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The Low Frequency Dielectric Constants of
 α -Quartz, Sapphire, MgF_2 , and MgO^*

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ABSTRACT

The 1000 Hz, 300°K dielectric constants were measured for crystalline α -quartz, sapphire, MgF_2 , and MgO , and polycrystalline sapphire (Lucalox), magnesium fluoride (IRTRAN 1), and magnesium oxide (IRTRAN 5). The measurements were performed using the method of substitution (two-fluid method).

The results are: single crystal α -quartz, $\epsilon_{s\parallel} = 4.6368 \pm 0.001$, $\epsilon_{s\perp} = 4.5208 \pm 0.001$; single crystal sapphire, $\epsilon_{s\parallel} = 11.589 \pm 0.005$, $\epsilon_{s\perp} = 9.395 \pm 0.005$; polycrystalline sapphire (Lucalox), $\epsilon_s = 10.154 \pm 0.007$; single crystal MgF_2 , $\epsilon_{s\parallel} = 4.826 \pm 0.01$, $\epsilon_{s\perp} = 5.501 \pm 0.01$; polycrystalline MgF_2 (IRTRAN 1), $\epsilon_s = 5.289 \pm 0.001$; single crystal MgO , $\epsilon_s = 9.830 \pm 0.001$; and polycrystalline MgO (IRTRAN 5), $\epsilon_s = 9.833 \pm 0.001$, where $\epsilon_{s\parallel}$ and $\epsilon_{s\perp}$ are the dielectric constants parallel and perpendicular, respectively, to the c-axis.

INTRODUCTION

Due to its interesting piezoelectric properties, crystalline α -quartz is probably our most widely studied anisotropic material. With the increase in availability of large single crystals, sapphire and magnesium fluoride have also attracted attention. Crystalline magnesium oxide is often studied in conjunction with the alkali halides since it has the sodium chloride structure but does not exhibit strongly ionic properties. Finally, Lucalox, IRTRAN 1, and IRTRAN 5 are of interest and use as polycrystalline forms of sapphire, MgF_2 , and MgO respectively. Since the low frequency dielectric constant, ϵ_s , is of fundamental importance in the characterization of these materials, it is felt that an accurate redetermination of ϵ_s for these materials is justified.

EXPERIMENTAL

Samples of crystalline α -quartz were obtained from Valpey Corp. (Holliston, Mass.) and P. R. Hoffman Co. (Carlisle, Pa.). The former were high purity materials grown by Valpey and the latter were either Brazilian natural quartz or synthetic quartz grown by P. R. Hoffman. The magnesium fluoride crystals were obtained from the Harshaw Chemical Co. (Solon, Ohio) and most of the sapphire was obtained from Union Carbide (Union, N. J.). Two samples of sapphire along with an MgO single crystal were obtained from Semi-Elements several years ago. The Lucalox samples were supplied by General Electric (Cleveland, Ohio) and the Kodak ITRAN materials were loaned to us by Charles Tilford of the National Bureau of Standards. All of the samples were 2.54 cm diameter disks and 1.5 mm thick with the exception of the Union Carbide sapphire samples which were slightly less than 1 mm thick.

The 1000 Hz, 300°K dielectric constants for each of the materials were determined by the method of substitution¹ (two-fluid technique²) using apparatus described previously by the authors.³ The present set of measurements differs from the previous work in that most of the data was obtained using a bridge constructed by one of the authors (C. A.) instead of the General Radio 1620-A.

The accuracy for individual measurements is placed at 0.01% for all but the sapphire materials. Since the single crystal sapphire samples were rather thin, uncertainties in positioning of the crystals produce errors of about 0.03% in the individual measurements. Surface irregularities and inhomogeneities resulted in errors of about 0.1% for the Lucalox samples.

The orientations of the anisotropic crystals were determined to 0.01° where necessary using refined back reflection Laue techniques including a data analysis involving angles only which avoids the usual ambiguities in the radial position of the spots.

The data for the anisotropic crystals were fitted to the equation:

$$\epsilon_s = \epsilon_{s\parallel} \cos^2 \theta + \epsilon_{s\perp} \sin^2 \theta \quad (1)$$

using the method of least squares. θ is the angle that the electric field makes with the c-axis.

The results of the measurements are tabulated in Tables I-IV.

