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Role of bromine on the thermal and optical properties of photo-thermo-refractive glass

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Abstract

Photo-thermo-refractive (PTR) glass is a photosensitive silicate glass doped with cerium, silver, and fluorine. The precipitation of a minor crystalline phase after UV-exposure and thermal treatment induces a refractive index change, which is large enough to create diffractive optical elements. In this work we present a first attempt to understand the role of bromine on thermal and optical properties of PTR glass. We reveal that at least 75% of the concentration of bromine of commercial PTR glass is necessary to produce photo-induced crystallization. We also show that an increase of the bromine concentration will increase the mean refractive index of virgin PTR glass. Further thermal treatments induce a decrease of the mean refractive index of PTR glass. This decrease is finally shown to be larger in UV-exposed glass if photo-induced crystallization is present. We also show that bromine concentration will decrease water concentration in PTR glass and have an impact on the losses in visible. We demonstrate that the higher the bromine concentration, the higher the shift of the silver containing particles absorption band. In addition, if bromine concentration is high enough to produce photosensitivity, an increase of scattering due to the crystallization process is observed.

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Keywords: Crystal growth; Glass ceramics; Nucleation; Nano-crystals; Optical spectroscopy; Secondary ion mass spectrocopy; Photo-induced effects

1. Introduction

Photo-thermo-refractive (PTR) glass is a sodium-potash-zinc-aluminum-silicate glass doped with cerium, silver, fluorine, and bromine that has been used for volume hologram writing for the past 15 years and is described in numerous original papers and several surveys, e.g. [1]. PTR glass exhibits refractive index changes after UV-exposure and thermal development above T_g resulting from the crystallization of about 0.1 wt% sodium fluoride nanocrystals.

It should be noted, however, that after a long-term study of this type of glass, the detailed mechanism of photo-thermo-induced crystallization is still unknown. In this paper, the role of bromine in photo-thermo-refractive glass crystallization is studied. We first introduce secondary ion mass spectroscopy (SIMS) measurements that permit to obtain a quantitative characterization of the relative concentration of bromine in as melt PTR glasses. Then we investigate the effect of bromine concentration on PTR glass crystallization by a combination of non-isothermal differential scanning calorimetry (DSC) and optical spectroscopy. Finally, we present the correlation between bromine concentration and refractive index, water content, and absorption band position of silver containing particles.

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2. Experimental – materials and methods

2.1. Glass sample preparation

Several photosensitive PTR glasses of approximate composition $15Na_2O$–$5ZnO$–$4Al_2O_3$–$70SiO_2$–$5NaF$–xKBr–$0.01Ag_2O$–$0.01CeO_2$ (mol%) were studied in this work. The variable x represents the bromine concentration which varied with values 0, 0.25, 0.5, 0.75 and 1 mol%. We designated these glasses: B0, B25, B50, B75 and B100, respectively. The glasses were melted in an electrical furnace in a 0.5 liter platinum crucible at 1460 °C for 5 h. Stirring with a Pt-blade was used to homogenize the melt. After melting, the glasses were cooled to the glass transition temperature (T_g ~460 °C), then annealed at T_g for 2 h, and finally cooled to room temperature at 0.1 K/min. Polished samples of 2 mm thick and 25×25 mm^2 lateral size were prepared from each melt. It has been previously shown [2] that the optical homogeneity of the samples plays a key role in their crystallization behavior. The homogeneity was thus tested by the shadow method in a divergent beam of a He–Ne laser and was quantified by measurements with a GPI Zygo interferometer. The samples selected for this study have shown refractive index fluctuations of less than 40 ppm (peak to valley variation of refractive index across the aperture).

2.2. Non-isothermal DSC measurements

Thermal analyses were performed by means of Differential Scanning Calorimetry using a Q10 DSC from TA instruments with typical sample weights of 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 designated as the crystallization temperature, T_c.

2.3. Spectroscopic measurements

Optical absorption spectra were determined with a Cary 500 optical spectro-photometer. Spectra were measured in the range from 200 to 3200 nm. In order to avoid any influence of surface contamination or incipient surface crystallization, each sample was re-polished before the measurements.

