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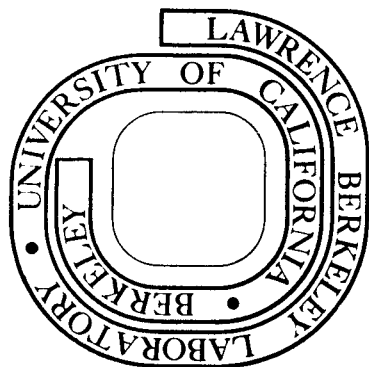
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DENSITIES OF $\text{SiO}_2\text{-Al}_2\text{O}_3$ MELTS

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DENSITIES OF $\text{SiO}_2\text{-Al}_2\text{O}_3$ MELTSIlhan A. Aksay^{*}, Robert F. Davis⁺, and Joseph A. Pask

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ABSTRACT

The densities of binary aluminosilicate melts have been measured x-radiographically as a function of Al_2O_3 concentration between 1800-2200°C. Within this temperature range, the density curves vary linearly and are parallel from fused SiO_2 to approximately 30-45 mole % Al_2O_3 , depending on the temperature. At higher Al_2O_3 contents, increasing negative deviation from linearity with rising temperature is noted. Recent supplementary research efforts on various aspects of the $\text{Al}_2\text{O}_3\text{-SiO}_2$ system indicate that the changing coordination and structural role of the aluminum ion may be a primary factor in determining the shapes of the density curves.

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I. INTRODUCTION

Boltzmann-Matano analysis of diffusion data derived from $\text{SiO}_2\text{-Al}_2\text{O}_3$ melts (1) require accurate measurement of melt densities. These densities were determined for the entire binary system in the temperature range 1700° to 2000°C using an x-radiographic technique developed by Rasmussen and Nelson (2). The technique consisted of measuring the volume of a melt at temperature from its radiographed image and of relating this volume to its density. This method was especially suited for the alumino-silicate melts as the specimens had to be sealed in molybdenum containers to eliminate silica losses during measurements. The present study describes the density changes observed as a function of Al_2O_3 concentration and temperature and relates this data in terms of possible structural changes of the atomic species, primarily aluminum and oxygen.

II. EXPERIMENTAL

The binary composition chosen for this study contained 22.8, 42.2, 60.0 and 80.0 wt.% $Al_2O_3^*$. These mixtures were weighed and subsequently melted in electron beam sealed, He tight Mo capsules at 1953°C in vacuum for ≈30 to 60 min.

The x-radiographic measurements were performed by Rasmussen[†] using the system described in reference (2). The specimens were heated at a rate of 3°C/min to the range of 1700° to 2000°C. The temperature (IPTS-68) was monitored continuously with a two color pyrometer having an accuracy of ± 10°C. The specimen images were obtained at 25°C intervals using a 300 Kv x-ray source. The volume of the melt was subsequently calculated from the measured height and the crucible diameter and corrected for thermal expansion (3). In most instances, the column length could be measured repetitively to give a density variation of ± 0.004 gm/cm³. A typical set of radiographs used in the measurements is shown in Figure 1. The amount of molybdenum in the melts was below the detection limit of the electron microprobe.

*Mixtures were prepared using powders of Alcoa XA-16 reactive $\alpha-Al_2O_3$ (Aluminum Co. of America, Pittsburgh, Pa., Chemical analysis (wt%) Na_2O 0.08, SiO_2 0.05, CaO 0.03, MgO 0.05, Fe_2O_3 0.01, MnO 0.0015, B_2O_3 <0.001, Cr_2O_3 0.002) and Corning 7940 fused silica (Corning Glass Works, Corning, New York produced by hydrolyzation of $SiCl_4$ when sprayed into an oxygen-hydrogen flame. Practically free from metallic impurities, but contains a high amount of OH (~1000 ppm) and Cl (~100 ppm)).

[†]Rasmussen, J. J., Battelle Pacific Northwest Labs., Ceramics and Graphite Section, Richland, Washing. Now with Montana Energy and MHD Research and Development Institute, Butte, Montana.

III. RESULTS AND ANALYSIS

The densities of the aluminum silicate melts determined only during the cooling cycle are presented in Table I and Figure 2. The measurements obtained during the initial heating cycle were considered erroneous due to the formation of bubbles and the presence of cores in the melts. However, consistent results could be obtained during subsequent reheatings. This phenomenon has also been observed with $MgAl_2O_4$ and Al_2O_3 (4) during the formation of initial melts from single crystals usually grown in the presence of H_2 or Ar.

The abrupt volume decrease shown in the 46.9 and 70.2 mol % Al_2O_3 supercooled melts (Figure 2) took place due to the formation of a precipitate. On heating, a volume increase accompanied by complete melting occurred for these compositions at $1913^{\circ}C$ and $1993^{\circ}C$, respectively, which correspond to alumina liquidus temperatures as determined by Aksay and Pask (5). The 14.8 and 30.1 mole % Al_2O_3 melts formed glasses; thus, no abrupt volume changes were noted during cooling and reheating.

