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Journal of Non-Crystalline Solids 325 (2003) 275–281
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

Comparative study of photo-induced variations of X-ray diffraction and refractive index in photo-thermo-refractive glass

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Received 17 April 2002

Abstract

Spontaneous and photo-induced crystallization have been investigated in fluorinated silicate glass by means of X-ray diffraction and optical interferometry. This glass is a photo-sensitive material for high-efficiency phase volume hologram recording. Variations of a refractive index in this glass are controlled by UV irradiation followed by a thermal development which is photo-thermo-refractive (PTR) process. A method of discrimination of weak narrow crystalline lines from a broad diffractive pattern of a vitreous material was developed, and quantitative measurements of small concentrations of crystalline phase in glass matrix were performed. The sensitivity of the method was about 0.01 wt% of crystalline phase of NaF in a silicate glass. This crystalline phase with concentration below 0.1 wt% was detected even in a highly transparent PTR glass with a modified refractive index produced by PTR processing. A correlation between the intensity of X-ray diffraction peaks of NaF and the induced refractive index was found in equally developed PTR glass samples exposed to different dosages of UV radiation.

PACS: 42.70.C; 78.20; 61.10.N; 42.40.E

1. Introduction

The fast evolution of lasers and optical communications stimulated increasing demands for diffractive optical elements serving as different types of spectral and angular filters. However all commercially available holographic photo-sensitive materials do not satisfy the very strong requirements for such applications (see e.g. the recent book of Hariharan [1]). One of such new promising media is a photo-thermo-refractive (PTR) glass which demonstrates high diffraction efficiency at all spatial frequencies in both reflecting and transmitting

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doi:10.1016/S0022-3093(03)00310-7

geometries, low losses in the visible and near IR spectral regions, combined with high tolerance to elevated temperatures and laser radiation [2–5].

PTR glass is a sodium–zinc–aluminum–silicate glass usually doped with cerium, silver, fluorine, and bromine. A refractive index decrement after exposure of this glass to UV radiation followed by thermal development was described in Ref. [6]. This phenomenon was used for phase volume hologram recording in Refs. [7,8]. A mechanism of a refractive index variation in Refs. [6–8] was ascribed to a photo-thermo-induced crystalline phase precipitation in a softened glass matrix discovered by Stookey [9] and studied in details in Ref. [10]. The main idea was exploited in Refs. [6–8] that a refractive index of crystalline phase of NaF (1.32) is significantly lower than that of glass matrix (1.49), and, therefore, the exposed area enriched with nanocrystals should have a lower refractive index.

A series of researches [10–14] was directed to the elucidation of the role of crystalline phase precipitation in photo-thermo-induced variations of optical properties (absorption, scattering, and refraction) of those similar glasses named differently depending on authors and applications (photo-sensitive opal, polychromatic, multichromatic, and PTR). Properties of different crystalline phases were studied by X-ray and electron diffraction, optical and electron microscopy, and optical scattering. It was found that an exposure of this glass to UV radiation resulted in a decrease of the incubation period of the photo-induced thermal crystallization compare to the spontaneous precipitation of crystalline phase. This is why a concentration of crystalline phase in exposed areas can be higher than that in unexposed areas, if proper conditions of exposure and development are found. However, all direct observations of the crystalline phase were conducted in glasses having high concentration of large crystals which produce a strong scattering of optical radiation (opalescence).

No data on crystalline phase detection were reported for the most practically important case of small exposures and low-temperature development for short holding periods which provides a maximal refractive index variation but minimal losses and, thus, was mainly used for hologram recording. Therefore, the goal of this research is to develop a method of detection of low concentrations of crystalline phase in the glass matrix and compare crystalline phase precipitation with refractive index variations in PTR glass samples exposed to UV radiation and subjected the thermal development.

