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Letter

Glass transition T_g, thermal expansion, and quenched-in free volume ΔV_f in pyrex glass measured by time-resolved X-ray diffraction

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Abstract

Using high-energy, high-intensity synchrotron light, we have obtained diffraction patterns in transmission during in situ heating of a pyrex glass. We have found that, as compared to conventional dilatometric measurements, the evolution with temperature (and time) of the position of the first diffraction maximum of the diffraction pattern accurately reflects the thermal expansion coefficient α_{th} and the relaxation behavior of the pyrex glass. The results allow quantitative determination of the glass transition T_g by diffraction that compares well with T_g obtained by calorimetry as was previously reported for metallic glasses [A.R. Yavari, J.L. Uriarte, N. Nikolov, N. Nishiyama, T. Zhang, A. Inoue, G. Heunen, Mater. Sci. Eng. A 375–377 (2004) 709]. The excess quenched-in free volume ΔV_f and its relaxation kinetics can also be determined [A.R. Yavari, M. Tonegaru, N. Lupu, A. Inoue, E. Matsubara, G. Vaughan, A. Kvick, W.J. Botta, Mater. Res. Soc. Symp. Proc. 806 (2004) 203].

Keywords: Glass transition; Amorphous materials; Synchrotron radiation; Thermal expansion; Free volume; Amorphisation; Thermal analysis; Liquid quenching

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1. Introduction

During cooling of a glass-forming material from the liquid state or from above the glass-transition temperature T_g, some excess quenched-in free volume ΔV_f is trapped into the glassy state the quantity of which will depend on the cooling rate [2].

Coherent diffraction from glassy materials forms a succession of halos or diffraction maxima in reciprocal space as compared to the Bragg peaks of crystalline materials [3].

Precise determination of the structural evolution with temperature requires determination of radial distribution functions derived from experimental structure factors using Fourier transformation techniques, a process in which the material mass density or atomic number density and its evolution with temperature are inputs [4]. However, as in crystals, as long as there is no structural relaxation at various temperatures well below T_g, the structure of an isotropic glass is invariant except for the reversible effect of thermal dilatation the magnitude of which depends on the anharmonicity of the inter-atomic potentials. In this regime, variation with temperature of wave-vector Q_{max} or angular position of the first diffracted intensity $I(Q_{max})$ maximum below T_g can consequently be used to determine the volume expansion of glassy structure using [3,5]

$$\left\{\frac{Q_{max}(T_o)}{Q_{max}(T)}\right\}^3 = \frac{V(T)}{V(T_o)} = 1 + \alpha_{th}(T - T_o) \tag{1}$$

where α_{th}, the volume coefficient of thermal expansion below T_g, can be obtained from the temperature slope or derivative of $\{V(T)/V(T_o)\}$ for T_o corresponding to the reference temperature. How accurately the evolution of the position Q_{max}

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of the first diffraction maximum $I(Q_{\max})$ due to structural relaxation would follow variations of the material density as excess quenched-in free volume ΔV_f anneals out during heat treatment has not been established and will be tested here in comparison with relaxation data (length and volume changes due to heat treatment) from conventional dilatometry.

2. Experimental

Diffraction spectra obtained in transmission with a high-intensity high-energy monochromatic beam on the ID11 line at the ESRF were used to continuously follow the evolution of a pyrex oxide glass during heating from the glassy state to T_g and cooling. The pyrex glass was a product of SOVIREL (code 732.01) with commercially specified composition (silica 80.00, anhydride boron oxide 13.00, aluminium oxide 2.25, iron oxide 0.05, sodium 3.50, potassium 1.15 wt.%). The pyrex about 1 mm in diameter was melted and formed into a rod about 1 mm in diameter, and then air-cooled. The pyrex rod was cut into 3 cm long pieces to place on a computer-controlled Linkam hot stage. The radiation was monochromatised using a double-crystal nitrogen-cooled silicon monochromater [6]. The photon energy was 65 keV corresponding to an X-ray wave-length of 0.0193 nm. The heating and cooling rates were 20 K/min. The diffracted intensity in transmission through the specimen on the hot stage was recorded by 2-D CCD camera placed perpendicular to the incident beam. A full spectrum was obtained every 20 s including data processing time.

3. Results and discussion

An in situ heating cycle was designed consisting of heating up from room temperature to T_g (first heating), cooling down to 373 K, and heating up again to T_g (second heating) as in Fig. 1.

