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LOW FREQUENCY DIELECTRIC CONSTANTS OF THE ALKALINE EARTH FLUORIDES BY THE METHOD OF SUBSTITUTION

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The 1000 Hz $300^{\circ}K$ dielectric constants of the alkaline earth fluorides were measured to an accuracy of 0.01% by the method of substitution. Reproducibly different values for various crystals of the same type were obtained which varied beyond the experimental error. The ranges of results for various crystals of each type measured, along with further separation by manufacturer are: CaF_2, Harshaw, 6.7984-6.7988, Optovac, 6.8074-6.8432; SrF_2, Harshaw, 6.4647-6.4664, Optovac, 6.4700-6.4703; and BaF_2, Harshaw, 7.3590-7.3595, Optovac, 7.3606-7.3630. The spread for each type of crystal is thought to be attributable to random trace impurities.

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INTRODUCTION

The alkaline earth fluorides have been extensively studied in recent years. Belonging to the space group O_h^5, CaF_2, SrF_2, and BaF_2 are of interest as a set of isomorphic cubic crystals with the fluorite structure. This series is particularly important in that the variation of the physical properties with the alkaline earth cation can be studied. Valuable details of electronic structure are then obtained, and one of the most productive areas of research yielding such information is that concerned with the dielectric properties of ionic crystals. There have been several studies[1-5] and reviews[6,7] dealing with these aspects of the alkaline earth fluorides. From these articles, it becomes apparent that one of the least well-determined parameters, yet one of the most important, is the static dielectric constant. Past literature values are collected in Table I where it is seen that in general the numbers are randomly scattered with the discrepancies reaching as high as 10%. There is one set of values, those tabulated by Hojendahl[7] who quotes the results of Errera and Ketelaar,[8] which, for CaF_2 and SrF_2, are in total disagreement with the values of the other workers. It is unfortunate that these have been the most commonly quoted results, and, for whatever reason, continue to

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appear.[9]

This work resolves the discrepancies by establishing highly accurate values of the static dielectric constants of the alkaline earth fluorides by the method of substitution.[10,11] In addition some information is given on the order of magnitude of the effect of random trace impurities.

THEORY

The method of substitution has been described previously.[10,11] The basic idea is to measure five capacitances:

$$C_1 = \frac{\varepsilon_s^1 \, A}{d} \qquad (1a)$$

: Fluid of static dielectric constant ε_s^1,

$$C_2 = \frac{\varepsilon_s^1 \, \varepsilon_s^s \, A}{\varepsilon_s^s \, d + (\varepsilon_s^1 - \varepsilon_s^s) \, t} \qquad (1b)$$

: Fluid 1 and sample of thickness t and static dielectric constant ε_s^s,

$$C_3 = \frac{\varepsilon_s^2 \, A}{d} \qquad (1c)$$

: Fluid of static dielectic constant ε_s^2,

$$C_4 = \frac{\varepsilon_s^2 \, \varepsilon_s^s \, A}{\varepsilon_s^s \, d + (\varepsilon_s^2 - \varepsilon_s^s) \, t} \qquad (1d)$$

: Fluid 2 and sample,

$$C_5 = \frac{A}{d} \qquad (1e)$$

: Vacuum

using a fixed-electrode, parallel plate capacitor of
area A and plate separation d. Combining the above
equations, one arrives at the working equation:

$$\varepsilon_s^s = \frac{C_1 \, (1 + C_3/C_2 - C_3/C_1 - C_3/C_4)}{C_5 \, (C_1/C_2 - C_3/C_4)} \, . \qquad (2)$$

The significant feature of this approach is that the
static dielectric constant of the sample is determined
only from ratios of capacitances, the values of which
can be known extremely well via three-terminal methods.

APPARATUS

The three-terminal capacitances were determined
using an appropriately modified General Radio Type
1620-A capacitance measuring assembly. Details of the
alterations are given elsewhere.[10,11] The bridge was
operated at 1000 Hz and 30 V.

An exploded view of the capacitance cell assembly
is shown in Figure 1. An important feature is that
there are four electrodes, an inner and an outer on each
plate, which can be combined to give two separate three-
terminal combinations. The inner and outer electrodes
are separated by epoxy and 0.00025 in. mylar. The 0.002
in. thick mylar shims center both the sample insertion
tool, which is free to move vertically upward to receive
and discharge the sample, and the sample which is placed
in the circular gap in the tool. The dimensions of the
cell are such that for one inch diameter samples the
condition that the fringing field effects be insignificant:

$$\frac{\text{Effective Guard Ring Width}}{\text{Gap Width}} > 3 \qquad (3)$$

is more than satisfied.