2. Experimental

2.1. Glass samples fabrication

The same photo-sensitive glass of approximate composition (mol%) $15Na_2O$–$5ZnO$–$4Al_2O_3$–$70SiO_2$–$5NaF$–$1KBr$–$0.01Ag_2O$–$0.01CeO_2$ was studied in this work as in previous works [2–5,7,8]. The glass was melted in an electrical furnace in 400 ml fused silica crucibles at 1460 °C for 5 h. Stirring was applied to homogenize the melt. After the melting, the glass was cooled to the glass transition temperature in the open air by casting on to a thick metal slab or in the crucible. The glass casting (or boule) underwent annealing at 460 °C for 2 h and then cooled with a rate in the region of structural and stress relaxation of 0.1 °C/min. Polished glass samples from 0.5 to 2 mm thickness of 25 mm × 25 mm size were prepared. Optical homogeneity of samples was tested by the shadow method in the divergent beam of a He–Ne laser and by the liquid-cell shearing interferometer described in Ref. [15].

2.2. Exposure and thermal development

Radiation from the CW He–Cd laser at 325 nm emitting a single transverse mode was used for exposure of the samples as was done in Ref. [15]. The transverse distribution of intensity in the laser beam was determined by measuring the intensity of the radiation transmitted through a pinhole of 50 μm in diameter, which was scanned across the beam. It was found that the transverse distribution of intensity could be fitted to a Gaussian function with the accuracy of better than 5%:

$$I(y) = I_{\max} \exp\left(-2\frac{y^2}{\omega^2}\right), \tag{1}$$

where y is the spatial coordinate, $I(y)$ is the intensity distribution, $I_{\max}$ is the maximal intensity in

the center of the beam, and ω is the half width of the beam at the level of $1/e^2$. This beam having a Gaussian spatial profile was directed onto a sample fixed on a motorized translational stage. While the sample was being exposed, the motorized stage scanned the sample with a constant speed V. Due to the motion of the stage, the irradiated area was a straight stripe with a Gaussian distribution of dosage in the lateral direction. It can be shown that the dosage at any distance from the center of the irradiated stripe will be described by the equation

$$D(y) = \sqrt{\frac{2}{\pi}}\frac{P}{\omega V}\exp\left(-2\frac{y^2}{\omega^2}\right), \quad (2)$$

where P is the total power of the laser beam. Typical scanning speed values of the 1 mW beam having about 2.5 mm width were ranged from units to hundreds of micrometers per second to provide maximal dosage from hundredths to units of joules per squared centimeter.

Thermal development was produced in a Lindberg/BlueM box furnace by keeping the exposed specimen on the flat surface of temperature resistant Pyrex glass at the temperature of 520 °C for holding periods ranging from a few minutes to several hours. After thermal development, the specimen slowly cooled down to the room temperature.

2.3. Induced refractive index measurement

A liquid-cell shearing interferometer was developed [15] to measure refractive index variations (Δn) in the volume of transparent materials. The cell was filled with a liquid having a matched refractive index with respect to the specimen. An interference pattern was formed by the reflections of a radiation of He–Ne laser at 633 nm from the high-quality surfaces of the cell, while no reflections from the surfaces of the specimen were observed. This construction combined with in-house software allowed elimination of the effect of surface imperfections on the measurement of volume variations of a refractive index. The achieved resolution was better than 1/1000th of a fringe shift and resulted in a Δn measurement sensitivity down to 10^{-7} for 1 mm thick samples. The use of Gaussian distribution of dosage in the direction perpendicular to the exposed stripe on the sample (Section 2.2) allows a calculation of an induced refractive index versus dosage in a single measurement.

2.4. X-ray diffraction measurement

Data were acquired using an X-ray diffractometer Rigaku model 'D/B max' with a CuK_α radiation and optimized operating conditions of 30 mA and 35 kV. All analyses presented in this paper were carried out at room temperature, scanning from 10° to 80° of 2θ angle. Different scanning rates were studied to provide maximum sensitivity of the method of the crystalline admixture detection. The desirable fractions of the glass sample (virgin or exposed) were cut out and pounded until a fine powder was obtained. Then, the powder was evenly spread out on a double-face adhesive tape and placed on the sample holder. The whole assembly was then inserted into the chamber for the angular distribution of X-ray diffraction (XRD) measurement and crystalline phase determination. These XRD patterns were matched to the corresponding Joint Committee of Powder Diffraction Standard (JCPDS) files.

