Nano-Structured Optical Glasses

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Abstract—A variety of oxide glasses and glass-ceramics that contain thermally or optically developed nanostructures will be described along with the properties that derive from the nano-phase, or structural rearrangement. The derived properties include photosensitive, photochromic, photo-adaptable color, photorefractive (induced refractive index), photo-machinable, and polarizing.

I. Introduction

Oxide glasses provide a wide range of static optical properties, like color, refractive index, dispersion, deep UV transparency to name a few. One can extend the range of properties by adding components to the glass that can be ultimately be phase separated from the matrix glass by an appropriate thermal treatment. The generic term glass-ceramics could be applied. Here for the most part the particle size of the developed phase is on the nanometer scale rendering the glass essentially transparent in spite of relatively large refractive index mismatch. The bulk of what will be discussed here involves the development nano-phases of Ag-halide, LiF, or Li-metasilicate. From these phases and with in most cases an additional optical treatment the following properties can be exhibited; photosensitive, photochromic, photo-adaptable color, photorefractive, photo-machinable, and polarizing to name the most interesting. Although we will not discuss them here, where the separated phase is crystalline then the incorporation of rare-earth or transition metal ions for laser and amplifier applications is possible.

II. List of Glass Systems and Derived Properties

In Table 1 we list the matrix glass system(s), the phase separated component, and the property exhibited. We will proceed to give examples of the properties listed above in the Table with a brief explanation of what physical processes are involved in the process as well as the some of the applications.

A. Photosensitive glasses

Class of alkali silicate glasses (sufficient non-bridging oxygen) that incorporate Ag^{+1} Au^{+1} or Cu^{+1} at a level of 0.01-0.1% and a photosensitizing agent usually Ce^{+3} at a level of 0.03% into the glass composition. Light exposure into the absorption of the Ce^{+3} (310nm) followed by a thermal treatment produces an image formed by Ag, (Au) nanoparticles as shown in Fig. 1.

Figure 1. Example of Ag-based (top) and Au-based photosensitive glasses

B. Augmented Photosenstive (Photorefractive and Photo-machinable)

The nanoparticles produced in the process described above can in select glasses be nucleation sites to effect phase separation leading to the formation of a nano-crystalline phase. In one case a NaF phase is produced where the particle size of the NaF nanocrystal can be controlled by the thermal treatment rendering the exposed region either opaque or transparent. In the latter case the refractive index of the exposed region is lowered, so that high resolution diffraction grating structures can be made. In Fig. 2 is shown an example of both the photo-written opaque effect and a hologram produced from the transparent effect.

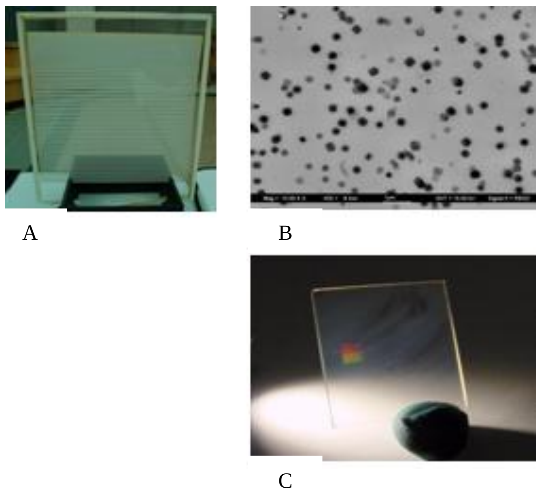

Figure 2 NaF-based glasses. (A) opaque pattern, (B) fine grain particles leading to transparency, (C) hologram made from B-type samples.

Classification	matrix glass	derived phase	property
Photosensitive[1,2]	Alkali silicate	Ag, or Cu	Photo-induced color patterns
Photochromic[3,4,]	Alkali borosilicates	Ag or Cu-halides	Reversible darkening
Polarizing[5]	Alkali borosilicates	Elongated Ag or Cu-halides +(reduction)	Waveplates polarizers
Photoadaptive[6]	Alkali borosilicates	Ag halides	Change color corresponding to exposure color
Photorefractive[7]	Alkali silicate	NaF	UV-induced refractive index change after HT
Photrefractive[8,]	Ge-silicate	Structural rearrange	Direct deep UV induced index change
Photo-machinable[2]	Li-alumino silicate	$Li_2O.SiO_2$	Preferentially etched And lens arrays

Table I Summary of Phenomena.

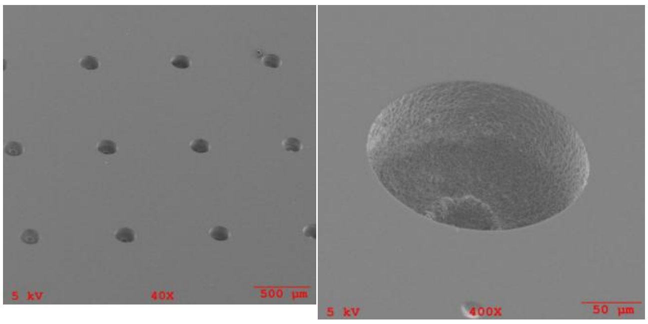

Figure 3 Example of photo-machinable Fotoform ™.

