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Influence of UV-exposure on the crystallization and optical properties of photo-thermo-refractive glass

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Abstract

Photo-thermo-refractive (PTR) glass is a photosensitive multi-component silicate glass. Photoinduced crystalline phase precipitation results in refractive index variations in UV exposed areas of PTR glass. The precipitation of silver containing particles which occurs during photo-thermo-refractive process increases the optical absorption of the samples in the range 350 nm to NIR wavelengths and the growth of sodium fluoride crystals and their aggregation increases light scattering in visible and NIR regions. We show that one effect of the UV-exposure is a decrease in the crystallization temperature by ~50 °C compared to the unexposed areas as measured by differential scanning calorimetry, which we attribute to an increase in nucleation rate. Using spectro-photometric measurements, a linear function is fitted to the changes in the amplitude of the absorption band of the silver containing particles versus the UV-dosage. The root mean square scatter of the data from the linear function is better than 0.99 and the slope of the function is 0.32 ± 0.01 cm/J. The IR absorption of PTR sample, measured by laser calorimetry shows that the increase of the absorption in infrared region at 1.1 μm, is due to the tail of the absorption band of silver containing particles having maximum at 465 nm. We finally show that after hyper-development, one effect of UV-exposure at 325 nm on the crystallization kinetics of PTR glasses is a decrease in particle sizes from micron size to nanometers size. But additional investigations demonstrate that smaller dosage UV-exposures (a few tens of milliwatts) increase the optical scattering by one order of magnitude. Optical micrographs taken after UV-exposure and hyper-development reveal the use of smaller dosages enhances nucleation rate without preventing the growth of large crystals and therefore induces higher scattering.

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Keywords: Crystal growth; Glass ceramics; Nucleation; Nanocrystals; Optical spectroscopy; Optical microscopy; Absorption; Photoinduced effects

1. Introduction

Photo-thermo-refractive (PTR) glass is a sodium–zinc–aluminum–silicate glass doped with cerium, silver, fluorine, and bromine. The class of glasses which demonstrated photo-thermo-induced crystallization was invented many years ago by Stookey [1] and has been studied as a possible candidate for hologram writing in the last 15 years [2–5]. PTR glass exhibits refractive index changes after UV-exposure and further thermal treatments above the glass transition temperature T_g, which results from the crystallization of about 0.1 wt% sodium fluoride nanometer size crystals [6]. Therefore this glass composition and the possibility of recording phase holograms has potential for many applications, such as optical filtering [7] or spectral beam combining [8]. A description of the complex photo-thermo-induced crystallization mechanisms is given in reference [9]. The evolution of the material and optical properties of PTR glass after UV-exposure are reported in several publications [6,10–13] and described in surveys, e.g. [15].

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In this paper, we first study the affect of UV-exposure on PTR glass crystallization using non-isothermal differential scanning calorimetry (DSC) and optical spectroscopy. Then we investigate the effect of UV-exposure time (dosage) on DSC thermograms and on the absorption spectra. Finally, we present correlation between various optical properties of PTR glass such as absorption and scattering at visible and near-infrared (NIR) wavelengths.

2. Experimental – materials and methods

2.1. Glass sample preparation

Samples of several photosensitive PTR glasses of composition $15Na_2O$–$5ZnO$–$4Al_2O_3$–$70SiO_2$–$5NaF$–$1KBr$–$0.01Ag_2O$–$0.01CeO_2$ (mol%) were studied in this work as in previous works [3–6]. The glasses were melted in an electric furnace in 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, the glasses were cooled to the glass transition temperature ($T_g \sim 460$ °C), then annealed at T_g for 2 h, and finally cooled to room temperature at the rate of 0.1 K/min. Polished samples $25 \times 25 \times 2$ mm^3 were prepared from each batch. The optical homogeneity of the samples being a critical parameter in their crystallization properties, their homogeneity was thus tested by the shadow method in a divergent beam of a He–Ne laser and was quantified by measurements with an interferometer (GPI Zygo). The samples selected for this study have refractive index fluctuations of less than 40 ppm [peak to valley] across the aperture.

