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Density and Thermal Expansion Measurements of Several Mixed Oxide Glasses in the Solid and Liquid Regions

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Density and Thermal Expansion Measurements of Several Mixed Oxide Glasses in the Solid and Liquid Regions

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ABSTRACT

The density and thermal expansion of a number of mixed oxide glasses were measured in the solid and liquid regions by gamma densitometry. With this non-contacting technique, both physical regimes may be investigated as the temperature is varied and the glass viscosity varies over a wide range. Where rate-dependent crystallization can occur, the technique allows the continuous measurement of density as the liquid cools to a supercooled glass or a crystalline solid. Lead borate glasses were investigated in the range from 27 to 42 mol% PbO. The liquid phase volumetric thermal expansion coefficient was observed to decrease with increasing PbO content, in contrast to the solid phase linear thermal expansion coefficient. In soda-baria phosphate glasses (50 mol% P_2O_5), liquid phase volumetric expansion coefficients were found to vary as the solid phase linear expansion coefficients. Two soda-alumina silicate glasses (60 mol% SiO_2) were investigated as well. Measurements on a lithia-aluminosilicate glass ceramic were obtained by this method to approximately 400 C above the limit of conventional dilatometry, thereby allowing the measurement of the thermal expansion of high temperature crystalline phases, as well as the liquid phase density.

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INTRODUCTION

Measurements of the density of glasses in the molten state and through the glass transition region can be useful in the study of crystallization processes in glasses. Conventional density measurement techniques may be used in either solid or liquid region, but the gamma densitometry technique allows measurements in both physical states with the same experimental arrangement. In particular, the measurement of the density through liquid/solid or glass transitions is well suited to this technique, because the measurement may be made through a wide range of viscosity. In this report, we describe the results of gamma densitometry measurements on the density and thermal expansion of a number of glasses through the solid and liquid regions. Depending on the heating and cooling rates employed in the experiments, crystallization occurred in some of the materials. The glasses measured here are of technological importance. They consisted of lead borate glasses, soda-baria phosphate glasses, alumina-silicate glasses, and a lithia-aluminosilicate glass ceramic.

EXPERIMENTAL DETAILS

The sample specimens were prepared by mixing of the starting materials, melting in a high temperature furnace in platinum crucibles, and casting into the required parallelepiped shape in high purity graphite crucibles. For each glass composition, the mass attenuation coefficient was measured at ambient temperature using the gamma densitometry facility. Absolute ambient density values were determined by submersion densitometry. Complementary measurements of the glass transition temperature (Tg) and linear thermal expansion in the solid phase were made by pushrod dilatometry.

For the high temperature density measurements, the glass was contained in a covered crucible (high purity graphite or platinum) of rectangular cross section and heated in a high temperature furnace in a helium atmosphere. Temperature measurements were made using a calibrated type S thermocouple in contact with the crucible support. Typical sample dimensions were 2 cm x 2 cm x 2 cm.

At a temperature (usually the highest) in the liquid phase, the gamma count rate was measured and used to determine the molten glass density. Subsequent gamma flux measurements as a function of temperature yielded the changes in attenuation due to the changes in the product of specimen density and pathlength parallel to the collimated gamma beam. Data were obtained during cooling from the melt at various rates to observe the effect of the quenching rates. In the melt, the glass conformed to the size and shape of the crucible, so that the pathlength was known and the glass density was determined directly. If the material separated from the crucible at some temperature, the glass density was only approximately determined. In some cases, the glass deformed the platinum crucible during freezing, typically contracting the crucible dimension by about 0.5%. In these cases, the solid phase density results suffer a corresponding reduction in precision. In cases where voids were present in the ambient temperature glass, a fully dense glass was not formed. The resulting porosity also contributed to imprecision in the solid phase density measurements.

Data were obtained on both virgin and remelted glass specimens. The initial data were obtained during cooling from the melt, typically at a rate of approximately 2.5 C/min. Subsequent data were obtained during heating, at various isothermal holds in the molten state, and at various cooling rates to investigate crystallization in the glasses.

Corrections were made for the variations in crucible dimension with temperature, the dead time of the counting system, and the variation with temperature of the gamma flux through the measurement device in the absence of a sample material. Typical density results were precise to within ±0.2%. Additional details of the gamma densitometry measurement technique may be found in Ref. [1].

RESULTS

Ambient temperature data for the measured glasses may be found in Table 1. These measurements consist of the ambient density and the material's mass attenuation coefficient determined experimentally. (The latter parameter, though determined at ambient conditions, is valid throughout the range of measurement, as it depends only on the chemical composition of the material.[1]) Data obtained from pushrod dilatometry were used to determine a mean thermal expansion coefficient in the solid phase and to calculate the solid phase density variation with temperature, assuming isotropic behavior. This density variation was compared with that obtained by gamma densitometry. Vertical offsets of the density data from test to test are largely the result of the imprecision in the ambient density values, due to voids, crucible deformation, etc. Mean expansion

TABLE 1. Ambient Temperature Parameters.

Glass	Composition (mol%)	Density (g/cm^3)	Mass Attenuation (cm^2/g)	Glass Transition Temperature Tg (C)
Lead Borates	27 PbO - 73 B_2O_3	3.87	0.0954	480
	33.3 PbO - 66.7 B_2O_3	4.40	0.0974	460
	42 PbO - 58 B_2O_3	5.14	0.0981	440
Soda-baria phosphates	50 BaO- 50 P_2O_5	3.41	0.0784	410
	50 Na_2O- 50 P_2O_5	2.50	0.0775	290
	40 Na_2O- 10 BaO- 50 P_2O_5	2.64	0.0787	280
soda-alumina silicates	20 Na_2O- 20 Al_2O_3- 60 SiO_2	2.46	0.0787	790
	26.6 Na_2O- 13.3 Al_2O_3- 60 SiO_2	2.48	0.0786	570
lithia-aluminosilicate		2.35	0.0775	470

coefficients were determined from linear least squares fits to the linear expansion or density data, over the specified temperature range. Since the liquid density variation with temperature typically shows some positive curvature, a comparison of expansion coefficients is meaningful only when similar temperature ranges are used in the fitting procedure. Typical deviations in the expansion coefficients are on the order of ±5%.

A. Lead Borates.

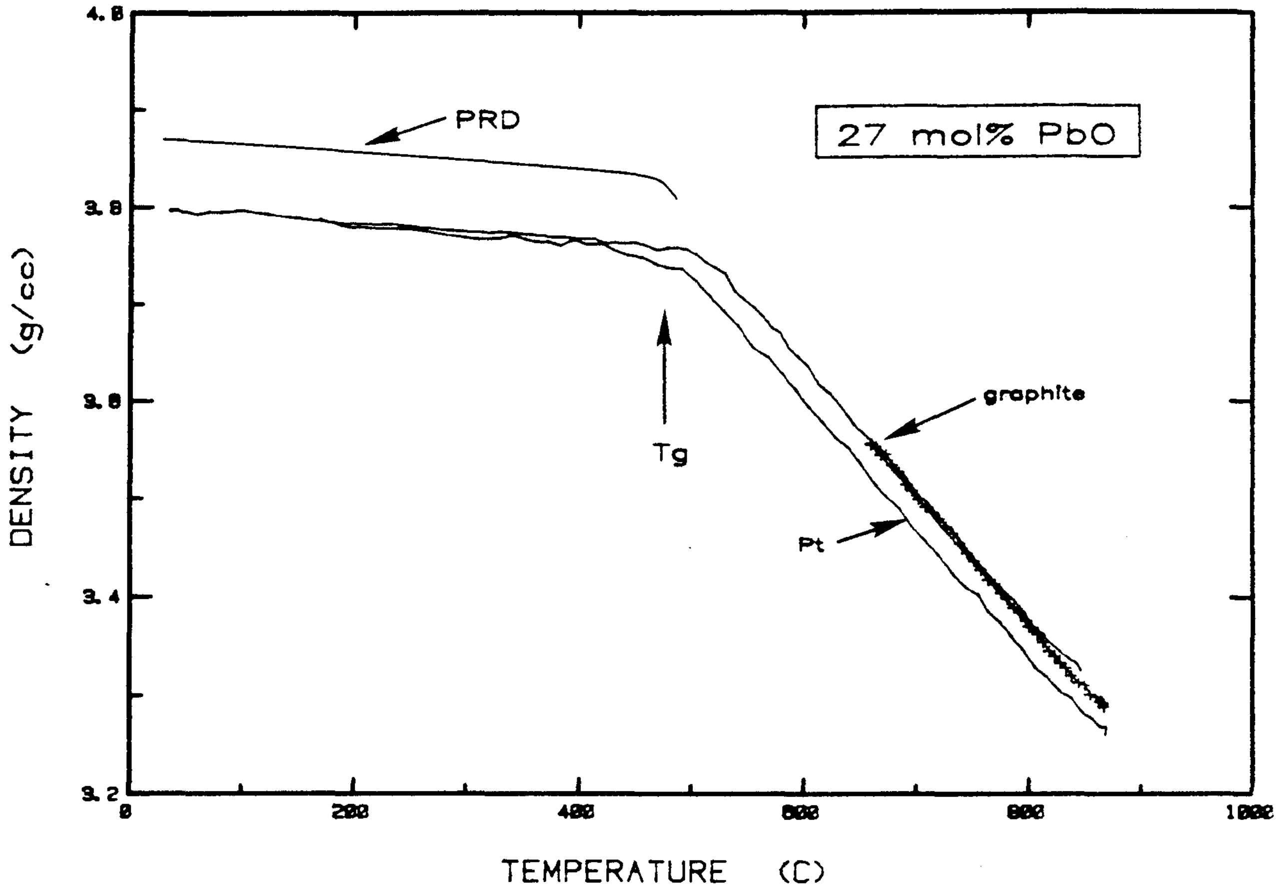
Three compositions of lead borate glasses were prepared for study. The compositions consisted of 27, 33.3, and 42 mol% PbO, with the remainder B_2O_3. The three initial glasses were formed by melting the starting components at 850, 850, and 950 C, respectively, prior to casting.

Differential thermal analysis (DTA) measurements on these glass compositions revealed Tg endotherms corresponding to the glass transitions observed by dilatometry. In the highest PbO glass, a sharp exotherm was observed near 570 C, presumably due to the formation of a crystalline phase in the glass. (DTA results were obtained during heating of the glasses at approximately 10 C/min.) The $PbO-B_2O_3$ phase diagram [2] reveals a liquidus for the three glass compositions at about 740 C.

