

# Spontaneous and photo-induced crystallisation of photo-thermo-refractive glass

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Photo-thermo-refractive (PTR) glass is suitable for phase hologram recording resulting from photo-thermo-induced precipitation of a sodium fluoride crystalline phase. A detailed knowledge of its properties is necessary for the successful development of optical components. In this paper we present a systematic DSC and spectroscopy study of several (nominally identical) PTR glass melts. These studies revealed that when these glasses are nucleated at temperatures higher than 480°C, the crystallisation peak shifts down to 650°C. For the samples previously ultraviolet exposed and nucleated in the same conditions the crystallisation peak shifts down to 600°C and in both samples another peak appears at 625°C. Thus photo-exposure clearly catalyses crystallisation. It was also found that absorption band of the ultraviolet exposed samples moves from 410 to 485 nm. This shift is tentatively associated with the creation of silver bromide nuclei. Experiments with a ultraviolet exposed bromine-free glass did not show any crystallisation peak up to 720°C, and no absorption peak shift occurred in case of irradiated samples.

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## 1. Introduction

Photo-thermo-refractive (PTR) glass is a sodium zinc aluminium silicate glass doped with cerium, silver, fluorine, and bromine, which was invented many years ago by S. D. Stookey<sup>(1)</sup> for photography and has been studied as a possible candidate for hologram writing in the last 15 years.<sup>(2–5)</sup> PTR glass exhibits refractive index changes after ultraviolet exposure and further thermal development above  $T_g$  resulting from the crystallisation of less than 2 wt% sodium fluoride nanocrystals. Therefore this glass and its resulting phase holograms are attractive for many advanced applications, such as optical filtering<sup>(6)</sup> or spectral beam combining.<sup>(7)</sup> A description of the complex photo-thermo-induced crystallisation mechanisms in PTR glass is given in reference.<sup>(8)</sup> The precise control of PTR glass crystallisation in both ultraviolet exposed and unexposed areas require a deep knowledge of its nucleation mechanisms and kinetics. In this paper, we describe a study of the effect of nucleation treatment in PTR glasses by associating non-isothermal differential scanning calorimetry (DSC) and optical spectroscopy. The first method is used to determine the optimum thermal treatment to enhance photo-induced nucleation and frustrate (or at least decrease) spontaneous nucleation, i.e. crystallisation in unexposed regions of the specimen.

The second technique is used in an attempt to gain a deeper insight into the nucleation mechanism in PTR glass.

## 2. Experimental: materials and methods

### 2.1. Glass sample preparation

Several photosensitive PTR glasses of approximate composition 15Na<sub>2</sub>O–5ZnO–4Al<sub>2</sub>O<sub>3</sub>–70SiO<sub>2</sub>–5NaF–1KBr–0.01Ag<sub>2</sub>O–0.01CeO<sub>2</sub> (mol%) were studied in this work. The glasses were melted in an electrical furnace in 1 l platinum crucible at 1460°C for 5 h. Stirring with a Pt blade was used to homogenise the melt. After melting, the glasses were cooled in air to the glass transition temperature ( $T_g \sim 460^\circ\text{C}$ ), then annealed at  $T_g$  for 2 h, and finally cooled to room temperature at 0.1°C/min. Polished samples of 2 mm thick and 25×25 mm lateral size were prepared from each melt. It has been previously shown<sup>(9)</sup> that the optical homogeneity of the samples plays a key role in their crystallisation behaviour. 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 commercial Zygo interferometer. The samples chosen for this study presented a degree of homogeneity of better than 40 ppm (peak to valley variation of refractive index). Finally, chemical analyses were carried out on all the glass melts that were studied in this paper. However, due to the high volatility of some elements, the presence of light

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elements and the low concentration of dopants, the exact composition cannot be easily determined. These chemical analyses showed that studied PTR glass melts have quite constant composition, very close to the batch composition, excepted for dopants such as fluorine and bromine for example. In that case, the error of the concentration determined by chemical analysis is larger than the real amount.

### 2.2. Non-isothermal DSC measurements

Thermal analyses were performed using a Q10 DSC from TA instruments with monolithic sample having weights of typically 30 mg and a heating rate of 30°C/min. Due to the limited temperature range of our differential scanning calorimeter, we measured thermograms up to 720°C and show the resulting curves in the range 450–720°C. The position of the inflexion of the endothermic peak (the glass transition temperature,  $T_g$ ) was then determined in each spectrum. Similar determination was done for the exothermic peaks, with the position of maximum being denominated as the crystallisation temperature,  $T_c$ .

