Properties and Characteristics of Optical Glass II

Alexander J. Marker III
Chair/Editor

12–13 July 1990
San Diego, California

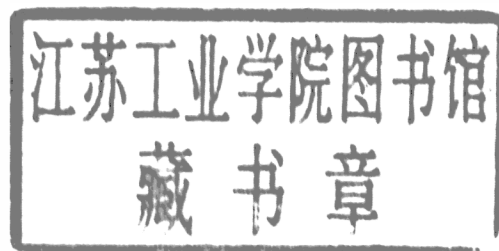# Properties and Characteristics of Optical Glass II

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Volume 1327

PROPERTIES AND CHARACTERISTICS OF OPTICAL GLASS II

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INTRODUCTION

Glass is a remarkable optical material. With applications across the electro-magnetic spectrum from the far ultraviolet to the far infrared, this optical material is unique in that it can be engineered to meet design requirements. This capability to be tailored can be seen in processing, interactions with radiation, nonlinear applications, and fiber optic applications.

By tailoring the glass composition, one can alter the microstructure, formation of defects, luminescence, crystalization and viscosity, as well as the more common physical properties such as refractive index and dispersion. Numerous examples of these engineered glasses are discussed in this proceedings.

An important parameter for optical engineers is the refractive index of the optical material. Homogeneity of the refractive index as well as the determination of the refractive index itself via holographic interferometry are discussed along with a more conventional method of measuring the index from the ultraviolet through the near infrared.

I would like to thank all the cochairs and authors who have made this conference on optical glass a success.

Alexander J. Marker III
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PROPERTIES AND CHARACTERISTICS OF OPTICAL GLASS II

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SESSION 1

Processing and Measurement Techniques

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Hydrogen-induced absorption in glasses containing arsenic and antimony

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ABSTRACT

Borosilicate, potassium and sodium silicate and potassium borate glasses containing small quantities of As_2O_3 and Sb_2O_3 darken from the surface when exposed to H_2 in the glass transformation range. The depth of surface darkening is a function of time, temperature, and H_2 pressure. Change in absorbance at constant wavelength increases with time but shows neither linear nor square root dependence on time. In addition, the absorbance change (λ = constant) does not show Arrhenius behavior as a function of treatment temperature, but instead appears to approach saturation.

The same phenomena are observed for D_2 treatments. Absorbance change at 300 nm from the H_2 treated sample under identical temperature and pressure conditions differs by a factor of the square root of 2. Relative permeability of H_2 and D_2 is given by the square root of their mass ratio, i.e. $\sqrt{2}$. This finding suggests a direct proportionality between the induced-absorption and the permeability of the diffusing species.

The coloration is attributed to the reduction of the fining agent (As/Sb) and is accompanied by an increase in the hydroxyl concentration in the glass. The effect of base glass permeability, fining agent identity and fining agent concentration on the optical absorption will be discussed. Metallic colloidal scattering is proposed as the mechanism for the coloration. Evidence to support the mechanism is presented and discussed.

2. INTRODUCTION

Lens' designed to collimate light and produce apertures for cameras and scopes[1] contain a central region of transmitting glass with a perimeter which absorbs energies in the visible region of the spectrum. Heat and applied pressure are traditionally used to fuse a dark glass cladding to a clear glass core to make a single component for this use.

Recent studies[1,2] have discovered a method for producing surface darkened materials which achieve the same objective. Glasses containing 0.2 to 10.0 wt% addition of As_2O_3[2] and Sb_2O_3[1] are treated in an H_2 atmosphere at temperatures in the glass transformation region. This process eliminates the interface imperfections and pitting, etc., which result from polishing a core/clad unit.[1]

A number of H_2 induced-absorption processes have been reported.[3-8] The optical absorption has been found to result from tungsten bronze centers[3,4] in tungsten phosphate glasses, reduction of elements such as iron in soda-lime-silicate glasses[5] and ceramics[6], reduction of silver to form silver colloids[7], and reduction of lead to form lead colloids.[8] The present H_2 induced-absorption process is similar to the other processes[3-8] in that the absorbing region grows from the surface of the sample with increasing time of exposure to hydrogen. The difference found in this process is that the change in absorbance with treatment time is neither linear with treatment time nor with the square root of treatment time.[2] In addition, Kohli et. al.[2] found that the absorption process does not follow Arrhenius behavior as a function of treatment temperature but appears to approach saturation with increasing temperature.

