Journal of Non-Crystalline Solids 354 (2008) 4730–4736

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Effect of cooling on the optical properties and crystallization of UV-exposed photo-thermo-refractive glass

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ARTICLE INFO

Article history:
Available online 23 August 2008

PACS:
42.70.Ce
42.40.Eq
61.46.Hk
78.20.Ci
81.40.−z

Keywords:
Crystallization
Optical microscopy
Nanocrystals
Absorption
Lasers
Optical spectroscopy
Photoinduced effects
Calorimetry

ABSTRACT

Photo-thermo-refractive (PTR) glass is a multi-component silicate glass that undergoes a refractive index change after UV-exposure and thermal treatment. This photo-thermo-refractivity is due to the precipitation of sodium fluoride nano-crystals; thus the glass remains highly transparent in the visible and near-IR regions. Up to now, most studies focused on the influence of temperature and duration of thermal treatment on the PTR glass properties, but no attention was given to the cooling step after thermal treatment. In this paper, the influence of cooling on crystallization and resulting optical properties of UV-exposed PTR glass is studied. We show that cooling between the nucleation and growth treatments is a mandatory step to achieve the full benefits of the first heat-treatment, i.e., a large number of small crystals. We also show that the main part of the refractive index change occurs on the cooling path after pre-nucleation. Non-isothermal DSC study associated with in situ pre-nucleation treatment shows that pre-nucleation enhances crystallization only if the temperature is decreased below T_g before the second (development) treatment. Using high temperature photometric measurements of the absorption spectra of UV-exposed PTR glasses, we tentatively associate that effect with the presence of liquid drops of a silver containing phase during regular pre-nucleation treatment. This fact explains the necessity to cool such drops below their melting point to obtain nucleation centers for efficient precipitation of NaF nano-crystals.

1. Introduction

Photo-thermo-refractive (PTR) glass is a sodium–zinc–aluminum–silicate glass containing small amounts of fluorine and bromine, doped with cerium, silver, antimony, and tin. Glasses which undergo photo-thermo induced crystallization were invented many years ago by Stookey [1] and have been studied as possible candidates for hologram writing in the last 15 years [2–5]. PTR glass exhibits significant refractive index change after UV-exposure and thermal treatments (pre-nucleation + development) above the glass transition temperature, T_g, which results from the crystallization of about 0.1 wt% sodium fluoride nanocrystals [6]. After partial crystallization the glass remains highly transparent in the visible. Therefore, the possibility of recording phase holograms in this type of glass has numerous potential applications, such as optical filtering [7] or spectral beam combining [8]. A simplified description of the complex photo-thermo crystallization mechanisms is given in Ref. [9].

The evolution of the crystallization and optical properties of PTR glass after UV-exposure is reported in several publications [6,10–14], and described in reviews, e.g. [15]. In this paper, we first analyze the correlation between the end temperature before quenching and the refractive index change that occurs after the thermal development of a UV-exposed PTR glass sample. Then, we show the effect of cooling on the crystallization kinetics and microstructure of UV-exposed PTR glass. In a complementary analysis of crystallization, the effect of cooling temperature is studied by non-isothermal differential scanning calorimetry. Finally, the evolution of the nucleation process is followed by spectro-photometric measurements. Insights on the mechanism of nucleation in PTR glass are advanced.

2. Experimental – materials and methods

2.1. Glass sample preparation

Samples of a photosensitive PTR glass containing $15Na_2O$–$5ZnO$–$4Al_2O_3$–$70SiO_2$–$5NaF$–$1KBr$–$0.01Ag_2O$–$0.01CeO_2$ (mol%) and minor amounts of Sn and Sb were used in this work as in

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doi:10.1016/j.jnoncrysol.2008.06.103

previous studies [3–6]. The glass was melted in an electric furnace in a 0.5 l platinum crucible at 1460 °C for 5 h in air. Stirring with a Pt blade was used to homogenize the liquid. After melting, homogenizing and fining, the glass was cooled to the glass transition temperature ($T_g \sim 460$ °C), then annealed at T_g for 2 h, and cooled to room temperature at a rate of 0.1 K/min. Polished $25 \times 25 \times 2$ mm^3 samples were prepared from the batch. The chemical homogeneity of the samples is a critical parameter affecting crystallization properties [16], thus homogeneity was tested by the shadow method in a divergent beam of a He–Ne laser and was quantified by measurements using an interferometer (GPI Zygo). The samples selected for this study had refractive index fluctuations of less than 40 ppm (peak-to-valley) across the aperture. UV-exposure of samples was performed by a He–Cd laser (4 mW, 325 nm). Except for the characterization of the refractive index change (Section 2.2), all samples were homogeneously exposed with a dosage of 0.9 J/cm^2.