The density of liquid alumina has been measured by several investigators (2, 4, 6). Mitin and Nagibin used a hydrostatic technique between the melting point and $2550^{\circ}C$ and their results are reproduced in Figure 2. The density of solid alumina was calculated up to its melting point using the coefficient of expansion data of Wachtman et al. (7) and the room temperature density of 3.965 gm/cm^3 (8).

The five density values of liquid silica shown in Figure 2 are by Bacon, et al. (9). A straight line is drawn through the data points excluding the one at 2326°C; since, an extension of a weighted line through all the points gives a density at the melting temperature of cristobalite which is higher than that of the solid. Thus it is concluded that either the density of liquid silica varies linearly only up to ~2200°C (Figure 2) and deviates from linearity thereon or the value reported at 2326°C is erroneous.

The variation of the melt densities with alumina content in the temperature range of 1800° to 2200°C is illustrated in Figure 3. In this temperature range, the densities increase linearly only up to ~45 mole % Al₂O₃. The negative deviation from linearity at higher alumina contents is indicative of the breakdown of the network structure.

Also included in Figure 3 are the room temperature densities of the glasses quenched from 1803°C (10). On the basis of the data of Figure 2, these room temperature densities correspond to a fictive temperature of ~1200°C.

No attempt has been made to calculate the partial molar volume of Al₂O₃ and SiO₂ in the melt. However, the data compiled by Huggins and Sun (11), Bottinga and Weill (12), and others (13) indicate that partial molar volumes are essentially constant in a certain range of silicate compositions and thus may be used to calculate the density of any silicate liquid within that range. The values for ternary alkali and alkaline earth aluminosilicates reported by Bottinga and Weill (12) were extrapolated to 1900°C and used to calculate the densities of binary

aluminosilicate melts in the range of 20 to 60 mole % Al_2O_3 . As shown in Figure 3, the agreement between these calculated values and the measured ones is poor, especially at higher alumina contents. Similar results are also obtained if the values compiled by Huggins and Sun (11) are used. It therefore appears that the partial molar volumes obtained from ternary aluminum-silicates may only be satisfactorily used to predict the densities of other ternary or more complex silicates of similar composition.

The experimental density data may also be used to determine the fractional volume change of mullite and alumina upon melting or solidification. Tyrolerova and Lu (14) have reported a volume decrease of 10.3% during solidification for a fused-cast mullite specimen of 75.1 wt% Al_2O_3 . The density of stoichiometric mullite (71.8 wt% Al_2O_3) at its metastable congruent melting temperature, 1890°C (15), is 3.10 gm/cm³ when calculated from the expansion data of mullite (16). The density of the corresponding melt at the same temperature is 2.774 gm/cm³ based on the data presented in Figure 3. Thus, the fractional volume decrease of mullite on solidification is 10.28% which agrees with the value reported by Tyrolerova and Lu (14).

The fractional volume decrease of alumina on solidification is 20.7%, based on the data of Figure 2. Similar values have been reported by Kingery (17) as 20.4%* and by Tyrolerova and Lu (18) as 19.9-20.1%. Kirshenbaum and Cahill (6b) and Bates et al. (4) have reported values on 22.0 and 24.0% respectively; however, for comparison, these values should be expressed as fractional volume change on solidification.

*This value was erroneously reported by Kingery (17) as fractional volume change on melting instead of solidification.

The new values are 18.2 and 19.4%, respectively, and compare well with the values reported by the other workers.

IV. DISCUSSION

The density and any changes in density of a system are a function of the percentages and molecular weights of the components, the structural positions and the bonding energies of the atomic species as well as the temperature and the resulting thermal expansion of the structure. Furthermore the particular structural roles of the atomic or molecular components may also be considerably influenced by both the concentration of each component and the temperature, thus producing second order effects on the density of the overall system. The density-temperature-composition relationships displayed graphically in Figure 3 are produced by and must be understood in relation to the above variables and their interaction.

The approximate parallelism of the melt density curves in the range 0 to 40 % Al_2O_3 is an indication that as the temperature increases at each Al_2O_3 concentration, the densities are controlled either by pure thermal expansion or by a combination of the thermal expansion and equivalent proportional changes of the coordination of the Al^{+3} ion. Experimental evidence for the latter postulate may be derived from research conducted on glasses quenched from these high melt temperatures and on mullite which is in two major primary phase fields in this region of the diagram (5).