Studies of the characteristics and mechanism of the induced-absorption process began with a commercial borosilicate glass containing ≈0.25 wt% addition of As_2O_3. Preliminary experiments were conducted using the commercial glass and a similar borosilicate laboratory melt. The present study considered the parameters which influence the rate and intensity of the induced-absorption in simple alkali borate and silicate compositions in order to define the relative roles of various experimental variables. This paper reports and discusses the effect of base glass composition, fining agent identity, concentration and mixture, and sample thickness on the rate of formation and intensity of the induced-absorption. A permeation-controlled reduction mechanism leading to the formation of metallic colloids, which cause the optical absorption process, will be proposed and discussed.

3. EXPERIMENTAL PROCEDURE

A variety of glasses were considered in this study. These glasses include the commercial borosilicate glass used by Kohli et. al. [2] and borosilicate, simple potassium borate, and potassium silicate glasses prepared in our laboratory. These glasses were melted in platinum crucibles. The compositions of undoped glasses are listed in Table I. Alumina was added to the borate glasses to increase their chemical durability. Three variations of each glass were made; dopant free, arsenic doped, and antimony doped. Most experiments were conducted using 0.25 wt% addition of dopant (as found in the commercial glass). Deviation in dopant concentration will be noted for the applicable experiments. Samples for spectral measurement were prepared by cutting 1.0 to 2.0 mm slices and polishing using standard techniques.

Table I. Laboratory base glass compositions studied (mol%).

Oxide	A	B	C	D	E
SiO_2	65.46	--	--	80.0	80.0
B_2O_3	19.94	79.2	74.25	--	--
K_2O	12.94	19.2	24.75	20.0	--
Na_2O	--	--	--	–	20.0
Al_2O_3	1.66	1.0	.1.0	–	--

Samples were placed in a vitreous silica tube that was attached to a gas treatment apparatus which allows evacuation to $\approx 10^{-8}$ kPa and desired gas atmospheres with pressures up to ≈ 100 kPa. A preheated tube furnace was placed over the evacuated silica tube. The interior of the tube reached the desired temperature in ≈ 10 minutes. The last 20 K of heating was completed in less than 2 minutes. After the interior reached the specified temperature, H_2 gas was introduced into the tube to the desired pressure (93.3 kPa unless otherwise stated). Treatment time periods were cumulative. Unless otherwise stated, the data were measured in a geometrical progression of hours (i.e. 1, 2, 4, 8, etc.) Since treatment times were much longer than the time for samples to cool (< 100 K in 2 to 3 minutes), cooling times were neglected.

Spectra were measured using a Varian uv-vis-nir Model 2300-Spectrophotometer in an "absolute" mode with the reference cell empty. The change in the absorbance was measured after each treatment time and the absorbance change relative to that of the same sample prior to treatment was calculated from these data. Infrared spectra were measured using a Mattson 2020 FTIR spectrometer to assess hydroxyl formation.

X-ray diffraction patterns were measured for solid samples of composition A with >4 wt% dopant, which had been treated in H_2 at 600 °C for more than 120 hours, to determine if crystals exist in the treated glasses.

Permeation measurements were made for deuterium gas using the equipment and procedure described previously.[9] Deuterium was used due to high system background from hydrogen. The permeation coefficient, K, of composition D was determined from the steady-state flow rate of gas through the sample as determined by a mass spectrometer. The details of the experimental procedure are discussed elsewhere.[8] Permeation coefficients for glasses of composition B and C are currently being measured; no results have yet been obtained. Samples were sliced and polished to 0.3 mm thicknesses. They were also pre-reacted with deuterium to eliminate effects due to isotope exchange with the hydroxyl in the glasses.

