica–Al₂O₃ diffusion couple and stable phase equilibrium diagram is drawn for 1753°C at bottom; C_1 corresponds to 100% Al₂O₃.

(B) *Stable Phase Equilibria:* The interfacial compositions listed in Tables I and II, data reported on the mullite liquidus,¹¹ the melting temperatures of cristobalite¹⁹ and corundum,¹⁵ and the cristobalite-mullite eutectic temperature²⁰ were used to construct the SiO₂-Al₂O₃ stable phase diagram in Fig. 1. The most important feature of this diagram is that, under stable equilibrium conditions, mullite melts incongruently, the liquid compositions in equilibrium with sapphire at 1853°C to 2003°C being the critical supporting evidence. The incongruent melting temperature (determined as 1828°C from the intersection of the extrapolated liquidus lines of mullite and alumina) and the position of these liquidus are essentially identical to the results of Bowen and Greig.¹

(2) Diffusion-Zone Microstructures

Typical diffusion-zone microstructures of the sapphire–fused-silica couples annealed at 1803°C and 1853°C are shown in Fig. 2.* Extensive crystallization of prismatic mullite in the melt portion of these and other couples occurred during cooling. The alumina content of these grains (determined by electron microprobe analysis) varied between 73 and 79 wt% Al₂O₃. In contrast, the stable mullite solid-solution range (determined from mullite grown at sapphire interfaces) varied from 70.5 to 74.0 wt% Al₂O₃ below 1753°C and from 71.6 to 74.0 wt% Al₂O₃ at 1813°C (Fig. 1).

Based on the kinetic data of mullite growth,^{11,13} if the stable mullite solid-solution field extended up to 1853°C, a growth layer 5.3 μm thick with a composition gradient across it would have been observed at the sapphire interface of the couple shown in Fig. 2(B). The essentially continuous mullite layer observed at the interface of

*All micrographs are by reflected light, Nomarski differential interference-contrast microscopy using a Zeiss Ultraphot II metallograph, Carl Zeiss, Wuersttemberg, West Germany.

