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Determination of the absorptivity of OH in a sodium borosilicate glass

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The absorptivity of OH in a sodium borosilicate glass has been determined. The method consisted of measuring the weight loss and the decrease in absorbance at 2825 nm after heat-treatment of polished slices of glass in a dry nitrogen atmosphere. The confusion in the literature involving "water" content and OH content of glasses is also discussed.

1. Introduction

The presence of chemically bound water as hydroxyl groups in inorganic glasses causes an absorption at about 2800 nm due to the fundamental OH antisymmetric stretching vibration. The first and second overtones of this absorption occur at about 1400 and 930 nm, respectively.

Optical communication systems are expected to use gallium arsenide or gallium aluminium arsenide laser diodes or LEDs as optical sources, at least in initial deployments. These devices emit in the wavelength range from 820 to 900 nm depending upon composition. Therefore, the short wavelength tail of the second overtone of the OH absorption is likely to cause unwanted absorption in the wavelength region of interest if "wet" glasses are used to fabricate the optical waveguides which carry the signal.

Thus it is useful to know the absorptivity for OH so as to be able to calculate the "water" content. Values have been reported for vitreous silica [1] and vitreous boric oxide [2], but no information is available for borosilicate compositions. Since sodium borosilicate glasses are of interest for optical waveguide fabrication, it was decided to determine the absorptivity for a representative composition.

Initially, attempts were made to diffuse water into a polished slice of glass. The intensity of the fundamental OH absorption at 2800 nm would be determined before and after treatment and the increase in water content would be determined by weighing. Unfortunately, this method failed because the risk of chemical reaction between the water and the glass surface at high temperatures and high humidities caused uncertainties in the sample weights. It was therefore decided to diffuse water out of the samples by high temperature heat-treatment of "wet" glasses in a dry nitrogen atmosphere over relatively long time periods, and record the spectra and sample weight before and after heat-treatment.

2. Glass preparation

The glass, of composition SiO_2, 45; B_2O_3, 35; Na_2O, 20 mol%, was prepared by melting together reagent-grade powdered silica, boric acid and sodium carbonate, in a clear fused silica crucible* at 1200° C. A wire-wound electrically heated pot-furnace was used. After all the starting materials had been crudely melted, a fused silica bubbler tube was inserted into the melt and a stream of oxygen (460 cm^3 min^{-1}) saturated with water vapour was bubbled through it. This served to ensure that the glass was "wet" and also provided a mixing action so that a reasonably homogeneous glass resulted. The bubbling was continued for 2 h, after which the glass was allowed to fine at 1200° C for 3 h in a wet oxygen atmosphere. The molten glass was then cast into a heated brass mould and cooled slowly from 700° C to room temperature. Slices 2.5 cm × 2 cm × 0.15 cm were cut from the block and were ground and polished to final thicknesses of about 0.02 cm.

3. Mass spectroscopic examination

Since it was planned to measure water loss by

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*TO-8, Amersil Inc, Sayreville, NJ, USA.

weighing before and after heat-treatment, it was necessary to determine exactly what chemical species were given off on heating.

The mass spectrum of the evolving species was therefore measured [3] as a function of temperature from 120 to 990° C. At temperatures up to 770° C, water was essentially the only species evolved.

4. Experimental procedure

Previous investigations [2, 4, 5] of water in B_2O_3 glass have shown that an absorption band at 3100 nm overlaps the 2800 nm band. The 3100 nm absorption is attributed to the OH stretching vibration in H_3BO_3 which is formed on the glass surface by reaction with atmospheric water.

In order to ensure that this effect would not be a problem in the present work, identical slices of our glass were ground and polished using water as the lubricant in one case and a dry halocarbon oil in the other. The spectrum of the 2800 nm band was recorded for both samples. The spectra were identical and the 3100 nm band was not detected in either sample, indicating that the glass surface did not react with water to any appreciable degree in the time taken to carry out the experiment.

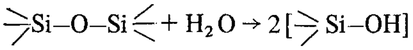
Each polished slice of glass was cleaned with water, dried, and the 2800 nm absorption band was recorded using a Perkin-Elmer Model 283 infra-red spectrophotometer. Multiple determinations were made in most cases on different areas of each slice in order to be able to average out concentration inhomogeneities. The samples were then cleaned again for 5 min in 50:50 acetone: chloroform in an ultrasonic bath, followed by an acetone rinse and two de-ionized water rinses. The glass slices were then placed in a platinum holder and inserted carefully into a horizontal furnace with a fused quartz muffle tube. The furnace was maintained in the temperature range 490 to 500° C, the highest temperature the samples could withstand without sagging. After 15 min, it was assumed the surfaces were dry, and the samples were removed and allowed to cool. The slices were then weighed to the nearest microgram.

The samples were then replaced in the furnace. Samples E, F and G were heat-treated in the furnace for 330 h and H, J, and K for 280 h. During this time a slow stream of clean dry nitrogen was passed through the furnace tube. After the heat-treatment, the samples were removed, allowed to cool, then reweighed under exactly the same conditions as before.

The spectra were then redetermined using the same conditions as before. In order to be able to calculate the molar absorptivity it was necessary to know the density of the glass. This was measured using the Archimedes method of displacement of carbon tetrachloride. The average of three values was 2.495 g cm^{-3}.