2.2. Photosensitivity characterization

The method used for characterizing the photosensitivity of PTR glass was the same as in Ref. [10]. Glass samples for refractive index measurements were fixed onto a computer-controlled translation stage and moved across a laser beam (He–Cd laser, 4 mW, 325 nm) at constant velocity in order to record a stripe with controlled distribution of dosages (Gaussian distribution with maximum of 0.9 J/cm^2). After exposure, the samples were thermally developed for 30 min at 520 °C. Refractive index changes were measured in each sample using a shearing interferometer setup [10]. Its basic principle is to create an interferogram that converts the phase change at propagation through the glass to a fringe shift. A liquid cell with an index matching fluid was used to prevent thickness variations of the sample which would contribute to fringe shift. Therefore the interferometer fringe distortions resulted only from refractive index variations.

2.3. Differential scanning calorimeter (DSC) measurements

Thermal analysis was performed using a DSC (Q10 DSC, TA Instruments) with sample weights of typically 30 mg and a heating rate of 30 K/min. Pre-nucleation of the samples was carried out in situ, inside the heating chamber of the DSC. DSC curves are shown in the temperature range of 500–720 °C, where relevant thermal events take place. The position of the maximum of the exothermic peak was denominated crystallization temperature, T_c.

2.4. Absorption spectra measurements

Optical absorption spectra were measured with the setup shown in Fig. 1. It is composed of a UV/visible white light (deuterium tungsten halogen) source. Light is coupled inside a 200 μm fiber and then collimated using a lens. The beam diameter is around 2 mm. This beam passes through the sample and is collected by a collimator associated with a 200 μm fiber. The collected light is sent to an Ocean Optics S2000 spectrometer that allows for spectral measurement of the transmitted power in the range of 380 up to 800 nm. The sample is placed inside a heating cell, which guarantees precise control of temperature in the range of 25 up to 600 °C. Therefore, this cell was also used for the thermal treatments of the samples. The transmitted power (P_s) was measured in situ for different durations of thermal treatment. In order to convert these power measurements into absorption spectra, preliminary measurements were carried out. The power was first measured when the beam was hidden ($P_{0\%}(\lambda)$), then a new measurement was performed with no sample placed in the sample holder ($P_{100\%}(\lambda)$). Finally, absorption spectra ($A(\lambda)$) were calculated as follows:

$$A(\lambda) = -\frac{1}{t}\log(T(\lambda) - R(\lambda)) = -\frac{1}{t}\log\left(\frac{P_s(\lambda) - P_{0\%}(\lambda)}{P_{100\%}(\lambda) - P_{0\%}(\lambda)} - R(\lambda)\right), \quad (1)$$

where t is the sample thickness ($t \sim 1.2$ mm) and $R(\lambda)$ the losses corresponding to Fresnel reflections on the faces of PTR glass sample, previously determined.

3. Results

3.1. Effect of cooling temperature on refractive index change

Several homogeneous samples from the same melt were prepared with the method described in Section 2.1. Each sample was UV-exposed with a Gaussian stripe and dosage of 0.9 J/cm^2 at 325 nm, and then heat-treated for 30 min at 520 °C to induce partial crystallization, which triggered a refractive index change. In order to study the effect of cooling, samples were left inside the hot furnace where unforced decrease of temperature in furnace occurred (estimated rate of ~2.5 °C/min). Each sample was then quenched (drawn from the furnace and placed on top of a metal plate at room temperature) from a different temperature starting at 520 °C down to 420 °C with a 20 °C step. A typical thermal treatment schedule is shown in Fig. 2a. Refractive index was measured using the liquid-cell shearing interferometer. The refractive index change was also measured in a sample that was not quenched from high temperature, but annealed down to room temperature (left cooling down inside the furnace). Evolution of the ratio between refractive index changes measured in each quenched sample and

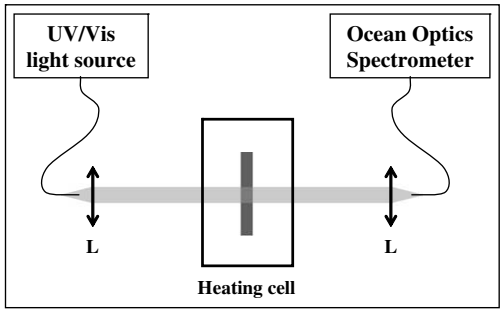

Fig. 1. Spectrometric setup developed for the measurement of the evolution, at high temperature, of the absorption band of silver containing particles in PTR glass.

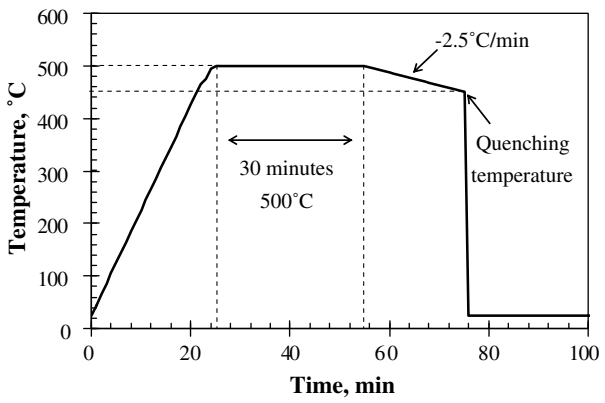

Fig. 2a. Thermal treatment schedule used for the analysis of the influence of cooling on PTR glass refractive index change.