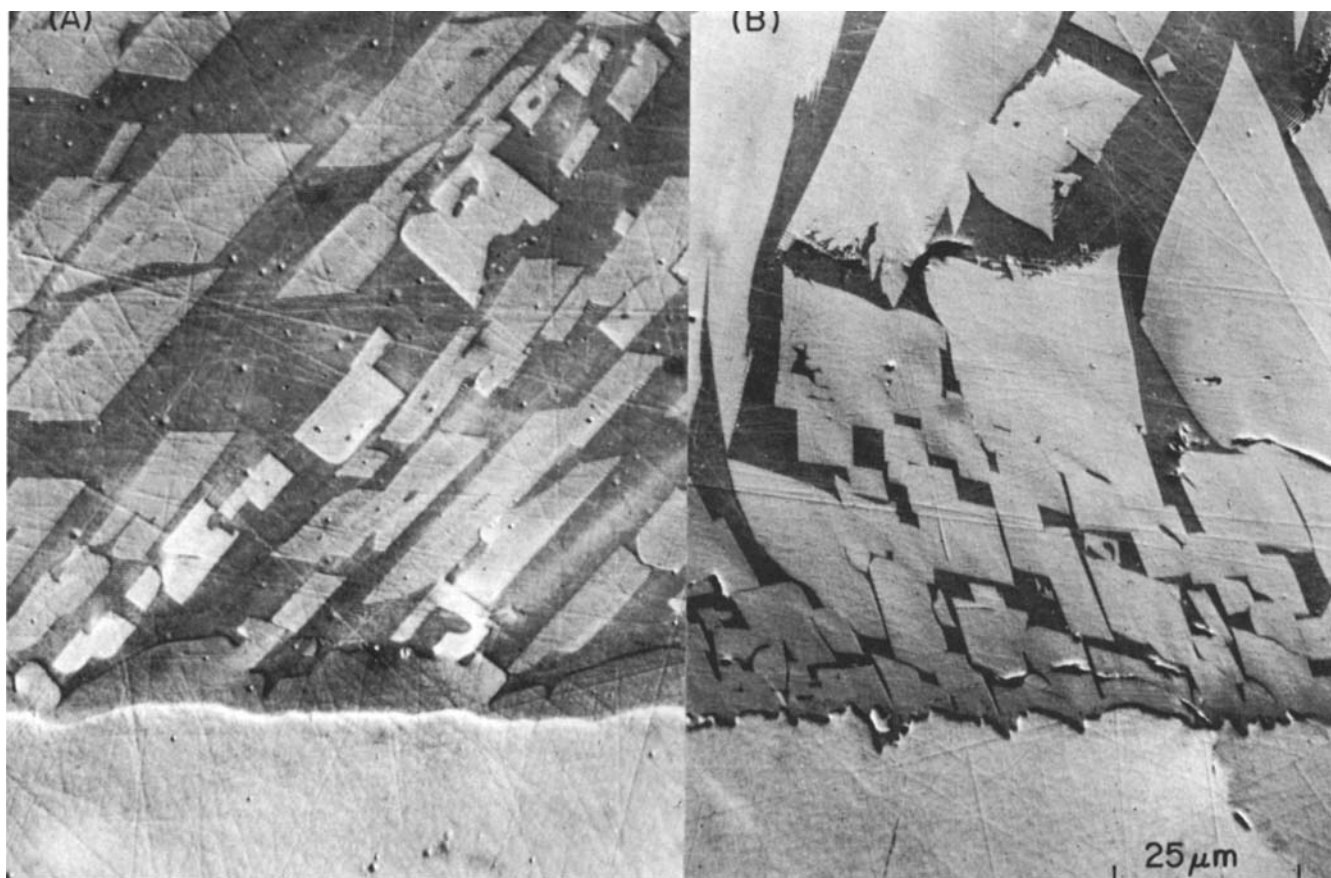


Fig. 2. Microstructures of diffusion zones in couples of sapphire (bottom) and fused silica annealed at (A) 1803°C for 10,035 min and (B) 1853°C for 120 min. Prismatic precipitates (light gray) in top portion of diffusion zone are mullite that crystallized during cooling; mullite layer at sapphire-melt interface of microstructure (A) grew at interface at temperature.

this couple, however, has a constant composition throughout which is identical to the precipitates in the adjoining diffusion zone. Furthermore, the prismatic morphology of the mullite layer is similar to that of the precipitates and differs from that of the layer grown at 1803°C (Fig. 2(A)), whose composition differs distinctly from that of the precipitates. The composition of the 1803°C layer varies from 71.1 wt% Al_2O_3 at the mullite-liquid interface to 74.0 wt% Al_2O_3 at the mullite-alumina interface. In addition, the appearance of the alumina interfaces in both couples is different. Thus, all the mullite observed in the diffusion zone at 1853°C formed during cooling, with nucleation occurring at the sapphire interface.

Since the liquid composition in the diffusion zone adjacent to the sapphire at 1853°C has 54.0 wt% Al_2O_3 (Fig. 1) and becomes oversaturated with alumina just below 1853°C, alumina should precipitate under equilibrium conditions. Below 1828°C precipitated alumina would then be completely resorbed by reacting with the liquid to form a mixture of mullite and liquid. The realization of such an equilibrium is rare, especially in silicates, since the crystal phase to be resorbed becomes unavailable for a direct reaction because of incrustation,⁹ i.e. a mullite layer forms around the alumina. However, a metastable mullite could also form if the liquid is sufficiently supercooled and no Al_2O_3 precipitation occurs. The absence of Al_2O_3 in the rapidly cooled diffusion zone thus indicates that such supercooling occurred.

Direct evidence for the importance of the rate of supercooling in the diffusion zone was established in 3 diffusion couples which were annealed together at 1903° for 15 min but cooled at relatively different rates as a result of the directional flow of He into the hot zone during quenching. Their microstructures differed drastically (Fig. 3) although the average diffusion profile in each case was identical, with a range of 0 to 62.5 wt% Al_2O_3 .¹² The precipitated crystalline phase, as determined by electron microprobe and X-ray diffraction, was only mullite when the couple was quenched (Fig.

3(A)), only alumina when the couple was cooled relatively slowly (Fig. 3(C)), and alumina and mullite when cooled at a moderate rate (Fig. 3(B)). In all cases, the matrix was a high-silica glass. Since the liquidus composition at the peritectic temperature is 52.3 wt% Al_2O_3 , $\approx 350 \mu\text{m}$ of the diffusion zone adjacent to the sapphire¹² would have experienced some alumina precipitation under equilibrium cooling. The absence of alumina in this portion of the diffusion zone of a quenched couple (Fig. 3(A)) and the presence of alumina in a slowly cooled couple (Fig. 3(C)) can be explained only by considering nucleation and supercooling phenomena in the liquid. The coexistence of alumina, mullite, and liquid (glass) in the diffusion zone of the couple cooled at a moderate rate (Fig. 3(B)) is in violation of the phase rule. In this case, after some equilibrium precipitation of alumina, the remaining liquid did not maintain equilibrium with alumina and behaved independently with the precipitation of mullite.