DISCUSSION

Quartz

The data for crystalline quartz is plotted in Fig. 1 vs. $\sin^2\theta$ along with the best fit straight line. It is seen that ϵ_s for quartz from two different sources is well represented by the equation:

$$\epsilon_s = 4.6368 \cos^2\theta + 4.5208 \sin^2\theta \quad (2)$$

While the individual measurements are good to 0.01%, variations from sample to sample place the uncertainties on the coefficients in Eq. (2) slightly higher. The value of $\epsilon_{s\parallel}$ is thus taken to be 4.6368 ± 0.001 . This value is in close agreement with the recent work by Loewenstein et al.⁴, Russell and Bell,⁵ and Roberts and Coon⁶ who arrive at values of 4.635 ± 0.004 , 4.639 ± 0.004 , and 4.635 ± 0.01 respectively. All three of these results were obtained by extrapolating far infrared refractive index data to zero frequency. In order to compare their results for $\epsilon_{s\perp}$ with the present work, a correction must be made for the effect of piezoelectric strain since the present work measures the "free" dielectric constant while theirs measure the "clamped" dielectric constant. Cady⁷ writes the relation between the "free" and "clamped" dielectric constants in a direction perpendicular to the c-axis, $\epsilon_{s\perp}$ and $\epsilon'_{s\perp}$ respectively, as:

$$\epsilon_{s\perp} = \epsilon'_{s\perp} + 4\pi(2e_{11}d_{11} + e_{14}d_{14}) \quad (3)$$

where e_{11} , e_{14} , d_{11} , and d_{14} are the appropriate stress and strain constants of quartz. Recent work⁸⁻¹⁰ indicates that the value for $4\pi(2e_{11}d_{11} + e_{14}d_{14})$ should be only slightly lower than the value of 0.087 given by Cady.⁷ The value of $\epsilon'_{s\perp}$ for the present work is thus 4.4348 ± 0.002 which agrees with the value of 4.436 ± 0.004 given by Russell and Bell.⁵ However, it disagrees with the values 4.460 ± 0.004 and 4.418 ± 0.01 arrived at by Loewenstein et. al.⁴ and Roberts and Coon⁶ respectively. Loewenstein et. al. have noted the discrepancy between their data and Russell and Bell's but provide no explanation. This agreement is in rather sharp contrast to the rest of the literature where values of $\epsilon_{s\parallel}$ range from 4.27 to 4.66 and $\epsilon_{s\perp}$ from 4.32 to 4.55, though the most commonly quoted values for these constants are 4.6 and 4.5 respectively.

Sapphire

The best fit of the data for sapphire yields the equation:

$$\epsilon_s = 11.589 \cos^2 \theta + 9.395 \sin^2 \theta. \quad (4)$$

The individual measurements are accurate at about the 0.03% level, but variations from sample to sample place the uncertainty in the coefficients of Eq. (4) at about 0.05%. Since

all of the samples cluster around three points, the data is not plotted.

Once again there is good agreement between the present capacitance measurements and extrapolated infrared refractive index data since the present values, 11.589 ± 0.005 and 9.395 ± 0.005 compare favorably with the values 11.601 ± 0.008 and 9.413 ± 0.008 ; $11.61_4 \pm 0.01_4$ and $9.40_6 \pm 0.01_2$; 11.58 ± 0.02 and 9.370 ± 0.02 , quoted by Loewenstein et. al.⁴, Russell and Bell¹¹, and Roberts and Coon⁶, respectively. (Roberts and Coon also quote a value of 9.357 ± 0.02 obtained on a sample with its optic axis perpendicular to the surface whereas the other values were obtained for a sample whose optic axis was parallel to the surface.) The values also compare well with the values quoted by Von Hippel¹² which are 11.54 and 9.34.

The low frequency dielectric constant was also determined for two samples of polycrystalline sapphire (Lucalox). The values were found to be 10.150 ± 0.01 and 10.158 ± 0.01 . It is interesting to note that these values are close to an average value of the single crystal constants, 10.128, which is calculated from $(2\epsilon_{s\perp} + \epsilon_{s\parallel})/3$.