SAMPLES AND PROCEDURE

Samples of all three alkaline earth fluorides were obtained from both the Harshaw Chemical Co. and Optovac, Inc. in the form of one inch diameter disks. The preparation of the samples and the measurement procedure were the same as those given in our article on the static dielectric constants of some alkali halides.[11] The samples are 0.062 in. thick unless otherwise indicated. The raw data from a typical data run are listed in Table II.

RESULTS AND DISCUSSION

The results for the 1000 Hz 300°K dielectric constants of various crystals of CaF_2, SrF_2, and BaF_2 are listed in Tables III-V respectively. The accuracy for an individual measurement is probably better than 0.01%.

Table III shows some interesting results. Note that the numbers for all Harshaw crystals, samples I-XIII are within 0.01% of each other. This includes two bi-crystals, samples IX and X, for one of which the grain boundary splits the crystal into two half-moons, and two thin crystals, samples XII and XIII. In addition the two 0.048 in. thick crystals had been purchased three years prior to the experiment, and stored in a desiccator during the interim. There is, however, grouping around the value 6.79845 and at 6.7988. This is thought to be a real difference due to trace impurities since the crystals came from two separate lab packs, and thus, possibly from two different boules.

The Optovac CaF_2 samples show both deviation from the Harshaw crystals and internal spread well beyond the uncertainty for an individual measurement. Clues to the apparent discrepancies are given by the dissipation factor.

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The loss for all Harshaw-Simplex oil combinations is on the order of 25 ppm. The losses for Simplex oil and samples XIV, XV, XVI, XVIII, and XIX are 25, 50, 65, 110, and 150 ppm. respectively.. Thus, there is a direct correlation between the loss and the low frequency dielectric constant. This implies that impurities or defects are responsible for the variations in ε_s^s. It is anticipated that experiments relating dielectric constant and loss to known impurity level content will soon be undertaken. It should be noted that accurate values of dissipation factor and conductance can be obtained from an analogous method of substitution. Sample XVII is a thin Optovac CaF_2 and was purchased three years prior to the experiment. Note that its dielectric constant fits into the spread nicely. The effects of polishing have been investigated previously,[11] and that there is no effect from our preparation process is confirmed by sample XVIII.

Samples I-IX of Table IV show that the Harshaw SrF_2 crystals are not quite as uniform as the Harshaw CaF_2 in that the spread amounts to 0.03%. The 0.048 in. thick crystals, samples V and IX, fit into the spread of values confirming that there is no thickness effect. Also, there was a slight green tint evident in samples VIII and IX, but no anomalies were noted in the dielectric

constant. The Optovac samples had a higher value of ϵ_s^s than did the Harshaw crystals, and, exhibited a correspondingly higher loss.

Samples I-VIII of Table V show that the static dielectric constants of the crystals of BaF_2 obtained from Harshaw were all within 0.01% of each other. The static dielectric constants and loss of the Optovac samples are again higher than for the Harshaw specimens. There was also a rather large difference between the two Optovac BaF_2 crystals, samples IX and X.

From Table I it is seen that only the work of Lowndes[2] and the numbers of Kaiser et al.[5] obtained by geometrical methods agree with our values for all three crystals within quoted experimental uncertainties. Other work[11] has indicated that Lowndes has done about as well as is possible with the geometrical method. The numbers of Kaiser et al. overlap ours only because they quote large uncertainties.

Thus, the static dielectric constants of the alkaline earth fluorides have been determined very accurately and found not to vary monotonically with the atomic number of the cation. In addition, the value of ϵ_s^s tends to be fairly sensitive to trace impurities, the quantitative investigation of which is soon to be undertaken. The pressure and temperature derivatives of the

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low frequency dielectric constants of these crystals are currently being studied to a high level of accuracy. Preliminary results for Harshaw CaF_2 and the uniformity of ε_s^s shown here for those crystals indicate the possibility of the use of CaF_2 as a pressure standard. The results from this investigation will be forthcoming shortly.

