The Effect of OH^- on the Low Frequency Dielectric
Constant of Vitreous Silica*

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ABSTRACT

The 1000 Hz, 300°K dielectric constant, ϵ_s , of twenty-four kinds of commercially available vitreous silica has been measured to an accuracy of 0.01% and a precision of about 1 part in 300,000 by the method of substitution (two-fluid technique). The observed dielectric constant ranges from 3.8073 to 3.8304. These results are correlated with hydroxyl ion content and other imperfections. It is found that $\epsilon_s = 3.8073 + 2.72 \times 10^{-22} N$ where N is the hydroxyl concentration in ions/cm³, and observed deviations from this rule are attributed to metallic impurities and inclusions. From the results, it appears that 3.8073 closely approximates the low frequency dielectric constant of pure vitreous silica.

INTRODUCTION

Vitreous silica¹ has played a prominent role in recent technology by virtue of its useful optical transmission characteristics and its low thermal expansion coefficient. Scientifically, it is probably our most widely studied amorphous solid.

One parameter that has not been particularly well determined for this material is the low frequency dielectric constant, ϵ_s . Literature values of ϵ_s for vitreous silica range from 3.70 to 4.00. These values were most likely determined using geometrical techniques which can result in errors of greater than 1%.

The present paper reports the results of measurements two orders of magnitude more accurate, obtained by a two-fluid method, the method of substitution,² which is often referred to as the two-fluid technique.³ The low frequency dielectric constants for twenty-four kinds of commercially available fused silica were determined.

PROCEDURE AND RESULTS

The Amersil, General Electric 151, and some of the Corning samples were obtained from the respective manufacturers. It is not certain that these G.E. samples are Type 151 since they were purchased with no numeric designation. However, since they were purchased several years ago and since they are distinct from Types 101, 124, and 125, the conclusion was drawn that they are Type 151. The remainder of the Corning, along with the two Dynasil samples, were purchased from the Muffoletto Optical Co. of Baltimore, Md. The Japanese Industries and the remainder of the G.E. samples were obtained from Bond Optics of Lebanon, N.H. All of the samples were in the form of 25 mm diameter disks approximately 1.6 mm thick.

The 1000 Hz, 300°K dielectric constant for each disk was measured by the method of substitution (two-fluid technique) using apparatus described previously by the authors.⁴ The present set of measurements differs from the previous work in that a capacitance bridge constructed by one of the authors (C.A.) was used in place of the General Radio Type 1620-A. The results are listed in Tables I-III.

As a test of the reproducibility, measurements on two samples, a Suprasil W-2 and an Optosil 2, were repeated.

The values in parentheses are the remeasured values. The values are seen to be reproducible to better than one part in 300,000. It is also significant that the values of ϵ_s for all three of the Suprasil W-2 samples are within one part in 300,000 of one another. This figure, then, gives an indication of the precision of the measurements. The reason for the high precision is that the dielectric constant of vitreous silica is close to that for castor oil, one of the fluids used in the measurements, and hence most of the random errors associated with sample geometry are greatly reduced due to the fact that the samples almost "disappear" in the castor oil. (Dielectric constant matching is, of course, a technique which is sometimes used in dielectric constant determinations.)

While the precision approaches 0.0003%, systematic errors leave the absolute dielectric constant uncertain at about the 0.01% level.²⁻⁴ Between samples, however, variations of up to 0.6% are observed. As an attempt to explain these results, the hydroxyl ion content, N, was determined for each of the samples using the equation:⁵

$$N = \frac{d}{t} \times 7.77 \times 10^{18} \frac{\text{ions}}{\text{cm}^3} \quad (1)$$

where d is the optical density at 2.72 μm and t is the

sample thickness in cm. The optical density was determined using a Perkin-Elmer 257 spectrophotometer. The calculated values of N are listed in the tables and are thought to be accurate at about the 3% level.

Further information on the level of imperfections can be gained from the room temperature dielectric loss, $\tan \delta$, of the samples since it has been suggested that this quantity possibly reflects the presence of aluminum in vitreous silica. A reasonable approximation to $\tan \delta$ for the samples is given by $\tan \delta$ of the Simplex oil-sample combination since the samples are of rather uniform thickness and fill the gap of the substitution cell almost completely. This quantity is listed in the tables under the heading "Approximate $\tan \delta$."