2.4. Refractive index measurement

Measurement of the absolute local refractive index of each sample was carried out with a Fisher Scientific Abbe refractometer. The precision of each measurement was estimated to be about 100 ppm. Refractive index change due to photosensitivity was measured by an interferometric method described in reference [3].

3. Results

3.1. Measurement of the relative concentration of bromine in melted glasses

Since bromine is a very volatile component, its final concentration is difficult to predict. Therefore, it was necessary to carry out measurements of the final concentration of Br in PTR glass after melting. However, the determination of bromine is not trivial due to its high volatility and its very low concentration. Regular chemical analysis methods could not be applied in order to precisely determine the final bromine concentration in the PTR glasses. It was recently demonstrated that Secondary Ion Mass Spectroscopy (SIMS) can be adjusted for the determination of the concentration of bromine in PTR glass [4]. Relative bromine concentration was directly measured with the use of a cesium primary beam and detection of negative secondary ions. The bromine concentration was then normalized to the silicon concentration in order to compensate for a different ion yield and/or extraction at different locations on the sample. This method does not permit to know the absolute concentration of bromine in PTR glass, but its relative concentration normalized to the concentration of silicon could be determined with high precision, i.e. within a few percent. Thus, SIMS was applied to the measurement of the relative bromine concentration in each glass melt. The bromine concentration was measured at different places on the different PTR glasses and average values and standard deviations were calculated. The evolution of the measured bromine concentration in arbitrary units (counts per minute) is represented as a function of initial bromine concentration in Fig. 1. One can see that measured bromine SIMS signal is proportional to the initial bromine concentration introduced in the batch.

3.2. Influence of bromine on glass crystallization

The influence of bromine concentration on PTR glass crystallization was investigated by non-isothermal DSC.

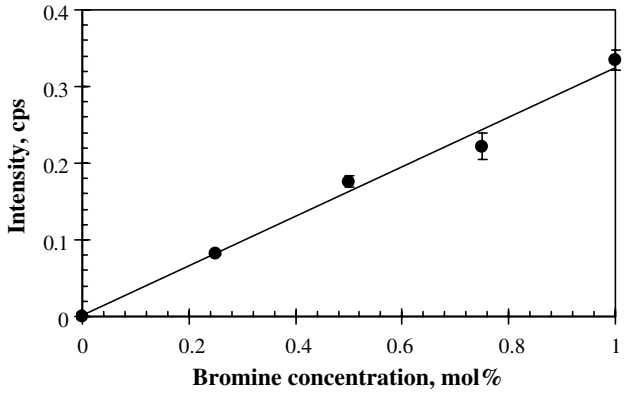

Fig. 1. Dependence of the bromine intensity signal measured by SIMS on initial bromine concentration by synthesis.

Two samples from each melt were considered in this study. The first one was kept unexposed, and the second one was UV-exposed. Previous studies [4] indicated that 0.9 J/cm^2 at 325 nm is an optimum dosage to reach sufficiently high refractive index changes and low optical losses for efficient hologram writing. Therefore, each sample for UV-exposure was exposed to a dosage of 0.9 J/cm^2 at 325 nm. Then heat-treatments were performed to induce crystal nucleation. All the samples were nucleated with the same duration and temperature for 30 min at 510 °C. Finally non-isothermal DSC thermograms were obtained for each of the 10 nucleated samples, which are shown in Fig. 2. First of all, one can see that T_g is almost the same whatever the bromine concentration. Moreover, unexposed glass samples do not show any crystallization peak when the bromine concentration is less than or equal to 0.5 mol%. In the case of UV-exposed samples, no crystallization peak appears if the bromine concentration is less than or equal to 0.25 mol%. Moreover, it is important to note that when crystallization peaks are detected in the range of our measurements, the crystallization peaks for UV-exposed samples are positioned at a lower temperature than the unexposed (homogeneous crystallization) peaks.