Initial gamma densitometry measurements were made in high purity graphite crucibles, but the materials were visibly altered after melting at high temperature. For the low PbO composition, the glass appeared to have a metallic luster, and the high PbO composition clearly displayed metallic Pb particles on the surface of the glass. The high PbO glass also showed areas of white, opaque polycrystalline material imbedded in the glassy bulk. Reduction of the PbO to metallic lead appeared to have taken place in the graphite crucibles. Subsequent measurements were performed using platinum crucibles, where the results were obtained with no visible evidence of oxide reduction.

<u>1. 27 PbO - 73 B_2O_3.</u> Figure 1 summarizes the 27 mol% PbO results. The upper curve, marked "PRD", shows the solid phase glass density up to the glass transition temperature Tg. These data were derived from pushrod dilatometry measurements of the linear thermal expansion. The expansion results compare well with the below-Tg data shown in the figure from gamma densitometry results. The two sets of data marked "graphite" were obtained with a graphite crucible. One curve was obtained during cooling at 2.5 C/min, and the other was determined while heating at 1 C/min with periodic isothermal holds. The final curve was obtained during cooling of a different sample in a platinum crucible. There were no apparent differences in the above-Tg expansion behavior between the the two crucible materials. The mean expansion coefficients are summarized in Table 2. The material was in a glassy state following each of the high temperature measurement cycles, independent of the heating and cooling rates employed.

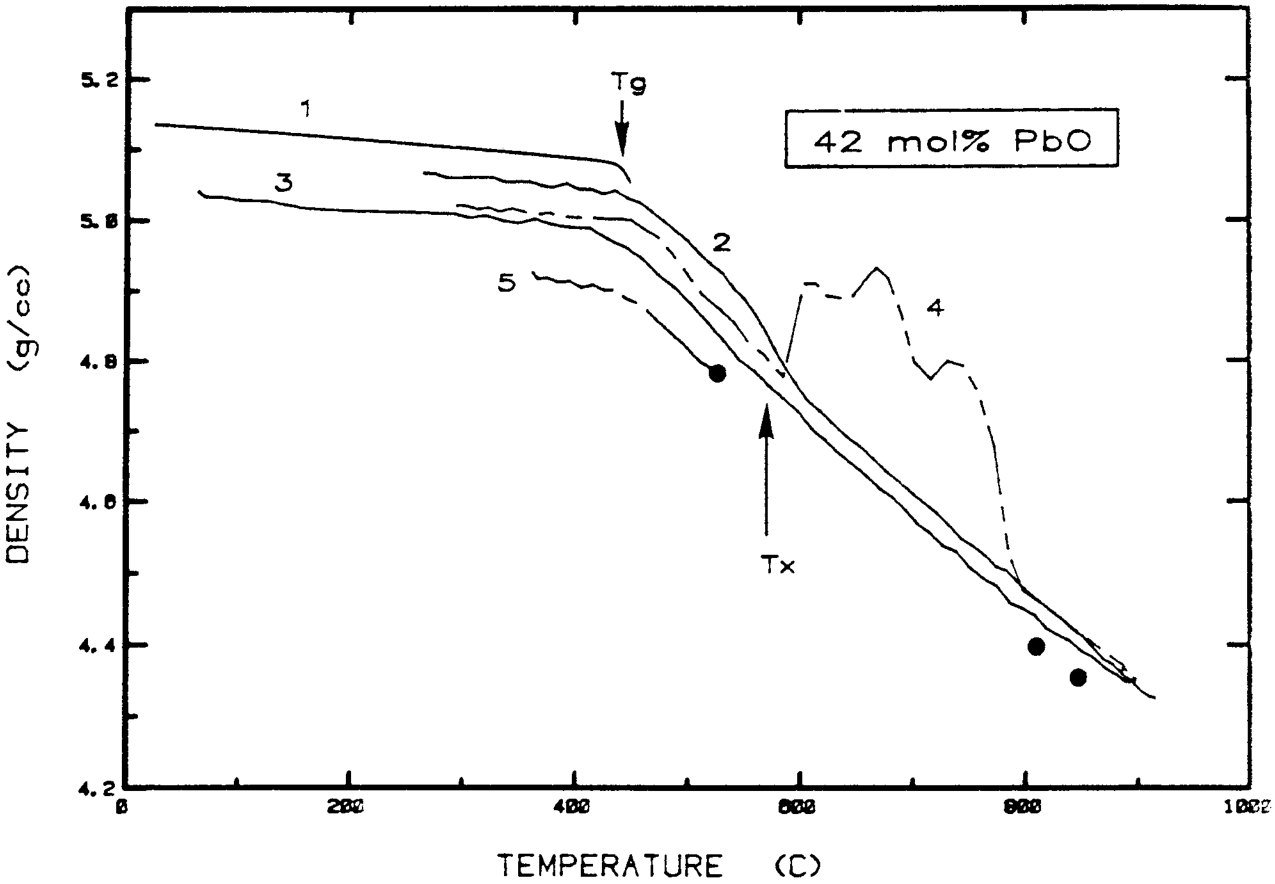
<u>2. 42 PbO - 58 B_2O_3.</u> Results from the measurements on the high PbO content glass are shown in Fig. 2. For this 42 mol% PbO glass, the Tg temperature was found by DTA and pushrod dilatometry (curve 1) to



1. Density vs temperature for 27 PbO - 73 B_2O_3 glass. PRD refers to results from pushrod dilatometry. Tg is the glass transition. Two crucible materials (graphite and platinum) were used in the measurements. Data above Tg were obtained for both cooling and heating.

TABLE 2. Lead Borate Glass Results

Composition (mol% PbO)	Mean Linear Thermal Expansion Coefficient 50 to 300 C (1E-6 /K)	Mean Density Coefficient, (1E-4 g/cm^3-K)		Liquid Density at 800 C (g/cm^3)
		T > 550 C	T > 750 C	
27	7.0	-12.8	-12.1	3.38
33.3	7.3	-----	-11.7	3.82
42	8.2	-13.2	-11.8	4.46



2. Density vs temperature for 42 PbO - 58 B_2O_3 glass. 1 -- pushrod dilatometry, 2 -- graphite crucible, cooling at 2 C/min, 3 -- platinum crucible, cooling at 3 C/min, 4 -- heating at 2.5 C/min, with crystallization at Tx, 5 -- liquid state density values (above 800 C) and density values below 525 C after cooling from 800 C at > 50 C/min.

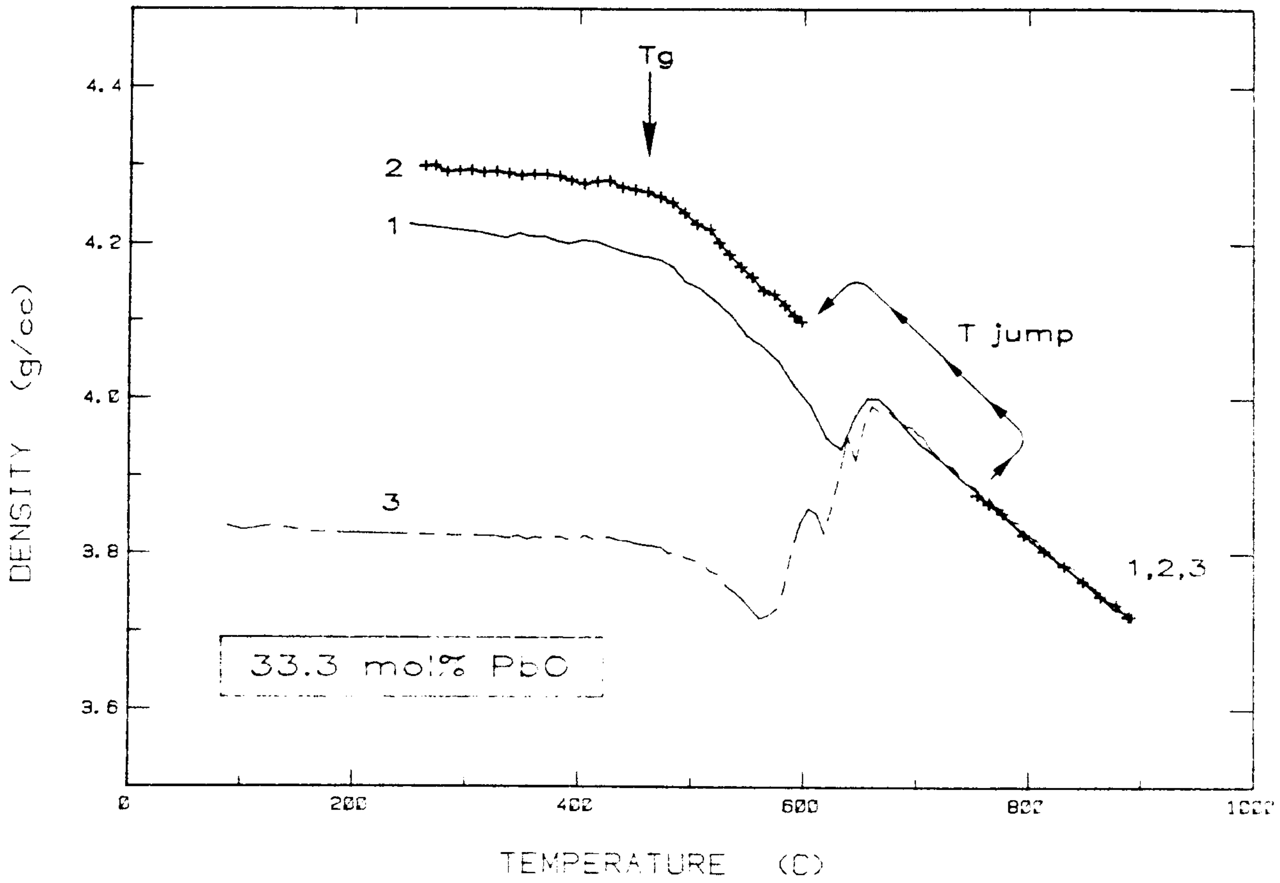
be about 440 C. Density measurements from gamma densitometry showed a marked dependence on the heating cycle during measurement, as seen in the figure. Curve 2 was obtained using a graphite crucible; data were obtained during cooling from the melt at about 2 C/min. After the test, PbO reduction was observed (metallic Pb particles on the glass surface), and there was visible evidence of polycrystalline material (opaque white crystals) dispersed throughout the glass. The departure from non-linear density vs temperature behavior which occurred at 570 C appears to correspond to the DTA crystallization peak; the crystalline phase would be expected to exhibit a higher density than the glass. The change in slope at Tg characteristic of the glass is due to the remaining glassy matrix.

