Uniaxial stress relaxation measurement in fluoroindate glasses

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Abstract

Glasses of composition $40InF_3$–$20SrF_2$–$16BaF_2$–$20ZnF_2$–$2GdF_3$–2NaF (mol%) have been prepared under controlled atmosphere. The time response of the stresses under the application of a constant strain was determined by microellipsometer technique, performed in ambient atmosphere at $T < T_g = 294$°C. The glasses show a Newtonian behavior at small stress level. During the relaxation process, very small grooves perpendicular to the applied strain appeared on the glass surface and affected its behavior after a time. The formation of these grooves is associated with the ambient atmosphere. Measurements in dry atmosphere showed that humidity was an important parameter in the relaxation process.

1. Introduction

The production of optical fibers operating in the infrared range to 5 μm became possible with the advent of the fluoroindate glasses [1]. The analysis of stress relaxation of these materials at temperatures less than the transition glass temperature (T_g) is, therefore, of great importance. The stress in transparent materials can be measured by ellipsometry technique. A microellipsometer, to measure the stress profile in SiO_2 thin films and able to compensate residual birefrigencies of the system due to non-ideal optical components, has been used to measure the stress relaxation of fluoroindate glasses at ambient temperature. The time response of the stresses under the application of a constant strain showed a Newtonian behavior at a small stress level. During the relaxation process, a delayed dilation phenomenon was observed that has been associated to O_2 or H_2O molecules present in the atmosphere. Small grooves have also appeared on the surface of a glass sample, perpendicular to the applied strain which affect its behavior at long times.

2. Viscoelastic behavior of fluoroindate glasses

Stresses on glasses can be divided into two kinds: structural and mechanical. The first one is due to the thermal history. In this case, relaxation is realized with heat treatments close to T_g. The second kind is caused by mechanical deformations after a load has been applied to a glass surface.

Glasses can be considered as viscoelastic materials (VE), for which only the temperature can change their viscosities. The application of a strain, ϵ_0, on VE materials produces a stress relaxation controlled by viscous flow. According to Scherer [2], the following relation is valid for uniaxial stress, where the shear relaxation is dominant:

$$\psi = \frac{\sigma}{\sigma_0} = e^{-\frac{t}{\zeta_u}},$$

where ζ_u is the uniaxial relaxation time which is proportional to the viscosity η; σ is the uniaxial stress; t is the time; σ_0 is the stress at $t = 0$ and Ψ is the normalized stress function.

At high temperature, the time, ζ_u, for the stress relaxation is small. If this dependence does not change in a range of temperature, the glass has a thermorheological simple behavior (TRS).

The main rheological feature for glasses that obey the thermorheological simple behavior is a constant time shift for the stress relaxation curve at different temperatures. In this way, it is possible to determine a master curve for a particular glass.

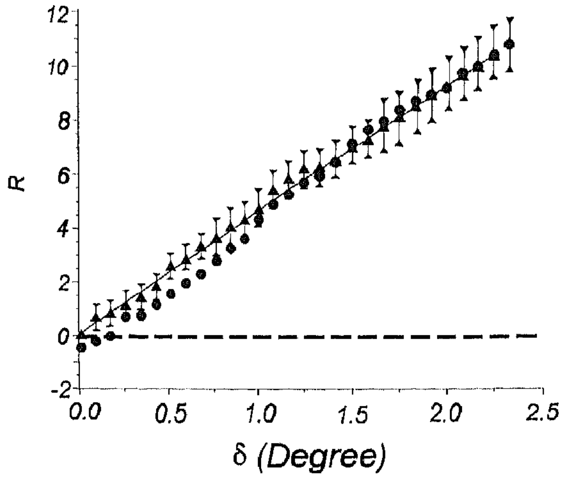

Fig. 2. Calibration curve determined by the application of lead weights on a quartz block: lead placement (▲); lead withdrawal (●). |, error bars. R is the ratio between the ac voltage $V(\omega_m)$ and dc voltage V_{dc} of the detector; δ, dephasing of the sample due to weight application.