Figure 1. Capacitance cell assembly: a, 0.002 in. thick mylar centering shims; b, sample insertion tool; c, guard ring; d, teflon FEP washers; e, aluminum guarded electrode; h, 0.00025 in. thick mylar film; i, 0.070 in. thick glass spacers.
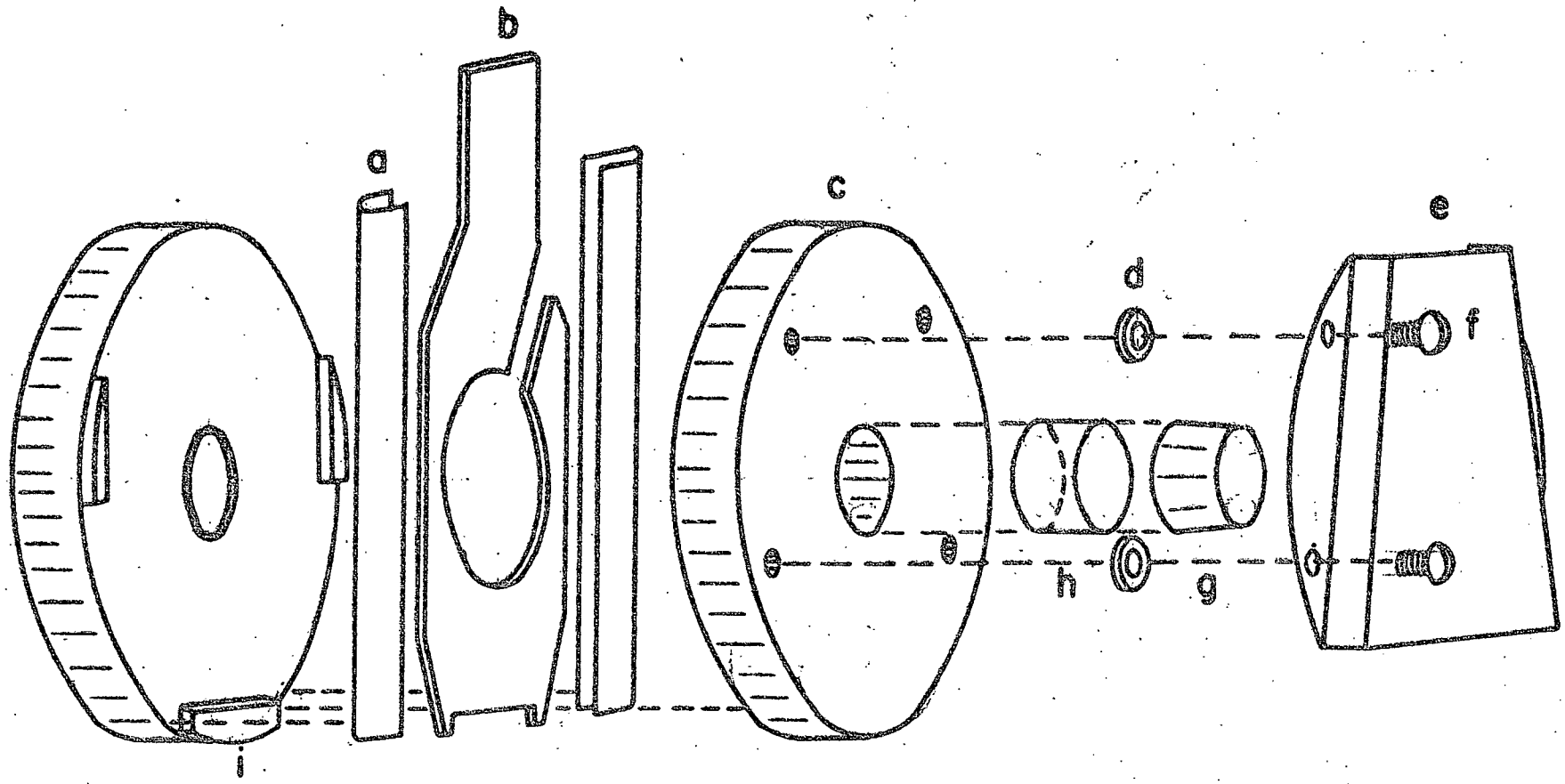
TABLE I: Comparison of literature values for the static dielectric constants of the alkaline earth fluorides.