Subsequent measurements on the 42 mol% PbO glass were done using the platinum crucible. No further evidence for oxide reduction was seen, although crystalline behavior was observed. Curve 3 in Fig. 2 shows the data obtained during cooling at 3 C/min from the melt in a Pt crucible. After the test, the material was a clear glass. As with the low PbO glass, the data show a high expansion, approximately linear with temperature, above Tg, and a lower expansion, consistent with pushrod dilatometry, below Tg. From the density data, there is no evidence of a "melting" transition, but only the continuous change with temperature of the glass density in the above-Tg state.

Cooling from the melt at about 1 C/min was sufficiently slow to allow crystallization of the entire sample. The specimen exhibited white opaque crystals throughout the crucible, and large internal voids were present (determined by the high gamma flux in this state), but no sample weight loss was observed. Subsequent reheating of the crystalline material showed a melting above 700 C. The data points and curve 5 in the figure show the subsequent density measurements obtained after melting the crystalline phase. At isotherms above 800 C, liquid state density values were obtained. The specimen was then rapidly cooled to about 525 C at an average cooling rate in excess of 50 C/min. The data point on curve 5 shows the density at the 525 C isotherm. Subsequent cooling at 2 C/min yielded the density variation with temperature and Tg representative of the glassy state. After this measurement, a clear glass was observed, although some bubbles were present, which may account for the low measured density.

Curve 4 shows the heating of the glass at 2.5 C/min. At the crystallization temperature Tx, the apparent density increases. Structure in the density curve 4 above Tx is not meaningful until temperatures are achieved where all phases are molten, since the crystallization (transition to a higher density phase) also induces porosity, which is observed by gamma densitometry as a low density material.

3. 33.3 PbO - 66.7 B_2O_3. Figure 3 shows the measured density vs temperature for the lead borate glass of intermediate composition, 33.3 mol% PbO. Curve 1 obtained from cooling the glass from the melt at a rate of 3 C/min. Liquid-like contraction with decreasing temperature occurred until approximately 660 C. The data near and below Tg indicate substantial remaining glass structure. After this test, the material exhibited some crystalline material imbedded in the predominantly glassy specimen. Curve 2 was obtained by cooling

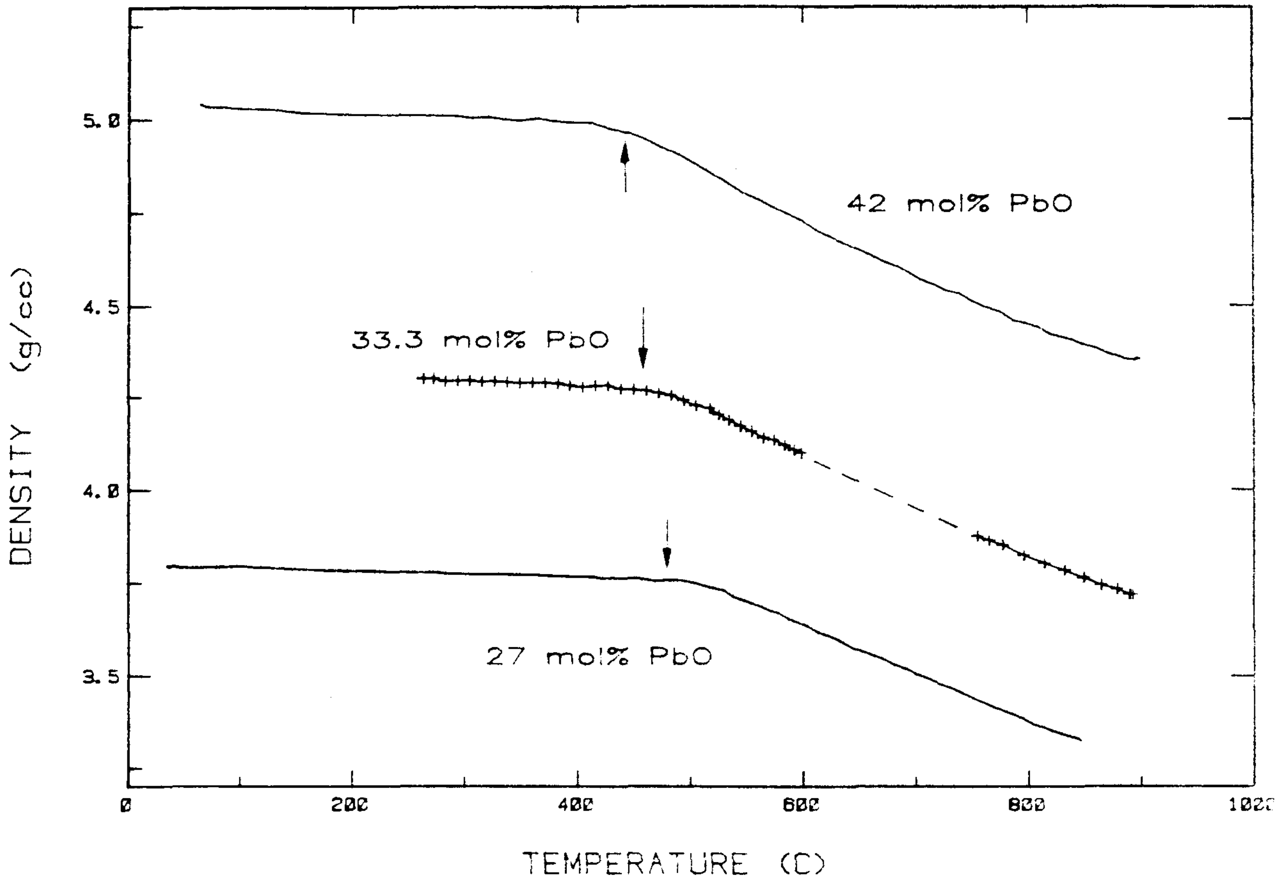


3. Density vs temperature for 33.3 PbO - 66.7 B_2O_3 glass. 1 -- cooling at 3 C/min, 2 -- cooling at 3 C/min to 740 C, followed by quench to 600 C, 3 -- cooling at 1.5 C/min.

from the melt at 3 C/min to about 740 C, whereupon the glass was quenched to about 600 C at a rate of at least 50 C/min. The subsequent density data below 600 C were obtained while cooling at 3 C/min again. Following the test, a clear glass was observed. The temperature jump during the fast quenching through the crystallization temperature was sufficient to maintain the glassy behavior, where the density variation with temperature is essentially linear from the melt to Tg.

Cooling from the melt at 1.5 C/min yielded curve 3. Again, crystallization occurred at about 660 C. The material at ambient temperature appeared as largely crystalline with voids throughout the crucible. As a result of the void volume, the apparent final density for curves 1 and 3 is lower than the ambient glass density. The reduction in apparent density indicates the amount of crystallization, which correlates with the cooling rate.

The lead borate glass density vs temperature is summarized in Fig. 4. In this figure, only data are shown which exhibit the above-Tg "liquid-like" density behavior. The mean expansion coefficients for these glasses are summarized in Table 2. As the PbO content of the glass increased, the solid phase thermal expansion coefficient was observed to increase slightly. However, the density coefficient in the liquid phase was remarkably independent of PbO content. In fact, on a fractional basis (relative to the liquid phase density), the liquid phase volumetric expansion coefficient decreased with increasing PbO content.



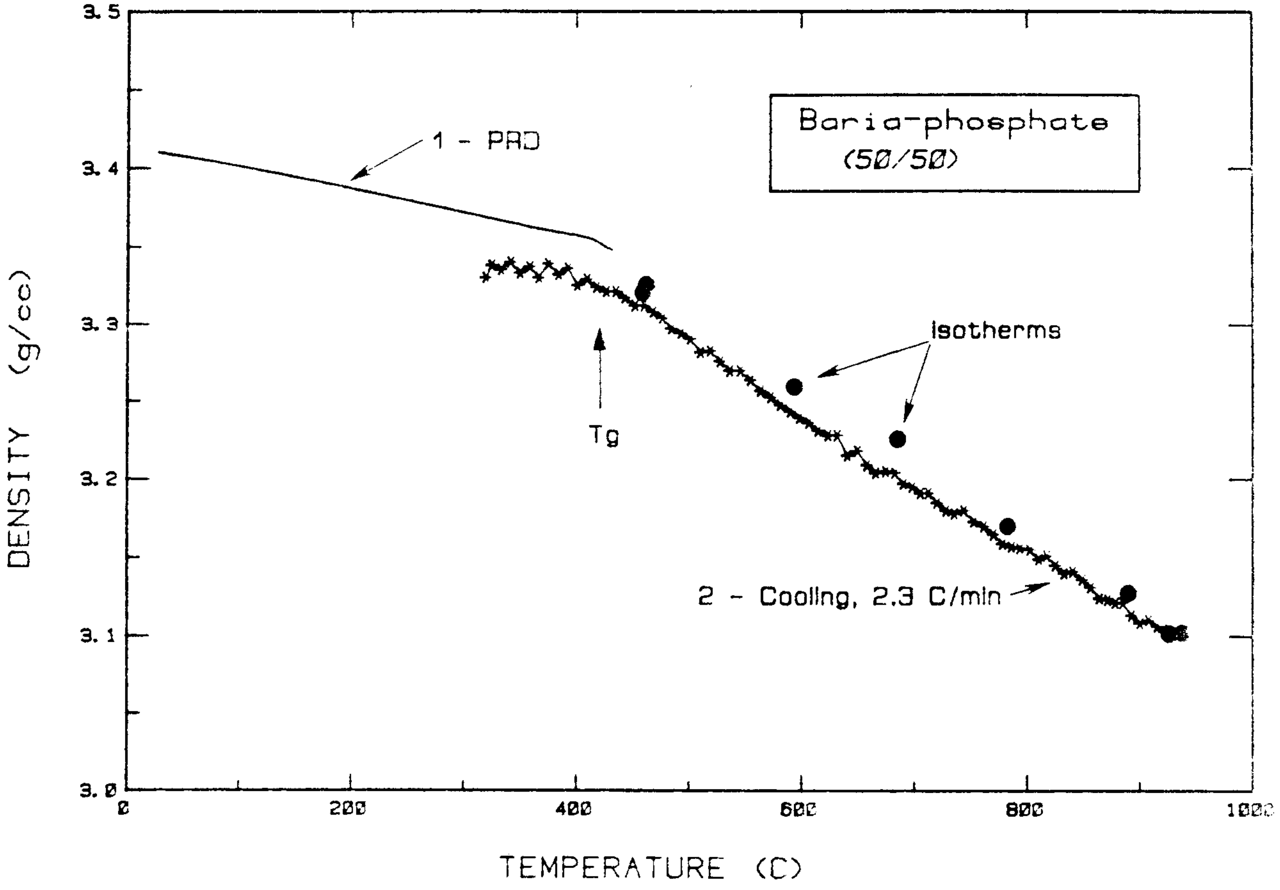
4. Lead borate glass density vs temperature. Data shown here exhibit "liquid-like" behavior above Tg.