Davis and Pask,¹¹ who observed the formation of an interfacial nonequilibrium liquid in cristobalite-sapphire couples at subsolidus temperatures, suggested the existence of an $\text{SiO}_2\text{-Al}_2\text{O}_3$ metastable phase diagram with a eutectic and no mullite, which was represented by extensions of the SiO_2 and Al_2O_3 liquidus curves. The diffusion-zone microstructure shown in Fig. 3(C) further supports their observations since the absence of mullite indicates a cooling rate sufficiently slow to maintain equilibrium between the liquid and alumina, resulting in the metastable extension of the alumina liquidus below the peritectic temperature.

Diffusion-zone microstructures of 1953° and 2003°C couples showed only alumina precipitates in a high-silica glassy matrix within the high-alumina (≥ 50 wt% Al_2O_3) portion of the diffusion zones even when they were quenched at the fastest rate experimentally possible. The sapphire substrate acted as a site for heterogeneous nucleation of alumina. Mullite precipitates, however, were always present at the low-alumina end of the zones.

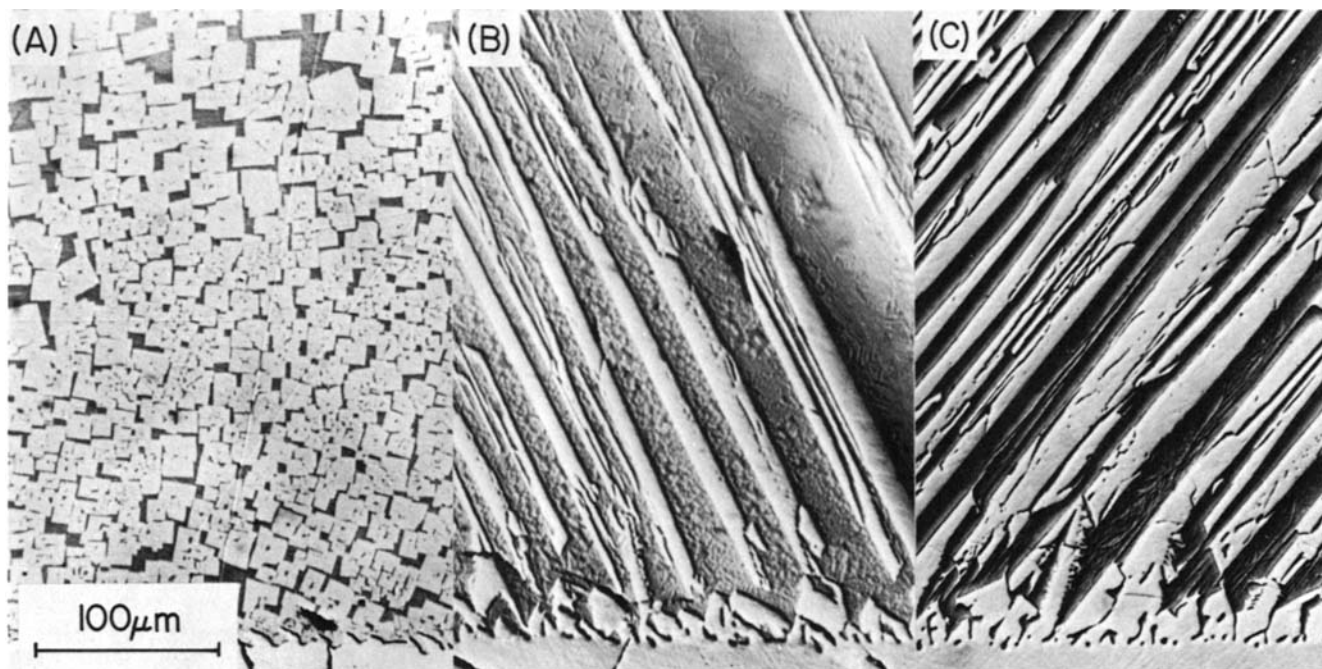


Fig. 3. Microstructures of diffusion zones in couples of sapphire (bottom) and fused silica annealed at 1903°C for 15 min and (A) quenched, (B) cooled at a relatively moderate rate, and (C) cooled relatively slowly. Precipitates in diffusion zone in (A) are mullite (light gray), in (B) alumina (light gray needles) and mullite (fine precipitates between alumina needles), and in (C) alumina (light gray needles); precipitates along interface in (B) and (C) are also alumina.

(3) Microstructures of Quenched Mixtures

At the outset of a quenching experiment, the mixtures of α - Al_2O_3 and fused SiO_2 were, unless otherwise stated, homogenized above the corresponding alumina liquidus temperature. Within the present homogenization periods, the fact that the crystalline phases completely dissolved in the melt was established by an X-radiographic technique.²² When a mixture containing 60.0 wt% Al_2O_3 was homogenized at 1953°C and cooled slowly (≈ 60 min) below the peritectic temperature before quenching, its microstructure showed mullite and glass. In comparison, a melt of similar composition (62.5 wt% Al_2O_3) in the diffusion zone adjacent to the sapphire (Fig. 3) had only precipitates of mullite when quenched; slower cooling rates resulted in precipitates of alumina. This difference in behavior can be attributed to the presence of sapphire in the diffusion couple, which acted as a site for heterogeneous nucleation of alumina for the more slowly cooled specimens.

