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Thermal Expansion of Glasses in the Solid and Liquid Phases[1]

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In this study, the thermal expansion of a number of mixed oxide glasses was measured in the solid and liquid regions by gamma densitometry. Conventional density measurement techniques are limited to either the solid or the liquid phase; however, with this noncontacting technique, the density and thermal expansion of both the solid and the liquid phases may be investigated as the temperature is varied and the glass viscosity varies over a wide range. This technique allows the continuous measurement of density as the liquid cools to a supercooled glass or to a crystalline solid. 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. 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. Measurements on a lithia-aluminoscilicate glass ceramic were obtained by this method to approximately 400°C above the limit of conventional dilatometry. The gamma densitometry technique can yield density, thermal expansion, glass transition and crystallization information, and quenching-rate dependence data on glasses to temperatures in excess of 1500°C, and thus provides a means for high-temperature characterization of glasses which complements conventional dilatometry, calorimetry, and thermal analysis.

KEY WORDS: gamma densitometry; glasses; liquids; thermal expansion.

1. 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

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in glasses. Conventional density measurement techniques may be used in either the solid or the liquid region, but the gamma densitometry technique allows measurements in both physical states with the same experimental arangement. 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 viscosity range. 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. Greater detail of these measurements as well as data for the soda-alumina silicate glasses may be found in Ref. 1.

2. EXPERIMENTAL DETAILS

Detailed descriptions of the gamma densitometry apparatus and its application to the measurement of the density and thermal expansion of liquids and solids are found in Refs. 2 and 3. Briefly, the high-temperature gamma densitometer employs a collimated gamma beam as the noncontacting measurement probe. The attenuation of the gamma beam is used to determine the density (or changes in density) of a material as a function of the temperature. For these glasses, absolute density values were determined by submersion densitometry at ambient temperature. Complementary measurements of the glass transition temperature (T_g) 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 $2 \times 2 \times 2$ cm.

At a temperature (usually the highest) in the liquid phase, gamma densitometry was 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 to the solid 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 to within $\pm 0.2\%$. In some cases, voids were present in the ambient-temperature glass after cooling from the melt so that a fully dense glass was not formed. The resulting porosity contributed to imprecision in the solid-phase density measurements. Ambient-temperature glass densities are also known to vary, depending on the cooling rates.

In most cases, the initial data were obtained during cooling from the melt, typically at a rate of approximately 2.5°C·min^{-1}. 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.

3. RESULTS AND DISCUSSION

Ambient-temperature data for the measured glasses may be found in Table I. These measurements consisted of the ambient density and the material's mass attenuation coefficient determined experimentally at the gamma energy of 662 keV. Data obtained from push-rod 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. Generally, these density variations compared well with those obtained by gamma densitometry. Mean expansion 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 showed 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 of the order of ±5%.

Table I. Ambient-Temperature Parameters

Glass	Composition (mol%)	Density (g·cm^{-3})	Mass attenuation (cm^2·g^{-1})	Glass transition temperature, T_g (°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
Lithia-aluminosilicate	See text	2.35	0.0775	470

3.1. Lead Borates

Three compositions of lead borate glasses were examined. The compositions consisted of 27, 33.3, and 42 mol% PbO, with the remainder B_2O_3. The three 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 T_g 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. The $PbO–B_2O_3$ phase diagram [4] reveals a liquidus for each glass composition at about 740°C.

For the 27 mol% PbO glass, the data above T_g were obtained from both heating and cooling at rates from 1 to 3°C · min^{-1}. The material was in a glassy state following each of the high-temperature measurement cycles, independent of the heating and cooling rates employed. A representative plot of density vs temperature is shown in Fig. 1 for the three compositions. This figure displays the lead borate glass density vs temperature where the behavior could be described as "liquid-like," that is, the density varied smoothly with the temperature through and above T_g, no crystalline behavior was observed, and the expansion coefficient was larger above T_g than below T_g.