We have taken the beginning of second heating, 373 K, as reference temperature T_o. Fig. 2 shows a plot of Eq. (1) during heating and cooling of the as-formed and air-cooled pyrex rod. $V(T)/V(T_o) = 1 + \alpha_{th}(T - T_o)$ near T_g shows a slope corresponding to α_{th}, the volume coefficient of thermal expansion, but the slope drops with increasing temperature due to structural relaxation. Subsequent cooling and heating do not result in significant further relaxation and the first heating, cooling, and second heating curves meet at T_g as determined for the same rod by DSC calorimetry trace of Fig. 3. From the slope, the volume coefficient of thermal expansion is seen to be near $2.2 \times 10^{-5}\,\mathrm{K}^{-1}$ below T_g. Whether the irreversible relaxation observed below T_g in the range $730\,\mathrm{K} < T < T_g$ corresponds quantitatively to a volume shrinkage must be determined by comparison with dilatometric measurements.

Turner and Winks [7] studied the difference of the dilatation behavior of a similar pyrex (borosilicate) glass after air-cooling from high temperature and after thermal annealing

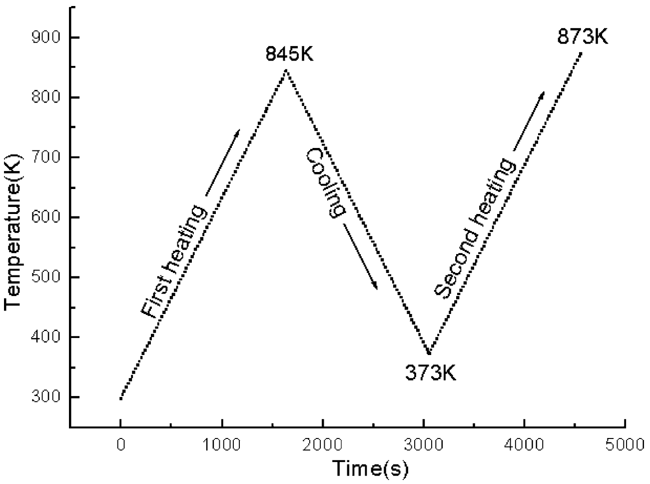

Fig. 1. In-the-beam temperature vs. time cyclic heating of an air-cooled pyrex oxide glass.

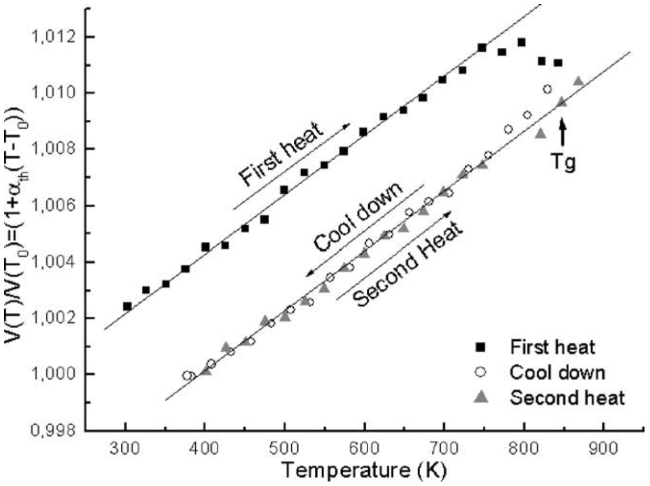

Fig. 2. Plot of $V(T)/V(T_o)$ vs. T during in-the-beam thermal cycling of air-cooled pyrex oxide glass using the diffraction method of Eq. (1).

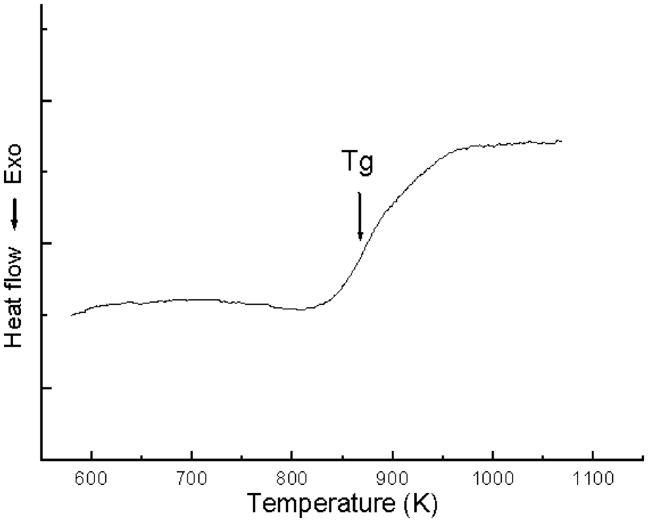

Fig. 3. Calorimetric (DSC) trace of air cooled pyrex oxide glass showing T_g at about 850 K.