In another example the glass the phase produced that is photo-nucleated is a Li-meta-silicate phase. This phase develops an overlapping dendritic morphology which is 20 times more soluble in acid than that of the unexposed glass leading to a method to photo-machine patterns. An example of making wells using this material is shown in Fig. 3. Another utilization of this material/process as a consequence of the fact that the crystalline phase is denser than the unexposed glass is able to fabricate microlenses [9]. The method involves exposing through a mask where a circular region is blocked. During the thermal treatment to 600C the denser surround squeezes the soft glass out and surface tension produces the spherical surface (Fig. 4).

C. Photocromic

There are a special class of glasses that allow the incorporation of Ag and halogens then when thermally treated form a nano-dispersion of silver-halide particles. Analogous the photographic process, when exposed to UV-blue light the glass darkens from the absorption produced by the photo-reduction of Ag on the Ag-halide particle. This darkening and fading behavior is shown in Fig. 5.

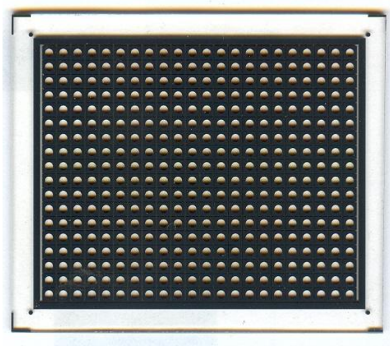

Figure 4 Example of lens array.

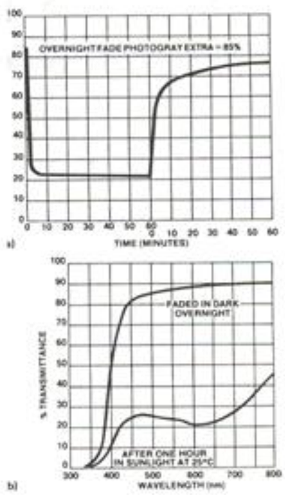

Figure 5 Example of darkening and fading of a photochromic glass.

Unlike the photographic process the absorption in this case is reversible because the hole is not trapped so it can diffuse and ultimately recombine with the reduced Ag.

D. *Polarizing Glass*

The process described above for the formation of Ag-halide nanoparticle in glass was the basis for another useful optical material, namely a polarizer. After the Ag-halide phase is produced by the thermal development the glass is reheated while being subjected to a load (uniaxial stress) at around the softening temperature. This elongates the glass and in the process applies a shear stress to the then liquid Ag-halide particle causing it to elongate. Upon cooling one the elongated Ag-halide is frozen in as an elliptical shape the extent of elongation (aspect ratio) is dependent on how much stress was applied. The elongated silver halide particle is then chemically reduced to Ag-metal by a thermal treatment in pure H_2. The anisotropy in shape produces two distinct absorption bands corresponding to the two surface plasmon resonances, parallel and perpendicular to the long axis of the particle as shown in Fig. 6. Using this process one is able to make polarizing glass with >50db extinction over the 800-2000nm wavelength range. (Polarcor™)

E. *Photorefractive*

Photorefractive in this context refers to permanent UV-induced refractive index changes in glass. In Table I we have listed two different glasses and the methods by which the photorefractive effect is achieved. The first is related to the glass mentioned in section B as that where a NaF nano-phase is photo-initiated. By a slight modification of the composition and a different thermal development schedule one can maintain the nanoparticle small enough to render the glass transparent. Because the refractive index of NaF is 1.32, the exposed and thermally developed region will have an overall lower refractive index than the unexposed region; order of 10^{-4} to 10^{-5}. The permits holographic patterns to be made (see Fig. 2C) The other photorefractive glass has an entirely different mechanism from the one described above. It is based on the Fiber Bragg Grating (FBG) phenomenon. The mechanism has been much conjectured, especially the augmented molecular H_2-impregnated version, but it inarguably involves the optical alteration of Ge bonding in the otherwise silica network.[10]We have exhibited the bulk glass version of this phenomenon; that is we made basically a $xGeO_2$-$(1-x)SiO_2$ composition. The exposure uses a spatially filtered KrF 248nm laser through a silica phase mask to produce the grating. The induced refractive index that can be achieved is of the order of 0.001. An example of a grating performance made on the glass is shown in Fig. 7.