B. Soda-baria phosphates.

Three compositions of soda-baria phosphate glasses were prepared for study. Compositions and experimental parameters for the glasses are given in Table 1. For these phosphates, graphite crucibles were used for the high temperature density measurements.

1. Baria phosphate (50 BaO - 50 P_2O_5). The glass transition temperature for the baria phosphate (50/50 mol%) glass was found to be 410 C. DTA measurements showed an exotherm peak near 485 C during heating at 10 C/min. Fig. 5 summarizes the results for this baria phosphate glass. High temperature data from gamma densitometry are in good agreement with pushrod dilatometry results. The glass was melted at temperatures in excess of 900 C. Density data were obtained during cooling at 2.3 C/min (curve 2 in Fig. 5) and during isothermal holds at selected temperatures above Tg. No differences were observed in the high temperature density measurements between these different cooling cycles. The density data show the typical glass behavior, where the above-Tg thermal expansion is essentially the liquid expansion, and no density discontinuity is observed as the viscosity varies from Tg to the melt. At ambient temperature, the baria phosphate was a clear glass with a few small bubbles throughout.

Thermal expansion data for the baria phosphate glass, below and above Tg, are shown in Table 3. The mean density thermal expansion coefficient in the high temperature region is based on the glass liquid-like behavior. This coefficient was determined from a linear fit to the density vs temperature data. The slope of the linear fit



5. Density vs temperature for 50 BaO - 50 P_2O_5 glass. Pushrod dilatometry data (1 -- PRD), cooling data (2) and isothermal data (3).

TABLE 3. Soda-baria Phosphate Glass Results (all glasses are 50 mol% P_2O_5)

Composition (mol%)	Mean Linear Thermal Expansion Coefficient 50 to 270 C (1E-6 /K)	Mean Density Thermal Expansion Coefficient* (1E-5 /K) and T range	Liquid Density (g/cm^3) at 700 C
50 BaO	13.9	-13.8 (550-800 C)	3.20
50 Na_2O	24.6	-19.8 (550-700 C)	2.27
40 Na_2O/ 10 BaO	22.1	-18.0 (550-800 C)	2.44

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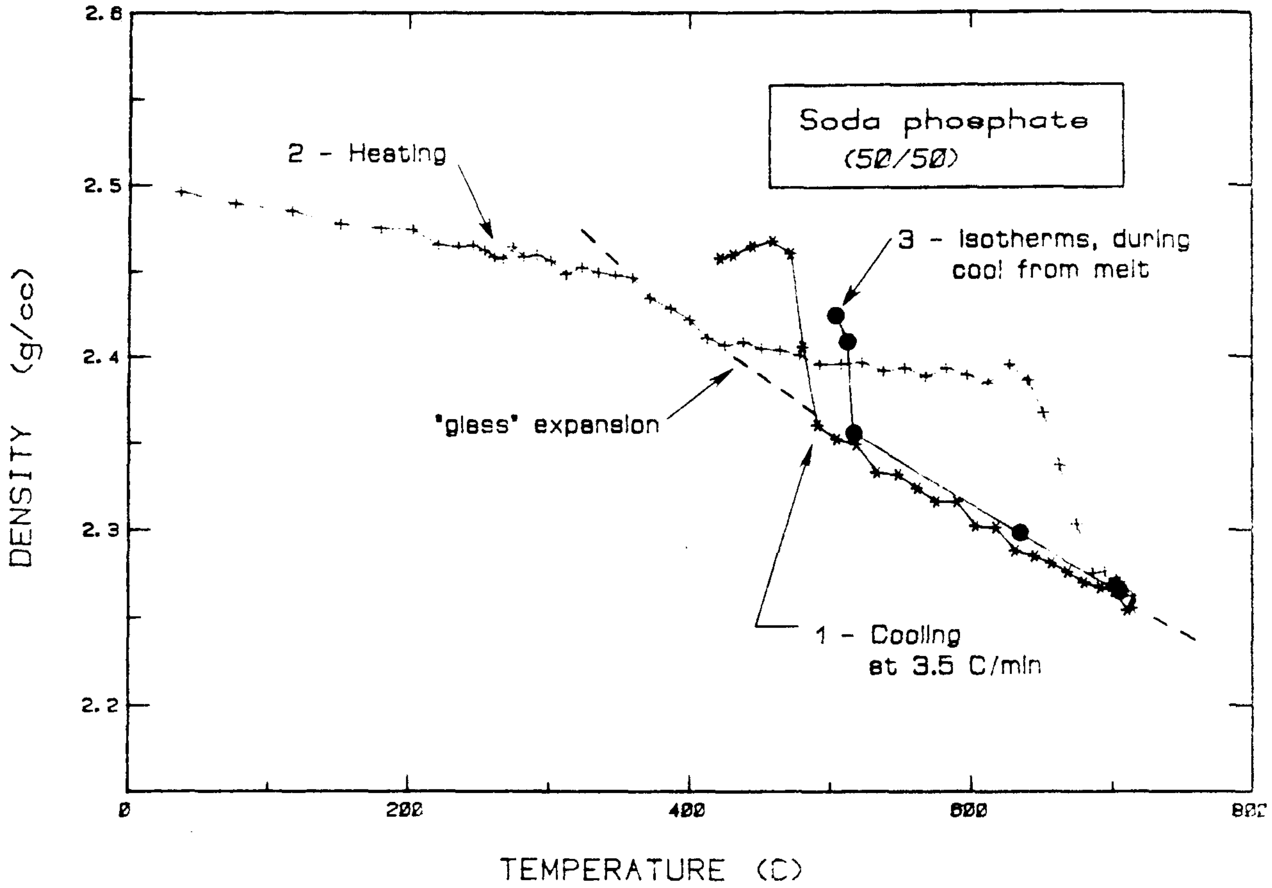
* Slope of linear fit to density vs temperature, divided by density at 700 C.

was divided by the density at 700 C to yield the density thermal expansion given in the table.

2. Soda phosphate (50 Na2O - 50 P_2O_5). The soda phosphate glass showed a glass transition temperature near 290 C. DTA measurements revealed a broad crystallization exotherm near 380 C, and a sharp endotherm near 625 C caused by the melt of the crystalline phase formed at the lower temperature (m.p. 628 C [2]).

In the gamma densitometer, the glass was melted at about 700 C and the density was measured during cooling at 3.5 C/min. Density was observed to increase during cooling in the usual fashion until 480 C, where the measured density showed an abrupt increase (approximately +0.1 g/cm^3). Subsequent cooling showed a decrease in density (expansion on cooling) until the crucible broke apart at 420 C (see Fig. 6, curve 1). At ambient temperature, the specimen appeared white and crystalline with a beady, textured surface. Porosity was evident. The material crumbled easily under slight pressure. On some of the textured surfaces, the material appeared glassy.

A second specimen was melted at 700 C and cooled to 560 C at 3 C/min, then cooled rapidly (tens of degrees per minute) to ambient temperature. The cooled material slipped from the containment crucible and showed a glassy (with bubbles) outer surface, while a volume about 1 cm diameter in the center of the specimen was opaque and white, due to the slower cooling rate in this region. This material was then heated from ambient to 700 C at 3 C/min (curve 2, Fig. 6). A departure from the typical glass expansion curve (above



6. Density vs temperature for 50 Na_2O - 50 P_2O_5 glass. Curves 1 and 3 show data during cooling from the melt at 3.5 C/min and infinitely slowly, respectively. The dashed curve shows the expected glass expansion behavior which would result from cooling at a rate sufficiently rapid to avoid crystallization.

Tg) was observed near 400 C; the measured density remained higher than the glass density until about 640 C. At this temperature, the density decreased to the liquid state density. Density measurements were made during isothermal holds (typically 30 min. for each data point) on cooling from the melt (filled circles, curve 3, Fig. 6). At temperatures of 516 C and above, the density values appeared to fall on the expansion curve for the glassy material. At 512 C and 505 C, a sharp increase in density was observed. Subsequent rapid cooling to ambient temperature revealed a white, opaque, polycrystalline material with porosity. Further measurements indicated that rapid cooling (typically 50 C/min or higher) from 700 C yielded a clear glass at ambient conditions.

These data may be interpreted as the partial or complete crystallization of the specimen in the temperature range from 380 to 515 C, depending on the heating or cooling rate and the initial state. Heating of the glass at 10 C/min (in the DTA) yielded crystallization at 380 C and subsequent melting at 625 C. Heating at 3 C/min (curve 2) displayed crystallization behavior (increase in density above the glass density) slightly above 400 C, and melting of the crystalline phase near 640 C. Cooling from the glassy melt at 3.5 C/min showed crystallization (increase in density) at 480 C, while infinitely-slow cooling showed crystallization near 515 C. Rapid cooling from the melt yielded no apparent crystallization. Since the onset of crystallization depends on crystal nucleation and growth rates, the observed dependence on heating and cooling rates is not unexpected. Some of the temperature differences from the different experiments (e.g. heating at 3 C/min in the gamma densitometer and heating at 10

C/min in the DTA) may of course be device dependent, owing to differences in thermal mass and temperature sensor calibration.

Thermal expansion results for the soda phosphate glass are given in Table 3. The mean density thermal expansion coefficient is given for the range 550 to 700 C, and is representative of the liquid glass (non-crystalline) regime. Since the density and porosity of the polycrystalline phase in the high temperature region (380 to 640 C) is unknown, the expansion coefficient for this phase can not be determined.

