

The Dielectric Constant of Barium Oxide*

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(Received January 15, 1951)

The availability of crystals of BaO made possible an investigation of the low frequency dielectric constant κ of BaO. This has been measured over the frequency range 60 to 6×10^7 cycles per second and the temperature range -25° to 60°C . Over these ranges κ is about 34, which is quite different from the value of 14 frequently quoted. There is some evidence for a rise in κ at the lowest frequencies. Data on dielectric loss is presented.

I. INTRODUCTION

THE purpose of this investigation was to measure the low frequency dielectric constant κ of barium oxide. A knowledge of κ is useful in the interpretation of the relation between optical and thermal excitation processes, since estimates of the energy of lattice relaxation can be made¹ using the values of κ and of κ_0 (the "optical" or "high frequency" dielectric constant).² The value of κ of BaO has also been used³ in attempts to explain the high dielectric constant of barium titanate, but such attempts appear⁴ to have been approximations.

κ for BaO does not appear to have been measured,⁵ but a value of 14.3 is sometimes quoted.³ This has its origin in a paper by Højendahl,⁶ who extrapolated this number on the basis of immersion-method determinations of the static dielectric constants of BeO, MgO, CaO, and SrO. His immersion liquids were dried with silica gel, which is thought to be a less effective drying agent than CaO.⁷ Hence, the values for CaO of 11.8 and SrO of 13.3 may be in error because of contamination by hydroxide.

In the work reported here, the dielectric constant was determined from 60 cycles to 60 Mc to find out whether it was frequency sensitive. In this connection the dissipation factor was also measured, since any dispersion phenomena are often more easily detectable in this quantity than in the dielectric constant.

II. EXPERIMENTAL PROCEDURE

A method for growing crystals of barium oxide from the vapor phase has recently been developed in this

laboratory.⁸ Thus it was possible to use the plate method of measuring the dielectric constant of single crystals. The same technique of measurement was also used on dense polycrystalline deposits grown directly on circular platinum electrodes, as shown in Fig. 1(a). The use of such deposits allowed a more easily controllable geometry. The plate method is greatly superior to the immersion method in the case of BaO, since this substance is exceedingly hygroscopic,⁷ very reactive, and has a conductivity high compared with that of most immersion liquids.

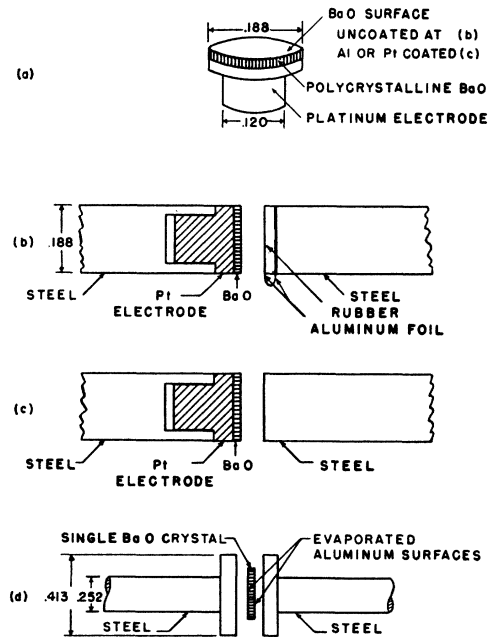


FIG. 1. Parts (a), (b), and (c) illustrate the use of a sample composed of dense, polycrystalline BaO grown on a platinum electrode. (a) shows the electrode with BaO coating. (b) is a cross section of the electrode configuration using a thin aluminum foil contact pressed against the BaO surface. (c) is an arrangement similar to (b) but using an evaporated aluminum or sputtered platinum contact to the BaO. (d) shows the configuration for study of a single crystal with plane parallel faces on which aluminum electrodes have been evaporated. Dimensions are given in inches.

* This work has received support from the ONR and from the Research Corporation.

¹ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948), pp. 160 ff.; J. H. Simpson, Proc. Roy. Soc. (London) **197**, 269 (1949).

² κ_0 has been found by M. Haase, Z. Kryst. **65**, 534 (1927), to be 4.0.