3. Sample preparation

In the experimental work, the stress relaxation for fluoroindate glasses was analyzed in an air atmosphere. The glass composition was $40InF_3$–$20SrF_2$–$16BaF_2$–$20ZnF_2$–$2GdF_3$–2NaF (mol%). The samples were prepared following the procedure given in Ref. [3]. In_2O_3 was converted into InF_3 at 400°C during 1 h by addition of $NH_4F{:}HF$ and was thereafter treated at 500°C in order to eliminate the fluoridating agent. Then, all components were mixed and melted in a dry box under argon atmosphere at 700°C and then at 800°C for fining. After this process, the liquid was cast into a preheated mould and annealed at 260°C for 2 h. The sample had typical dimensions of $3 \times 10 \times 10$ mm^3. All faces were optically polished including those to which the stress was applied.

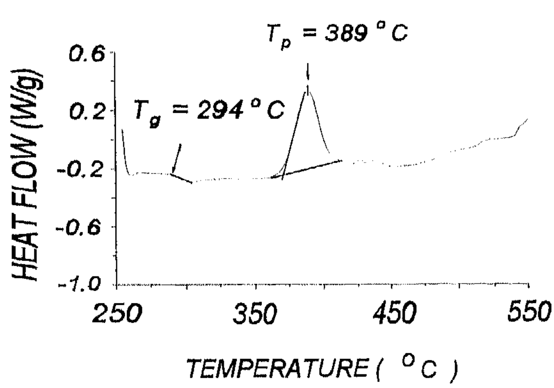

Fig. 1. Differential scanning calorimetry (DSC) curve for $40InF_3-20SrF_2-16BaF_2-20ZnF_2-2GdF_3$–2NaF glass composition (mol%) measured at a 10°C/min heat rate in N_2 atmosphere. T_g, glass transition temperature; T_p, exotherm peak crystallization.

Fig. 1 shows the differential scanning calorimetry (DSC) curve of this sample, measured in the range of 250–550°C with a 10°C/min heat rate in N_2 atmosphere. The glass transition temperature, T_g, for this sample is 294°C and the crystallization begins at 388°C.

4. Microellipsometer description

The microellipsometer used in this work was described by Barros et al. [4]. This equipment measures the stress using polarized light modulation at 50.3 kHz. For uniaxial stress, σ, less than 1×10^6 N/m^2, the following relation holds:

$$\sigma = \frac{\lambda R}{2\pi c_0 K d},$$

where R is the ratio between the ac voltage, $V(\omega_m)$, and dc voltage, V_{dc}, of the detector; d is the sample thickness; c_0 is the stress optical coefficient of the material; K is an experimentally determined constant and λ is the wavelength of the He–Ne laser light source ($\approx$ 632.8 nm).

Fig. 2 shows the calibration curve of the system using a quartz block standard. Its dimensions were $50 \times 50 \times 7$ mm and it was stressed by loading with lead weights. According to Cerqua et al. [5], the stress optical coefficient of silica is 3.29×10^{-12} m^2/N. In this way, the sample dephasing corresponds to $\delta = 3.66 \times 10^{-4} m$, where m is the applied mass in grams. The linear fit determined K to be 264 ± 3. The equipment is able to measure stress in the range 0.3 to 400 N/m^2. The glass sample is pressed by two steel rods in a cylindric oven. The top and bottom temperatures of the glass is measured by two chromel–alumel thermocouples. The temperature difference was less than 1°C.

5. Experimental results

Two samples have been used to determine the stress relaxation curve in an ambient atmosphere as shown in Fig. 3. An estimate of the relative error of ψ was 10% and is not shown in order to better analyze the relaxation phenomenon. The normalization ($\psi = 1$) has taken into consideration the stress initially applied. The value $\psi = 0$, in this case, refers to the stress value of the glass before the strain application and was determined after maintaining the sample at the measurement temperature for 2 h. Initially, the sample was strained at 249°C and then at 260°C. No significant variation of ψ was observed at these temperatures.