Alumina, mullite, and glass were found in a mixture containing 71.8 wt% Al_2O_3 (corresponding to $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) which had been annealed at 1953°C, cooled slowly (≈ 30 min) to 1753°C, annealed further for ≈ 29 days, and quenched (Fig. 4). The presence of alumina clearly indicates the incongruity of mullite; alumina could not be present under any circumstances if mullite solidified congruently from a melt. The presence of mullite around the alumina also indicates that the peritectic reaction was incomplete because diffusion through the mullite layer was slow. The diffusion mechanism is indicated by the presence of concentration profiles through the mullite layers ranging from 74 wt% Al_2O_3 at the alumina interfaces to 70.5 wt% Al_2O_3 at the glass interfaces (Fig. 1). However, when this mixture was homogenized at 2003°C and rapidly cooled to 1753°C, the fact that, in the absence of sapphire nucleation sites, the microstructure showed no alumina precipitates could easily be misinterpreted as being indicative of the congruency of mullite.

Typical microstructures of the silicate mixtures of 78.3 and 80.0 wt% Al_2O_3 were homogenized at 2003°C (Fig. 5); the degree of mullite and/or alumina precipitation in these melts was highly dependent on the cooling rate. A quench by turning off the power and rapid introduction of He into the furnace always resulted in mullite with compositions varying up to 83.2 wt% Al_2O_3 and some residual high-silica glass (Fig. 5(A)). Occasional precipitation of alumina was observed around the crucibles' sharp edges, which must have acted as nucleation sites. When the melts were moder-



Fig. 4. Microstructure of 71.8 wt%- Al_2O_3 -containing silicate melted in sealed Mo crucible at 1953°C for 460 min, cooled to 1753°C in 30 min, annealed at 1753°C for 42,392 min (29.4 days), and quenched from 1753°C to room temperature. Light gray precipitates are alumina completely surrounded by layer of mullite (gray). Dark gray portions between mullite layers are glass containing fine precipitates of mullite formed on quenching.

ately cooled by just turning off the power to the furnace, alumina precipitated readily (Fig. 5(B)). The intermediate liquid phase apparently did not maintain equilibrium with the precipitated alumina and cooled independently to form mullite and residual