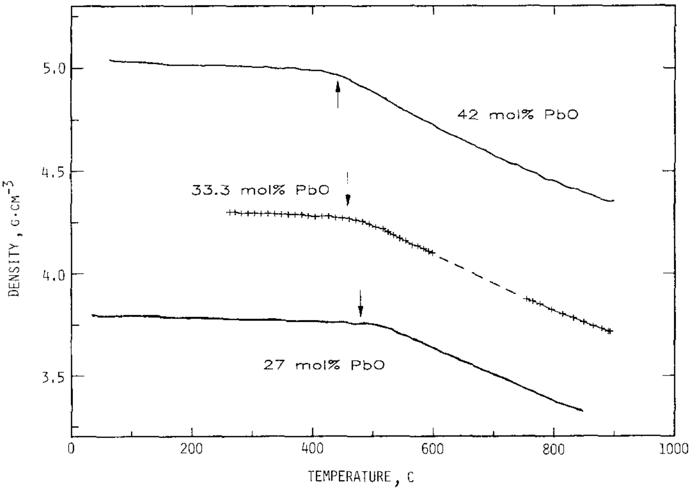

Fig. 1. Lead borate glass density vs temperature. Data shown here exhibit "liquid-like" behavior above T_g (indicated by arrows). For the 33.3 mol% PbO glass, the dashed line represents quenching to avoid crystallization. Otherwise, data were obtained during cooling from the melt at about 3°C · min^{-1}.

In the 33.3 mol% PbO glass composition, liquid-like contraction (densification) occurred with decreasing temperatures (at 3°C·min^{-1}) from the melt until approximately 660°C, at which point the density departed from a linear behavior with temperature. After this test, the material exhibited some crystalline material imbedded in the predominantly glassy specimen. Cooling from the melt at 1.5°C·min^{-1} also exhibited crystallization at about 660°C. At this lower rate, the material at ambient at ambient temperature appeared to be largely crystalline with voids. Cooling from the melt at 3°C·min^{-1} to 740°C, quenching to 600°C at a rate of at least 50°C·min^{-1}, and cooling from 600°C to ambient at 3°C·min^{-1} yielded a clear glass and the liquid-like density behavior shown in Fig. 1. In this case, the quench through the crystallization temperature was sufficient to maintain the glassy behavior, where the density variation with temperature was essentially linear from the melt to T_g.

For the 42 mol% PbO glass, T_g was found by DTA and push-rod dilatometry to be about 440°C. Gamma densitometry showed a marked dependence of the density on the heating cycle. During cooling at 3°C·min^{-1} from the melt, the material was a clear glass after the test. Cooling from the melt at about 1°C·min^{-1} was sufficiently slow to allow crystallization of the entire sample. As with the lowest-PbO glass, the data obtained at 3°C·min^{-1} show a high expansion above T_g, approximately linear with temperature, and a lower expansion below T_g, as depicted in Fig. 1. From the density data, there was no evidence of a "melting" transition, but only the continuous change with temperature of the glass density in the above-T_g state at this cooling rate.

The mean density thermal expansion coefficients for these glasses are summarized in Table II. As the PbO content of the glass increased, the solid-phase thermal expansion coefficient was observed to increase slightly. However, the liquid-phase volumetric expansion coefficient decreased with increasing PbO content.

Table II. Lead Borate Glass Results

Composition (mol% PbO)	Mean linear thermal expansion coefficient, 50 to 300°C (10^{-6} K^{-1})	Mean density thermal expansion coefficient (10^{-5} K^{-1}) for $T > 750$°C[a]	Liquid density at 800°C (g·cm^{-3})
27	7.0	−35.8	3.38
33.3	7.3	−30.6	3.82
42	8.2	−26.5	4.46

[a] Slope of linear fit to density vs temperature, divided by density at 800°C.

3.2. Soda-Baria Phosphates

Three compositions of soda-baria phosphate glasses were examined, as listed in Table I. Graphite crucibles were used for the high-temperature density measurements.

The glass transition temperature for the baria phosphate (50 BaO–50 P_2O_5) glass was found to be 410°C. Density data were obtained during cooling from 900°C at 2.3°C · min^{-1} and during isothermal holds at selected temperatures above T_g. No differences were observed in the high-temperature density measurements between these different cooling cycles. The density data showed the typical glass behavior, where the above-T_g thermal expansion was essentially the liquid expansion, and no density discontinuity was observed as the viscosity varied from T_g to the melt. At ambient temperature, a clear baria phosphate glass was obtained. Thermal expansion data for the soda-baria phosphate glasses are shown in Table III. The mean density thermal expansion coefficient in the high-temperature region was based on the glass liquid-like behavior.