3.3. Influence of bromine on refractive index

The influence of bromine on the optical properties of PTR glasses before and after thermal development was studied. Three PTR glasses from each melt were polished. The first samples were kept unexposed and undeveloped. The second samples were also unexposed but thermally developed. The third samples were UV-exposed and thermally developed. For UV-exposure the samples were exposed to a dosage of 0.9 J/cm^2 at 325 nm. Thermal development was carried out with the standard procedure used for holographic optical element recording (i.e. 2 h at 520 °C). Refractive indices were measured with an Abbe refractometer in all types of samples: unexposed and undeveloped, unexposed and developed, and UV-exposed and developed. The dependence of the refractive index on bromine concentration is shown in Fig. 3. One can see that the refractive index of virgin (unexposed and undeveloped) and unexposed and developed samples increases almost linearly with bromine concentration, while the refractive index of the developed samples is slightly lower than to those of the undeveloped samples. The slightly lower index can be assigned to a change of the specific volume of the glass [7]. One can also see that for UV-exposed and thermally developed PTR glass samples the linearity of the refractive index evolution is broken when the bromine concentration is higher than 0.5 mol%. This behavior can be explained by photo-induced crystallization, which occurs in PTR glasses having a high concentration of bromine, and results in a decrease of refractive index.

Absolute measurement of the refractive index, with an Abbe refractometer had an accuracy of 100 ppm. Hence in order to improve the precision with which photosensitivity is characterized, the refractive index difference between UV-exposed and unexposed areas in the same sample was measured with the interferometric setup introduced above. The sensitivity of this interferometer is about 1 ppm (10^{-6}), but only *refractive index differences* can be measured and not the absolute value of the refractive index in each area. No refractive index change was detected in samples having bromine concentrations of 0, 0.25 and 0.5 mol%. This result demonstrates that photo-induced refractive index changes, if they exist, are below 1 ppm. The samples doped with 0.75 mol% of bromine showed a refractive index change of 375 ppm, and the samples doped with 1 mol% of bromine showed a refractive index change of 670 ppm. We found that additional thermal development for 1 h did not change this tendency, i.e. the glass samples having bromine concentration of 0.5 mol% or less showing no crystallization at all and no refractive index change. The higher the bromine concentration, the higher the refractive index changes after thermal development.

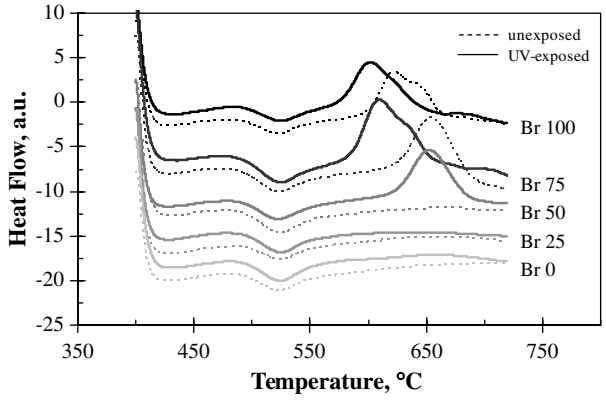

Fig. 2. Non-isothermal DSC spectra measured in pre-nucleated PTR glass samples with different bromine concentration. Solid and dashed lines represent UV-exposed and unexposed samples, respectively.

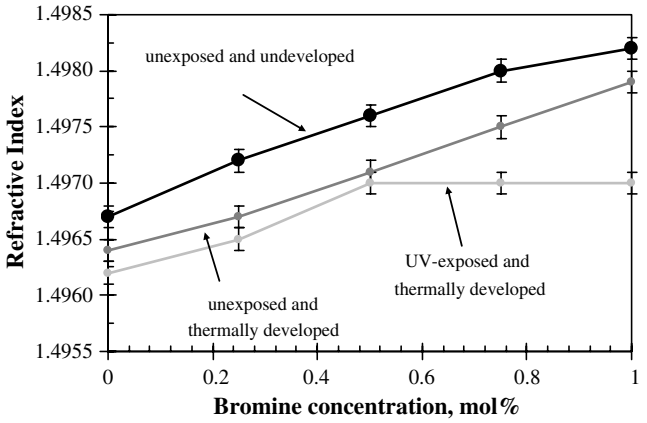

Fig. 3. Dependence of refractive index of PTR glass on bromine concentration (by synthesis).