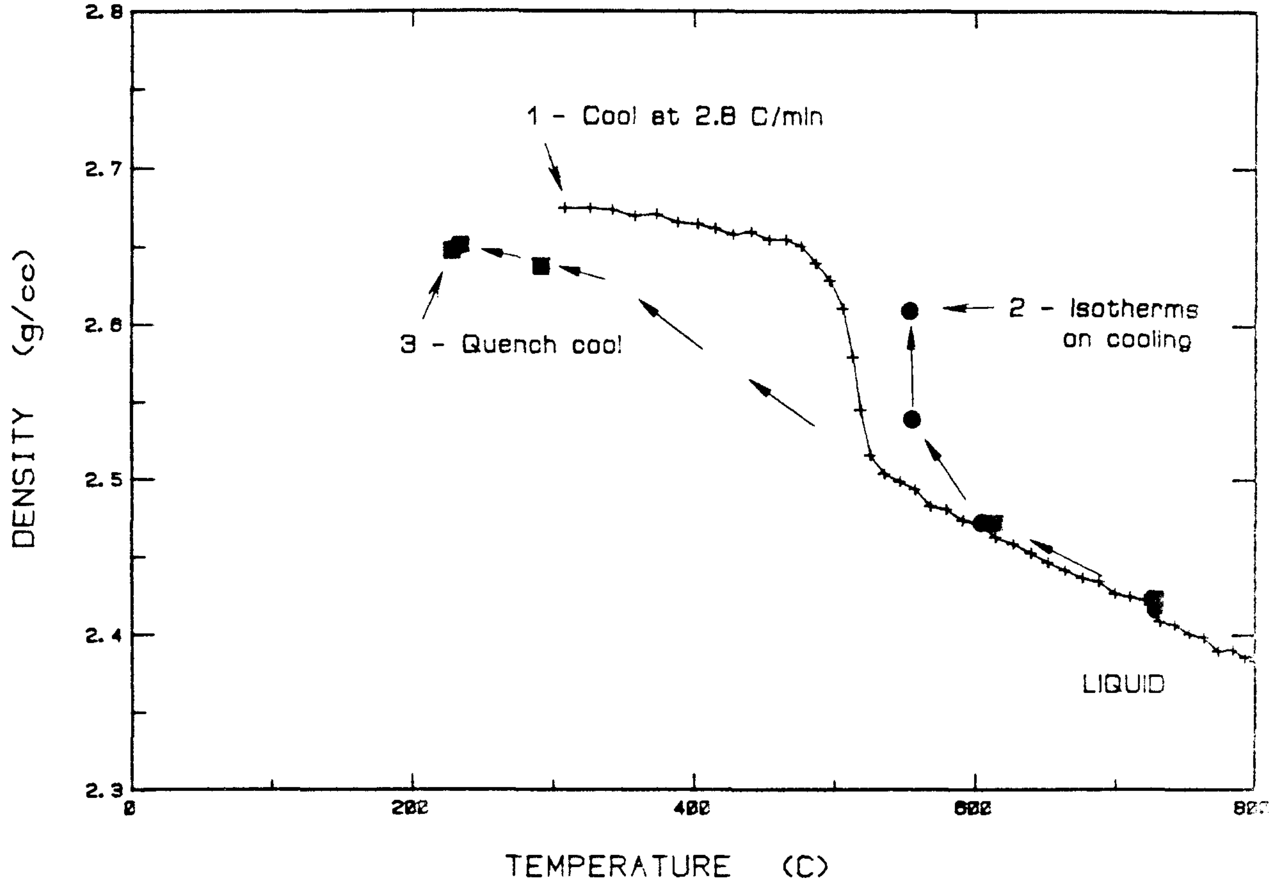
3. Soda-baria phosphate (40 Na_2O - 10 BaO - 50 P_2O_5). This composition glass was studied as the parent glass for a glass ceramic with high thermal expansion properties for potential aluminum sealing applications. Additional information on this glass composition is described by Wilder [3]. The ambient density and thermal expansion values were found to scale with composition between the soda phosphate and baria phosphate glass compositions described in the two previous sections.

Pushrod dilatometry and DTA measurements revealed a Tg near 280 C; dilatometric softening occurred at about 300 C. The DTA measurements (heating of a powder sample of the glass at 10 C/min) revealed a broad crystallization exotherm from 300 to 400 C, possibly consisting of two (or more) crystallization peaks. The DTA results also showed two melting endotherms at 580 C and 640 C during further heating of the specimen. A sodium metaphosphate crystal phase was identified in a previous study [3] during the heat treatment of this glass composition.

Differential scanning calorimeter (DSC) measurements were performed [4] on bulk glass samples identical to the glass specimens employed in the gamma densitometry measurements. In addition to the similarity in specimens, the DSC results were obtained using heating and cooling profiles similar to those used in the gamma densitometry tests. This was performed to assist in the interpretation of the density and thermal expansion results. During cooling at 2.5 C/min from the melt at 700 C to 200 C, a broad exotherm was observed between 543 and 515 C. Subsequent heating from 200 to 600 C at 10 C/min (simulating the DTA scan) showed no thermal activity. Thus, the original exotherm was interpreted as crystallization of the glass, as subsequent heating showed no Tg and no additional crystallization in the region around 530 C. Additional cooling showed no thermal transitions, again indicating that the sample was already in the crystalline state. Identical behavior was observed using a 10 C/min cooling rate from the melt (temperature above 700 C).

A second sample of bulk glass was measured using the DSC at a 10 C/min heating rate to compare with the DTA results. A Tg transition was observed near 290 C and a strong exotherm region was observed between 362 and 452 C. Cooling and subsequent reheating from 200 to 700 C showed no transitions, indicating that the initial exotherm was a glass-to-crystal transition. Two melting endotherms were observed above 567 C. The material was then cooled at a rapid rate (100 to 300 C/min) to achieve a glassy state. Additional heating at 10 C/min showed behavior similar to the original scan, except that the crystallization exotherm was shifted about 40 degrees to higher temperatures (now residing from 412 to 492 C). The differences in crystallization temperature between DTA and DSC scans appear to be dependent on thermal history and scan direction, and also dependent on the physical form of the specimen (powdered vs bulk glass).

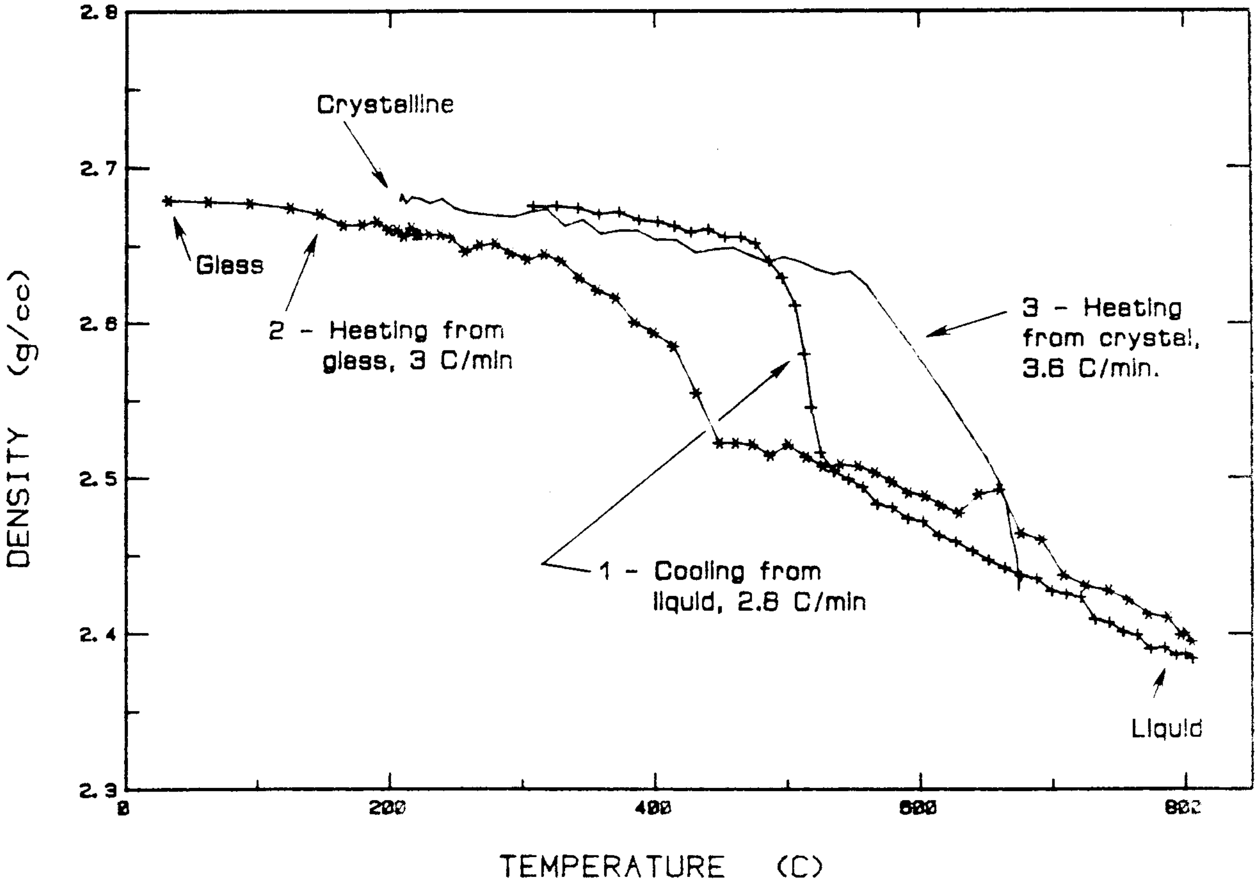
The gamma densitometry results agreed most closely with the transitions and rate dependences observed in the DSC measurements. This is most likely due to the use of bulk glass specimens in both measurements (as opposed to powdered samples in the DTA) and the similarity in heating and cooling profiles which were employed. As with the soda phosphate glass discussed in the previous section, the soda-baria phosphate composition displayed a cooling rate dependence of the onset of crystallization. Fig. 7 shows the variation in the cooling behavior, where densitometry data were obtained during cooling of the glass from the liquid regime at 800 C. Curve 1 was obtained while cooling at 2.8 C/min. Liquid-like thermal expansion was observed to about 510 C, where continued cooling showed a rise in density indicative of the crystalline transition. Examination at ambient temperature revealed an opaque, white polycrystalline material with porosity. Curve 2 shows the isothermal (infinitely-slow cooling) density values obtained during cooling from the liquid. The crystalline transition appears at a slightly higher temperature, near 550 C. Curve 3 represents isothermal density values obtained throughout the glassy region. The glass was obtained by rapid cooling of the liquid from the isotherm at 600 C to 280 C at a rate of 30 to 40 C/min. The ambient density was reduced and the specimen appeared as a clear glass.



7. Density vs temperature for 40 Na_2O - 10 BaO - 50 P_2O_5 glass. Density behavior on cooling varies with the cooling rate.

The hysteresis in the crystallization temperature between heating and cooling is displayed in Fig. 8. Curve 1 shows the onset of crystallization at 510 C during cooling from the liquid at 2.8 C/min. A crystalline specimen resulted. Curve 2 shows the density scan during heating from the glassy state at 3 C/min. The Tg transition is evident near 300 C; departure from glass expansion is observed at about 400 C, in agreement with the DSC data. Some additional structure in curve 2 near 650 C is probably due to the melting of the crystalline phase(s). Curve 3 shows the density behavior during heating of a crystalline material at 3.6 C/min. Clearly, no Tg or additional crystallization (in the region from 300 to 500 C) was observed. The reductions in density observed near 540 and 640 C are caused by the melting of the crystal phases, in agreement with the melting endotherms observed by DTA.