³ G. H. Jonker and J. H. van Santen, Chem. Weekblad **43**, 672 (1947); B. T. Matthias, Phys. Rev. **75**, 1771 (1949); S. Roberts, Phys. Rev. **76**, 1215 (1949).

⁴ A. von Hippel, Revs. Modern Phys. **22**, 236 (1950).

⁵ A preliminary value of 37 was reported from this laboratory in Tech. Rept. No. 2 (unpublished).

⁶ K. Højendahl, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. **16**, No. 2 (1938).

⁷ J. H. Bower, J. Research Natl. Bur. Standards **33**, 199 (1944). From the chemical properties of MgO, CaO, SrO, and BaO it appears likely that SrO is an even better drying agent than CaO.

⁸ Sproull, Dash, Tyler, and Moore, Rev. Sci. Instr. **22**, 410 (1951).

TABLE I. Dielectric constant of BaO at 0.5 Mc.

Sample No.	Electrode assembly	Measuring instrument	ΔC $\mu\mu f$	Area cm^2	Thickness cm	κ
3P	Fig. 1c	C-meter	24.5±0.2	0.181±0.004	0.0231±0.0005	36±2
4P	1c	C-meter	18.3±0.2	0.181	0.0283	33±2
5P	1c	C-meter	25.4±0.2	0.181	0.0193	31.5±2
6P	1b	C-meter	7.1±0.2	0.172	0.0676	32.5±2
7P	1c	Q-meter	13.3±0.5	0.181	0.0393	33.5±2.5
2S	1d	C-meter	15.0±0.2	0.226	0.0437	34±1.5
3S	1d	C-meter	10.3±0.2	0.106	0.0297	33.5±2.5
4S	1d	C-meter	6.0±0.2	0.044	0.0198	32±5
5S	1d	Q-meter	14.0±0.5	0.482	0.0940	32±2

(1) Sample Preparation

All samples were prepared in the atmosphere of a dry box, containing porous BaO and a liquid air trap as desiccants.

For polycrystalline BaO, the free surface was polished in a jig so that it was parallel to the platinum-BaO interface, to a tolerance of 0.0004 in. The diameter at the electrode-BaO interfaces was made equal to that of the electrodes, 0.188 in., to within ± 0.003 in., as shown in Figs. 1(b) and 1(c). An attempt was made to grind the peripheral surface to a curvature qualitatively like that expected for the lines of force near the edge of an air condenser. This was done to minimize distortion of the field lines when BaO was used as the dielectric and made estimation of the edge effects easier, as discussed in the Appendix.

Single crystal samples were prepared by manually grinding the major surfaces plane parallel to one another to a tolerance of 0.0008 in. The electrode configuration shown in Fig. 1(d) was used with these samples. The electrode area was always considerably larger than the BaO crystals. Therefore, to avoid distortion of the field lines upon insertion of the sample, the peripheral surfaces were ground flat and perpendicular to the electrode surfaces. The crystals were rectangular in shape, and their dimensions are given in Table I.

Good electrical contacts to the major surfaces of the BaO were very important, since all specimens were thin and κ was found to be high compared with that of air. Both sputtered platinum and evaporated aluminum coatings were used, against which the bare steel electrodes were pushed as shown in Figs. 1(c) and 1(d). The samples could be mounted and sealed in the evaporator while it was inside the dry box. The sealed evaporator was then transferred to a pumping station, thus avoiding exposure of the BaO to moist air. The undesirable metallic coating on the peripheral surfaces was later carefully removed with a razor blade under a microscope.

To check whether the above technique caused any penetration of metallic material into the polycrystalline deposits, contact to the BaO surface was also made by pressing aluminum foil against it as shown in detail in

Fig. 1(b). Use of this method also permitted rapid changing of the sample thickness.

(2) Measuring Method and Apparatus

The measurements had to be carried out in a dry atmosphere, so a small, 6-inch diameter dry box was constructed which contained porous BaO as desiccant. While the small box was inside the large dry box, the sample was inserted between the electrodes and the small box sealed. One electrode in the small dry box was fixed, the other movable by means of a micrometer screw. A General Radio Type 846 CK variable capacitor (called " C_B " below) was mounted inside the small dry box close to the sample and connected in parallel with it by short leads. Short, wide copper strips were used as leads to outside measuring equipment to minimize lead inductance. All seals in the box were "O-ring" gaskets.