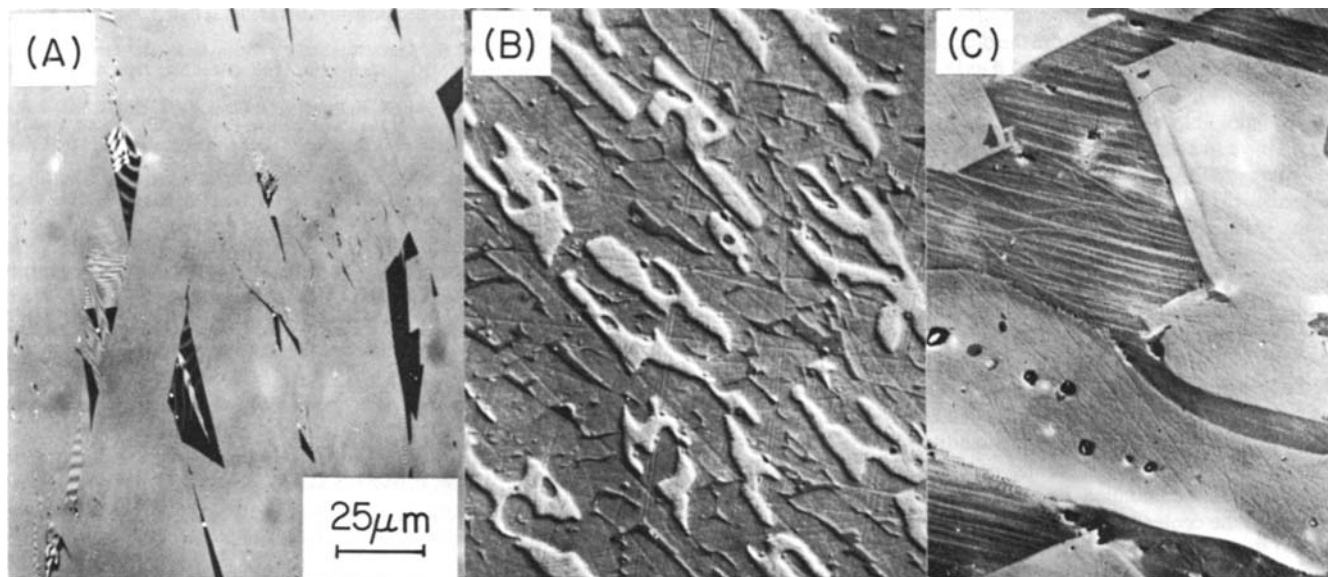


Fig. 5. Microstructures of (A) 78.3-wt%- Al_2O_3 -containing silicate melted at 2003°C for 30 min and quenched in He (matrix is mullite but contains glassy inclusions); (B) 80.0 wt% Al_2O_3 melt cooled at moderate rate in vacuum by turning off power to furnace (light gray portions are alumina; gray, mullite; and dark gray, glass); and (C) 80.0 wt% Al_2O_3 melted at 2003°C for 90 min, cooled to 1753°C in 60 min, and quenched in He to room temperature (both large and needlelike precipitates are alumina set in glass matrix).

glass. When the melts were cooled slowly to 1753°C and quenched, only precipitates of alumina were present (Fig. 5(C)). The needles in the glassy matrix were only a few microns thick and thus were too small for electron microprobe analysis; X-ray diffraction analysis of such specimen surfaces, however, indicated $\alpha\text{-Al}_2\text{O}_3$ as the only crystalline phase. The overall composition of the matrix surrounding the primary alumina precipitates, as determined by scanning-beam electron microprobe analysis, was ≈ 48 wt% Al_2O_3 . This composition is identical to that of the alumina liquidus at 1753°C when it is extended below the peritectic temperature (Fig. 1) and provides additional evidence for the existence of a metastable $\text{SiO}_2\text{-Al}_2\text{O}_3$ binary without any mullite phase.

(4) Melting Behavior and Composition of Mullite

The melting behavior of mullite was studied using polycrystalline stoichiometric 3:2 mullite²³ (71.8 wt% Al_2O_3) specimens.* They were placed in Mo crucibles and heated in vacuum. Temperature was measured using blackbody conditions with a hole drilled directly into the specimen. Heating to 1800°C was rapid (5 to 10 min) followed by a 5°C/min heating rate to maintain thermal equilibrium. The temperature of complete liquidation was assumed to be that at the first instant of specimen slumping. Some specimens were only partially melted before quenching.

The melting temperature was consistently 1880°C. The same melting temperature was determined independently by Mazdiyasi and Brown²³ using an identical material and similar experimental conditions. This value is considerably higher than the peritectic melting temperature of 1828°C, as determined from the diffusion studies (Fig. 1). Furthermore, the microstructure of the completely molten portion showed only recrystallized mullite and some glass. No alumina formed because of nucleation difficulties. Thus, when superheated, stoichiometric mullite behaved as a congruently melting compound.

According to the stable phase diagram (Fig. 1), a mullite of 71.8 wt% Al_2O_3 becomes unstable at 1816°C and dissociates to a mixture of a silica-rich liquid phase and to a higher-alumina mullite above 1816°C. The nonslumped portion of the specimens after heating to a blackbody temperature of 1880°C showed a mixture of glass and mullite grains (≈ 5 to $10\ \mu\text{m}$) whose composition was consistently 75.8 wt% Al_2O_3 , as determined by point-beam microprobe analysis.

Incongruently melting silicates can be superheated above the peritectic temperature and are represented by the metastable prolongation of the corresponding liquidus and solidus.¹⁰ The extension of the stable mullite liquidus of Fig. 1 intersects the 71.8 wt% Al_2O_3 line at $\approx 1875^\circ\text{C}$, which closely corresponds to the present complete liquidation temperature. Such metastable congruent melting of mullite necessitates higher alumina contents in the recrystallized mullite and thus provides an explanation for the measured shift to 75.8 wt% Al_2O_3 . Also, since liquid is present, the indifferent point of the metastable extensions has to be higher than 75.8 wt%.

The phase relations developed thus far do not provide an explanation for the higher alumina contents in the mullite (≈ 73 to 79 wt% Al_2O_3) precipitated from the liquid phase. Under stable equilibrium conditions the mullite composition in contact with liquid should contain 70.5 to ≈ 72 wt% Al_2O_3 (Fig. 1). A possible explanation could be the formation, under these conditions, of a "disordered" mullite phase with a broader shifted alumina solid-solution range.