Galakhov and Konovalova (19) and Eipeltaufer and Hrushka (20) attributed the observation of unusual structural features in quenched glasses containing 12-48 mole % Al_2O_3 to phase separation. The latter

authors found the crystallization temperatures (T_x) of these glasses to be 950-1000°C in agreement with the later work of Takamori and Roy (21). TEM work by Takamori and Roy also revealed direct evidence of metastable phase separation between 20 and 50 mole % Al_2O_3 (20% was the lowest concentration examined). MacDowell and Beall (22) have conducted the most comprehensive experimental study on the microstructure of these glasses and report considerable evidence that phase separation exists within a metastable immiscibility dome having limits from 7-55 mole % Al_2O_3 and an estimated approximate consolute point of 1650°C. According to recent thermodynamic calculations the consolute temperature is $\sim 1540^\circ C$.²³ Finally, Shaw and Uhlmann (24) have shown theoretically and experimentally that the curve of density vs. weight percent composition for binary vitreous systems must always have a positive (concave upward) curvature across a two-phase immiscibility gap. Accurate knowledge of the density data across a compositional region will reveal those regions which are most amenable to phase separation as well as those which are likely to be homogeneous. The equation derived by these authors and shown below

$$\rho = \frac{\rho_1 \rho_2}{[(X-X_1)/(X_2-X_1)](\rho_1-\rho_2) + \rho_2} \quad (1)$$

has been used by the present writers to check the validity of the immiscibility gap reported by MacDowell and Beall (22). The meaning of the variables and the values used are as follows:

ρ_1, ρ_2 = densities of the first and second phases = 2.743 and 2.276 g/cc, respectively.

X_1, X_2 = composition (wt. fraction) of the end points = 0.68 and 0.10 Al_2O_3 , respectively, of the immiscibility gap (ref.22).

X = arbitrary compositions between X_1 and X_2

The calculations utilized the present authors' room temperature density data extended to 68 wt% (55 mole %) using the equation $\rho(\text{g/cc}) = 0.00806 (\text{wt\% Al}_2\text{O}_3) + 2.195$. The justification for this extension is derived by noting that in the melt density curves, the lower the temperature of the melt, the smaller the deviation from linearity and the greater the Al_2O_3 concentration at which this deviation begins. For example if one extrapolates the 2000°C curve of Figure 3 to pure Al_2O_3 following the general shapes of the higher temperature curves as well extrapolates linearly the density curve for molten Al_2O_3 given by Mitin and Nagibin (Figure 2) to 2000°C, the density values are found to be 2.98 g/cc and 3.08 g/cc, respectively. The value of the room temperature density for 68 wt% (55 mole %) Al_2O_3 is thus thought to be at least as accurate. The resulting curve shown in Figure 4 reveals a moderate positive curvature typical of vitreous systems over the range of experimentally determined metastable immiscibility gaps such as the $\text{Li}_2\text{O-SiO}_2$, $\text{Na}_2\text{O-SiO}_2$ and $\text{Li}_2\text{O-B}_2\text{O}_3$ binaries (Figures 4, 5, and 6 of ref. 24). Agreement between the predicted density relation and the measured values is apparent; however, the preparation of these high silica glasses is difficult and no doubt contributes to the scatter of the measured data and to the lack of overlap between the two curves. This agreement further strengthens the evidence for the existence of an immiscibility gap in the $\text{Al}_2\text{O}_3\text{-SiO}_2$ system. The exploration of the underlying structural-chemical reasons for this proposed gap should, in turn, help to explain the density data in this region of the diagram.

The mullite structure consists of a quasi-ordered distribution for four and six coordinated aluminum atoms and four coordinated silicon atoms (25,26);* however the ratio of the AlO_4 and AlO_6 polyhedra is variable within this nominal crystal structure. Roy (27), as well as other investigators⁺, have attributed the formation from the melt of the metastable $2Al_2O_3 \cdot SiO_2$ mullite to a "structural inheritance from the melt which favors more Al^{+3} ions in four coordination". In addition, heat treatment of mullites of fixed composition over a temperature range of 1300^0-1790^0C increases the room temperature unit cell dimensions, particularly along the a axis, again indicating coordination changes in the aluminum ion (27). Thus the structural position of the aluminum species is seen to vary even in the crystalline mullite as a function of Al_2O_3 concentration and temperature. This same effect may also be assumed to exist in aluminosilicate glasses. This prior research leads to at least three explanations which may act separately or in combination to produce the parallelism of the melt density curves in the 0-40 mole % range.

a) At high temperatures above the liquidus and therefore above the consolute point, the ratio AlO_4 to AlO_6 becomes relatively constant for each concentration and the decrease in density as temperature increases is only a function of the increase in the thermal vibrations of the structure.

*The 40% point (x) (Figure 5) may contain mullite. Thus; if ignored would allow better agreement.

⁺For a discussion of this phenomenon, see reference (28).

b) The pure thermal expansion of the structure is accompanied by small decreases in the number of oxygens surrounding the normally octahedrally coordinated aluminum ions as well as, to a smaller extent, the more strongly bonded tetrahedrally coordinated aluminum and silicon ions. This common high temperature structural-chemical effect maintains the structural role of the ions, e.g., a modifying position, but decreases their average oxygen coordination.

c) The pure thermal expansion of the structure is accompanied by slight increases in the AlO_4 to AlO_6 ratio which are proportional to the Al_2O_3 concentration up to 30-45 mole %, depending on the temperature.