3. Results and discussion

3.1. Spontaneous crystallization of the virgin glass

It is well known that fluorine containing glasses have a high tendency to crystallization. Hence, the technology of PTR glass was designed in such manner that no evidences of any type of crystallization could be found in the as-melted glass samples. The virgin glass samples used in all experiments had no optical scattering (no visible Tindal cone under excitation by 30 mW He–Ne laser at 633 nm). No sharp lines appeared in the XRD pattern depicted in Fig. 1(A). The single broad band observed on the XRD pattern had a maximum approximately at 23° and full width from 15° to 40°. This band is usual for all silicate glasses. No traces of crystalline quartz were found

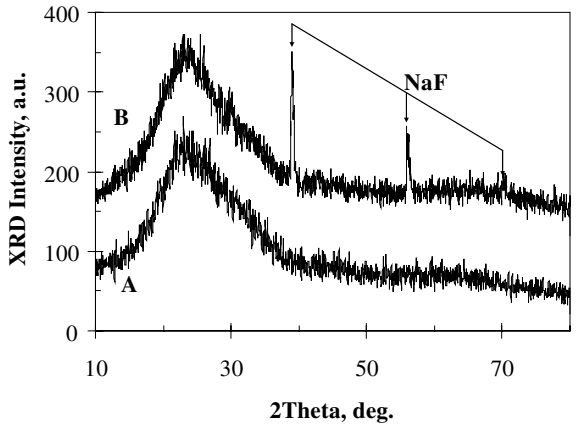

Fig. 1. X-ray diffraction patterns recorded on PTR glass: (A) as-melted and (B) baked at 600 °C for 15 h. The curve B is shifted up for 100 units to separate the curves.

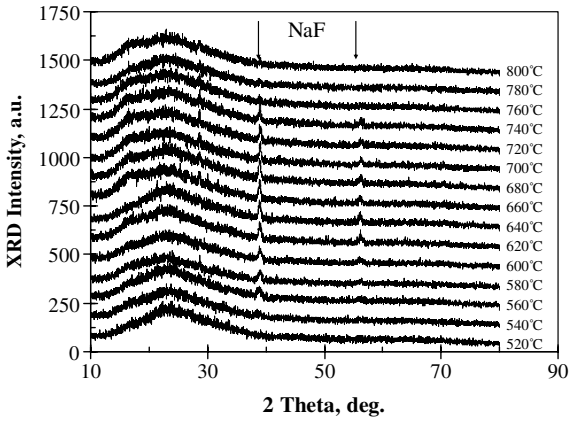

Fig. 2. X-ray diffraction patterns recorded on virgin PTR glass samples after heat treatment for 60 min at different temperatures. Each consequent pattern is shifted up for 100 units to separate the curves.

in the virgin PTR glass samples used in this study, as it was reported in Ref. [11].

To demonstrate the ultimate level of spontaneous crystalline phase precipitation in PTR glass, we baked the virgin glass samples at a temperature of 600 °C for 15 h. Indeed, the resulting object was a completely white opal glass. The XRD pattern of this totally crystallized glass is shown in Fig. 1(B). One can see the three sharp peaks match with the expected NaF Villaumite crystalline phase [JCPDS # 36-1455] located at 39°, 56° and 70.5° as was described in earlier works [10–14]. A weak singularity that can be classified as a small peak can be found in the region of 30° which is a signature of NaBr [JCPDS # 36-1456]. These data mean that the main crystalline phase precipitated in PTR glass is NaF with possible small admixture of NaBr. No other crystalline phases detectable by XRD were found in totally crystallized PTR glass samples. It should be noted that a bright yellow residue was precipitated on the abraded surfaces of thermally treated samples which could be due to a silver containing compound. However, we did not study this surface phenomenon in the current work. Thus, the main crystalline phase precipitating in the unexposed PTR glass after thermal treatment is a cubic NaF one.