The soda phosphate glass (50 Na_2O–50 P_2O_5) 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 (mp, 628°C [4]). The densitometry data may be interpreted as the partial or complete crystallization of the material in the temperature range from 380 to 515°C, depending on the heating or cooling rate and the initial state. Heating of a glass at 3°C · min^{-1} displayed crystallization behavior (increase in density above the glass density) slightly above 400°C, and melting of the crystalline phase near 640°C, corresponding to the DTA measurements. Cooling from the glassy melt at 3.5°C · min^{-1} showed crystallization (increase in density) at 480°C, while infinitely slow cooling

Table III. Soda-Baria Phosphate Glass Results (All Glasses Are 50 mol% P_2O_5)

Composition (mol%)	Mean linear thermal expansion coefficient, 50 to 270°C (10^{-6} K^{-1})	Mean density thermal expansion coefficient (10^{-5} K^{-1})[a] and T range	Liquid density ($g \cdot cm^{-3}$) at 700°C
50 BaO	13.9	−13.8 (550–800°C)	3.20
40 Na_2O/10 BaO	22.1	−18.0 (550–800°C)	2.44
50 Na_2O	24.6	−19.8 (550–700°C)	2.27

[a] Slope of linear fit to density vs temperature, divided by density at 700°C.

showed crystallization near 515°C (see Fig. 2). 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.

The soda-baria phosphate ($40\,Na_2O$–$10\,BaO$–$50\,P_2O_5$) composition 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 [5]. The ambient density and thermal expansion values were found to scale with composition between the soda phosphate and the baria phosphate glass compositions described above. Like the soda phosphate results, the mean density thermal expansion coefficient is given (Table III) for the liquid glass (above T_g) region, not for the crystalline phases which appeared at slow cooling rates. 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.

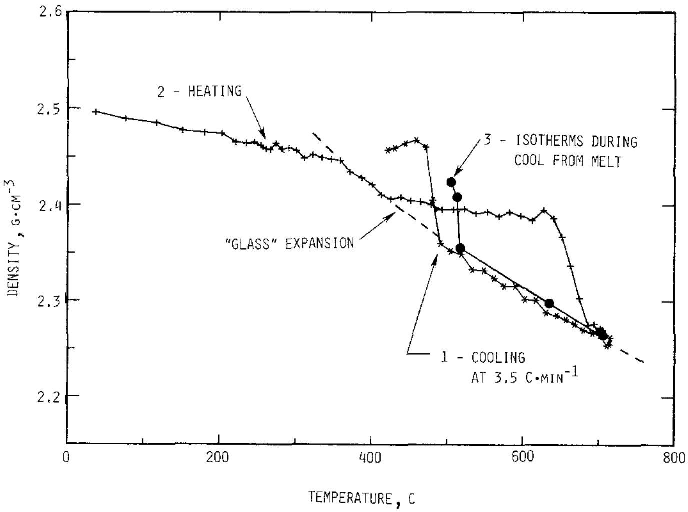

Fig. 2. Density vs temperature for $50\,Na_2O$–$50\,P_2O_5$ glass. Curves 1 and 3 show data during cooling from the melt at 3.5°C·min^{-1} and infinitely slowly, respectively. Curve 2 was obtained during heating at 3°C·min^{-1}. The dashed curve shows the expected glass expansion behavior which would result from cooling at a rate sufficiently rapid to avoid crystallization.

3.3. Lithia-Aluminosilicate Glass Ceramic

A lithia-aluminosilicate glass was investigated, which, on proper heat treatment, forms a glass ceramic useful for metal sealing applications. The final glass composition, by weight percent, was 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 a crucible. DTA measurements on the glass revealed a glass transition T_g at 454°C, two crystallization exotherm peaks near 620 and 825°C, and a melting endotherm at 950°C (see Fig. 3). Analysis by transmission electron microscopy and X-ray diffraction assigned these peaks to crystallization of lithium metasilicate (LS) and lithium disilicate (LS_2) and LS_2 melting, respectively [6]. Push-rod dilatometry on the glass revealed a mean expansion coefficient of 9.1×10^{-6} K^{-1} over the range from 50 to 300°C. A glass