The well-known substitution or compensation method was employed, measurements being made on the entire electrode assembly first with and then without the sample. The dissipation factor, D , and change of parallel capacitance, ΔC , caused by the BaO was then calculated (D is the same as $\tan \delta$, which is defined as the ratio of the imaginary part to the real part of the complex dielectric constant). In the case of the polycrystalline BaO the background measurements were made after either replacing the BaO-coated electrode by a dummy platinum electrode, or introducing an air gap of thickness equal to that of the sample between one electrode and the free BaO surface. The latter method causes an error of about 0.1 percent in the measured capacitance change for a substance of dielectric constant about 30. In the case of single crystals, the background measurements could be made after simply removing the sample while leaving the electrode spacing constant.

Several measuring circuits were employed. The most accurate capacitance measurements (to $\pm 0.1 \mu\mu f$) could be made with a 0.5-Mc heterodyne beat oscillator capacitance meter (called "C-meter" in Table I), developed by Dr. H. S. Sack, which supplied 66 volts across the sample. It was realized that shunting the tank circuit of a feed-back oscillator with a high loss

condenser causes a decrease of voltage output and a frequency change greater than to be expected from the capacitance of the condenser. By calibration with parallel combinations of resistance and capacitance it was found that this effect caused negligible error in this work, the BaO shunt resistance being of the order of several hundred megohms. In order to test the validity of our method, single cleaved crystals of magnesium oxide⁹ were measured on this instrument. The dimensions were similar to those of the BaO samples. With the aluminum foil contact on uncoated crystals an average of 9.3 ± 0.1 was obtained for κ . Electrode assembly Fig. 1(d) gave κ as 9.5 ± 0.05 . This latter value is in satisfactory agreement with the results cited by Højendahl,⁶ which range from 9.25 to 9.93.

The range from 50 kc to 60,000 kc was explored with a Boonton Q-meter, Type 160-A, using the condenser C_B for compensation. C_B was calibrated with a General Radio Type 722N precision condenser, and capacitance increments could be measured to $\pm 0.5 \mu\mu\text{f}$. As a check of possible lead inductance errors at high frequencies, a thin plate of mica was used as the dielectric in the electrodes of Fig. 1(c). The capacitance increments at 500 kc agreed with those measured on the 0.5-Mc capacitance meter to ± 2 percent and stayed constant within random errors up to 60 Mc. The accuracy of the D measurements was good to about ± 0.002 up to 20 Mc. Above this frequency the inductance of the leads external to the dry box became important and caused greater scattering of the points when different inductors were used.

A General Radio Type 650-A Impedance Bridge served from 0.060 kc to 3 kc. At higher frequencies than this, ground capacitance errors became appreciable. The audiofrequency power for the bridge was supplied through a step-up shielded transformer from a Hewlett-Packard Type 200-B oscillator. The voltage across the crystal was usually about 50 volts. A Hewlett-Packard Type 400-H vacuum tube voltmeter was used as detector. Capacitance increments could be measured to $\pm 0.5 \mu\mu\text{f}$. Dissipation factor measurements were usually better than 10 percent. The direct reading bridge dials gave series capacitance; from this and the dissipation factor the equivalent parallel capacitance could be calculated. The instrument was calibrated with both MgO crystals and artificial dielectrics made up of parallel combinations of carbon resistors and mica condensers. The parallel capacitance of these samples stayed constant to within $\pm 0.3 \mu\mu\text{f}$ from 0.06 to 3.0 kc. These measurements agreed with the 0.5-Mc capacitance meter measurements within $\pm 0.5 \mu\mu\text{f}$. The parallel resistance stayed constant from 0.06 to 0.75 kc, but decreased beyond this due to ground capacitance errors, reaching a value 20 percent lower at 3 kc than at 0.75 kc.

The dc resistance of the BaO crystals was estimated by putting 45 volts in series with them and measuring

the current. Accurate values could not be obtained, due to a current decay effect with time which is not as yet well understood.

