The densities of binary aluminosilicate melts were measured X-radiographically as a function of $\text{Al}_2\text{O}_3$ concentration between 1800° and 2000°C. Within this temperature range, the density curves vary linearly and are parallel from fused $\text{SiO}_2$ to $\text{SiO}_2$-2000°C. The X-radiographic measurements were made by Rasmussen and Nelson.2 The technique involved measuring the volume of a melt at temperature from its radio-graphed image and relating this volume to its density. This method was especially suitable for the aluminosilicate melts, since the specimens had to be sealed in molybdenum containers to eliminate silica losses during the measurements. The present study describes the density changes observed as a function of $\text{Al}_2\text{O}_3$ concentration and temperature and relates this data in terms of possible structural changes of the atomic species, primarily aluminum and oxygen.

II. Experimental Procedure

The binary compositions chosen for this study contained 22.8, 42.2, 60.0, and 80.0 wt% $\text{Al}_2\text{O}_3$. These mixtures were weighed, then melted in electron-beam-sealed, He-tight Mo capsules at 1953°C in vacuum for 30 to 60 min. The X-radiographic measurements were made by Rasmussen using the system described in Ref. 2. The specimens were heated at a rate of 3°C/min at 1700°C to 2000°C. The temperature (International Practical Temperature Scale (IPTS) 68) was monitored continuously with a two-color pyrometer accurate to ±10°C. The specimen images were obtained at 25°C intervals using a 300 kV X-ray source. Volume of the melt was calculated from the measured height and crucible diameter and corrected for thermal expansion. In most instances, the column length could be measured repetitively to give a density variation of ±0.004 g/cm². A typical set of radiographs used in the measurements is shown in Fig. 1. The amount of molybdenum in the melts was below the detection limit of the electron microprobe.

III. Results and Analysis

Densities of the aluminosilicate melts determined during the

Densities of $\text{SiO}_2$-$\text{Al}_2\text{O}_3$ Melts

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1 A portion of this work was conducted while the author was a Graduate Research Assistant at the University of California.
cooled only are shown in Table I and Fig. 2. The measurements obtained during the initial heating cycle were considered to be 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 (Ref. 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 (Fig. 2) was caused by formation of a precipitate. When heated, a volume increase accompanied by complete melting occurred for these compositions at 1913°C and 1993°C, respectively, corresponding to alumina liquidus temperatures as determined by Aksay and Pask.9 The 14.8 and 30.1 mol% 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.5-8 Mitin and Nagibin6 used a hydrostatic technique between the melting point and 2550°C; their results are reproduced in Fig. 2. The density of solid alumina was calculated up to its melting point using the coefficient of expansion data of Wachtman et al.9 and the room temperature density of 3.965 g/cm³ (Ref. 10).

The five density values of liquid silica shown in Fig. 2 are by Bacon et al.10 A straight line is drawn through the data points, excluding the one at 2326°C, since extending 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 (Fig. 2) and then deviates from linearity or the value reported at 2326°C is erroneous.

Figure 3 shows the variation of the melt densities with alumina content at 1800°C to 2200°C; the densities increase linearly only up to ~45 mol% Al_2O_3. The negative deviation from linearity at higher alumina contents indicates breakdown of the network structure. The figure also includes room temperature densities of the glasses quenched from 1803°C.12 On the basis of the data of Fig. 2, these room-temperature densities correspond to a fictive temperature of ~1200°C.

The partial molar volume of Al_2O_3 and SiO_2 in the melt was not calculated. However, the data compiled by Huggins and Sun,13 Bottinga and Weill,14 and others15 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 were extrapolated to 1900°C and used to calculate the densities of binary aluminosilicate melts containing 20 to 60 mol% Al_2O_3. The agreement between these calculated values and the measured ones is poor, especially at higher alumina contents (Fig. 3). Similar results are obtained if the values compiled by Huggins and Sun are used. It therefore appears that the partial molar volumes obtained from ternary aluminosilicates may be satisfactorily used only to predict