To determine the temperature region of sodium fluoride precipitation, the unexposed PTR samples were baked for 60 min at temperatures ranging from 500 to 800 °C. The associated diffraction patterns displayed in Fig. 2 show that spontaneous precipitation of a sodium fluoride crystalline phase starts at about 540 °C and this phase becomes completely dissolved at temperatures above 800 °C. No crystalline phase was detected in our samples below 540 °C, which agreed with results of Astakhova et al. [11] who observed low-temperature crystallization after 16 h of baking only. Thus, the regime of thermal development at 520 °C revealed in Refs. [6,7] corresponds to the maximum temperature when no significant spontaneous crystallization should be observed after a few hours of treatment. No other crystalline phase than NaF was detected in PTR glass in the studied range of temperatures and holding periods.

3.2. Photo-induced crystallization – discrimination of the weak bands

Standard procedure of high-efficiency hologram recording [2–5,15] consists of PTR glass exposure to radiation at 325 nm with dosage ranged from 50 mJ/cm^2 to 5 J/cm^2 followed by a thermal development at 520 °C for one or two hours. This treatment results in a refractive index decrement which was traditionally ascribed to the crystalline phase precipitation in the exposed areas. It should be noted that total losses (absorption and scat-

tering in red and near IR spectral regions) of the area with the modified refractive index are usually below 1%. The following procedure was performed to check the presence of crystalline phase in the exposed area of PTR glass with known dosage of UV irradiation. To provide a uniform distribution of dosage in the sample for XRD measurements, the PTR glass blank was exposed to four straight stripes of UV radiation with Gaussian lateral distribution of dosage (Section 2.2) which were consequently shifted in the lateral direction. In this case, fluctuations of dosage in the central part of the stripe with width of about 8 mm did not exceed 10%. After exposure, the sample was developed in the oven. A refractive index profile was measured, and it was found that the central part of the wide stripe actually had a flat top. This uniform central part of the exposed stripe was cut out and used for XRD measurement (Section 2.4).

A typical XRD pattern for exposed and developed at 520 °C sample of PTR glass is shown in Fig. 3(A) and by light circles in Fig. 3(B). This XRD pattern looks similar to that obtained for the virgin sample (Fig. 1(A)) and no sharp peaks on the noisy background of the XRD band of the glass matrix can be detected in the pattern of the exposed glass with the modified (it was measured before the sample preparation) refractive index. To discriminate the possible XRD peaks of NaF, we exploited the following traditional approaches for noise elimination by signal accumulation and the use of additional a priory information. The first one is the increase in the number of experimental points in the vicinity of the expected informative region. We restricted the area of measurement in the vicinity of 39° where the most intensive line of NaF is placed (Fig. 3(B), light circles) and produced repeatable measurements of the same angular region. The solid circles in Fig. 3(B) show the accumulated result of 32 scans of the same sample. One can see that the completely random distribution of the experimental points is reorganized to the band with a maximum at 39°. We know from Fig. 1(B) that the angular width of the measured NaF bands is about 1°. The density of experimental data shown in Fig. 3 was 25 points per degree. This means that averaging of these data over the angular space below 0.5° would not result in the missing of valuable information while the noise could be suppressed. The solid line in Fig. 3(B) shows the result of averaging over nine consequent points in a summarized pattern. The well-defined band of NaF crystalline phase is seen in this figure with the level of noise below 10% of its intensity. The same treatment of XRD patterns of virgin glass does not show any evidences of the crystalline phase presence. Thus, these results prove a photo-induced precipitation of a crystalline phase of NaF in transparent PTR glass with a refractive index modified after exposure to UV radiation and thermal development at 520 °C.