It is impossible from the current status of research to differentiate between these effects and their contribution, if any, to the formation of parallel density curves; however, all of the above structural changes have been shown to occur in this binary system. Also the apparent linearity of these melt density curves can be explained as a result of the additive volume relationships between Al_2O_3 and SiO_2 ; however, what combination of the above mechanisms produce this phenomenon is not known.

As one cools the melts, those aluminum ions having an increasing tendency to transform into 6 coordination exert an increasing force on the surrounding oxygens which eventually causes phase separation within certain compositional limits into alumina-rich and silica rich glasses. The former has been shown by MacDowell and Beall (22) to crystallize to mullite on heating. It is reasonable that this microphase separation would tend to produce a slight increase in

the density of the system and would explain the somewhat higher slope of the room temperature density curve (Figure 3) as compared to those of the melts*.

Studies concerning the direct determination of the coordination of aluminum ion in silicate glasses and melts, have been primarily limited to alkali aluminosilicates (29). Both tetrahedral (the tricluster [see footnote on page 12] and network-forming types) and octahedral coordinations of aluminum have been proposed under certain conditions. Evidence for the presence of the aluminum ion in both tetrahedral and octahedral coordination, in binary $\text{SiO}_2\text{-Al}_2\text{O}_3$ glasses, has been provided by Davis (10) utilizing Al $K\alpha$ x-ray fluorescence derived from electron beam microprobe measurements on the 5-40 wt% (3-28 mole %) Al_2O_3 glasses with a fictive temperature of $\sim 1200^\circ\text{C}$ (Figure 2). It was shown that Al $K\alpha$ wavelength of these aluminum-silicate glasses, when compared to the x-ray emission of metallic aluminum, AlPO_4 , and $\alpha\text{-Al}_2\text{O}_3$ (Table II), corresponded to that of a tetrahedrally coordinated aluminum at 5 wt% (3 mole %) Al_2O_3 and octahedrally coordinated aluminum at and above 10 wt% (6 mole %) Al_2O_3 . Similar more refined research has been carried out by Aksay (30) on 10.9 wt%

*Lacy (296) has argued that in low concentrations of Al_2O_3 , AlO_6 octahedra cannot exist. He postulated the existence of triclusters of AlO_4 tetrahedra accompanied by tribridging oxygen. The aluminum species in these triclusters is 4 coordinated to oxygen but only bonded to 3 to maintain charge balance. It is of note that no phase separation is detected in this low Al_2O_3 range even on slow cooling (22a).

(7 mole %) and 22.8 wt% (15 mole %) Al_2O_3 binary glasses using similar standards plus kyanite and mullite. The deconvoluted curves[†] revealed in both samples the presence of 6 and 4 coordinated aluminum ions as well as an increase in the former in the higher Al_2O_3 composition. Wardle and Brindley (31) have recently pointed out that although the x-ray fluorescence technique provides a means for determining coordination numbers; when more than one coordination state occurs simultaneously, the results reflect the weighted average of the two coordinations. Thus, the findings of Davis do not necessarily indicate a sudden change from four-fold to six-fold coordination at 10 wt% Al_2O_3 but could also indicate a gradual change from a predominantly four-fold coordinated structure to a predominantly six-fold coordinated one as demonstrated by Aksay. This gradual change is also substantiated by the density data.

As one increases the Al_2O_3 concentration (>40 mole %), the resulting compositions represent melts above the primary phase field of Al_2O_3 ; thus, it is feasible that the percentage of aluminum in octahedral positions structurally similar to that occupied in the oxide will increase with increasing concentrations of Al_2O_3 . The viscosities of these melts have also decreased dramatically from that of the high silica liquids (32) indicating that the structural network is becoming increasingly broken down coupled with lowered bond energies between the atomic species. These two premises would allow for a continual decrease in the average coordination of oxygen around the quasi-octahedrally

[†]Work conducted at Walter C. McCrone Associates using a DuPont 310 Curve resolver.

coordinated aluminum atoms as the temperature increased at each Al_2O_3 concentration. Such an effect coupled with static or increased coefficients of thermal expansion would explain the increasing deviation from linearity as a function of temperature and composition in the high Al_2O_3 range noted in Figure 3. Considerable research integrated with the development of presently unknown techniques will have to occur before a complete understanding of the density-temperature-composition phenomena can be achieved.