3.4. Influence of bromine on the absorption spectra

Finally, the influence of bromine on the absorption spectra of PTR glass was studied. We first studied the influence of bromine on unexposed PTR glasses. The absorption spectra were measured in the range 200–3200 nm (Fig. 4). One can see that in the ultraviolet–visible–near-infrared ranges, no important changes appear with the different concentrations of bromine. In the UV, the Ce^{4+} and Ce^{3+} absorption bands are almost the same. In the range 360 nm up to 2.6 μm, no absorption band appears, as expected. The main difference between the measured absorption spectra appears at longer wavelengths. The range of wavelengths from 2.5 μm up to 3.2 μm corresponds to the absorption of hydroxyl groups; see e.g. Ref. [5]. One can see that an increase of bromine induces a decrease of the absorption at these wavelengths from ~0.45 down to ~0.25 cm^{-1}. Hence the increase of bromine concentration induces a decrease of the amount of structural water in PTR glass.

We then studied the influence of bromine on the absorption spectra of UV-exposed and thermally developed PTR glasses. Absorption spectra were measured in UV-exposed (dosage of 0.9 J/cm^2 at 325 nm) and thermally developed for 2 h at 520 °C PTR glass samples having different bromine concentrations (Fig. 5). First of all, it is important to note that UV-exposure associated with thermal development does not produce any visible change of the absorption spectra in the NIR part of the spectra. Hence we limited our spectra (Fig. 5) to the visible range. It is important to note that due to the basic principles of the photo-thermo process, atomic silver will appear and after thermal development form silver containing clusters inducing the appearance of an additional band centered between 400 and 500 nm. However, the exact composition of these clusters is not known. One can see in Fig. 5 that the absorption band of these silver containing particles seems to shift to longer wavelengths with the increase of bromine. In order to confirm this evolution, the position of the maximum of this absorption band was extracted from the absorption spectra by calculations. Then, the evolution of the position of this maximum was plotted as a function of bromine concentration (Fig. 6). These calculations show that an increase of bromine concentration effectively shifts this absorption band to longer wavelengths. Finally, the last effect that can be seen in Fig. 5 is that PTR glasses with bromine concentration equal to or less than 0.5 mol% do not show any significant scattering after UV-exposure followed by thermal treatment; and the higher the bromine concentration, the higher the resulting scattering.

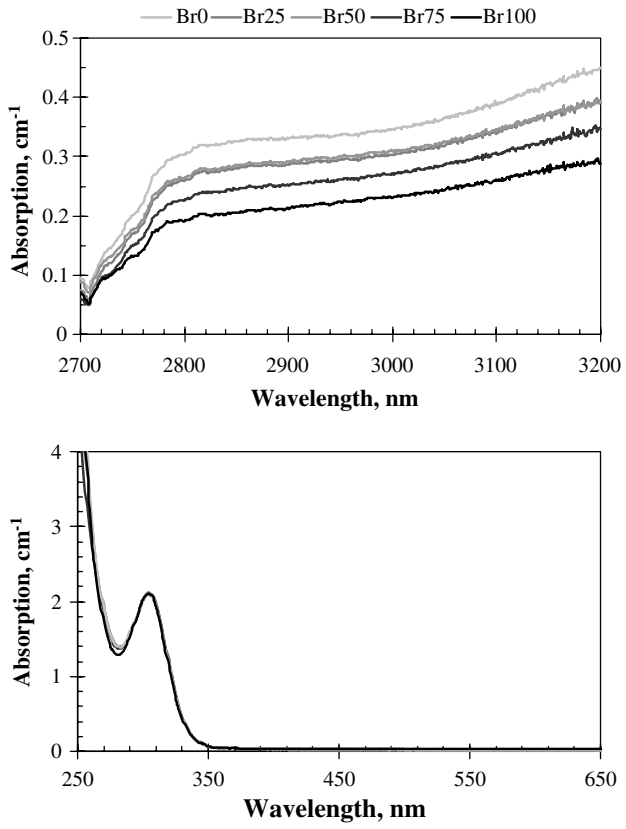

Fig. 4. Absorption spectra of virgin (unexposed and undeveloped) PTR glass samples doped with different bromine concentrations.