F. *Photoadaptive*

This behavior refers to phenomena whereby the glass color or state of polarization is altered permanently by the exposure to light. In an alkali boro-silicate glass one can initiate a process that is essentially a combination of the photochromic and photosensitive mechanisms described above. The glass after

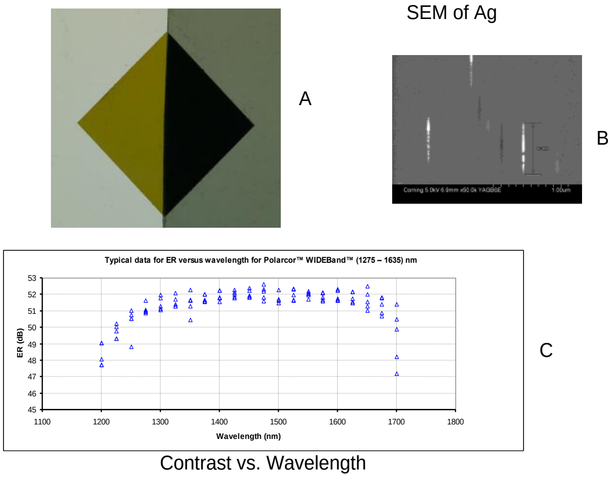

Figure 6 Polarizing glass; (A) visual contrast, (B) SEM of elongated silver particles

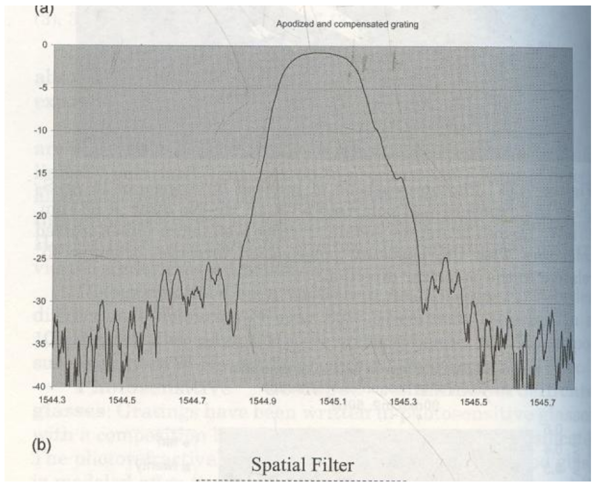

Figure 7 example of the performance (db vs. wavelength) of a grating made in the Ge-silicate glass.

heat treatment develops an Ag-halide phase; (blue curve in Fig. 8B and lowest band of Fig. 8A). The absorption feature is attributed to silver nanoparticles on the Ag-halide particle. Exposure to Hg-lamp (310nm) produces a pink color (middle band of Fig. 8A) which is not reversible (yellow curve of Fig. 8B);.This corresponds to some kind of rearrangement of the Ag on the Ag-halide particle; (note the appearance of two absorption peaks) Exposure to a black light 365nm source produces a reversible photochromic effect (not shown). Further exposure to a pulsed 355nm laser produces yet another altered absorption state (pink curve of Fig. 8B and upper band in Fig. 8A) which is a "bleaching" effect. A dichroic behavior can be produced by an exposure to the polarized Ar-ion 508nm laser (Fig. 8C).

III. Discussion

We have described a wide variety of optical effects in a number of glasses attributable to photo-thermal induced nanostructures in the respective glass. What is common to all of them derives from the fact that glass presents a multi-component system from which a number of stable and meta-stable phases can be produced either thermally, or by a combination of heat and light. These induced phases often, more than not impart changes in either the optical, chemical, or mechanical properties from the mother glass. A number of the above glasses showing the derived properties have been commercialized under trade names like *Photogray Extra™ Fotoform™ FotaLite™ and Polarcor™.* Clearly because of limited space detailed description of the different phenomena is not possible. In any event the references attached will contain more detail. Ref. [10] below contains material relevant to a number of the effects discussed in more detail.

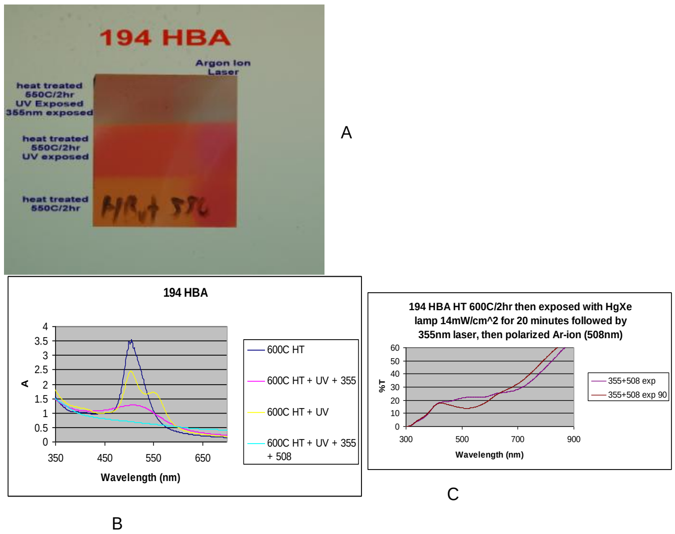

Figure 8 Examples of the photo-adaptive behavior, (A) color change as noted and described in text, (B) corresponding absorption spectra for the conditions noted, (C) evidence of dichotic behavior when bleached.

ACKNOWLEDGMENTS

The author thanks the members of the technical staff of the Corning Incoporated research laboratory, both past and present for their contribution to this paper.

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