**Table 1. Densities of SiO_2-Al_2O_3 Melts**

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>p(ρ/cm³)</th>
<th>Temp. (°C)</th>
<th>p(ρ/cm³)</th>
<th>Temp. (°C)</th>
<th>p(ρ/cm³)</th>
<th>Temp. (°C)</th>
<th>p(ρ/cm³)</th>
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<tr>
<td>1707</td>
<td>2.319</td>
<td>1758</td>
<td>2.475</td>
<td>1755</td>
<td>2.736</td>
<td>1966</td>
<td>2.811</td>
</tr>
<tr>
<td>1752</td>
<td>2.319</td>
<td>1789</td>
<td>2.466</td>
<td>1773</td>
<td>2.732</td>
<td>1993</td>
<td>2.799</td>
</tr>
<tr>
<td>1813</td>
<td>2.320</td>
<td>1813</td>
<td>2.461</td>
<td>1803</td>
<td>2.724</td>
<td>1995</td>
<td>2.791</td>
</tr>
<tr>
<td>1858</td>
<td>2.316</td>
<td>1838</td>
<td>2.465</td>
<td>1808</td>
<td>2.724</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1907</td>
<td>2.313</td>
<td>1858</td>
<td>2.460</td>
<td>1835</td>
<td>2.629</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1909</td>
<td>2.313</td>
<td>1880</td>
<td>2.454</td>
<td>1859</td>
<td>2.627</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1963</td>
<td>2.305</td>
<td>1881</td>
<td>2.455</td>
<td>1882</td>
<td>2.626</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1988</td>
<td>2.302</td>
<td>1909</td>
<td>2.448</td>
<td>1910</td>
<td>2.625</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2008</td>
<td>2.302</td>
<td>1913</td>
<td>2.449</td>
<td>1938</td>
<td>2.615</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1941</td>
<td></td>
<td>1941</td>
<td></td>
<td>1959</td>
<td></td>
<td>2.612</td>
</tr>
<tr>
<td></td>
<td>1975</td>
<td></td>
<td>1975</td>
<td></td>
<td>1985</td>
<td></td>
<td>2.608</td>
</tr>
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</table>
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 on melting or solidification. Tyrolerova and Lu\textsuperscript{16} reported a volume decrease of 10.3\% during solidification for a fused-cast mullite specimen of 75.1 wt\% Al\textsubscript{2}O\textsubscript{3}. The density of stoichiometric mullite (71.8 wt\% Al\textsubscript{2}O\textsubscript{3}) at its metastable congruent melting temperature, 1890°C\textsuperscript{17} is 3.10 g/cm\textsuperscript{3} when calculated from the expansion data of mullite.\textsuperscript{18}

The density of the corresponding melt at the same temperature is 2.774 g/cm\textsuperscript{3}, based on the data given in Fig. 3. Thus, the fractional volume decrease of mullite on solidification is 10.52\%, which agrees with the values reported by Tyrolerova and Lu.\textsuperscript{16}

The fractional volume decrease of alumina on solidification is 20.7\%, based on the data of Fig. 2. Similar values were reported by Kingery\textsuperscript{19} (20.4\%)\textsuperscript{19} and Tyrolerova and Lu\textsuperscript{19} (19.9 to 20.1\%). Kirshenbaum and Cahill\textsuperscript{8} and Bates et al.\textsuperscript{4} reported values of 22.0 and 24.0\%, respectively; however, for comparison, these values should be expressed as fractional volume change on solidification. The new values are 18.2 and 19.4\%, respectively, and compare well with those reported by the other workers.

![Diagram](https://example.com/diagram.png)

**Fig. 3.** Variation of aluminosilicate melt densities with Al\textsubscript{2}O\textsubscript{3} content. Densities of quenched specimens, pure SiO\textsubscript{2}, and pure Al\textsubscript{2}O\textsubscript{3} are from Refs. 12, 11, and 8, respectively.

The density and any changes in density of a system are a function of the concentrations 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 the concentration of each component and the temperature, thus producing second-order effects on the density of the overall system.

The approximate parallelism of the melt-density curves for 0 to 40\% Al\textsubscript{2}O\textsubscript{3} indicates that, as the temperature increases at each Al\textsubscript{2}O\textsubscript{3} concentration, the densities are controlled by either pure thermal expansion or a combination of the thermal expansion and equivalent proportional changes in the coordination of the Al\textsuperscript{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.\textsuperscript{3}