2.2. Non-isothermal differential scanning calorimeter (DSC) measurements

Thermal analysis was performed using a DSC (Q10 DSC from TA instruments) with sample weights of typically 30 mg and a heating rate of 30 K/min. Thermograms were measured up to 720 °C and the resulting curves are shown in the range 450–720 °C. Then, the position of the maximum of the exothermic peak was determined and denominated crystallization temperature, T_c.

2.3. Losses and absorption measurements

Optical absorption spectra were measured with an optical spectrophotometer (Cary 500) in the range from 200 to 1500 nm. To avoid effects of surface contamination or incipient surface crystallization, each sample was re-polished before the measurements. Small losses ($<10^{-2}$ cm^{-1}) at 1096 nm were measured with an original optical setup. With this Yb-doped fiber laser based setup we measured the transmitted and reflected power and therefore losses (sum of absorption and scattering) with a precision of ~0.1%. Absorption was also measured with a setup based on laser calorimetry [13] and permitted us to measure an absorption coefficient with a precision $<10^{-4}$ cm^{-1}.

3. Results

3.1. Effect of UV-exposure on the nucleation properties of PTR glass

Effect of UV-exposure on crystallization was studied by non-isothermal DSC with heating rate of 30 °C/min. Non-isothermal DSC thermograms were measured on adjacent PTR glass samples from the same melt and having identical refractive index ±40 ppm: one sample was un-exposed, and the other one was UV exposed to 0.9 J/cm^2 at 325 nm and positions of crystallization peaks were determined. These measurements showed that the temperature of the crystallization peaks of UV exposed samples decreases a few degrees (typically between 2 and 10 K) compared to un-exposed PTR glass samples. Moreover, previous studies [14] demonstrated that UV-exposure (0.9 J/cm^2, 325 nm wavelength) associated with proper nucleation treatment (e.g. 30 min at temperature higher than 495 °C) decreased crystallization temperature up to more than 70 °C compared to crystallization temperature of an un-exposed sample. In this case, crystallization temperature could be decreased 50 K from that in unexposed glass (Fig. 1). Actually it was demonstrated that crystallization temperature of UV-exposed glasses is [600 ± 5] °C and for unexposed PTR glasses crystallization temperature is [650 ± 5] °C. By such treatments, photo-induced and spontaneous crystallization can be easily separated. Additional samples from the same melt were UV-exposed with different dosages from 0.5 J/cm^2 to 8 J/cm^2. Then these samples were nucleated for 30 min at 480 °C and DSC spectra were recorded (Fig. 2). With such a treatment, we show that DSC thermograms have 2 crystallization peaks: the peak at lowest temperature is due to photoinduced crystallization while the other peak is due to spontaneous crystallization. Moreover, whatever the dosage, the same peaks appear at the same temperatures. But in the case of smaller dosages, the spontaneous crystallization peak is larger while at larger dosages the peaks are comparable.

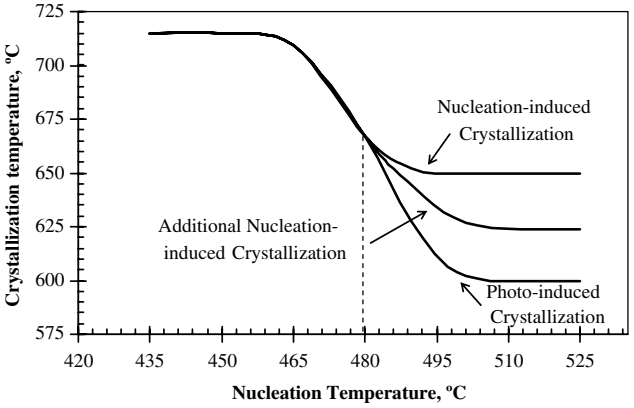

Fig. 1. Dependence of crystallization temperature versus nucleation temperature of virgin and UV-exposed PTR glass measured by non-isothermal DSC. Nucleation time was 30 min.