Aramaki and Roy⁵ observed that heat treatment of mullite prepared by quenching caused almost as much variation in its lattice parameters as in its composition and suggested Al-Si order-disorder as a possible explanation. Later, similar observations were made by Mazdiyasi and Brown²³ and Majumdar and Welch.²⁴ Previous studies⁶ strongly support the existence of such a disordered mullite phase, frequently referred to as 2:1 or melt-mullite. The upper limit of the disordered-mullite solid-solution range is uncertain but has been set at 83.2 wt% Al_2O_3 since this was the highest alumina content detected in any mullite. This limit agrees well with the compositions of mullite single crystals grown from a melt by Bauer *et al.*⁷ (82.57 wt% Al_2O_3), by Neuhaus and Richartz²⁵ (77.5 wt% Al_2O_3), and by Guse and Mateika²⁶ (77.3 wt% Al_2O_3). Temperatures as high as 1913°C have been associated with the melting behavior of 2:1 mullite^{4,25}; an average of the reported values is $\approx 1900^\circ\text{C}$.

(5) Metastable Phase Equilibria

Based on the above information, the possibility of the existence of ordered and disordered mullites with metastable congruency necessitates two overlapping mullite solid-solution fields that exist in the absence of alumina. Metastable phase equilibrium diagrams are formed by each mullite with SiO_2 , as shown in Fig. 1.

The phase diagram for SiO_2 -ordered-mullite in the absence of alumina shows an extension of the stable mullite liquidus and solidus, the indifferent point of the extensions being ≈ 77 wt% Al_2O_3 . The SiO_2 -disordered-mullite diagram in the absence of alumina indicates a mullite solid-solution range of ≈ 73 to ≈ 83

*Provided by K. S. Mazdiyasi, Air Force Materials Laboratory, Wright-Patterson Air Force Base, OH.

wt% Al_2O_3 . (The values that were used to position the disordered mullite liquidus were taken from the diagram of Aramaki and Roy.⁵)

MacDowell and Beall²¹ observed evidence for metastable liquid immiscibility in the system SiO_2 - Al_2O_3 and outlined an immiscibility and a possible spinodal region as shown in Fig. 1. Takamori and Roy²⁷ have questioned the existence and especially the location of this immiscibility region on the grounds that inadequate data existed to locate it. The present results similarly cast doubt on the location of the spinodal region as proposed by MacDowell and Beall since the extension of the alumina liquidus cuts through the center of this region. Below the critical temperature of an immiscibility region, the free-energy-of-mixing curve of a liquid as a function of composition will have two minima. Common tangents drawn at the immediate vicinity of these minima define the composition of the liquid that should be at metastable equilibrium with alumina and the boundary of the immiscibility region. Therefore, the extension of a liquidus must be close to the immiscibility region boundaries and can never cut through the center of the spinodal. However, the extension of the alumina liquidus as shown in Fig. 1 directly intersects the center of the proposed immiscibility region, in violation of this rule. Any proposed spinodal region must then be either completely under or outside the extension of the alumina liquidus.

VI. Summary

Diffusion-couple experiments in the system SiO_2 - Al_2O_3 yielded information on stable and several metastable phase equilibria. Mullite, under stable equilibrium conditions, was shown to melt incongruently at $1828^\circ \pm 10^\circ\text{C}$, as originally determined by Bowen and Greig.¹ The measured stable solid-solution range of mullite in the presence of alumina was 70.5 to 74.0 wt% Al_2O_3 below 1753°C and 71.6 to 74.0 wt% Al_2O_3 at 1813°C .

Diffusion-zone microstructures and microstructures of specimens heat-treated by the static method of quenching indicated the incongruency of mullite as well as the existence of metastable equilibria. The congruent melting of mullite during superheating in the absence of alumina indicates the existence of an SiO_2 -ordered-mullite metastable phase diagram. The precipitation of disordered mullite from melts indicates the existence of an SiO_2 -disordered-mullite metastable phase diagram in the absence of alumina, with a broader and shifted solid-solution range of mullite. Direct evidence was also provided for the existence of an SiO_2 - Al_2O_3 metastable binary without any mullite phase, as represented by the extensions of the silica and alumina liquidus curves to form a eutectic.

Metastable phase equilibria result from various difficulties associated with nucleation of phases. When a melt is supercooled into an alumina primary phase region, alumina nucleates less readily as the silica content of the melt increases (with the consequent precipitation of disordered mullite) and sapphire provides a heterogeneous nucleation site, allowing alumina to precipitate more readily. Mullite grown at temperature by a solid-state reaction appears to be ordered and of the 3:2 type; mullite formed in the liquid phase by exsolution appears to be disordered and of the 2:1 type.

Acknowledgments: The writers thank George J. Georgakopoulos for assistance in electron beam microprobe analysis, Victor F. Draper and Norman Gardner for technical assistance, and Robert F. Davis for valuable discussions.