Galakhov and Konovalova\textsuperscript{21} and Eipeltauer and Hruschka\textsuperscript{22} attributed unusual structural features in quenched glasses containing 12 to 48 mol\% Al\textsubscript{2}O\textsubscript{3} to phase separation. Eipeltauer and Hruschka found that the crystallization temperature (T\textsubscript{c}) of these glasses is 950° to 1000°C, in agreement with the work of Takamori and Roy,\textsuperscript{24} whose TEM studies also gave direct evidence of metastable phase separation at 20 to 30 mol\% Al\textsubscript{2}O\textsubscript{3} (20\% was the lowest concentration examined). MacDowell and Beal\textsuperscript{24} conducted the most comprehensive study of the microstructure of these glasses and found much evidence for phase separation within a metastable immiscibility gap with limits of 7 to 55 mol\% Al\textsubscript{2}O\textsubscript{3} and an approximate consolute point of 1650°C. Thermodynamic calculations by Rishub and Pask\textsuperscript{25} indicate that this immiscibility gap extends from \approx 11 to 49 mol\% Al\textsubscript{2}O\textsubscript{3} at 1100°C with a consolute temperature of \approx 1540°C at a critical composition of \approx 36 mol\% Al\textsubscript{2}O\textsubscript{3}. Furthermore, their direct TEM and selected-area diffraction studies of the powdered glasses within this gap revealed phase-separated glassy droplets (\approx 400 Å) up to \approx 25 mol\% Al\textsubscript{2}O\textsubscript{3}; beyond this Al\textsubscript{2}O\textsubscript{3} concentration the glasses tended to crystallize rapidly. Indeed, studies 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\textsuperscript{8,26-27}; however, the ratio of Al\textsubscript{2}O\textsubscript{3} and AlO\textsubscript{2} polyhedra is variable within this nominal crystal structure. Aramaki and Roy\textsuperscript{28} and other investigators\textsuperscript{28} attributed the formation from the melt of the metastable 2Al\textsubscript{2}O\textsubscript{3}·SiO\textsubscript{2} mullite to a "structural inheritance from the liquid which favors more Al\textsuperscript{3+} ions in four coordination."\textsuperscript{28} In addition, heat-treating mullites of fixed composition at 1300° to 1790°C increases the room-temperature unit-cell dimensions, particularly along the a axis, again indicating coordination changes in the aluminum ion.\textsuperscript{28} Thus the structural position of the aluminum species varies even in the crystalline mullite as a function of Al\textsubscript{2}O\textsubscript{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 to 40 mol\% range.

1. At high temperatures (above the liquidus and therefore above the consolute point) the ratio of Al\textsubscript{2}O\textsubscript{3} to AlO\textsubscript{2} 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.

2. 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 lesser 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.

3. The pure thermal expansion of the structure is accompanied by slight increases in the Al\textsubscript{2}O\textsubscript{3} to AlO\textsubscript{2} ratio which are proportional to the Al\textsubscript{2}O\textsubscript{3} concentration up to 30 to 45 mol\%, depending on the temperature.

\textsuperscript{4}For a discussion of this phenomenon, see Ref. 29.
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 preceding structural changes have occurred in this binary system. Also, the apparent linearity of these melt density curves can be explained as a result of the additive volume relations between Al₂O₃ and SiO₂; however, what combination of the above mechanisms produces this phenomenon is not known.

As the melts cool, the aluminum ions have an increasing tendency to transform into six coordination and exert an increasing force on the surrounding oxygen ions, eventually causing phase separation (within certain compositional limits) into alumina-rich and silica-rich glasses. MacDowell and Beall showed that the alumina-rich glasses crystallize to mullite when heated. 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 (Fig. 3) as compared to those of the melts.

Studies of the direct determination of aluminum ion coordination in silicate glasses and melts have been primarily limited to alkali aluminosilicates. Both tetrahedral (the tricluster* and network-forming types) and octahedral coordinations of aluminum have been proposed under certain conditions. The presence of the aluminum ion in tetrahedral and octahedral coordination in binary SiO₂-Al₂O₃ glasses was shown by Davis, who used Al Kα X-ray fluorescence derived from electron-beam microscope measurements on 5 to 40 wt% (3 to 28 mol%) Al₂O₃ glasses with a fictive temperature of ~1200°C (Fig. 2). The Al Kα wavelength of these aluminosilicate glasses, when compared to the X-ray emission of metallic aluminum, AlPO₃, and α-Al₂O₃ (Table II), corresponded to that of a tetrahedrally coordinated aluminum at 5 wt% (3 mol%) Al₂O₃ and octahedrally coordinated aluminum ~10 wt% (6 mol%) Al₂O₃. Similar, more refined research was conducted by Aksay on 10.9 wt% (7 mol%) and 22.8 wt% (15 mol%) Al₂O₃ binary glasses, using similar standards plus kyanite and mullite. In both samples, the deconvoluted curves revealed the presence of six- and four-coordinated aluminum ions as well as an increase in the former in the higher Al₂O₃ composition. Wardle and Brindle 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, Davis's findings do not necessarily indicate a sudden change from fourfold to sixfold coordination at 10 wt% Al₂O₃ but could also indicate a gradual change from a predominantly fourfold-coordinated structure to a predominantly sixfold-coordinated one, as demonstrated by Aksay. This gradual change is also substantiated by the density data.

As the Al₂O₃ concentration increases (>40 mol%), the resulting compositions represent melts above the primary field of Al₂O₃; 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 Al₂O₃. The viscosities of these melts also decrease dramatically from that of the high-silica liquids, indicating that the structural network is becoming increasingly broken down and that bond energies between the alumina species are decreasing. These two premises would allow for a continual decrease in the average coordination of oxygen around the quasi-octahedrally coordinated aluminum atoms as the temperature increased at each Al₂O₃ concentration. Such an effect, coupled with static or increased coefficients of thermal expansion, could explain the increasing deviation from linearity as a function of temperature and composition in the high Al₂O₃ range (Fig. 3). Much research and the development of presently unknown techniques are necessary to achieve a complete understanding of the density-temperature-composition phenomena.