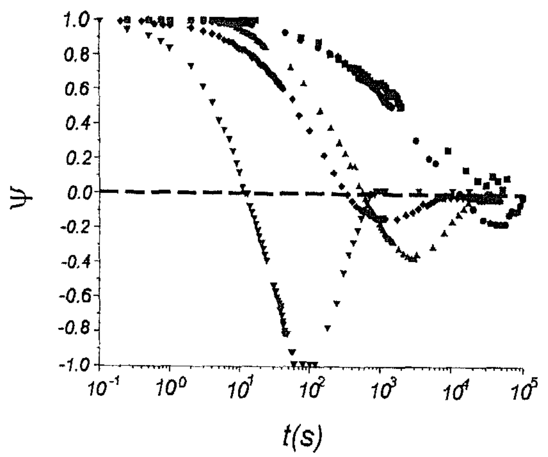

Fig. 3. Stress relaxation curve for a fluoroindate glass with $40InF_3$–$20SrF_2$–$16BaF_2$–$20ZnF_2$– $2GdF_3$–$2NaF$ (mol%) composition measured at various temperatures T in ambient atmosphere: (a) $T = 249$°C (●); (b) $T = 260$°C (■); (c) $T = 270$°C (▲); (d) $T = 275$°C (♦); (e) $T = 281$°C (▼). ψ, normalized relaxation curve in relation to the stress initially applied; t, measurement time.

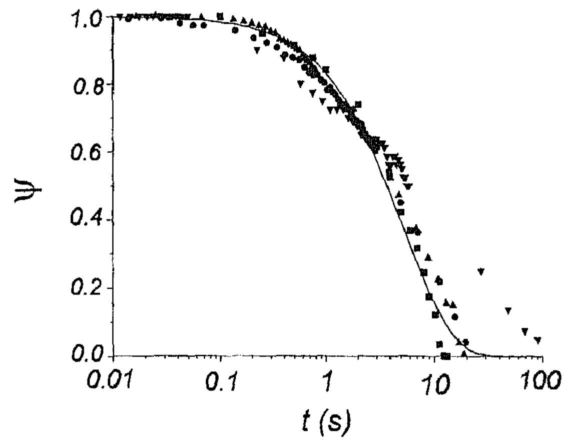

Fig. 4. Master curve $\psi = \exp(-t/\zeta_s)$ for the fluoroindate glasses with $40InF_3$–$20SrF_2$–$16BaF_2$–$20ZnF_2$– $2GdF_3$–$2NaF$ (mol%) composition submitted to different temperatures T at ambient atmosphere: (a) $T = 260$°C (■); (b) $T = 270$°C (▲); (c) $T = 275$°C (●); (d) $T = 281$°C (▼); (e) master curve (————). ψ, normalized relaxation curve in relation to the stress initially applied; t, measurement time; $\zeta_s = 5.4 \pm 0.3$ s, relaxation time with reference to 281°C temperature.

Ψ variation only occurred at higher temperatures, $T = 270$ and 281°C. Macroscopic changes of the lateral glass surface were also observed. The glass surface became translucent due to the presence of small grooves, perpendicular to the applied strain. A second sample, exposed to strain at 275°C behaved similarly. We also observed that Ψ became negative for long time measurements. This change is a delayed dilatant effect of the glass, possibly due to air atmosphere. The glass then returned to its original stress before the strain application. However, the appearance of ripples on the surface changes the optical behavior of the glass and the stress measurement is not reliable in this time range.

The curves for $0.1 < \psi < 1$ at $T = 260$, 270, 275 and 281°C showed a thermorheological simple behavior as seen in Fig. 4. The 10% relative error in ψ again is not shown in order to better analyze the master curve. The value for $\zeta_s = 5.4 \pm 0.3$ s was measured at 281°C. These results indicate that fluo-