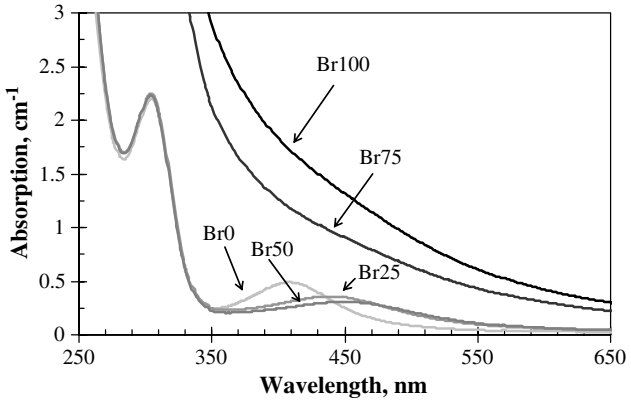

Fig. 5. Absorption spectra of UV-exposed and thermally developed PTR glass samples doped with different bromine concentrations.

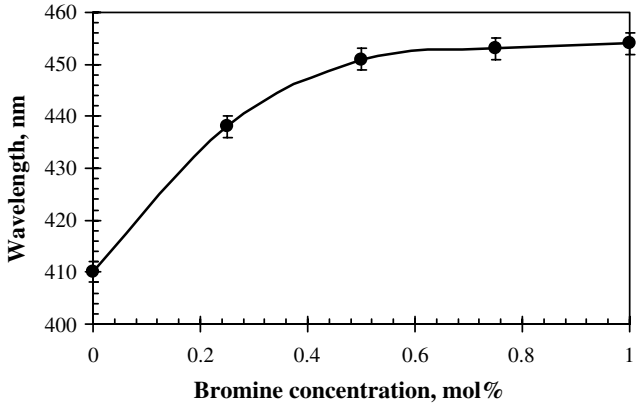

Fig. 6. Dependence of a silver related absorption band peak on bromine concentration.

4. Discussion

We have investigated the influence of bromine on the optical and crystallization properties of PTR glasses. Several PTR glasses with different bromine concentrations were melted in an electrical furnace and characterized. Secondary Mass Ion Spectroscopy (SIMS) was used to determine the actual bromine concentration in the melted glasses. The graph in Fig. 1 shows that after melting, the concentration of bromine in PTR glasses increases almost linearly as a function of initial bromine concentration. Therefore, this result first means that the volatility of bromine is the same in the glass samples and therefore its concentration by synthesis can be used as a relative measure of the actual bromine concentration. Secondly, this result enables us to use the nominal bromine concentration in the batch as a relative measure of the actual bromine concentration in the glass.