Table 3 gives the thermal expansion results for this glass. Like the soda phosphate results, the mean density thermal expansion coefficient is given for the liquid glass (above Tg) region, not for the crystalline phases. For the soda-baria phosphate glasses, both the linear (solid) thermal expansion coefficient and the liquid phase density (or volume) thermal expansion coefficient vary with the soda-baria content of the glass, in proportion to the relative amounts of the two oxides.



8. Density vs temperature for 40 Na_2O - 10 BaO - 50 P_2O_5 glass, showing hysteresis in crystallization temperature between heating and cooling.

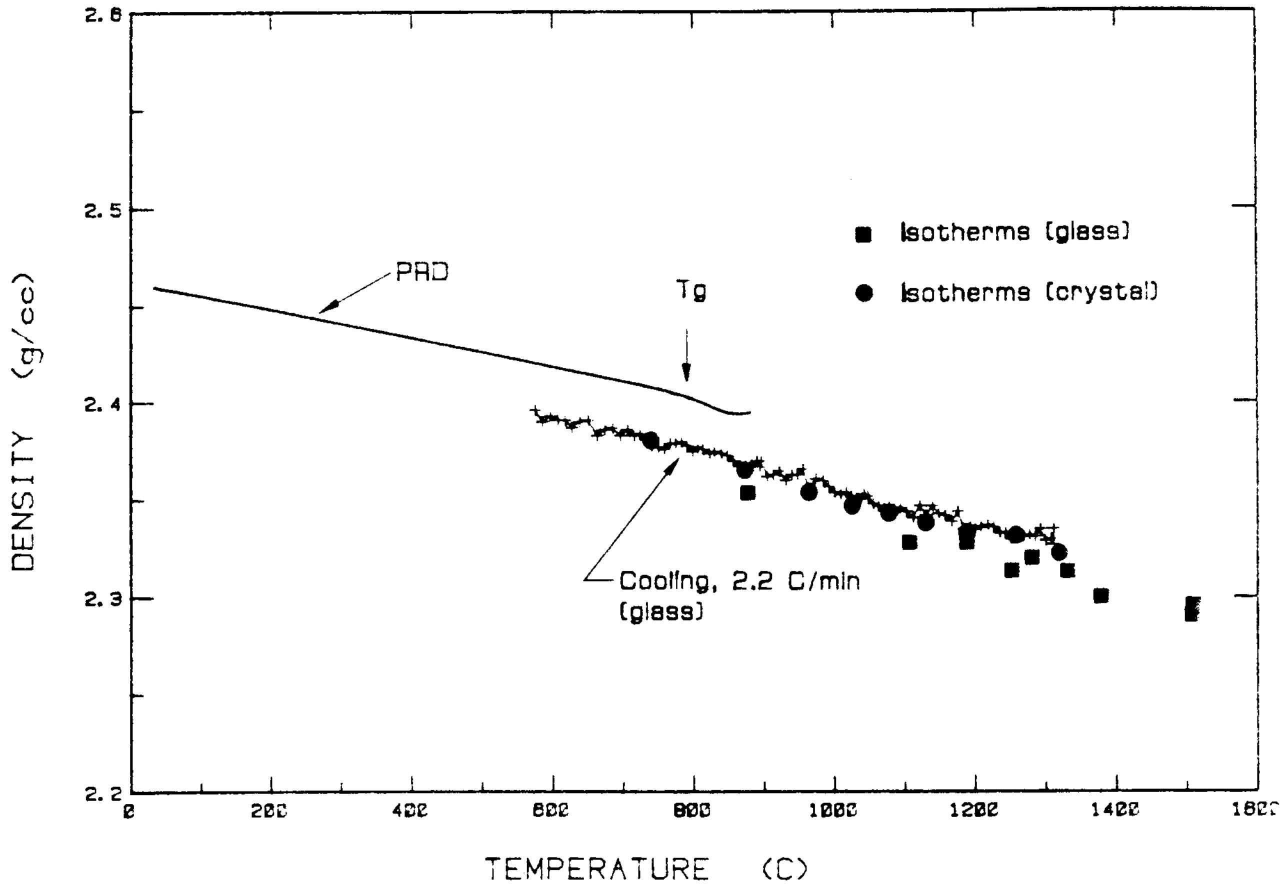
C. Soda-alumina silicates.

Two compositions of soda-alumina silicates, both with 60 mol% SiO_2, were prepared for study by gamma densitometry. Compositions and experimental parameters are shown in Table 1. For these glasses, graphite crucibles were employed. Because of the high temperatures used in some of the measurements, pyrometric thermometry was used to supplement thermocouple measurements where appropriate.

1. 20 Na_2O - 20 Al_2O_3 - 60 SiO_2. Pushrod dilatometry revealed a glass transition temperature Tg of 790 C, although DTA measurements showed no apparent endotherm in this region. Dilatometric softening occurred above 840 C. During an isothermal hold of a specimen at 1025 C, the viscosity was reduced enough to make smooth and glassy a previously ground surface on the glass, but the temperature was insufficient to cause flow of the glass to the crucible walls. Following heating to 1320 C, the glass flowed to conform to the crucible dimensions.

The density vs temperature results are shown in Fig. 9. The density data from the pushrod dilatometer (PRD) display the Tg transition at 790 C. Gamma densitometry results yielded density values generally lower than the PRD data, which was based on the ambient density value obtained by immersion pycnometry. This difference is likely due to the formation of bubbles in the glass during the high temperature experiments as well as the technique imprecisions discussed earlier.

Glass specimens melted at 1300 C and cooled at 2.2 C/min showed no apparent Tg, although the PRD and DTA data suggest that the



9. Density vs temperature for 20 Na_2O - 20 Al_2O_3 - 60 SiO_2 glass. PRD refers to pushrod dilatometry data; Tg identifies the glass transition.

manifestation of Tg is weak in this glass. This slow cooling scan yielded a clear glass at ambient temperature, though many bubbles were frozen in the glass. Isothermal density values obtained during cooling from 1300 C displayed values (filled circles in Fig. 9) similar to the density scan during cooling at 2.2 C/min. However, in the isothermal case, the specimen was not clear or glassy, but appeared to contain grainy, polycrystalline material. From the density values, no crystallization transition was apparent. (The lowest temperature isotherm measured was at 740 C.) Subsequent heating of this specimen to 1300 C and cooling at 2 C/min yielded no change in physical appearance, suggesting that the crystalline phase did not melt at or below 1300 C. A specimen heated to 1500 C displayed similar isothermal density values (filled squares) during cooling. The lowest temperature isotherm was 880 C in this case; the material was then rapidly cooled to ambient. This sample was a clear glass at ambient temperature, thus suggesting a crystallization transition in the 740 to 880 C region.

The linear thermal expansion of the solid glass yielded a mean expansion coefficient of 9.6 x 1E-6/K between 50 and 300 C. This corresponds to a density coefficient of -7.2 x 1E-5 g/cm^3-K over the same region. For the three runs above Tg shown in Figure 9, the average density coefficient was -9.3 x 1E-5 g/cm^3-K for temperatures 800 C and above, based on separate linear fits to each measurement set. This value corresponds to a mean density thermal expansion coefficient of -3.9 x 1E-5/K, relative to the density at 800 C. The results are summarized in Table 4.

TABLE 4. Soda-alumina Silicate Glass Results
(all glasses are 60 mol% SiO_2)

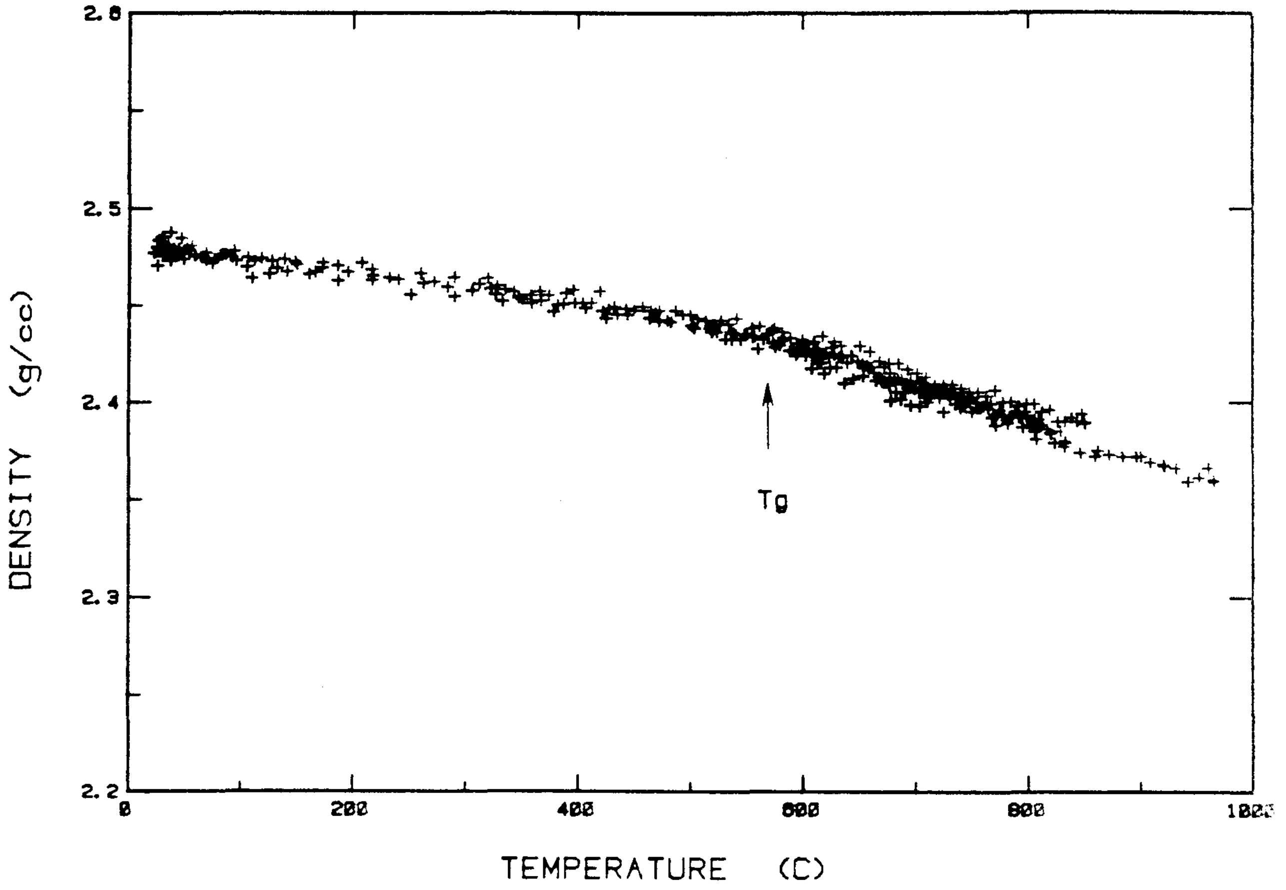
Composition (mol%)	Mean Linear Thermal Expansion Coefficient 50 to 300 C (1E-6 /K)	Mean Density Expansion Coefficient* (1E-5 g/cm^3-K) and T range	
20 Na_2O/ 20 Al_2O_3	9.6	-7.2 (50-300 C)	below Tg
		-9.3 (800-1600 C)	above Tg
26.6 Na_2O/ 13.3 Al_2O_3	9.8	-8.1 (20-550 C)	below Tg
		-18.0 (600-1000 C)	above Tg