### 2.3. Spectroscopic measurements

Optical absorption spectra were determined with a Cary 500 optical spectrophotometer. Spectra were measured in the range from 200–800 nm. Finally, in order to avoid any influence of surface contamination or incipient surface crystallisation, each sample was repolished before the measurements.

## 3. Results and discussion

### 3.1. Calorimetric study on PTR glass

Nucleation in PTR glasses was studied with non-isothermal DSC. However, it was previously demonstrated<sup>(9)</sup> that for different PTR glass melts,  $T_g$  is almost the same, but  $T_c$  varies from 660°C to more than 720°C. These large differences can be explained by changes in the concentration of the highly volatile components of the melt such as fluorine or bromine. However, as it was previously mentioned, no chemical analysis permitted us to make a reliable determination of these concentrations in PTR glasses. Therefore, we performed our study for two different melts having widely distinct crystallisation temperatures: melt 1, which has an initial crystallisation temperature equal to 720°C and melt 2, which has a crystallisation temperature about 50°C lower than the first. Then heat treatments were performed to induce crystal nucleation. All these samples were nucleated for 30 min at different temperatures ( $T_n$ ) from 435 to 525°C, with a step of 15°C. After these thermal treatments, a yellowish surface colouration

appeared that was associated with precipitation of metallic silver. Hence each sample was repolished and/or reground to remove this contamination and any incipient surface crystallisation that could have appeared during the preheating, and cleaned. Non-isothermal DSC measurements were then carried out. Figure 1(a) shows the changes in the DSC diagrams of each prenucleated sample from melt 1. First, it is clear that whatever the nucleation temperature,  $T_g$  remains constant and equal to about 498±2°C for all samples. Then, for nucleation temperatures below 480°C, the crystallisation peak does not significantly change from that of the original virgin glass (720°C for melt 1 and 670°C for melt 2). Afterwards the crystallisation peak starts to significantly shift to lower temperatures and a second crystallisation peak appears. Finally, for temperatures above 495°C, the crystallisation trace consists in two nucleation induced crystallisation peaks: one at 650±5°C and a second one at 625±5°C appear. This second peak can be associated with some kind of surface crystallisation. It is important

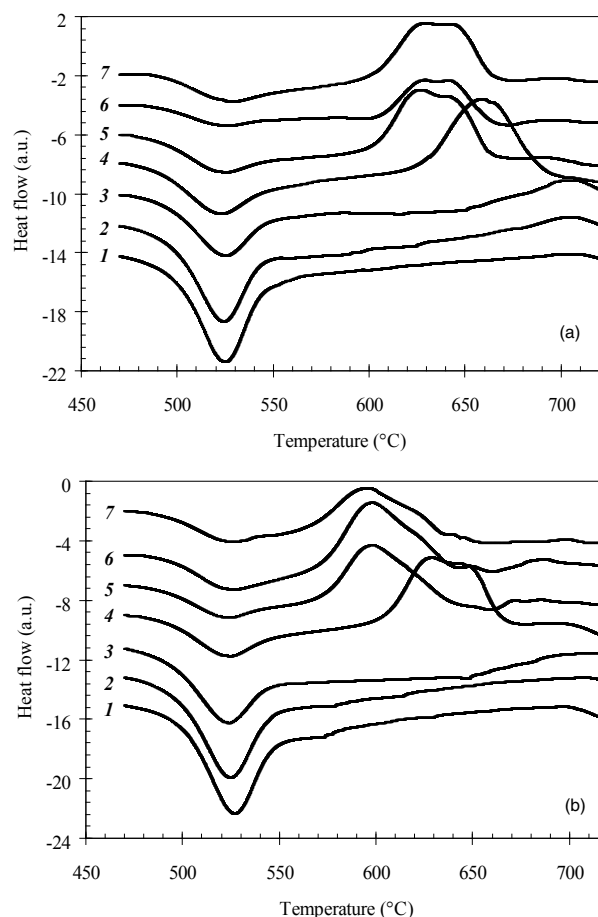


Figure 1. (a) DSC diagrams of melt 1, unexposed and nucleated for 30 min at different temperature from 435°C (curve 1) to 525°C (curve 7) with a step of 15°C. (b) DSC diagrams of melt 1, ultraviolet exposed and nucleated for 30 min at different temperature from 435°C (curve 1) to 525°C (curve 7) with a step of 15°C

to stress that the shift to lower temperature (650°C) of the crystallisation peak was observed for both melts. Therefore, nucleation for 30 min at temperatures over 495°C catalyses nucleation and permits the glass to reach the same regime of overall crystallisation, whatever the original glass melt is. Moreover, this thermal treatment will also permit one to have the most efficient nucleation in PTR glass, due to the fact that the minimum crystallisation temperature has been reached.