4. RESULTS

Optical spectra of treated glasses exhibit the same general shape; i.e. a broad absorption tail extending from the ultraviolet to the near infrared region of the spectrum. Fig. 1 shows the absorption spectra of glass B with a dopant level addition of 0.25 wt%, treated in H_2 for 128 hours at 455 °C (T_g=410 °C). Note the higher absorbance of antimony, for the same concentration of dopant. Fig. 2 emphasizes the increased intensity and shows the increased absorption rate for the antimony doped glass. Since greater detail of the absorbance change/time behavior was desired, more frequent measurements were taken for the antimony doped sample. This revealed that there appears to be a period of induction in the coloration process prior to onset of linear behavior. The curve through the As_2O_3 doped sample was drawn as a dashed line merely to show the relative rate of the induced-absorption due to different dopant identities.

Fig. 3 shows a comparison of the rate of coloration of compositions B, C, D and E. The glasses were treated at temperatures appropriate to make an iso-viscosity comparison. Compositions C and D have very similar coloration rates, with C slightly greater than D. Composition E colors slower . Composition B, however, is clearly the slowest darkening

glass. The curve for composition D is, again, a result of more frequent measurements. It suggests that there is a further effect of composition on the shape of the absorbance change/time behavior. The permeation coefficient for composition D and E are 4.5×10^8 and 2.5×10^8 molecules/s-cm-atm respectively, at 200 °C. Although the treatments are conducted at higher temperatures, the relative permeabilities will be the same since although the permeability temperature curves may converge, they will never cross. Measurement of the permeation coefficients for compositions B and C may also further indicate whether there are other factors of the matrix glass which influence the coloration rate that occurs for a particular dopant.
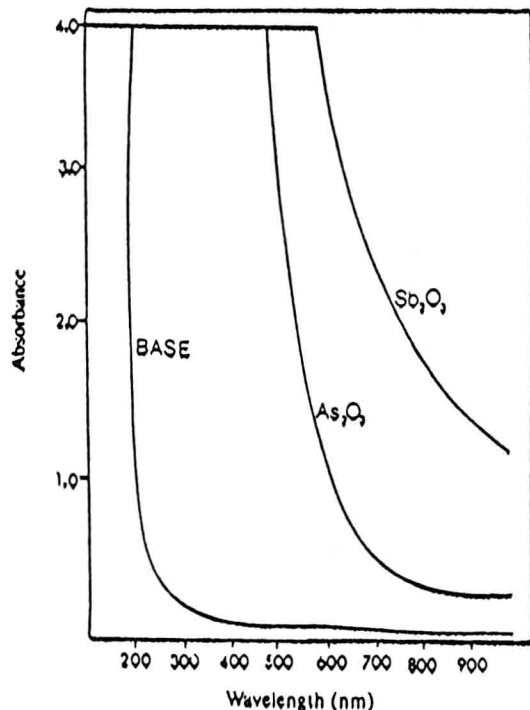
Fig. 1. Absorption spectra of composition B; base glass, As_2O_3 doped and Sb_2O_3 doped.
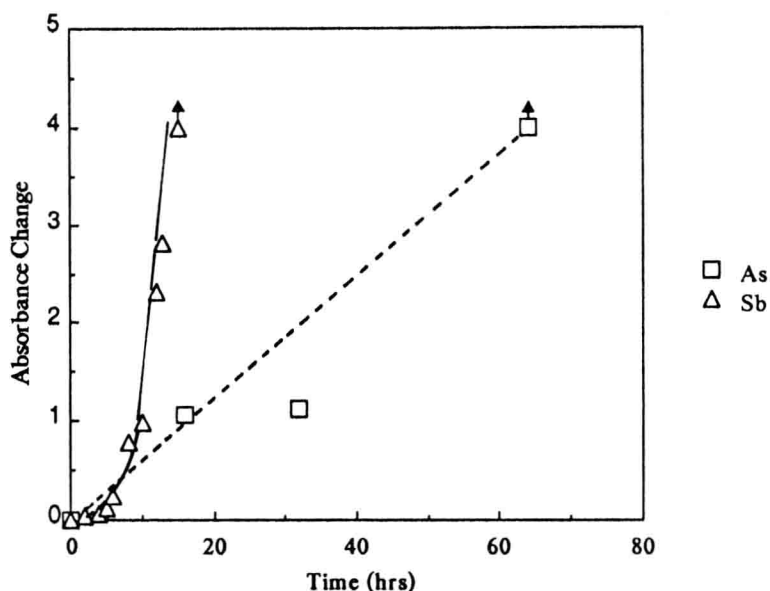
Fig. 2. Absorbance change versus time at 300 nm for Composition B with different dopants.
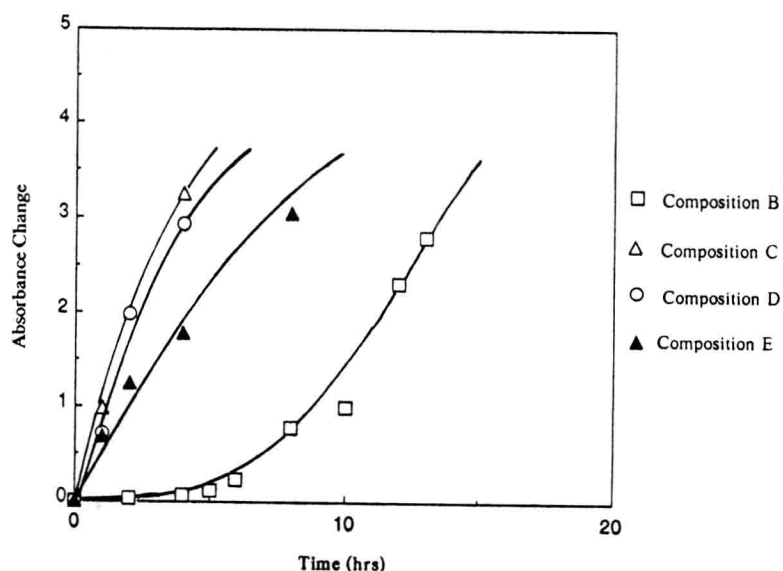
Fig. 3. Comparison of Absorbance change characteristics of glasses doped with 0.25 wt% Sb_2O_3.