Method	This Work	Lowndes (1969)[a]	Jones (1967)[b]	Bosomworth (1966)[c]	Rao & Smakula (1965)[d]	Kaiser et al. (1962)[e]	Hojendahl (1935)[f]
	Method of Substitution	Geom.	Geom.	Curve fit dispersion relation	Geom.	Geometrical curve fit Kramers - Kronig	Mixed - Liquid
Temp.	300°K	300°K	300°K	300°K	300°K	300°K	
CaF_2	Harshaw 6.7984 -6.7988	6.81	6.35	6.63	6.78	6.7	8.43
	Optovac 6.8074- 6.8432					6.65	
SrF_2	Harshaw 6.4647- 6.4664	6.50		6.20	6.48	6.6	7.69
	Optovac 6.4700- 6.4703					6.14	
BaF_2	Harshaw 7.3590- 7.3595	7.32	7.02	6.94	7.28	7.2	7.33
	Optovac 7.3606- 7.3630					6.73	

TABLE I:- Continued

	This Work	Lowndes (1969)[a]	Jones (1967)[b]	Bosomworth (1966)[c]	Rao & Smakula (1965)[d]	Kaiser et al. (1962)[e]	Hojendahl (1935)[f]
Quoted Error	.01%	.5%	1%	1%	.5%	5%	

TABLE II:- Raw data for sample I of Table III. The capacitances are in picofarads. Fluid 1 is Simplex projector oil and fluid 2 is castor oil.

	BRASS CELL		ALUMINUM CELL	
	Normal	Reverse	Normal	Reverse
C_1	.891016 .891016	.892550 .892553	.887718 .887720	.898471 .898478
C_2 (flip) (flip)	2.324319 2.324279 2.324328 2.324308	2.328436 2.328473 2.328400 2.328515	2.302438 2.302507 2.302461 2.302428	2.330274 2.330223 2.330205 2.330254
C_3	1.899940 1.900005	1.903213 1.903278	1.893005 1.893050	1.915937 1.915986
C_4 (flip) (flip)	2.677185 2.677181 2.677205 2.677206	2.681821 2.681844 2.681867 2.681845	2.663385 2.663367 2.663370 2.663385	2.695613 2.695631 2.695639 2.695602
C_5	.4114719	.4121805	.4099437	.4149131
ε_s^s	6.798852	6.798842	6.798831	6.798826

TABLE III. The 300°K 1000Hz dielectric constants of some CaF_2 crystals.

Sample	Source and Comments	Measuring group	ϵ_s^s
I	H	12	6.7988
II	H	12	6.7988
III	H	12	6.7985
IV	H	11	6.7984
V	H	11	6.7984
VI	H	11	6.7985
VII	H	11	6.7988
VIII	H	11	6.7984
IX	H-(Bi-crystal)	8	6.7985
X	H-(Bi-crystal)	15	6.7988
XI	H	16	6.7985
XII	H(.048 "old")	15	6.7986
XIII	H(.048 "old")	13	6.7986
XIV	O	13	6.8074
XV	O	13	6.8077
XVI	O	14	6.8123
XVII	O(.048 "old")	15	6.8291
XVIII	O(Bi-crystal)	6	6.8343
XVIII	Repolished	8	6.8344
XIX	O	13	6.8432

TABLE IV:- The 1000 Hz 300°K dielectric constants of some samples of SrF_2.

Sample	Source and Comments	Measuring group	ϵ_s^s
I	H	8	6.4648
II	H	12	6.4650
III	H	12	6.4664
IV	H	12	6.4651
V	H(.048")	13	6.4648
VI	H	14	6.4647
VII	H	14	6.4650
VIII	H (green tint)	14	6.4652
IX	H(.048") (green tint)	15	6.4653
X	O	8	6.4703
XI	O	15	6.4700

TABLE V:- The 1000Hz 300°K dielectric constants
of some crystals of BaF_2.

Sample	Source and Comments	Measuring group	ϵ_s^s
I	H	13	7.3591
II	H	13	7.3591
III	H	14	7.3593
IV	H	14	7.3591
V	H	14	7.3594
VI	H	15	7.3590
VII	H	15	7.3590
VIII	H	16	7.3595
IX	O	8	7.3630
X	O	12	7.3606

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* Work supported in part by the Atomic Energy Commission

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