Since PTR glass is a photosensitive material, the effect was studied of nucleation temperature on the overall crystallisation temperature of ultraviolet exposed samples. Melts 1 and 2 were used again, and were first ultraviolet exposed with a Helium-Cadmium laser (325 nm, 4 mW). Previous studies<sup>(4)</sup> indicated that 0.9 J/cm<sup>2</sup> is an optimum dosage to reach high refractive index changes and low optical losses for efficient hologram writing. Therefore, each sample was exposed to the same dosage. Then these samples were nucleated by the same method for the same times and temperatures, (i.e. 30 min at different temperatures from 435–525°C). Finally identical sets of DSC measurements were carried out for each sample. Figure 1(b) shows how spectra change for different nucleation temperatures (melt 1). First of all, these spectra show that ultraviolet exposure by itself (i.e. without further thermal treatment) did not shift  $T_g$ . Regarding the crystallisation temperature; ultraviolet exposure induces a small shift of the peak to lower temperatures, but it is less by than 5°C. When the samples are nucleated at a temperature below 480°C, the crystallisation peaks does not undergo any significant shift. For higher temperatures (e.g. 30 min nucleation at 480°C), the crystallisation peak starts to shift and reaches a minimum for nucleation temperatures above 495°C. This variation of the crystallisation peak of ultraviolet exposed glass is very similar to the changes observed in non exposed glass, and has the same critical temperatures. However, for ultraviolet exposed glasses, the minimum

crystallisation temperature is much smaller and equal to 600±5°C. Moreover, this change in of the crystallisation peak is identical for both melts. Finally, a second crystallisation peak caused by some kind of surface crystallisation also appears at 625±5°C, in ultraviolet exposed glass, for nucleation temperatures over 480°C.

The aim of this study is to reveal these details and to find a way to enhance photo-induced crystallisation and to frustrate spontaneous crystallisation. The thermal nucleation step permits us to improve the separation between these two types of crystallisation.

### 3.2. Spectroscopic study on PTR glass

Spectroscopic measurements were carried out in parallel with the calorimetric experiments. The optical and crystallisation properties of PTR glass were then compared. Absorption spectra were recorded from 200–800 nm just after nucleation. Figures 2 (a) and (b) show the changing spectra for different nucleation temperatures for (a) unexposed and (b) ultraviolet exposed samples.

First, we describe these absorption spectra. For unexposed samples, the absorption spectra show two absorption bands. The first one is the band centred in the far ultraviolet region and is linked to the presence of Ce<sup>4+</sup>, Sb<sup>3+</sup> and Ag<sup>+</sup>. However, the maximum cannot be measured due to its high intensity. The second absorption band is due to Ce<sup>3+</sup> and is centred at 305 nm. No matter what the nucleation temperature is, no noticeable changes in the absorption spectra are observed. In the case of ultraviolet exposed glasses, low temperature nucleated samples were yellowish. The higher the nucleation temperature, the more red the glass became. Absorption spectra show three distinct absorption bands. The first two are identical to that of unexposed glasses; they are a signature of cerium, but have different intensities due to the change of the ratio between the two oxidation states.