Samples of composition B were prepared for comparison of the effect of fining agent concentration with dopant levels of 0.25, 0.5, 1.0, 2.0, and 4.0 wt.% additions of Sb_2O_3. The 0.5 data presented are mean and standard deviation of 5 samples treated simultaneously to allow assessment of error inherent in the measurement. These glasses were treated in H_2 at 455 °C. Fig. 4 shows the absorbance change versus time for each dopant level. As expected, increasing the concentration of the dopant increases the intensity of induced-absorption. The increase appears to have some limiting value since the 2.0 and 4.0 wt% additions produce nearly the same absorbance change characteristics. The 0.5 wt% data indicates, again, that there is an induction period. Error in the measurement technique indicates that at small times data are fairly accurate, while at longer times and greater absorbance changes, the error is significant. Note, however, that error is not great enough to negate the dopant concentration trend. No curves were drawn for the 1.0 and 0.25 wt% data due to insufficient data for accurate shape determination.
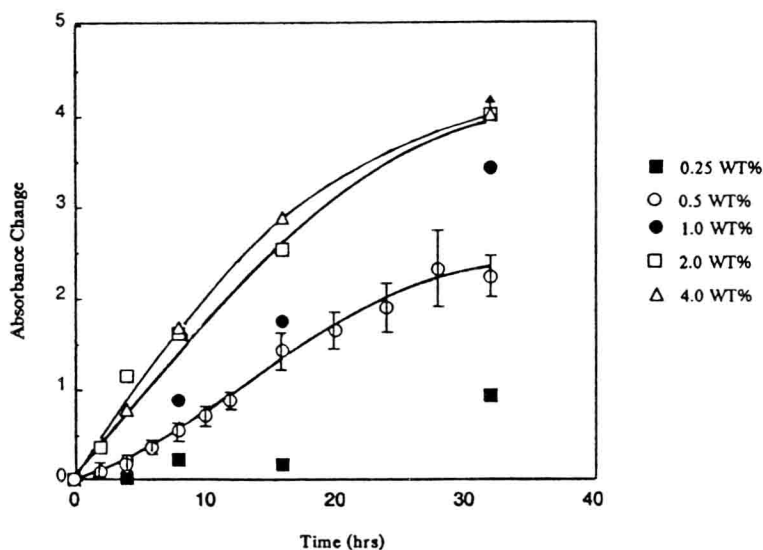
Fig. 4. Absorbance Change at 600 nm for potassium borate glass with different concentrations of added Sb_2O_3.