V. CONCLUSIONS

1. The x-radiographic technique represents an accurate method for measuring homogeneous single phase melt densities and fractional volume changes in single and multicomponent ceramic systems.
2. The extrapolation of available partial molar volume data of ternary aluminosilicates to the temperatures of the present research does not give accurate calculated values of density for the binary system.
3. Melt density curves in the $\text{Al}_2\text{O}_3\text{-SiO}_2$ system are parallel and linear to approximately 30-45 mole % Al_2O_3 , depending on the temperature. At high Al_2O_3 concentrations, increasing negative deviation from linearity is noted as a function of rising temperature and Al_2O_3 content.
4. A review of recent research on glasses in the $\text{Al}_2\text{O}_3\text{-SiO}_2$ system strongly indicates the existence of changing structural roles of the aluminum ion from AlO_4 to AlO_6 polyhedra with increasing Al_2O_3 content and decreasing temperature. This effect coupled with normal structural-chemical decreases in the coordination number of all cations with increasing temperature as well as pure thermal expansion of the structure play, at present, undifferentiable roles in determining both the absolute and relative values of densities in melts and quenched glasses of the Al_2O_3 system.

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Table I. Densities of the SiO₂-Al₂O₃ melts.

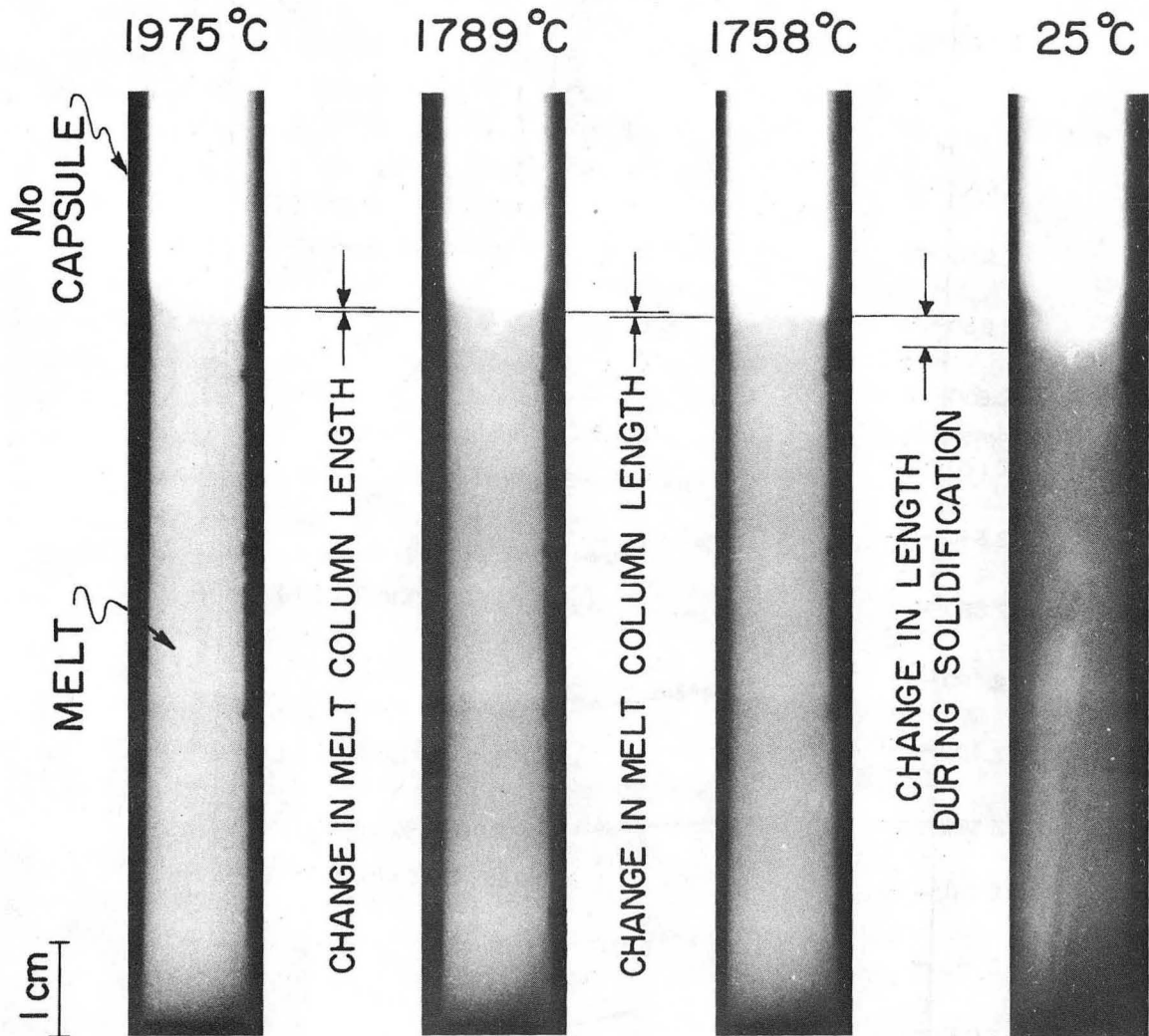
| 22.8 wt% Al ₂ O ₃ (14.82 mole%) | | 42.2 wt% Al ₂ O ₃ (30.08 mole%) | | 60.0 wt% Al ₂ O ₃ (46.92 mole%) | | 80.0 wt% Al ₂ O ₃ (70.21 mole%) | |
|--|----------------------------|--|-----------------------|--|-----------------------|--|-----------------------|
| Temp. (°C) | ρ (gm/cm ³) | Temp. (°C) | (gm/cm ³) | Temp. (°C) | (gm/cm ³) | Temp. (°C) | (gm/cm ³) |
| 1707 | 2.319 | 1758 | 2.475 | 1755 | 2.736 | 1966 | 2.811 |
| 1752 | 2.319 | 1789 | 2.466 | 1773 | 2.732 | 1993 | 2.799 |
| 1813 | 2.320 | 1813 | 2.461 | 1803 | 2.724 | 1995 | 2.791 |
| 1858 | 2.316 | 1838 | 2.465 | 1808 | 2.724 | | |
| 1907 | 2.313 | 1858 | 2.460 | 1835 | 2.629 | | |
| 1909 | 2.313 | 1880 | 2.454 | 1859 | 2.627 | | |
| 1963 | 2.305 | 1881 | 2.455 | 1882 | 2.626 | | |
| 1988 | 2.302 | 1909 | 2.448 | 1910 | 2.625 | | |
| 2008 | 2.302 | 1913 | 2.449 | 1938 | 2.615 | | |
| | | 1941 | 2.445 | 1959 | 2.612 | | |
| | | 1975 | 2.446 | 1985 | 2.608 | | |