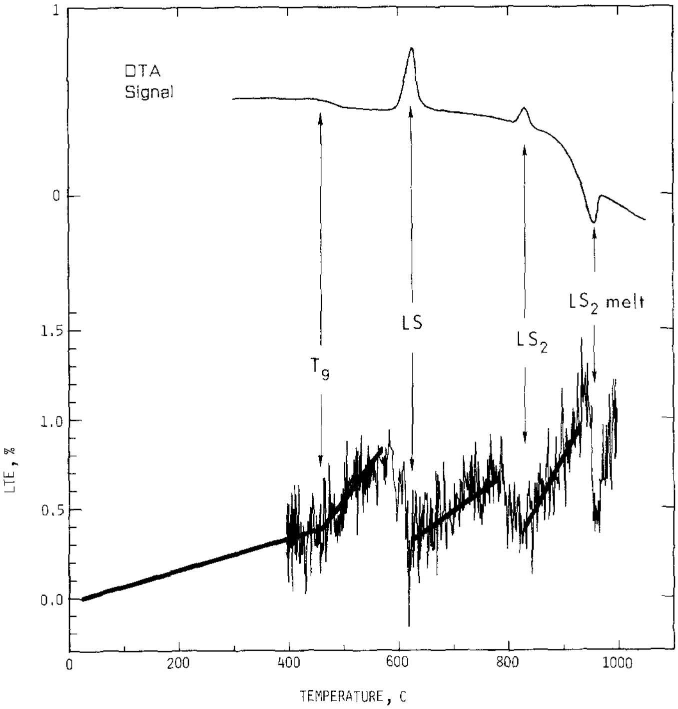

Fig. 3. DTA and linear thermal expansion (LTE) data vs temperature for lithia-aluminosilicate glass (see text for composition), obtained during heating. Broad, solid lines in the LTE curve show linear fits to several data scans. The glass transition T_g, two crystallization exotherms LS and LS_2, and LS_2 melting endotherm are displayed by both measurements. LS, lithium metasilicate; LS_2, lithium disilicate.

transition was observed at 470°C, and dilatometric softening occurred above 520°C. Following heat treatment [1], the glass ceramic exhibited a linear thermal expansion coefficient of $15.4 \times 10^{-6}\,K^{-1}$ calculated between 25 and 800°C.

Representative data for the linear thermal expansion (LTE as a percentage) of the glass, determined by gamma densitometry, are shown in Fig. 3. Linear fits on several runs were performed over selected temperature intervals and are shown in the figure as solid lines. There is good agreement between the densitometry and the DTA results. The glass displays a mean expansion coefficient of $8.8 \times 10^{-6}\,K^{-1}$ from ambient to 460°C, compared with $9.5 \times 10^{-6}\,K^{-1}$ from push-rod dilatometry. The expansion coefficient increases at T_g to a value of $40 \times 10^{-6}\,K^{-1}$ over the range from 460 to 570°C. At the lithium metasilicate (LS) crystallization exotherm (620°C), a volume reduction is observed due to the densification on crystallization. From 630 to 780°C, the mean expansion coefficient for this crystal/glass matrix mixture was $22 \times 10^{-6}\,K^{-1}$. At the lithium disilicate (LS_2) exotherm near 825°C, another volume reduction was observed. Over the range 830 to 930°C, the expansion coefficient was $56 \times 10^{-6}\,K^{-1}$. At the lithium disilicate melting temperature (950°C), the sample pathlength increased as the specimen flow to fill the crucible, causing a reduction in gamma flux and an apparent increase in density even though the density actually decreased on melting.

It is interesting to note here the utility of the gamma densitometry technique for linear thermal expansion measurements on glasses. Using conventional push-rod dilatometry, the maximum temperature investigated on this glass was 520°C, where glass softening prevented any higher-temperature expansion measurements. Using 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.

4. 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 mans of characterization of the high-temperature behavior of glasses. Push-rod dilatometry provides information only on the solid phase, typically limited to temperatures only slightly in excess of T_g. DSC and DTA measurements are typically limited to 700–1000°C by readily available commercial equipment. Gamma densitometry can provide density, thermal expansion, T_g, and crystallization information and quenching-rate dependence data on glasses to 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 a fashion similar to that of 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.

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 push-rod dilatomtry. This increase in temperature range allowed the quantitative investigation of the thermal expansion of crystalline phases in a glass matrix.

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