Composition B was also used to examine the effect of mixing dopants. Three doped glasses were compared. The first glass contained 0.5 wt% As_2O_3, the second 0.5 wt% Sb_2O_3, and the third a mixture of 0.25 As_2O_3 + 0.25 Sb_2O_3 wt% additions. Surprisingly, instead of additive behavior, mixing dopants shows only a marginal increase in the coloration rate of the glass from that of the As_2O_3 doped glass (fig. 5).
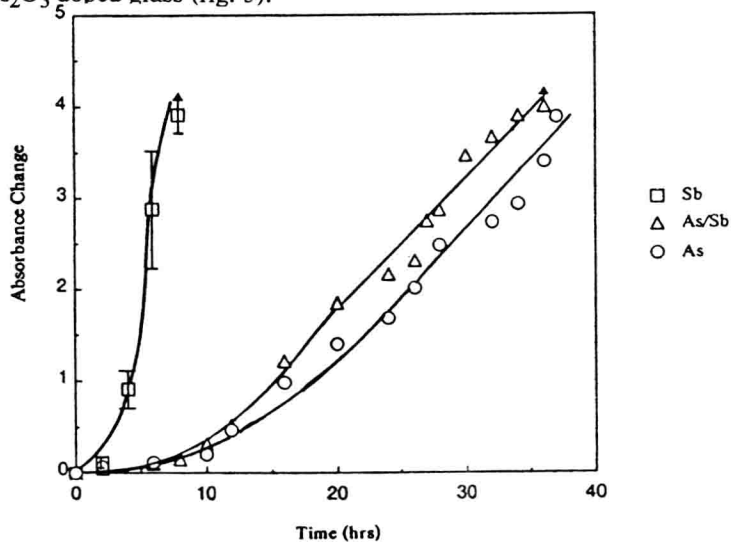
Fig. 5. Absorbance change of Composition B with 0.5 wt% additions of Sb_2O_3, As_2O_3, and an equal mixture of As_2O_3 + Sb_2O_3.

The commercial borosilicate glass was used to compare differences in the absorbance change/time characteristics for treatment in hydrogen and deuterium. Figure 6 shows the spectra obtained for each sample after 8 hours of treatment at 605 °C. The ratio of the absorbance change at 300 nm for H_2/D_2 is approximately 1.40 which is very near the theoretical value of $\sqrt{2}$ predicted for the diffusion coefficients of these gases. For a chemically controlled reaction, the isotopes would produce the same change in absorbance since they are chemically identical. These results strongly suggest a permeation controlled reaction.
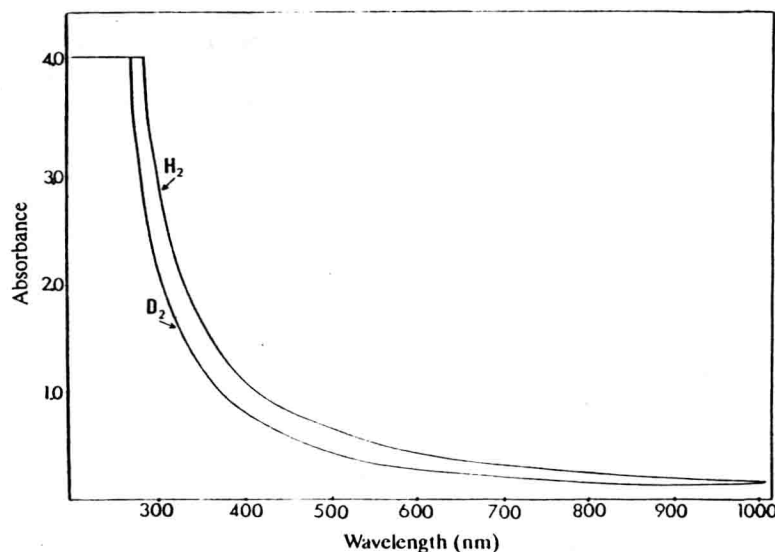
Fig. 6. Comparison of absorption spectra for the commercial borosilicate glass treated in H_2 and D_2.