Table II. Aluminum coordination data determined from AlK_α X-ray emission spectra. AlPO_4 and Al_2O_3 were the 4-fold and 6-fold coordinated standards. Al_2O_3 concentrations in the glasses are given in wt%.

| Material | Peak Position Half Height (\AA) | Displacement λ from Al Metal |
|-----------------------------|---|---|
| Al | 8.3390 | 0.0000 |
| AlPO_4 | 8.3357 | 0.0033 |
| Al_2O_3 | 8.3339 | 0.0051 |
| 5% Al_2O_3 | 8.3353 | 0.0037 |
| 10% Al_2O_3 | 8.3340 | 0.0050 |
| 15% Al_2O_3 | 8.3339 | 0.0051 |
| 20% Al_2O_3 | 8.3337 | 0.0053 |
| 25% Al_2O_3 | 8.3339 | 0.0051 |
| 30% Al_2O_3 | 8.3337 | 0.0053 |
| 35% Al_2O_3 | 8.3336 | 0.0054 |
| 40% Al_2O_3 | 8.3336 | 0.0054 |

FIGURE CAPTIONS

- Figure 1. Radiographs of molten and solidified alumino-silicate columns used in the determination of densities.
- Figure 2. Variation of the alumino-silicate melt densities with temperature.
- Figure 3. Variation of the alumino-silicate melt densities with Al_2O_3 content.
- Figure 4. Plots of calculated densities vs Al_2O_3 concentration across the immiscibility gap of ref. 22a using equation 1 and a least squares plot of the measured values of density (ref. 10.).