* Slope of linear fit to density vs temperature

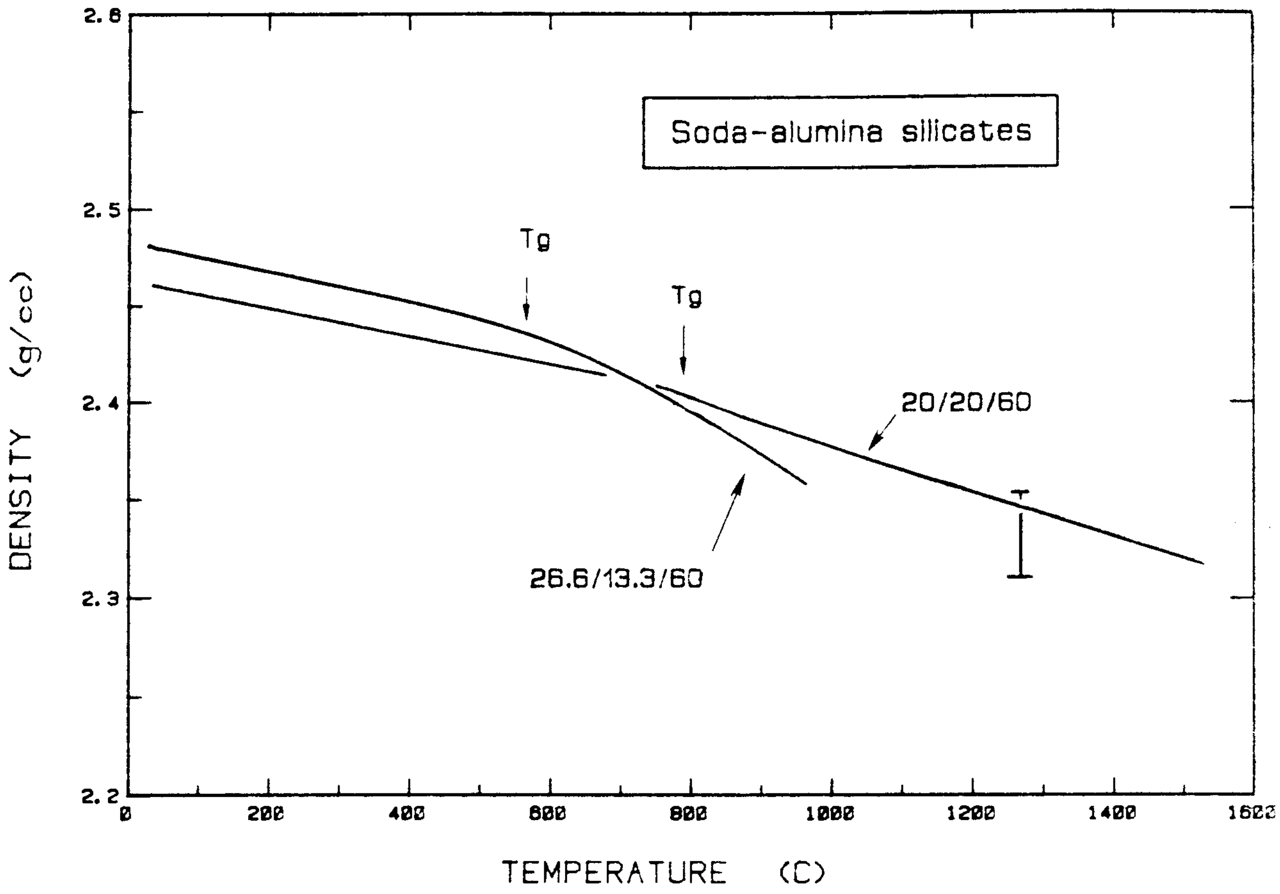
2. 26.6 Na_2O - 13.3 Al_2O_3- 60 SiO_2. This glass composition consists of a lower alumina content than the glass described in the previous section. The glass transition temperature Tg was reduced by 220 C (790 to 570 C) from the 20 mol% alumina glass (see Table 1).

Figure 10 shows the collected results from measurements of the density of this glass by both gamma densitometry and pushrod dilatometry. Solid density results from gamma densitometry agreed well with results from pushrod dilatometry. Data shown in the figure cover the solid and liquid regions of the glass, and a slope discontinuity is visible at Tg. The temperature dependence of the data is typical of the liquid/glass, where no density discontinuities are observed, and the expansion coefficient is higher above Tg. Data for the figure were obtained during heating and cooling of the glass, with cooling rates of 1 C/min, 2 C/min and infinitely long (isothermal holds during cooling). In all cases, a clear glass (with a few bubbles) resulted at ambient temperature; no evidence for crystallization transitions was found.

Thermal expansion results are given in Table 4. The expansion coefficients of the two silicate glass compositions are essentially identical in the ambient temperature region, 50 to 300 C. However, above Tg, the density coefficients for the two glasses differ by a factor of two. These values are depicted in Fig. 11, where representative curves are shown comparing the two silicate compositions. The large error bar associated with the higher alumina content glass reflects the uncertainty in the matching of the solid and liquid density values, as seen in Fig. 9.



10. Density vs temperature for 26.6 Na_2O - 13.3 Al_2O_3 - 60 SiO_2 glass. Both gamma densitometry and pushrod dilatometry data are shown, as well as data from both heating and cooling.



11. Representative temperature dependence of density of the two compositions of soda-alumina silicate glasses (Figs. 9 and 10).

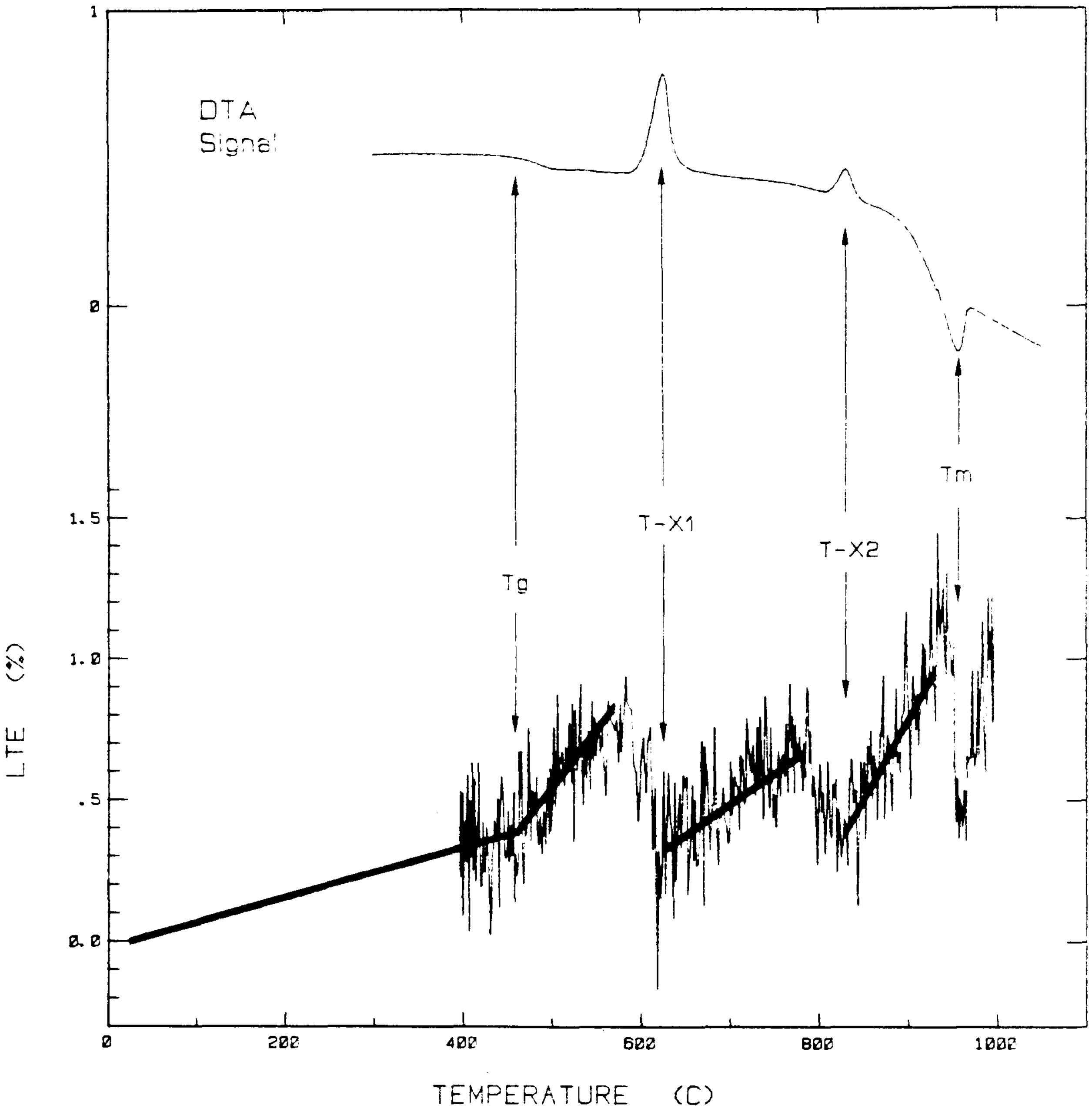
D. Lithia-aluminosilicate Glass Ceramic

A composition of lithia-aluminosilicate glass was investigated. On proper heat treatment, this glass forms a glass ceramic which is useful for metal sealing applications. The final glass composition, by weight %, consists of 71.7 SiO_2, 12.6 Li_2O, 5.1 Al_2O_3, 4.9 K_2O, 3.2 B_2O_3, and 2.5 P_2O_5. The starting constituents were melted at 1550 C; the glass was annealed at 465 C following the pour into the crucible. DTA measurements on the glass (heated at 10 C/min) revealed a glass transition Tg at 454 C, two crystallization exotherm peaks near 620 and 825 C, and a melting endotherm at 950 C. Pushrod dilatometry on the glass revealed a mean expansion coefficient of 9.1 x 1E-6/K over the range from 50 to 300 C. A glass transition was observed at 470 C, and dilatometric softening occurred above 520 C.