The crystallization properties of these glasses with different Br contents were studied by non-isothermal DSC. First of all one can see in Fig. 2 that T_g of glasses with different bromine concentration is almost the same. This independence of T_g on bromine concentration may be due to the fact that its concentration is very low and thus it does not change the glass viscosity significantly. Regarding crystallization, it was previously demonstrated [6] that PTR glasses pre-nucleated for 30 min at 510 °C would exhibit a typical behavior, i.e. the crystallization peak of unexposed glass shifts down to 650 °C, and the crystallization peak of UV-exposed glass shifts down to 600 °C. It was also shown that an additional peak associated to surface crystallization may appear at 625 °C in both unexposed and UV-exposed PTR glasses. Fig. 2 shows that identical behavior occurs in both B75 and B100 glass samples. Crystallization temperatures tend to be slightly higher in B75 than in B100, but this difference is less than 10 K. The striking effect is that if the bromine concentration is equal to or less than 0.5 mol%, unexposed glasses do not show any crystallization peak in the measurement window, and the crystallization peak of the UV-exposed samples also shifts to a higher temperature. Hence, this experiment shows that bromine has a significant impact on the crystallization of UV-exposed PTR glasses, but also on the crystallization of unexposed PTR glasses. This result is very surprising. Actually, the role of bromine on the PTR glass crystallization was recently inferred [6] and it was supposed that bromine plays an important role in the creation of silver containing nuclei in UV-exposed glasses. This experiment proves that bromine also plays a role in the so-called spontaneous crystallization, i.e. it affects the homogeneous crystallization rates of glasses without any UV-exposure. In order to confirm the association of lower bromine concentration with higher crystallization temperature, one PTR glass sample from each melt containing different bromine concentration was developed at a high temperature (600 °C) for several hours. Glasses with bromine concentration of 1 mol% crystallized after a few tens of minutes, glasses with 0.75 mol% crystallized after ~3 h, but glass with no bromine, 0.25 mol% or 0.5 mol% did not crystallize even after 12 h! Observations by optical microscopy showed some very large crystals with dendritic shape in B50 glass, very few crystals in B25, and no crystals in B0. Hence, as observed for fluorine [1], bromine is a key element in both spontaneous and photo-induced PTR glass crystallization processes.

The influence of bromine on PTR glass refractive index and photosensitivity was studied. First of all, Fig. 3 shows that the refractive index increased linearly from 1.4967 up to 1.4982 in virgin PTR glass when bromine concentration increased from 0 to 1 mol%. This linearity confirms that the present glasses effectively contain increasingly higher concentrations of bromine. Fig. 3 shows that whatever the bromine concentration, heat treatment locally decreases the refractive index by more than 2000 pm due to a change of the specific volume of the glass [7].

Finally, photosensitivity characterization is in perfect accordance with the crystallization study. As photosensitivity is directly linked to the crystallization of sodium fluoride crystals, a bromine concentration threshold appears (about 0.5 mol%) under which refractive index change due to photosensitivity does not occur.

Next, the effect of bromine on the absorption spectra was studied. It is first shown that the water content decreases as a function of bromine concentration (Fig. 4). This observation is very important since it is well known that water generally has an important impact on the crystallization kinetics of glasses.

Finally, regarding visible absorption, unexposed samples do not show any difference of absorption with a change of bromine concentration. Regarding UV-exposed and thermally developed PTR glasses, it can be seen that the absorption band of silver containing particles shifts to longer wavelengths when the bromine concentration increases (Figs. 5 and 6). Moreover, it is known that the silver absorption band is centered at about 410 nm [8], and the silver bromide absorption band is centered at about 485 nm [9]. Hence the shift of this absorption band may be tentatively associated with the appearance of silver bromide clusters when the bromine concentration is increased and, therefore, it is due to a competition between the absorption bands of silver and silver bromide. Finally, it can be seen in Fig. 5 that significant scattering only appears for glasses having bromine concentration higher than 0.75 mol%, and that scattering is higher in B100 than in B75. This increased scattering is associated with the appearance of sodium fluoride crystals and, therefore, with the refractive index change. Thus, there is a minimum concentration of bromine which enables crystallization of sodium fluoride in PTR glasses and the resulting refractive index changes after UV-exposure followed by thermal development.

5. Conclusions

PTR glass crystallization highly depends on bromine concentration. A minimum bromine concentration of

0.75 mol% is necessary to induce a crystallization temperature low enough to produce refractive index change associated with small crystals. Refractive index change and water content increase and decrease with bromine concentration, respectively. An increase in bromine concentration results in a shift of the absorption band of silver containing particles to longer wavelengths. This absorption band seems to be the combination of two different bands; the first one due to silver clusters, and the second one due to silver bromide.

Acknowledgements

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