DISCUSSION

The values for N and ϵ_s are plotted in Figure 1. It is evident that there is, indeed, a correlation between hydroxyl ion content and the observed low frequency dielectric constant. Not only are the values of both ϵ_s and N grouped for the various types of vitreous silica, but also in general the dielectric constant increases with increasing hydroxyl ion content both within and between the groups. The most important example of this behavior is the Suprasil W-Suprasil system. Since these fused silicas are produced from the same synthetic raw material, the basic difference between these glasses is the hydroxyl ion content. (There may be other differences because of the leaching process used on Suprasil W. In particular this could cause differences in halide ion content. No specific information is available on halide ion content at the present time.) The Suprasil W samples are essentially "water" free and show a characteristic dielectric constant of about 3.8073. Suprasil 1(2) on the other hand contains about $8.16(8.55) \times 10^{19}$ hydroxyl ions/cm³ and shows a dielectric constant of just under(over) 3.830. This is not a density effect since, if anything, the density tends to decrease slightly with increasing hydroxyl ion concentration.⁶

The Corning samples show a similar trend. In fact, as shown in Figure 1, the straight line:

$$\epsilon_s = 3.8073 + 2.72 \times 10^{-22} N \quad (2)$$

fits both the Suprasil and Corning data quite well. This might be expected since Corning 7940 is made from a pure, synthetic silicon dioxide similar to that used for the Suprasils. It then follows that:

$$\frac{d\epsilon_s}{dN} = 2.72 \times 10^{-22} \frac{\text{cm}^3}{\text{ion}}$$

represents the effect of the hydroxyl ion concentration on ϵ_s for fused silica and that 3.8073 is close to the ϵ_s for pure vitreous silica. The data for both the G.E. 151 and the Dynasil samples lie close to the line. This implies that these materials were manufactured using techniques and materials similar to those used to produce the "wet" Suprasils and the Corning 7940's. The actual details, however, are unknown to the authors.

It is noted, however, that the data for eleven of the remaining twelve kinds of vitreous silica lie above the line. It is significant that all eleven are produced from

naturally occurring rock crystal. Thus, the low frequency dielectric constant reflects the difference between the vitreous silicas produced from natural and synthetic starting materials. This difference is most likely due to metallic impurities, the most abundant being aluminum. As mentioned previously, the room temperature $\tan \delta$ of the samples is probably correlated with the aluminum content of the samples. The values of $\tan \delta$ for the pure synthetic materials support this assertion in that they are essentially zero with the exception of a few Corning 7940's. The authors have observed surface effects in the case of the Corning samples which might account for these deviations. The remaining samples also provide supporting evidence. In Figure 2 $\tan \delta$ is plotted vs. the deviation of the dielectric constant, $\Delta\epsilon_s$, of the remaining eleven samples from the reference line. (The loss of one sample out of twenty-nine, a G.E. 124 fused quartz, appears to be anomalous and consequently was not plotted.)

It is obvious that there is, indeed, a correlation between the $\tan \delta$ and $\Delta\epsilon_s$ and hence most likely between aluminum content and $\Delta\epsilon_s$. In addition, it appears that the Ultrasil and Japanese Industries samples contain concentrations of still other imperfections. A rather complete analysis of several samples would be necessary to make further comments

on these effects. This will be done in conjunction with experiments which are currently underway to determine the temperature, pressure, and frequency variation of ϵ_s for these materials.

One material, T08 Commercial fused quartz, however, lies below the reference line. Amersil quotes a rather large concentration of inclusions for this material, and it is conceivable that the lowering of ϵ_s could be connected with this or associated properties.

Thus, the deviations from Eq.(1) can be explained by imperfections other than the hydroxyl ion. This further substantiates the assertions that $d\epsilon_s/dN = 2.72 \times 10^{-22} \text{ cm}^3/\text{ion}$ reflects the effect of the hydroxyl ion on the low frequency dielectric constant of vitreous silica and that 3.8073 is close to ϵ_s for pure vitreous silica.