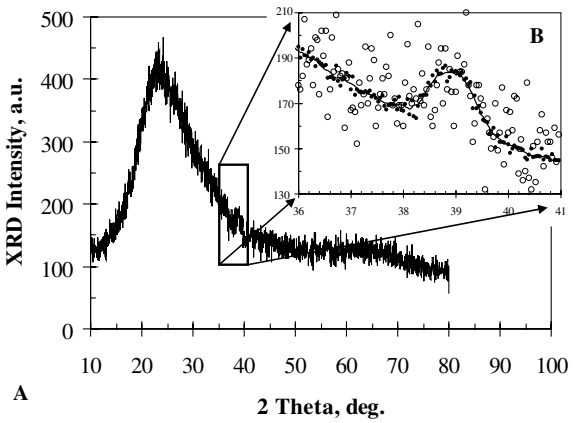

Fig. 3. X-ray diffraction patterns recorded on PTR glass sample after exposure to UV radiation at 325 nm for 2 J/cm^2 and developed at 520 °C for 1 h. Step interval for recording is 0.04°. (B) Shows the detailed part of the total pattern (A) in the vicinity of 39°. Light circles in (B) are the same data as in (A). Solid circles in (B) resulted from summarizing of 32 scans of the same sample. Solid line in (B) resulted from averaging over the consequent nine points in the summarized pattern.

3.3. Photo-induced crystallization – concentration measurement

A conventional XRD analysis with powdered samples does not allow quantitative determination of a crystalline phase concentration because of uncertainty of sample preparation which causes strong fluctuations of the signal. However, in the case of stability of a glass matrix composition this problem can be eliminated. The multiple measurements of XRD pattern of virgin and treated glasses (Figs. 1(A) and 3(A)) have shown that the

magnitude of the broad XRD band of glass matrix with maximum at 23° could vary from sample to sample up to several times while the shape of this pattern was very stable. This fact allows the normalization of XRD patterns in the region where no crystalline peaks occur and consequent subtracting of the vitreous background from the XRD pattern in the vicinity of crystalline peaks. Fig. 4 shows the result of such treatment for PTR glass samples with different dosages of UV radiation. One can see the presence of NaF peak at 39° in all samples including the lowest dosage of 150 mJ/cm^2 and increase of the concentration of crystalline phase with the dosage.

To estimate the concentration of crystalline phase of NaF in exposed and developed samples of PTR glass, a calibration of the signal is necessary. This calibration was made by the measurements of the mixtures of powdered virgin PTR glass with different concentrations of powdered sodium fluoride crystals. To provide uniformity of these mixtures, each batch was homogenized in the shaker for 1 h. The procedure of measurement and calculation of intensity of differential peak at 39° was the same as described above. Dependence of XRD peak at 39° versus concentration of NaF in the mixture is shown in Fig. 5. This calibration curve in comparison with data in Fig. 4 shows that

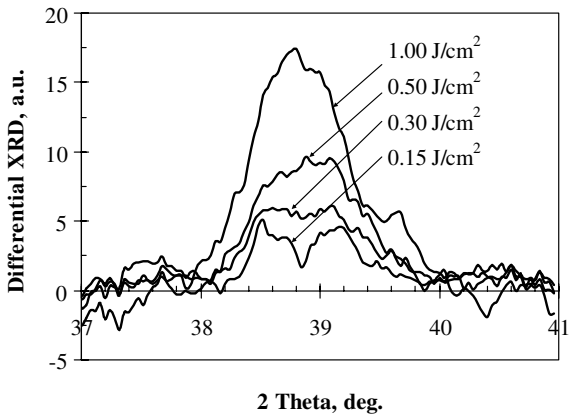

Fig. 4. Differential XRD patterns of PTR glass samples exposed to UV radiation at 325 nm and thermally developed at 520 °C for 1 h. Samples were scanned 32 times with step-period of 0.04°, patterns were summarized, averaged over nine consequent points and normalized. The pattern of virgin PTR glass was subtracted from the patterns of exposed glass samples.

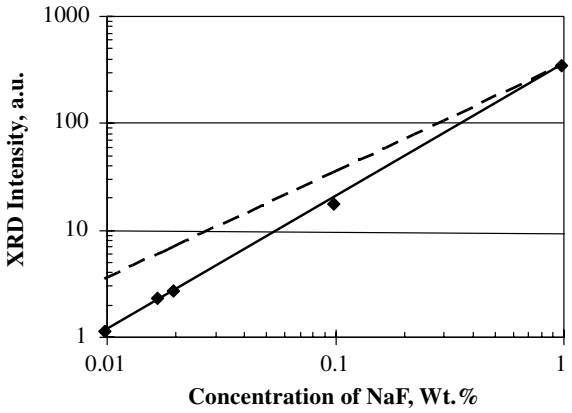

Fig. 5. Dependence of intensity of differential XRD peak at 39° in mixture of virgin PTR glass and sodium fluoride crystals on concentration of NaF. The dashed line is a linear function.