References

- N. L. Bowen and J. W. Greig, "The System: Al_2O_3 - SiO_2 ," *J. Am. Ceram. Soc.*, **7** [4] 238-54 (1924); "Corrections," *ibid.*, [5] 410.
- (a) N. E. Filonenko and I. V. Lavrov, "Melting of Mullite," *Dokl. Akad. Nauk SSSR*, **89** [1] 141-42 (1953).
- (b) J. H. Welch, "New Interpretation of the Mullite Problem," *Nature (London)*, **186** [4724] 545-46 (1960).
- (c) J. H. Welch, pp. 197-206 in Transactions of the VIIth International Ceramic Congress, British Ceramic Society, London, 1960.

- (d) H. R. Mueller, "Solidification Behavior of Mullite in Bulk," *Ber. Deut. Keram. Ges.*, **40** [5] 316-19 (1963).
- (e) Toshiyasu Horibe and Senzo Kuwabara, "Thermoanalytical Investigation of Phase Equilibria in the Al_2O_3 - SiO_2 System," *Bull. Chem. Soc. Jap.*, **40** [4] 972-82 (1967).
- (a) G. Troemel, K. H. Obst, K. Konopicky, H. Bauer, and I. Patzak, "Investigations in the SiO_2 - Al_2O_3 System," *Ber. Deut. Keram. Ges.*, **34** [12] 397-402 (1957).
- (b) K. Konopicky, "Equilibrium Diagram of the System SiO_2 - Al_2O_3 ," *Bull. Soc. Franc. Ceram.*, **1956**, No. 33, pp. 3-6.
- (c) G. Troemel; pp. 77-78 in Physical Chemistry of Steelmaking. Edited by J. F. Elliott. Massachusetts Institute of Technology Press, Inc., Cambridge, and John Wiley & Sons, Inc., New York, 1958.
- (d) K. Konopicky, "Equilibrium Diagram Al_2O_3 - SiO_2 ," *Ber. Deut. Keram. Ges.*, **40** [5] 286 (1963).
- (a) N. A. Toropov and F. Y. Galakhov, "New Data on the System Al_2O_3 - SiO_2 ," *Dokl. Akad. Nauk SSSR*, **78** [2] 299-302 (1951).
- (b) P. Budnikov, S. G. Tresvyatski, and V. I. Kushkovski, "Making the Phase Diagram of the System Al_2O_3 - SiO_2 More Precise," *ibid.*, [9] 281-83 (1953).
- (c) F. Y. Galakhov, "Crystallization of Mullite in Ternary Silica-Alumina Systems," *Bull. Soc. Franc. Ceram.*, **1958**, No. 38, pp. 11-16.
- (d) N. A. Toropov and F. Y. Galakhov, "The SiO_2 - Al_2O_3 System," *Ekspieriment Tekhn. Mineralog. Petrogr., Materialism Soveshch.*, **7th Lvov 1964**, pp. 3-8 (1966).
- (e) G. Rehfeld and H. E. Schwiete, "Recent Results on the Melting Behavior of Mullite," *Ber. Deut. Keram. Ges.*, **48** [6] 258-61 (1971).
- (a) Shigeo Aramaki and Rustum Roy, "Mullite-Corundum Boundary in the Systems MgO - Al_2O_3 - SiO_2 and CaO - Al_2O_3 - SiO_2 ," *J. Am. Ceram. Soc.*, **42** [12] 644-45 (1959).
- (b) Shigeo Aramaki and Rustum Roy, "Revised Equilibrium Diagram for the System Al_2O_3 - SiO_2 ," *Nature (London)*, **184** [4686] 631-32 (1959).
- (c) Shigeo Aramaki and Rustum Roy, "Revised Phase Diagram for the System Al_2O_3 - SiO_2 ," *J. Am. Ceram. Soc.*, **45** [5] 229-42 (1962).
- (a) Hermann Salmang, *Ceramics, Physical and Chemical Fundamentals*; pp. 105-12. Translated by Marcus Francis. Butterworth & Co. (Publishers) Ltd., London, 1961.
- (b) János Grofcsik, Mullite, Its Structure, Formation and Significance; pp. 31-37. Publishing House of the Hungarian Academy of Sciences, Budapest, 1961.
- (c) H. Mueller-Hesse, "Development of the Investigations and Present-Day Knowledge on the System Al_2O_3 - SiO_2 ," *Ber. Deut. Keram. Ges.*, **40** [5] 281-85 (1963).
- (d) Wilhelm Eitel, *Silicate Science*, Vol. 3; pp. 205-28. Academic Press, Inc., New York, 1965.
- (e) R. F. Davis and J. A. Pask; pp. 37-76 in High Temperature Oxides, Part IV. Edited by A. M. Alper. Academic Press, Inc., New York, 1971.