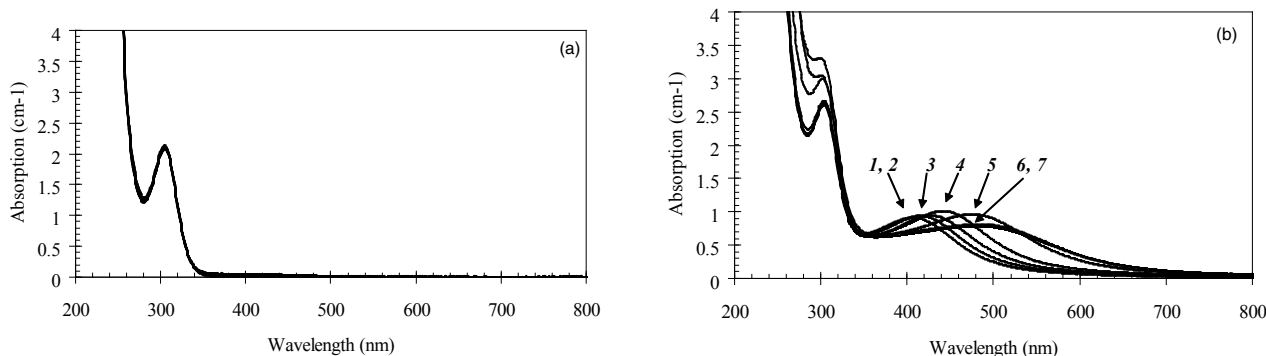


Figure 2. (a) Absorption spectra of unexposed PTR glasses nucleated for 30 min at different temperatures from 435–525°C with a step of 15°C. Spectra are identical for all melts and nucleation temperatures. (b) Absorption spectra of ultraviolet exposed PTR glasses nucleated for 30 min at different temperatures from 435°C (curve 1) to 525°C (curve 7) with a step of 15°C

The third one will be discussed later. It is originally centred at 410 nm and is linked to the presence of silver colloids in this glass. Moreover, this peak changes with temperature. For temperatures below 465°C, the peak slowly shifts from 410 up to 425 nm with a slow increase of intensity. Then, at 465°C, this peak shifts to 440 nm and saturates at about 485 nm when the temperature reaches 495°C. This peak stops shifting to higher wavelengths (it even starts to shift back to lower wavelengths) and its intensity starts to decrease. It is interesting to note that in case of melts, 1 and 2, the peak position is an identical function of temperature for both melts.

The origin of the peak centred between 400 and 500 nm was studied in more detail. First of all, this peak shifts and broadens when the temperature of thermal treatment is increased. Moreover, we know that this peak is directly linked to the presence of silver colloids in this glass. Therefore, if these particles are composed of pure silver, an explanation for this change could be an increase in the silver particle size with nucleation temperature and duration. This idea also allows us to explain why optical losses are systematically observed at longer wavelengths after heat treatment, such as 1 µm (increase of scattering due to the growth of the silver particles). However, other type of particles such as silver bromide could also explain such an absorption band. As a matter of fact, silver bromide shows an absorption band centred at about 485 nm, and which has a long tail that goes beyond 1 µm.<sup>(10)</sup> This effect was previously seen in photochromic glasses.<sup>(11)</sup> When the authors replaced chlorine by bromine, they noticed that the induced absorption extends to a longer wavelength. Hence, in order to have a better idea about the origin of this peak in our glass, its composition was changed. A modified PTR glass without bromine was melted with the same procedure described in part two. Then, several samples were cut and polished and their homogeneity was measured. Two samples were ultraviolet exposed with identical dosage to that previously used. One sample was then nucleated for 30 min at 435°C, and the other one was nucleated for 30 min at 510°C. Finally, nonisothermal DSC curves and absorption spectra were measured. In the case of nonisothermal DSC, we first measured the DSC curve of virgin glass, and compared it with the curves obtained with nucleated glasses. In all cases, no crystallisation peak appeared in our measurement

window. Moreover, the absorption spectra did not show any shift of the studied absorption band, but just an increase of its intensity. Therefore, bromine seems to play a key-role in the nucleation process and also in the origin of the band being studied.

#### 4. Conclusions

Non-isothermal differential scanning calorimetry measurements associated with spectroscopic characterisation of two photo-thermo-refractive glasses were conducted. This study revealed that even if some non-uniformity exists in the non-isothermal crystallisation temperature of the as made PTR glass samples, due to variations in chemical composition, heat treatments used as a prenucleation process permits one to homogenise the crystallisation behaviour of the glass in both unexposed and ultraviolet exposed PTR glass samples. Spectroscopic analysis revealed a parallel between the crystallisation temperature of PTR glasses and the chemical composition. The change of crystallisation temperature is correlated with a shift of an absorption band situated in the 400–500 nm range. Experiments carried out with bromine free PTR glasses indicate that this peak may be associated with the appearance of silver bromide particles that act as nucleation centres.

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