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### Table II. Aluminum Coordination Data Determined from AlKα X-ray Emission Spectra

<table>
<thead>
<tr>
<th>Material</th>
<th>Peak position half breadth (Å)</th>
<th>Displacement ( \Delta ) from Al metal</th>
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<tr>
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<td>8.3390</td>
<td>0.0000</td>
</tr>
<tr>
<td>AlPO₄</td>
<td>8.3357</td>
<td>0.0033</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>8.3339</td>
<td>0.0051</td>
</tr>
<tr>
<td>5 wt% Al₂O₃</td>
<td>8.3353</td>
<td>0.0037</td>
</tr>
<tr>
<td>10 wt% Al₂O₃</td>
<td>8.3400</td>
<td>0.0050</td>
</tr>
<tr>
<td>15 wt% Al₂O₃</td>
<td>8.3339</td>
<td>0.0051</td>
</tr>
<tr>
<td>20 wt% Al₂O₃</td>
<td>8.3337</td>
<td>0.0053</td>
</tr>
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</tr>
<tr>
<td>30 wt% Al₂O₃</td>
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</tr>
<tr>
<td>40 wt% Al₂O₃</td>
<td>8.3336</td>
<td>0.0054</td>
</tr>
</tbody>
</table>

*AlPO₄ and Al₂O₃ were the 4-fold and 6-fold coordinated standards (from Ref. 12).

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### 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. Extrapolating available partial molar volume data of ternary aluminosilicates to the temperatures of the present research does not result in accurate calculated values of density for the binary system.

3. Melt density curves in the system SiO₂-Al₂O₃ are parallel and linear to ~30 to 45 mol% Al₂O₃, depending on the temperature. At high Al₂O₃ concentrations, increasing negative deviation from linearity is noted as a function of increasing temperature and Al₂O₃ content.

4. A review of recent research on glasses in the system SiO₂-Al₂O₃ strongly indicates the existence of changing structural roles of the aluminum ion from Al₂O₃ to Al₂O₃ polyhedra with increasing Al₂O₃ content and decreasing temperature. This effect, coupled with normal structural-chemical decreases in the coordination number of all cations with increasing temperature, and pure thermal expansion of the structure have roles that cannot now be differentiated in determining the absolute and relative values of densities in melts and quenched glasses of the system SiO₂-Al₂O₃.

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### References


Delayed Failure in Chemically Vapor Deposited ZnSe

K. R. McKinney, J. J. Mecholsky, and S. W. Freiman

Naval Research Laboratory, Washington D.C., 20375

Room-temperature delayed failure of CVD ZnSe was tested in 4-point flexure. Fracture surfaces of specimens exhibiting delayed failure, i.e., failing after some time under a fixed load, showed an intergranular region of fracture, surrounding a mechanically induced flaw. This intergranular region was attributed to slow crack growth and the remaining transgranular fracture to high-velocity crack propagation. This behavior contrasts with that of specimens failing during loading, i.e., with little or no slow crack growth, which typically exhibited only transgranular failure, as was also observed in bend tests of specimens loaded to failure. Actual times to failure fell between failure-time predictions based on single-crystal and polycrystalline slow crack growth data, but were much closer to that for the single crystal.

1. Introduction

Moisture-assisted subcritical crack growth occurs in chemically vapor deposited (CVD) ZnSe. The primary objective of the present work was to experimentally measure times to failure of CVD ZnSe as a function of stress in deadweight loading and to compare these times to those predicted from slow crack growth data and fracture mechanics principles. A secondary objective was to investigate possible correlations of failure behavior with microstructure.

II. Experimental Technique

Thirty-two 4-point bend specimens (1.9 by 4.4 by 25.4 mm) were cut from a plate of CVD ZnSe, finished with a 1-μm diamond paste, and the corners rounded. Specimens were deadweight-loaded in 4-point flexure (outer span 22.9, inner span 7.5 mm) in air at 21°C and 50% rh, using eight test fixtures (Fig. 1). When a specimen fractured, a microswitch located at the pivot point of the loading bar opened, stopping a timer. Two stress levels, 46.9 and 55.8 MPa, were chosen based on statistical analysis of the strength distribution of bars previously tested in 4-point bending. Scanning electron micrographs of the fracture surfaces were used to determine the type, size, and geometry of failure origins.

III. Results and Discussion

(1) Fracture Surface Analysis

Fracture origins were identified in the 27 bars which failed in 300