the concentration of crystalline phase of NaF in PTR glass samples after photo-thermal treatment ranged from 0.01 to 0.1 wt%. It is important to note that this low concentration is enough to provide the refractive index variations necessary for high-efficiency holograms while no significant scattering occurs in the treated sample. However, there is a feature of this calibration curve that has no satisfactory explanation yet. One can see from Fig. 5 that the dependence of XRD signal on concentration of NaF is a superlinear function (it varies faster that the linear one). The origin of this non-linear behavior of XRD signal versus NaF concentration requires a separate study; however, the existing calibration curve enables the measurement of the crystalline phase concentration in PTR glass.

3.4. Correlation between XRD signal of NaF and a refractive index

A series of PTR samples was prepared, exposed to the straight UV stripes with a uniform lateral profile of dosage (Section 3.2) for different dosages, and then developed in the oven. The profile of induced refractive index was measured for each stripe (Section 2.3) and a value of induced refractive index in the uniform central part of each stripe was determined. Then, the central part of the exposed stripe was cut out and used for XRD

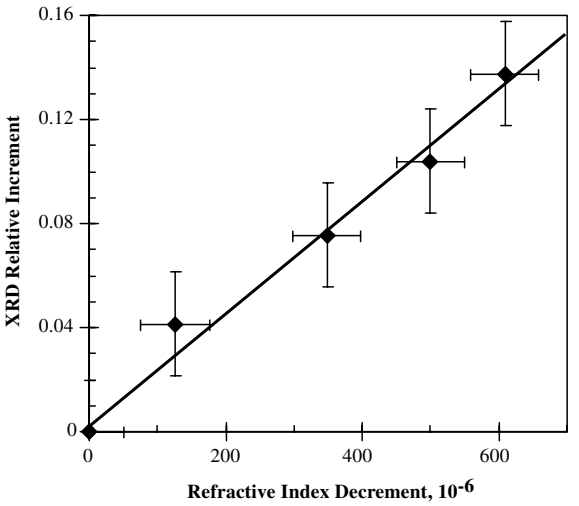

Fig. 6. Correlation between refractive index decrement ($-\Delta n$) and XRD relative increment (intensity of differential XRD signal at the major line of NaF at 39° normalized to the XRD intensity of PTR glass at the same angle) for PTR glass samples exposed to UV radiation at 325 nm and developed at 520 °C for 1 h.

measurement (Section 2.4). Fig. 6 shows the correlation between an induced refractive index decrement and intensity of XRD peak at 39° for samples exposed to different dosages of UV radiation. One can see a strong correlation which proves that the refractive index variation in PTR glass produced by UV irradiation followed by thermal development is the result of precipitation of crystalline phase of NaF in the exposed area. It is true even for highly transparent glasses which show no induced scattering. This result is the basis for the future study of the particular mechanism of refractive index variation in PTR glass.

4. Conclusions

The developed method of crystalline peaks discrimination in X-ray diffraction pattern on PTR glass allowed a detection of crystalline phase of NaF for concentrations down to 0.01 wt%. No crystalline phase was detected in a virgin PTR glass. A crystalline phase of NaF and traces of NaBr were detected in a totally crystallized PTR glass baked at 600 °C for 15 h. The single crystalline phase of NaF with concentration ranging from 0.01 to 0.1 wt% was detected in PTR glasses exposed to UV radiation at 325 nm and developed at 520 °C. There is a linear correlation between induced refractive index and intensity of X-ray diffraction of NaF in exposed and developed PTR glasses. Refractive index variations in exposed and developed PTR glass resulted from the precipitation of sodium fluoride nanocrystals in the volume of glass.

Acknowledgements

The work has been supported by BMDO contracts # 66001-97-C60008 and 6600198D6003. Authors appreciate useful discussions with Drs Andrea Bustamante and Kathleen Richardson.

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