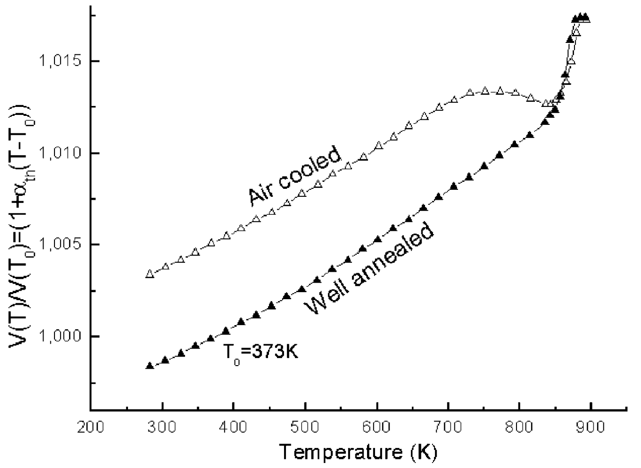

Fig. 4. Volume thermal expansion of pyrex (borosilicate) glass measure by dilatometry [7].

using conventional dilatometry, and presented linear thermal expansion curves with the linear $\alpha_{\text{th}}^{\text{L}}$ and the volume α_{th} coefficients of thermal expansion related via $\alpha_{\text{th}} = 3\alpha_{\text{th}}^{\text{L}}$. Using the linear thermal expansion curves of Turner and Winks, we have drawn the volume thermal expansion curves. We used 373 K of the well-annealed specimen as the reference temperature T_{o}, as we did for our X-ray data of Fig. 2. We then connected their dilatometric curves for the as-cooled and annealed glass at T_{g} as shown in Fig. 4.

Fig. 5 compares the volume thermal expansion curve of the borosilicate glass obtained by conventional dilatometry with those for the similar glass of Fig. 2 obtained by real-time X-ray diffraction during in situ thermal cycling using synchrotron light. Clearly, the two sets of curves reflect the same underlying densification during relaxation. In both sets of curves (from X-ray diffraction and dilatometry), the volume change (densification) due to relaxation (vertical difference for the air-cooled glass curves before and after heating up to T_{g} as signaled by vertical arrows in the figure) is 0.5 vol.% (corresponding to the annealing out of quenched-in free volume ΔV_{f} = 0.5 vol.%). Minor differences are likely due to small differences of the compositions of the two commercial pyrex glasses.

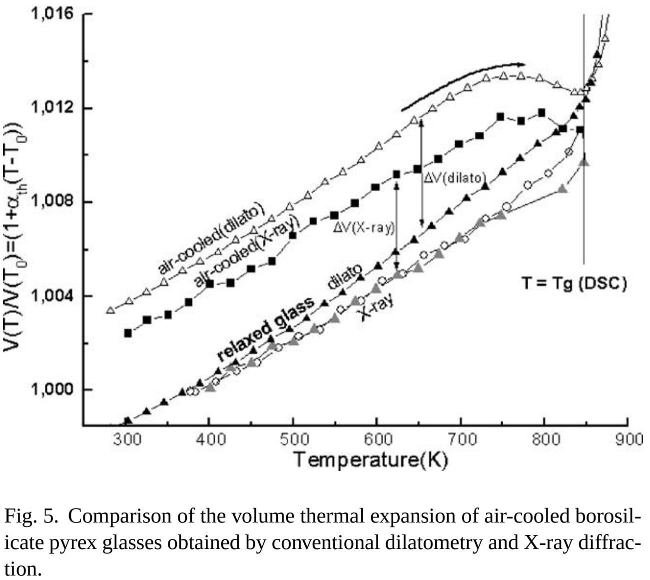

Fig. 5. Comparison of the volume thermal expansion of air-cooled borosilicate pyrex glasses obtained by conventional dilatometry and X-ray diffraction.

In conclusion, it has been found that measurement of the variation of the average volume per atom during annealing of air-cooled pyrex using the displacement of the first maximum of the diffraction intensity in Q-space yields nearly exactly the same results as measurements by dilatometry. This simple X-ray method, previously applied to metallic glasses [1], can therefore be applied also to oxide glasses to determine coefficients of thermal expansion, the glass transition temperature T_{g}, structural relaxation, and densification during thermal annealing and the amount of quenched-in free volume ΔV_{f}. The method may be useful in industrial and manufacturing processes where volume changes, quenching stresses, and relaxation at various joints and interfaces between oxide glasses and other materials are critical.

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