Fig. 7 shows the infrared spectra of a glass of composition A, doped with ≥ 4.0 wt% Sb_2O_3, treated for various times. The formation of hydroxyl is noted with the increase in intensity of the bands at ≈ 3200 cm^{-1}. Hydroxyl formation was not detected in glasses with small dopant concentration.
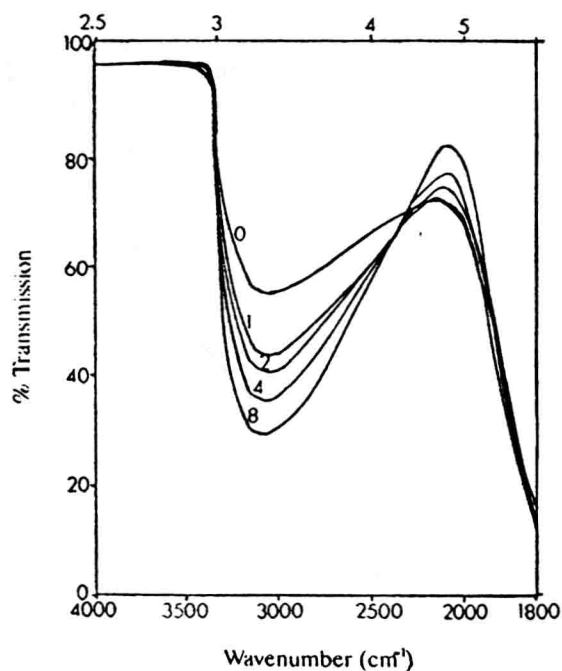
Fig. 7. Infrared spectra of Sb_2O_3 doped composition A at 0,1, 2, 4, and 8 hours to show hydroxyl formation.

Absorbance data versus $1/\lambda^4$ was plotted (fig. 8). The linearity of this plot suggests Rayleigh scattering behavior, which in turn, suggests a colloidal scattering mechanism.
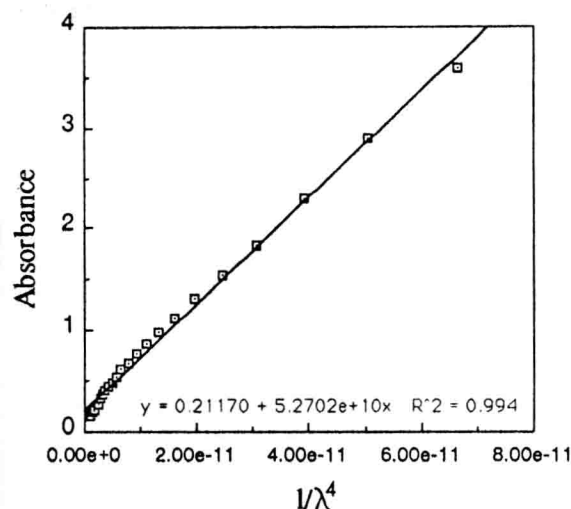
Fig. 8. Absorbance versus $1/\lambda^4$: Rayleigh Scatter behavior.