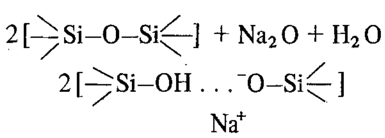
5. Results and discussion

Current thinking, which is the same as described by Adams and Douglas [6], is that each molecule of water which is introduced into a silicate glass results in the formation of two OH groups according to the reaction:



$$\equiv Si-O-Si\equiv + H_2O \rightarrow 2[\equiv Si-OH]$$

for bridging oxygens, or:



$$2[\equiv Si-O-Si\equiv] + Na_2O + H_2O \rightarrow 2[\equiv Si-OH\ldots{}^{-}O-Si\equiv]\ Na^+$$

if sodium oxide is also added. In the latter case, the OH groups are hydrogen-bonded to the singly bound oxygens. In both cases one hydroxyl group is formed completely from the water molecule and the other from an oxygen already present in the glass and the remaining hydrogen from the water. Thus we may write:

$$H_2O_{gas} + O_{glass} \rightarrow 2OH_{glass}$$

so that on a weight basis, 18 parts of water will result in the formation of 34 parts of OH in the glass. Similarly, the removal of water will result in the "destruction" of OH in this same ratio.

The absorbance values, A were obtained from the spectra by the baseline method, by drawing the baseline tangential to the spectral curve at 2675 and 3345 nm then reading the peak height at 2825 nm. Table I shows the data obtained on six slices of glass.

The values of the absorptivity $a_{(OH)}$ were calculated from the expression:

$$a_{(OH)} = \frac{\Delta A \times W \times 18}{t \times \Delta W \times 10^6 \times 34}\,\mathrm{cm}^{-1}$$

where ΔA is the difference in absorbance before and after heat-treatment, ΔW the loss in weight due to water removal before and after heat-

TABLE I

Sample	weight W(g)		$\Delta W(\mu g)$	Region sampled	Absorbance A		ΔA	Sample thickness (cm)	Absorptivity (cm^{-1}) $a_{(OH)}$	Molar absorptivity (litre mol^{-1} cm^{-1}) $\epsilon_{(OH)}$
	Before	After			Before	After				
E	0.230 059	0.230 020	39	1	0.268	0.247	0.021	0.0193	0.0034	23.1
				2	0.263	0.239	0.024	0.0190	0.0039	26.9
F	0.183 315	0.183 278	37	1	0.260	0.226	0.034	0.0189	0.0047	32.2
				2	0.250	0.220	0.030	0.0182	0.0043	29.6
G	0.276 669	0.276 637	32	1	0.314	0.285	0.029	0.0232	0.0057	39.0
H	0.267 780	0.267 753	27	1	0.324	0.305	0.019	0.0232	0.0043	29.3
				2	0.313	0.296	0.017	0.0221	0.0040	27.5
				3	0.293	0.276	0.017	0.0212	0.0042	28.7
J	0.189 213	0.189 185	28	1	0.242	0.221	0.021	0.0173	0.0043	29.6
				2	0.215	0.194	0.021	0.0149	0.0050	34.4
				3	0.197	0.176	0.021	0.0137	0.0055	37.4
K	0.285 308	0.285 275	33	1	0.317	0.297	0.020	0.0226	0.0041	27.6
				2	0.316	0.299	0.017	0.0228	0.0034	23.3
				3	0.331	0.311	0.020	0.0238	0.0039	26.2

treatment (g), W the sample weight (g), and t the sample thickness (cm). This formulation gives values of $a_{(OH)}$ based on OH concentrations in the glass in parts per million by weight.

The average value of the absorptivity is $a_{(OH)} = 0.0043\ cm^{-1}$ with a standard deviation of ± 0.0007.

Using the measured density of the glass and converting the OH concentration from ppm to mol $litre^{-1}$, the values of molar absorptivity for OH were calculated. The average was found to be

$$\epsilon_{(OH)} = 30 \text{ litre mol}^{-1} \text{cm}^{-1}$$

with a standard deviation of ±5.

In his paper on water in B_2O_3 glass [2], and binary alkali borate glasses [7], Franz makes his calculations of absorptivity on the basis of H_2O rather than OH contained in the glasses. This has been pointed out by Pasteur [8]. If the factor of two is applied to Franz's results [7] for a borate glass containing 20 mol % Na_2O, a value of about 38 litre mol^{-1} cm^{-1} is obtained for the molar absorptivity of OH, which is of the same order as our result of 30 litre mol^{-1} cm^{-1} Williams *et al.* [9] have studied the absorptivity of "water" in a variety of glass compositions by a mass spectrometric technique. The compositions they examined all contained fairly high percentages of silica. Two of them (Corning 7740 and 7251) were sodium borosilicates containing 2 wt % Al_2O_3 and 81 wt % SiO_2. They obtained values of 55 and 56 litre mol^{-1} cm^{-1} for the molar absorptivity based on H_2O rather than OH contained in the glass. Again applying the factor of two, we obtain values of 27.5 and 28 litre mol^{-1} cm^{-1} for the absorptivity of OH, which is in good agreement with our result of 30 litre mol^{-1} cm^{-1}. However, it is by no means certain that the agreement should be that good in view of the large differences in the composition of the glasses being compared.

It is not possible to compare our results with those of Stephenson and Jack [1] on water in fused silica, since although they quote a "% wt loss" on heat-treatment *in vacuo* in their Fig. 2 as 0.125% and state that this is "assumed to be water", in a companion publication [10], Hetherington and Jack refer to this same concentration as wt % (– OH) (their Table 2) and quote [1] in the text.

It would be desirable to have this confusion cleared up since Dodd and Fraser [11] have used Stephenson and Jack's molar absorptivity value of 77.5 litre mol^{-1} cm^{-1} as the basis for a method of calculating the OH concentration in samples of fused silica. The results obtained by this method may be in error by a factor of two.

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