- (a) W. H. Bauer, I. Gordon, and C. H. Moore, "Flame-Fusion Synthesis of Mullite Single Crystals," *J. Am. Ceram. Soc.*, **33** [4] 140-43 (1950).
- (b) W. H. Bauer and I. Gordon, "Flame-Fusion Synthesis of Several Types of Silicate Structures," *ibid.*, **34** [8] 250-54 (1951).
- (a) J. B. MacChesney and P. E. Rosenberg; pp. 113-65 in Phase Diagrams, Materials Science and Technology, Vol. 1. Edited by A. M. Alper. Academic Press, Inc., New York, 1970.
- (b) N. L. Bowen, *Evolution of the Igneous Rocks*; pp. 25-33. Dover Publications, Inc., New York, 1956.
- (a) Wilhelm Eitel, *Silicate Melt Equilibria*; paragraphs 25-29. Rutgers University Press, New Brunswick, NJ, 1951.
- (b) R. F. Davis and J. A. Pask, "Diffusion and Reaction Studies in the System Al_2O_3 - SiO_2 ," *J. Am. Ceram. Soc.*, **55** [10] 525-31 (1972).
- (a) I. A. Aksay and J. A. Pask, "Diffusion in SiO_2 - Al_2O_3 Melts"; for abstract see *Am. Ceram. Soc. Bull.*, **52** [9] 710 (1973).
- (b) I. A. Aksay, R. F. Davis, and J. A. Pask, "Diffusion in Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$)"; for abstract see *ibid.*
- (a) F. D. Rossini, "International Practical Temperature Scale of 1968," *J. Chem. Thermodyn.*, **2**, 447-59 (1970).
- (b) S. J. Schneider and C. L. McDaniel, "Effect of Environment Upon the Melting Point of Al_2O_3 ," *J. Res. Natl. Bur. Stand., Sect. A*, **71** [4] 317-33 (1967).
- (a) R. F. Davis, I. A. Aksay, and J. A. Pask, "Decomposition of Mullite," *J. Am. Ceram. Soc.*, **55** [2] 98-101 (1972).
- (a) R. Theisen, *Quantitative Electron Microprobe Analysis*. Springer-Verlag, New York, 1965.
- (b) J. Z. Frazier, R. W. Fitzgerald, and A. M. Reid, "Computer Programs EMX and EMX2 for Electron Microprobe Data Processing," Scripps Institute of Oceanography, University of California at San Diego, La Jolla, Calif.; unpublished work.
- (a) J. W. Greig, "Immiscibility in Silicate Melts: I," *Am. J. Sci.*, **13** [73] 1-44 (1927); "II," *ibid.*, [74] 133-54.
- (b) R. B. Sosman, *Phases of Silica*; pp. 156-58. Rutgers University Press, New Brunswick, NJ, 1965.
- (a) J. F. Schairer and N. L. Bowen, "The System K_2O - Al_2O_3 - SiO_2 ," *Am. J. Sci.*, **253** [12] 681-746 (1955).
- (b) J. F. MacDowell and G. H. Beall, "Immiscibility and Crystallization in Al_2O_3 - SiO_2 Glasses," *J. Am. Ceram. Soc.*, **52** [1] 17-25 (1969).
- (a) I. A. Aksay, R. F. Davis, and J. A. Pask, "Densities of SiO_2 - Al_2O_3 Melts"; for abstract see *Am. Ceram. Soc. Bull.*, **51** [9] 720 (1972).
- (b) K. S. Mazdyasni and L. M. Brown, "Synthesis and Mechanical Properties of Stoichiometric Aluminum Silicate (Mullite)," *J. Am. Ceram. Soc.*, **55** [11] 548-52 (1972).
- (a) A. J. Majumdar and J. H. Welch, "New Data on Synthetic Mullite," *Trans. Brit. Ceram. Soc.*, **62** [8] 603-13 (1963).
- (b) A. Neuhaus and W. Richartz, "Artificial Growing of Single Crystals of Mullite and the Phase Relationships Encountered," *Ber. Deut. Keram. Ges.*, **35** [4] 108-16 (1958).
- (a) W. Guse and D. Mateika, "Growth of Mullite Single Crystals ($2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) by the Czochralski Method," *J. Cryst. Growth*, **23** [3] 237-40 (1974).
- (b) W. Guse, "Compositional Analysis of Czochralski Grown Mullite Single Crystals," *ibid.*, **26** [1] 151-52 (1974).
- (a) Takeshi Takamori and Rustum Roy, "Rapid Crystallization of SiO_2 - Al_2O_3 Glasses," *J. Am. Ceram. Soc.*, **56** [12] 639-44 (1973).