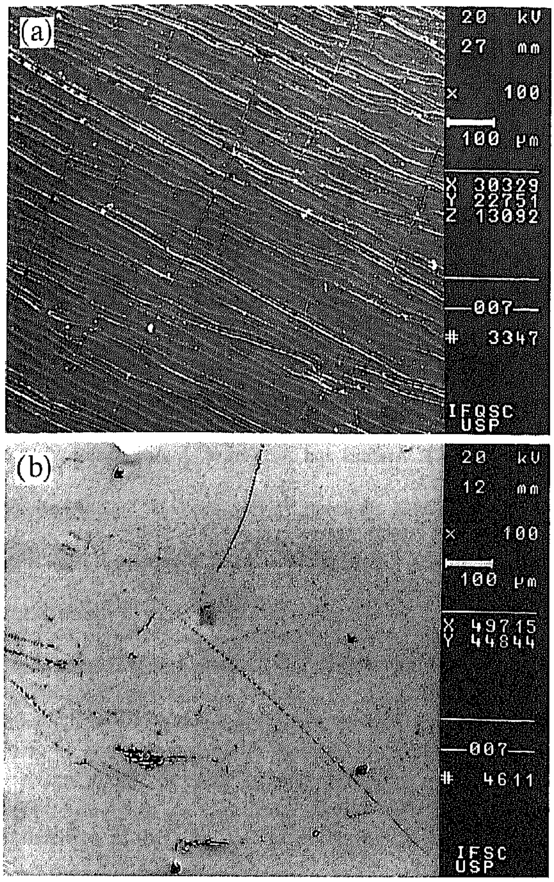

Fig. 5. Scanning electron microphotographs (100× magnification) of the lateral glass surface with $40InF_3-20SrF_2-16BaF_2-20ZnF_2-2GdF_3-2NaF$ (mol%) composition: (a) sample submitted to a constant strain at 281°C measured in ambient atmosphere; (b) sample submitted to a constant strain at 275°C in dry Ar atmosphere (≅ 30 ppm H_2O).

roindate glasses show a Newtonian behavior for the stress which was applied. However, this behavior occurs in a limited temperature range and describes only partially the temporal stress dependence.

Fig. 5 shows two scanning electronic microphotographies (SEM–Zeiss–960) of the glass surface. Fig. 5a shows the lateral surface after the relaxation at 281°C at 24 h; the grooves are observed to be perpendicular to the applied strain. These grooves can not be associated to the polishing procedure because the surface was polished. They are similar to those found by Abe et al. [6] for $Ca(PO_3)_2$ glasses and also by Iqbal et al. [7] during AlF_3 fiber drawing. There are also parallel scratches with dark spots at their edges that may be a consequence of a crystallization phenomenon. Fig. 5b shows the glass surface exposed to a constant strain at 275°C for 10 h in dry argon atmosphere (maximum: 30 ppm H_2O). There are neither grooves nor scratches on this glass surface. We conclude that these modifications of the glass surface are caused by H_2O molecules. The absence of grooves in Fig. 5b indicates that water directly influences the formation of these defects.

6. Discussion

It is possible to analyze the relaxation process in fluoroindate glasses without the determination of the stress applied value. The ψ behavior can give information about the changes in the mechanical properties of the glass. The Newtonian viscous flow is due to shear forces along the glass surface and low stress level. A dilational response has not been observed in oxide glasses, however, the measurement of the stress relaxation indicated that there was a dilational response for fluoroindate glasses (Fig. 3). This response can be attributed to changes in the surface glass structure, due for example, to the incorporation of O_2 or H_2O molecules which may produce surface oxyfluorides. This phenomenon creates a glass film that may make this microellipsometer technique susceptible to errors. The alterations of the glass surface observed by SEM indicates that atmospheric humidity alters the optical behavior of the glass (Fig. 5). Hence, it is necessary to measure the stress relaxation in a controlled atmosphere.

The Newtonian behavior for similar deformations can be thermorheological simple and has the same sequence of molecular events at different temperatures. According to Simmons et al. [8], who analyzed the behavior of the viscosity in soda lime silica glass, the Newtonian viscous flow is generally observed for low stress or strain rate. The viscosity depends on the strain rate and the glass can change from a pseudo-plastic material to a dilatant material because of structural modifications. The rheological behavior for fluoroindate glasses can be non-Newtonian similar to the flow of organic polymers [9,10]. In this case, the master curve can be obtained by the

Kohlrausch approach [11] and the thermorheological simple behavior can be described by an Arrhenius or Leonard–Jones equation.

7. Conclusions

The ellipsometry is an efficient technique to characterize the relaxation of uniaxial stresses of fluoroindate glasses. It was determined that the relaxation process was Newtonian for short time measurements and there was a dilational effect after long times. Air and/or atmospheric humidity alter the glass surface, resulting in the formation of grooves perpendicular to the applied strain. Surface oxyfluorides may form.

Acknowledgements

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