The starting glass material was clear and transparent. When heated to 730 C (above the lower crystallization exotherm) and cooled rapidly (~40 C/min) to ambient, the transparent material was yellow on optical transmission and blue on reflection, probably due to light scattering from small crystals. A volume reduction was also observed, consistent with a higher density crystal phase. Heating the starting glass to 900 C (above the higher temperature exotherm) and subsequent cooling to ambient revealed a glassy, white opaque material. A volume reduction was again observed, but no flow of the original specimen had occurred. Slow cooling (3 C/min) from 1000 C revealed a similar material, with the exception that flow had occurred, and the sample conformed to the crucible shape.

Representative data for the linear thermal expansion (LTE in %) of the glass, determined by gamma densitometry, are shown in Fig. 12. For clarity, only one of several raw data sets (the noisy trace) is shown in the figure. Linear fits on the several runs were performed over selected temperature intervals, and are shown in the figure as solid lines. The DTA signal for this glass is also shown. There is good agreement between the densitometry and DTA results. The glass displays a mean expansion coefficient of 8.8 x 1E-6/K from ambient to 460 C, compared with 9.5 x 1E-6/K from pushrod dilatometry. The expansion coefficient increases at Tg, the glass transition temperature, to a value of 40 x 1E-6/K over the range from 460 to 570 C. At T-X1 (approximately 620 C), the first crystallization exotherm, a volume reduction is observed due to the densification on crystallization. From 630 to 780 C, the mean expansion coefficient was 22 x 1E-6/K. At the second crystallization exotherm, T-X2, near 825 C, another volume reduction was observed. Over the range 830 to 930 C, the expansion coefficient was 56 x 1E-6/K. At the melting temperature Tm (950 C), the sample pathlength increased as the specimen flowed to fill the crucible. This caused a reduction in gamma flux (and an apparent increase in density) even though the density actually decreased on melting. (Because of the statistical noise in the LTE data, the mean expansion coefficients from gamma densitometry reported here have a precision of about ±20%.)

It is interesting to note here the utility of the gamma densitometry technique for linear thermal expansion measurements on glasses, in spite of the resultant imprecision due to statistical noise. Using conventional pushrod dilatometry, the maximum temperature investigated

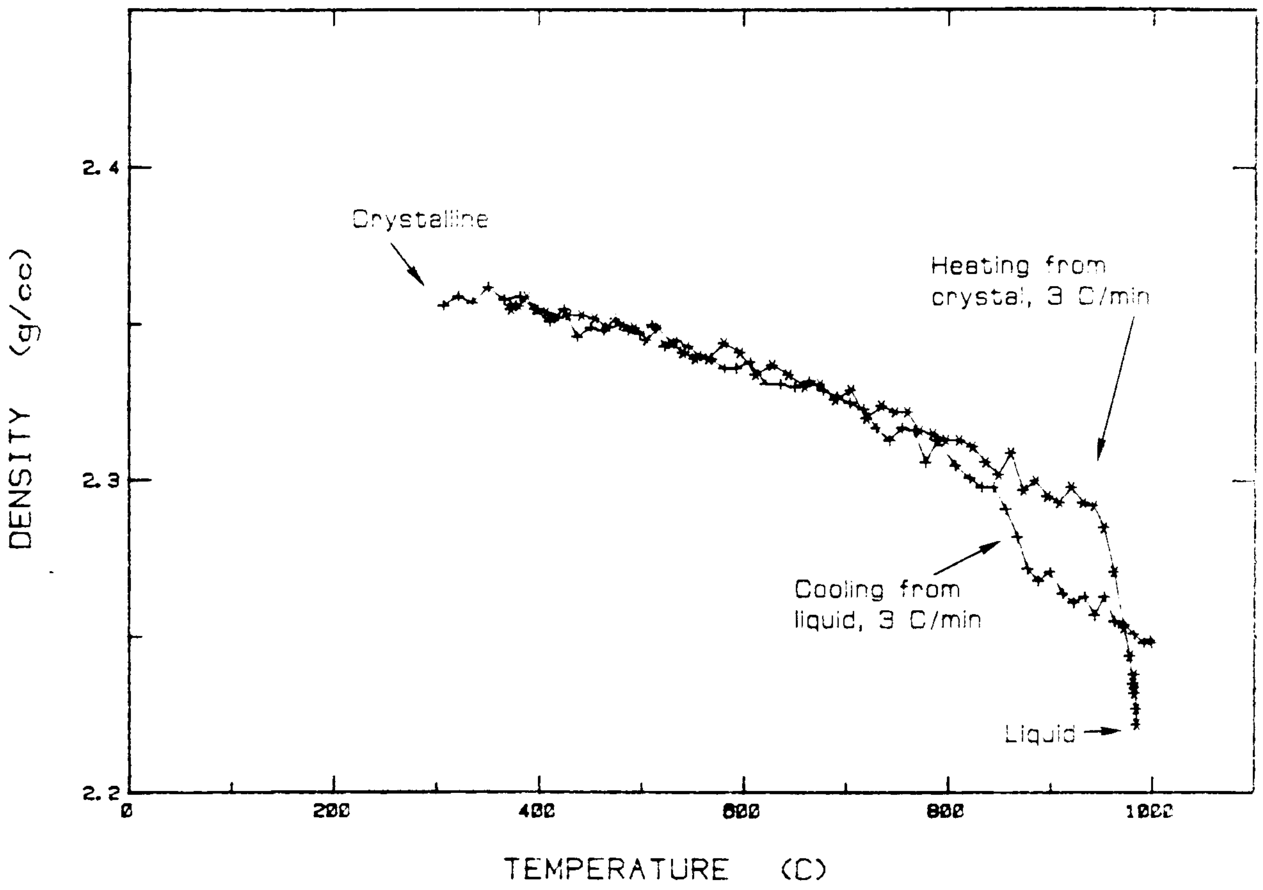


12. DTA and Linear Thermal Expansion (LTE) data vs temperature for lithia-aluminosilicate glass (see text for composition), obtained during heating. Broad, solid lines in the LTE curve show linear fits to several data scans. The glass transition Tg, two crystallization exotherms T-X1 and T-X2, and melting endotherm Tm are displayed by both measurements.

on this glass was 520 C, where glass softening prevented any higher temperature expansion measurements. In this case, by use of gamma densitometry, the temperature range for measurement of the solid glass (prior to flow) has been increased by 400 C. In this extended temperature range, data were obtained on two crystallization transformations which would have been inaccessible for study with conventional dilatometry.

Following melting of the glass, data were obtained during cooling from 1000 C at 3 C/min, as shown in Fig. 13. On cooling, a density expansion coefficient of -19 x 1E-5 g/cm^3-K was determined over the range from 900 to 1000 C. At this cooling rate, crystallization occurred at about 850 C. At ambient, the subsequent material was glassy but opaque and white, similar in appearance to the material formed from the glass after heating to 900 C and cooling. The melted-and-cooled specimen was then reheated at 3 C/min to 980 C. The density vs temperature on reheating is also shown in Fig. 13; the crystalline melt temperature again appeared at 950 C. The linear thermal expansion of the crystalline material, determined between 25 and 800 C, was 15.9 x 1E-6/K.

The glass ceramic was formed by heat treatment of the starting glass as follows [5]: 1) heat from 25 to 1000 C at 50-100 C/min, 2) hold at 1000 C for 15 min, 3) cool from 1000 to 650 C at -50 C/min, 4) hold at 650 C for 15 min, 5) heat from 650 to 820 C at 30 C/min, 6) hold at 820 C for 20 min, 7) cool from 820 to 650 C at -50 C/min, 8) cool from 650 to 400 C at -5 C/min, and 9) cool from 400 to 25 C at -2 C/min. The glass ceramic which resulted from this treatment was similar in



13. Density vs temperature for lithia-aluminosilicate glass ceramic, during cooling from liquid and heating from a crystalline state.

appearance to the glassy, opaque white specimen described above. Subsequent densitometry measurements on the glass ceramic displayed a density vs temperature scan similar to the heating curve shown in Fig. 13. The linear thermal expansion coefficient calculated between 25 and 800 C was 15.4 x 1E-6/K. These coefficients are in agreement with pushrod dilatometric results on the glass ceramic material reported by McCollister [5], where coefficients in the range 11.0 to 15.5 x 1E-6/K were found (25 - 800 C).

SUMMARY

Gamma densitometry measurements were made on a number of glasses in the solid and liquid phases and throughout the intermediate transition region where the material viscosity varies by several orders of magnitude. The gamma densitometry measurements provide an additional means of characterization of the high temperature behavior of glasses. Pushrod dilatometry provides information only on the solid phase, typically limited to temperatures only slightly in excess of Tg. DSC and DTA measurements are typically limited to about 700 C by readily-available commercial equipment. Gamma densitometry can provide density, thermal expansion, Tg and crystallization information, and quenching rate dependence data on glasses to very high temperatures, in excess of 1500 C.

Lead borate glasses were examined in the range 27 to 42 mol% PbO. The liquid phase volumetric thermal expansion coefficient was observed to decrease with increasing PbO content, in contrast to the solid phase linear thermal expansion coefficients, which displayed some increase with increasing PbO composition. At 33.3 and 42 mol% PbO, these glasses displayed crystallization behavior during cooling from the melt, depending on the cooling rate.

In the soda-baria phosphate system, measured volumetric thermal expansion coefficients were observed to scale with the glass composition, in similar fashion to the solid phase linear thermal expansion coefficients. For those phosphates with Na_2O, crystallization was observed on cooling from the melt. While the soda-baria phosphate glasses studied showed solid linear thermal expansion coefficients two to three times those observed in the lead borate glasses, the volumetric thermal expansion coefficients in the liquid state were larger, by a factor of two, in the lead borates than in the soda-baria phosphates.

Two soda-alumina silicate glasses were investigated. While the expansion coefficients in the solid were nearly identical, these glasses displayed volumetric expansion coefficients which differed by a factor of two above the glass transition. Generally, it appears that the solid phase linear thermal expansion coefficient of many glasses is not a good indicator of the volumetric expansion coefficient in the liquid phase, either in absolute magnitude or in dependence on composition.

Thermal expansion measurements were made on a lithia-aluminosilicate glass and glass ceramic from ambient to 1000 C. Using gamma densitometry, data were obtained on the solid phase thermal expansion of the glass some 400 C higher than attainable with conventional pushrod dilatometry. This increase in temperature range allowed the quantitative investigation of the thermal expansion of crystalline phases which were indicated by DTA measurements.

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