Magnesium Fluoride

The data for crystalline magnesium fluoride is plotted in Figure 2. It is apparent that the equation:

$$\epsilon_s = 4.826 \cos^2 \theta + 5.501 \sin^2 \theta \quad (5)$$

represents the dielectric constant of MgF_2 rather well. While individual measurements are accurate at about the 0.01% level, there are fairly large variations from sample to sample. The coefficients in Eq. (5) are thus considered correct at about the 0.2% level. These values are in agreement with the work of Barker¹³ who reports values of $\epsilon_{s\parallel} = 4.6$ and $\epsilon_{s\perp} = 5.4$ obtained from infrared reflectivity measurements.

The value of ϵ_s was also determined for a sample of IRTRAN 1 (polycrystalline MgF_2) and was found to be 5.289 ± 0.001 . This is rather close to the average value for crystalline MgF_2 which is 5.276.

Magnesium Oxide

Values of ϵ_s were obtained for both a single crystal and a polycrystalline form of MgO , IRTRAN 5. The value for the single crystal, 9.830 ± 0.001 is to be compared with the values of 9.958 and 9.65 as reported by Bartels and Smith¹⁴ and Von Hippel¹² respectively. The value for the IRTRAN 5 sample, 9.833 ± 0.001 , is slightly larger than the single crystal value.

CONCLUSIONS

Excellent agreement is found between the present capacitance measurements and recent far infrared determinations of the low frequency dielectric constants of α -quartz and sapphire. It thus appears that the low frequency dielectric constants for these materials are indeed well known. In addition it has been shown that the dielectric constants for polycrystalline forms of sapphire (Lucalox), MgF_2 (IRTRAN 1), and MgO (IRTRAN 5) are close to an average of the respective single crystal values.

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Table I. The 1000 Hz, 300°K dielectric constants of α -quartz.

<u>θ</u>	<u>ϵ_s</u>	<u>Source</u>
0.2°	4.6372	Hoffman
"	"	"
"	"	"
"	"	"
"	4.6373	"
1.7	4.6358	Valpey
15.31	4.6279	"
29.12	4.6087	"
45.08	4.5783	"
54.95	4.5590	Hoffman
54.95	4.5588	"
60.52	4.5486	Valpey
75.59	4.5279	"
89.9	4.5210	Hoffman
"	"	"
"	4.5209	"
"	"	"
"	"	"
89.8	4.5208	Valpey
"	4.5207	"
"	4.5203	Hoffman

Table II. The 1000 Hz, 300°K dielectric constants for sapphire.

<u>θ</u>	<u>ϵ_s</u>	<u>Source</u>
0.47	11.593	Union Carbide
0.83	11.590	"
2.85	11.584	Semi Elements
59.01	9.9646	Union Carbide
59.36	9.9625	"
59.57	9.9627	"
60.00	9.9322	"
60.33	9.9321	"
60.34	9.9254	"
87.26	9.4048	"
88.79	9.4025	"
88.82	9.4002	"
89.86	9.3986	Semi Elements

Table III. The 1000 Hz, 300°K dielectric constants for magnesium fluoride.

<u>θ</u>	<u>ϵ_s</u>
0.76	4.8220
0.87	4.8243
23.05	4.9397
23.10	4.9406
45.47	5.1526
45.63	5.1665
68.02	5.4063
68.16	5.4079
86.54	5.5069

Table IV. The 1000 Hz, 300°K principal dielectric constants
for several insulators.

<u>Material</u>	<u>$\epsilon_{s }$</u>	<u>$\epsilon_{s\perp}$</u>
α -QUARTZ	4.6368 $\pm$ 0.001	4.5205 $\pm$ 0.001
SAPPHIRE		
Single Crystal	11.589 $\pm$ 0.005	9.395 $\pm$ 0.005
Polycrystalline (Lucalox)	11.154 $\pm$ 0.007	
MAGNESIUM FLUORIDE		
Single Crystal	4.826 $\pm$ 0.01	5.501 $\pm$ 0.01
Polycrystalline (IRTRAN 1)	5.289 $\pm$ 0.001	
MAGNESIUM OXIDE		
Single Crystal	9.830 $\pm$ 0.001	
Polycrystalline (IRTRAN 5)	9.833 $\pm$ 0.001	

FIGURE CAPTIONS

Figure 1. Plot of the 1000 Hz, 300°K dielectric constant vs. $\sin^2\theta$ for crystalline α -quartz.

Figure 2. Plot of the 1000 Hz, 300°K dielectric constant vs. $\sin^2\theta$ for crystalline MgF_2 .