CONCLUSIONS

It has been shown that the effect on ϵ_s of hydroxyl ions in pure vitreous silica can be written as:

$$\epsilon_s = 3.8073 = 2.72 \times 10^{-22} N \quad (1)$$

Most of the deviations from Eq.(1) have been correlated with $\tan \delta$ of the samples which in turn is probably directly related to the aluminum content of the samples. A few deviations have been found and may be explained in terms of other impurities or imperfections.

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TABLE I. The 1000 Hz, 300°K dielectric constant of Amersil vitreous silica.

GRADE	HYDROXYL CONCENTRATION 10 ¹⁹ ions/cm ³	APPROXIMATE TAN δ (ppm)	ε _s
Suprasil W-1	0	0+	3.80729
	0	0+	3.80740
	0	0+	3.80732
Suprasil W-2	0	0	3.80727 (3.80726)
	0	0	3.80727
	0	0	3.80726
Suprasil 1	8.20	0	3.82990
	7.98	0	3.82946
	8.14	0+	3.82975
Suprasil 2	8.62	0+	3.83022
	8.56	0	3.83043
	8.58	0	3.83043
Ultrasil	1.04	13	3.81261
	1.13	9	3.81254
	1.02	13	3.81267
Homosil	0.91	11	3.81087
	1.10	8	3.81117
	0.90	12	3.81098
Infrasil 1	0.07	63	3.81297
	0.07	56	3.81263
	0.07	47	3.81156
Infrasil 2	0.07	73	3.81329
	0.07	71	3.81328
	0.07	72	3.81322
Optosil 1	1.19	8	3.81090
	1.10	7	3.81079
	1.11	7	3.81083
Optosil 2	0.92	15	3.81047
	1.19	16	3.81131 (3.81132)
	1.11	33	3.81300

TABLE I. Cont'd.

GRADE	HYDROXYL CONCENTRATION	APPROXIMATE TAN δ (ppm)	ϵ_s
	10^{19} ions/cm ³		
Optosil 3	1.05	15	3.81127
	1.06	19	3.81131
	1.07	17	3.81122
T08 Commercial	1.49	14	3.80969
	1.26	16	3.80931
	1.39	17	3.80973

TABLE II. The 1000 Hz, 300°K dielectric constant of Corning fused silica.

GRADE	HYDROXYL CONCENTRATION 10 ¹⁹ ions/cm ³	APPROXIMATE TAN δ (ppm)	ϵ_s
Ultraviolet	7.47	0+	3.82778
	7.18	20	3.82759
Schlieren	7.33	0+	3.82746
	7.17	0+	3.82695
Mirror	7.13	10	3.82691
	6.96	0+	3.82616
Optical 1	7.23	10	3.82726
	6.98	5	3.82633
Optical 2	6.44	3	3.82490
	6.98	5	3.82615
Industrial	7.37	0+	3.82747
	6.75	0+	3.82572
Muffoletto	7.35	0	3.82771
	7.39	0+	3.82807

Table III. The 1000 Hz, 300°K dielectric constant of
General Electric, Dynasil, and Japanese
Industries vitreous silica.

MANUFACTURER	GRADE	HYDROXYL CONCENTRATION $10^{19} \frac{\text{ions}}{\text{cm}^3}$	APPROXIMATE TAN δ (ppm)	ϵ_s
General Electric	101	0.05	17	3.80784
		0.02	18	3.80823
	124	0	6	3.80744
		0	70	3.80771
	125	0.06	43	3.80983
		0.03	39	3.81060
	151	7.36	0	3.82793
		7.48	0	3.82863
		7.32	0	3.82774
		7.46	0	3.82810
Dynasil	4000	7.06	0	3.82511
		-	0	3.82589
Japanese Industries		1.51	33	3.81261
		1.69	35	3.81291

FIGURE CAPTIONS

Figure 1. The low frequency dielectric constant plotted vs. hydroxyl concentration for each sample of vitreous silica.

Figure 2. The deviations from the reference line, $\Delta\epsilon_s$, of the low frequency dielectric constant of twenty-eight "high" samples plotted vs. approximate $\tan \delta$ for each sample.