Figure 9 shows the x-ray diffraction pattern obtained for a heavily heat treated antimony doped glass of composition A. The diffraction pattern indicates metallic antimony and strongly supports the contention that the scattering sites in these materials are metallic colloids. The pattern obtained for the arsenic doped glass, although treated for the same time period and conditions, which also produced an opaque sample, remained characteristic of an amorphous material.
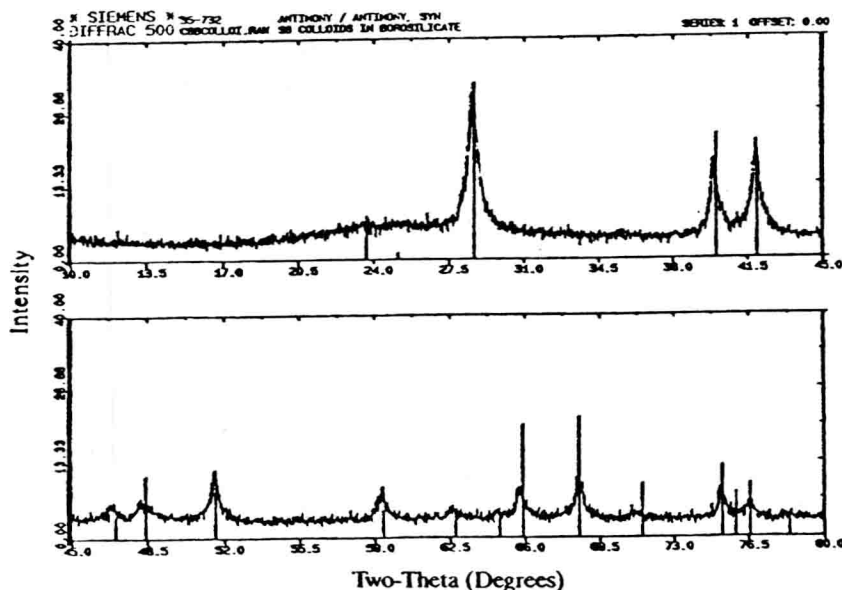
Fig. 9. X-ray diffraction pattern of ≥ 4.0 wt% Sb_2O_3 doped composition A after long H_2 treatment.

5. DISCUSSION

The proposed absorption mechanism of colloidal scattering from metallic As and Sb is strongly supported by the results of this study. The reactions which occur are a reduction of the 3^+ and 5^+ states to the elemental state, i.e.

$$2As^{3+} + 3H_2 = 2\ As^{\circ} + 6\ H^+$$

$$2\ As^{5+} + 5H_2 = 2As^{\circ} + 10\ H^+$$
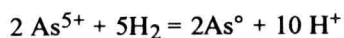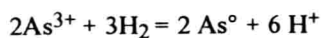
with analogous reactions for antimony. Other work[10] indicates that, for glasses of equal thermal history, the ratio of the 3^+ to 5^+ states is greater for antimony than for arsenic. Given the proposed mechanism, it would take a longer period of time to reduce arsenic than antimony to the metallic state, which would explain the greater coloration rate for Sb_2O_3 doped compositions.

Increased absorption change with increased dopant concentration should result from a higher concentration of ionic sites per unit volume, and thus per unit depth, in the glass. Therefore, although the absorption change with time is increased, the depth of coloration per absorbance change value is decreased. It is speculated that there are two controlling factors for the induced-absorption process. Initially, the process is controlled by the permeation of H_2 through the glass to the ions. At some later time, dictated by the differences between the activation energies, the diffusion of metal atoms to form colloids becomes the controlling process. This may be one reason for the limited increase in coloration versus dopant concentration. Asymptotic behavior of data taken at 600 nm may be attributed to one of two things. First, the color may be due to the size and/or shape of the colloids. Ellipsoidal colloids produce split band absorptions; the absorption which occurs when the electric vector of the light is parallel to the long axis of an oblate colloid moves toward longer wavelengths as the particle becomes more highly elongated and the absorption perpendicular to the long axis moves to shorter wavelengths. The other possibility is that there is an actual saturation in the coloring; the measurements at relatively long wavelengths are taken at long time periods.