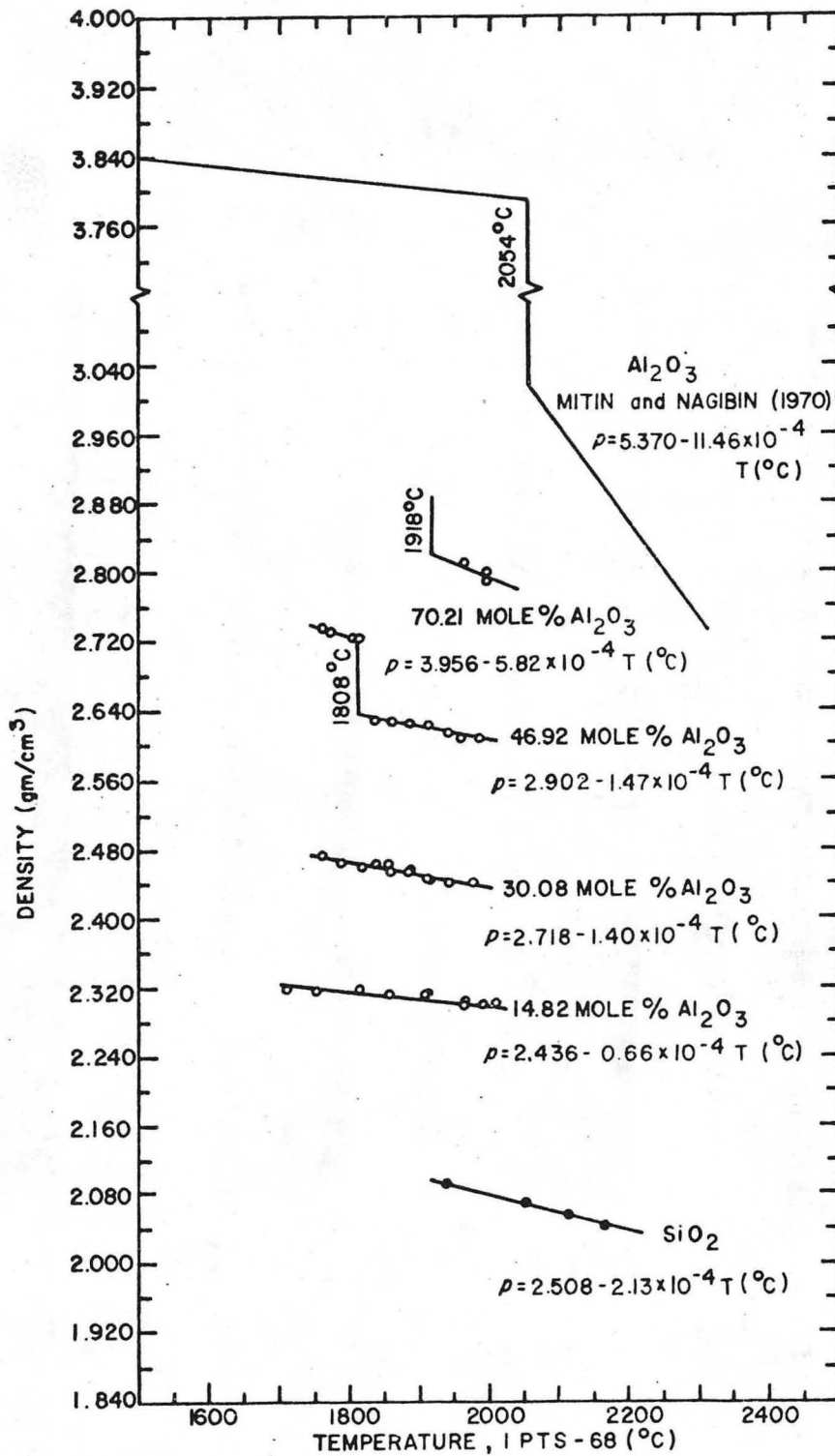


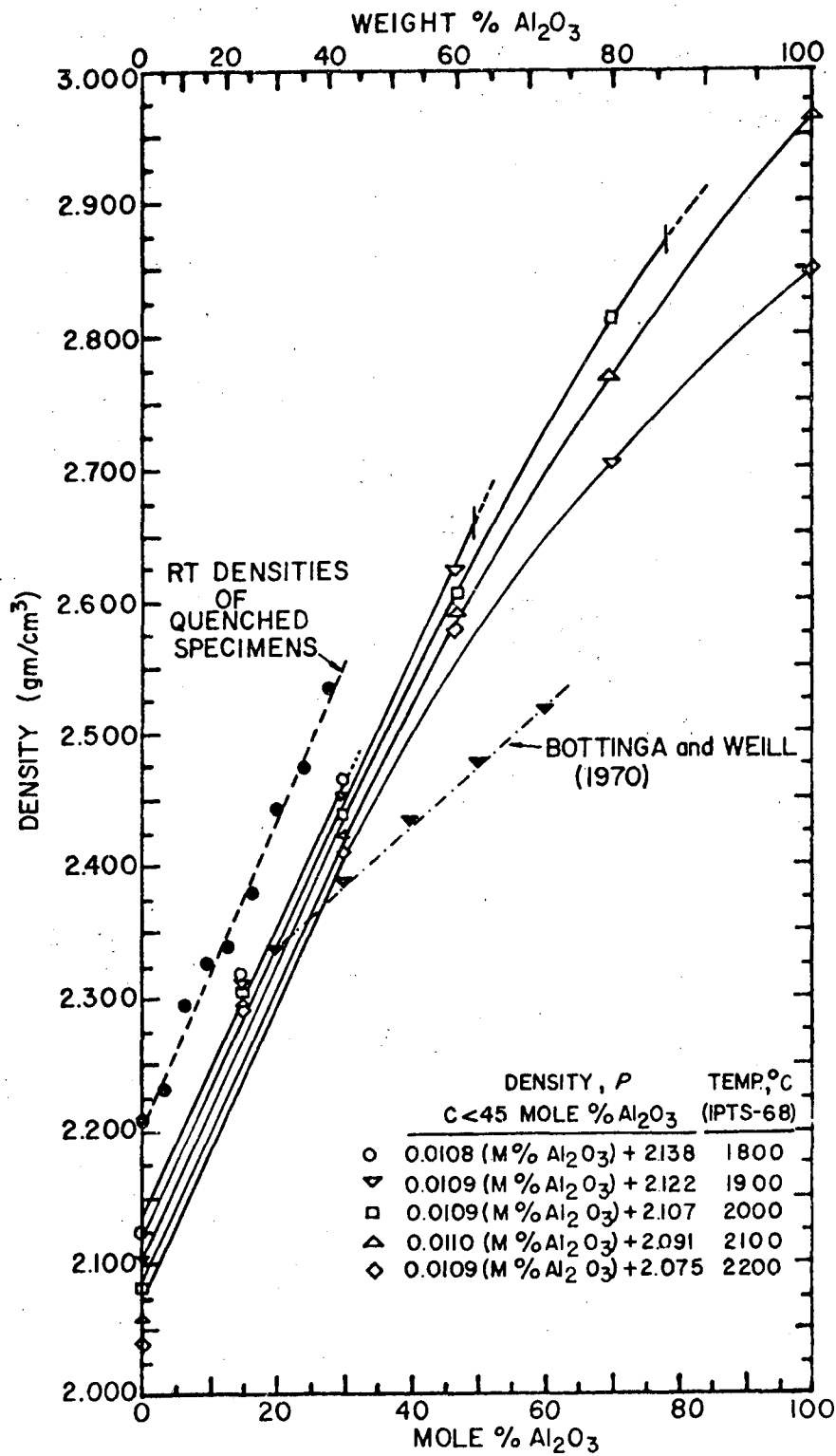
MELT COMPOSITION

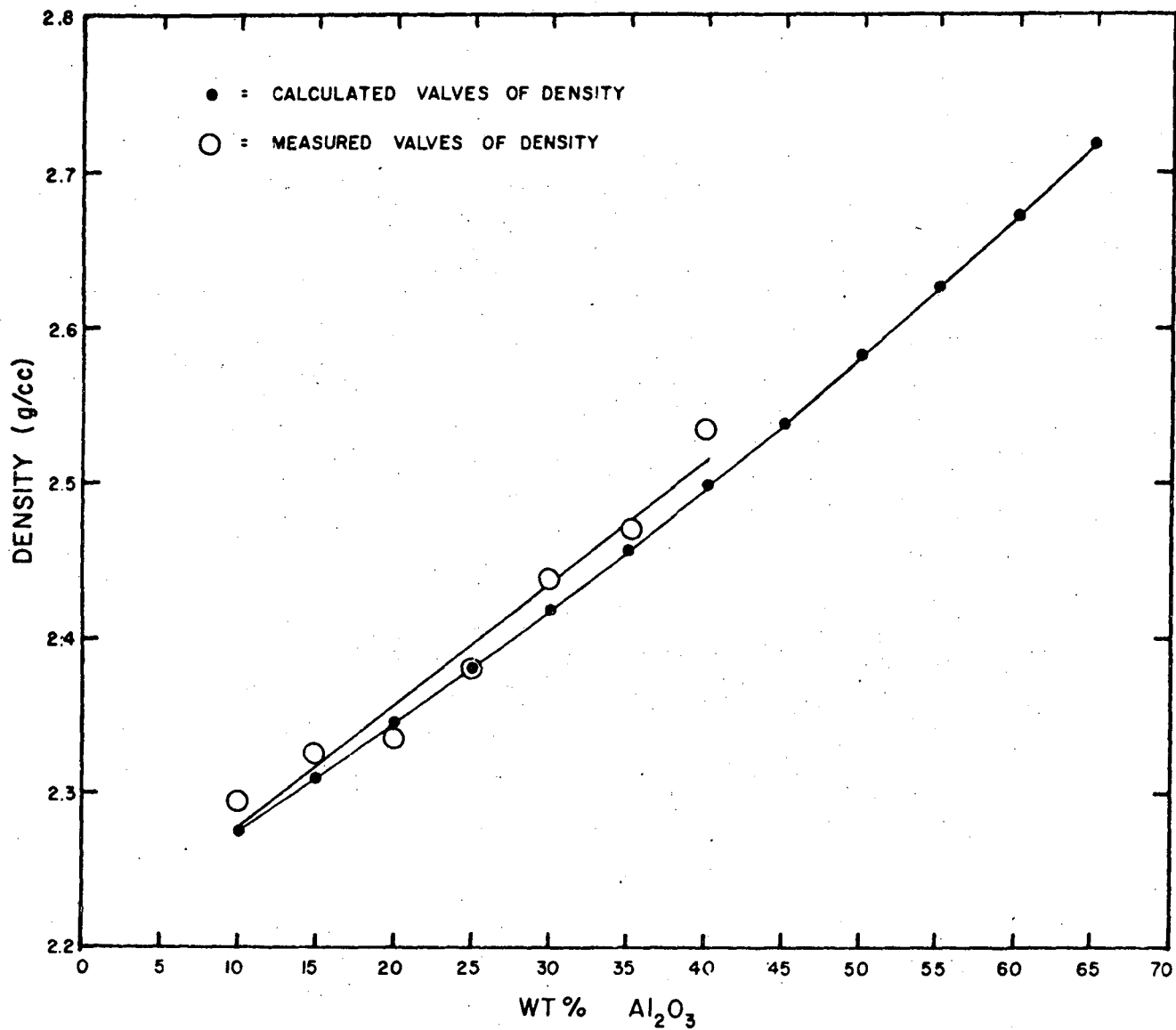
42.2 WT % Al₂O₃ + 57.8 WT % SiO₂

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Fig. 1







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