The cause of the lack of an additive coloring rate in a glass containing a mixture of dopants from that of As_2O_3 and Sb_2O_3 doped glass at the same total concentration can only be speculated. The authors suggest two possible reasons. Considering the above hypothesis, one possibility is that there is an interference of the two types of diffusing metal species thus decreasing the total metal that reacts and forms colloids. Another possibility is that there is an interaction between two simultaneous redox reactions, decreasing the rate at which each goes to completion. It is also a possibility that a combination of these things is occurring.

Hydroxyl formation as a result of H_2 treatment is consistent with the proposed reduction model. The H^+ formed during treatment reacts immediately with neighboring oxygen atoms to form OH^- as shown previously.[5] It is believed that glasses with small quantities of dopant do form OH^- during treatment, but that the quantities formed are too small to detect.

A previous study[11] presented an x-ray pattern which was inconclusively attributed to metallic antimony. The degree of peak broadening due to suspected small colloid size was sufficient to raise doubt of the pattern assignment. The same glass (composition A) was treated for a longer period of time and gave the diffraction pattern shown in figure 10. The degree of peak broadening was reduced due to colloid growth and hence more peaks were discernable; a conclusive assignment was made. It has been shown[12] that lead colloids form large ($\approx 0.15\ \mu$) metallic colloids following reduction in H_2. It is speculated that there is a trend toward increasing colloid size, given equal treatment times, with a progression down group VB in the periodic table. More work is needed to prove this hypothesis. Lack of sufficient colloid size is, however, suggested as a possible reason for the absence of an x-ray diffraction pattern in the arsenic doped sample.

6. CONCLUSIONS

From this study it can be concluded that the rate at which glasses doped with antimony darken is greater than that at which those doped with arsenic darken, at equal dopant concentrations. In addition, the rate was also found to be dependent on the base glass composition and dopant concentration. Furthermore, mixing the dopants does not produce additive induced-absorption single dopant compositions. Glasses with higher concentrations of dopant were also shown to form hydroxyl during the darkening process. This is consistent with the confirmation of metallic colloids as the source of Rayleigh scattering coloration from a reduction of the dopant ions.

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Primary and Secondary Phase Separation in GeS_2 - La_2S_3 Glasses

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ABSTRACT

GeS_2 is known to be a good chalcogenide glass former with a transmission cut off at $11\mu m$ and has been studied for its application in the mid infrared region. The rare earth sulfides (La-Er) form reasonably good and stable glasses when mixed with other chalcogenides such as Ga_2S_3. In this work, glass formation was studied in the GeS_2-La_2S_3 system. Two compositions containing 60 mol% and 92.5 mol% GeS_2 respectively were studied, and the effect of composition on the microstructure and thermal stability of these glasses were investigated. Microstructural analyses were performed on the as prepared and heat treated glasses using TEM and SEM/EDXA. Glasses rich in GeS_2 exhibited primary (6-80 nm) and secondary (3-13 nm) phase seperation at the molecular level. Differential thermal analysis performed on these glasses indicated glass transition temperatures (T_g) of 590°C and 420°C for the two compositions studied. The glasses were stable and the (T_g) was observed to decrease with increasing contents of GeS_2 in these glasses.

1. INTRODUCTION

Chalcogenides are compounds whose anions are from group VI of the periodic table, i.e., oxygen, sulfur, selenium, and tellurium. In vitreous systems, the term chalcogenide is commonly used incorrectly to distinguish sulfide, selenide, and telluride glasses from oxide glasses.

The nonoxide chalcogenide glasses transmit to longer wavelengths than oxide glasses[1]. They are very good glass formers and the glass forming tendency in these glasses varies in general as S > Se > Te, As > P > Sb, Si > Ge > Sn, mainly because of the large size of the anions. They are convalently bonded materials and form glasses with long chain networks. The non-oxide chalcogenides are typically weak solids with low hardness and low softening points when compared with normal oxide glasses[2] resulting from the small difference in the electronegativities of the metal-chalcogen bond.

Electronegativity difference itself can be taken as a rough measure of the bond energy between two atoms. It is known that ionically bonded materials have large differences in electronegativity in comparison with covalently bonded solids. A pure covalent bond will