III. EXPERIMENTAL RESULTS

The results of measurements of κ at 0.5 Mc are summarized in Table I, where ΔC stands for the capacitance increment caused by insertion of the sample, and κ is calculated from the simple formula (later justified in the Appendix):

$$\kappa = 1 + (4\pi t \Delta C)(1/A).$$

Here t is the sample thickness, and A is the sample area. Samples marked P were polycrystalline, those marked S were single crystals.

From Table I it can be concluded that the average dielectric constant is 34, with an average deviation from the mean due to random errors of ± 1 . A much more serious uncertainty is caused by hydroxide formation.¹⁰ It is thus felt that κ might be as high as 37, but probably not lower than 33.

Typical results of the measurements of κ and D as a function of frequency from 60 cycles to 60 Mc are shown in Fig. 2 for polycrystalline sample No. 5P, and in Fig. 3 for single crystals Nos. 2S and 5S.

In the region from 50 kc to 60 Mc, κ is constant within random errors. The slight decrease of κ towards 50 Mc for No. 5P is not thought to be significant and did not occur in other samples. The rise of D with frequency, beginning at about 1 Mc may indicate dispersion phenomena in the microwave region. This rise seemed to

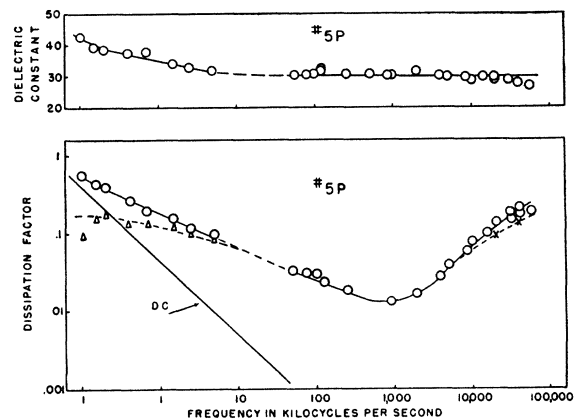


Fig. 2. Dielectric constant and dissipation factor as a function of frequency of a polycrystalline sample, No. 5P, at 25°C. The circles are measured data points. The line marked "dc" shows computed loss due to the measured dc resistance of 120 megohms. The triangles are total loss minus computed dc loss. The crosses represent the dissipation factor corrected approximately for lead inductance.

¹⁰ The measurements summarized in Table I were made immediately after sample preparation. When the same specimens were used to make measurements as a function of frequency several days later, κ had often decreased from 34 to about 32. Bridge measurements and Q-meter measurements as shown in Figs. 2 and 3 did not always join continuously because of this same deterioration with time.

⁹ Obtained from the Norton Company, Niagara Falls, Canada.

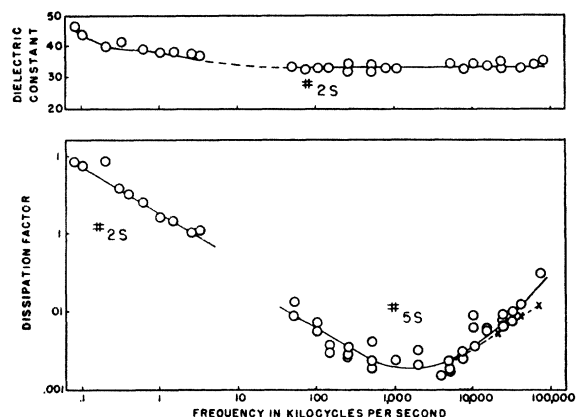


FIG. 3. Dielectric constant and dissipation factor as a function of frequency of single crystals No. 2S and No. 5S, at 25°C. The circles are measured data points. The crosses represent dissipation factor corrected approximately for lead inductance.

start at a somewhat higher frequency in the case of the single crystals than for the polycrystalline material. Above 20 Mc the effect of the inductance of the leads external to the dry box was to make D appear too high. Approximately corrected points are marked by crosses in Figs. 2 and 3 and were obtained using a lead inductance value of $0.15 \mu\text{henry}$ as calculated from a lumped circuit theory based on measurements at 40 and 55 Mc.

The behavior with decreasing frequency below 2 kc is somewhat unusual. The dielectric constant apparently increases, as does the dissipation factor, with a slope less steep than 1. This slope might be explainable as being due to a superposition of a nearly constant ac loss and a dc loss having a slope of magnitude 1. The dc loss

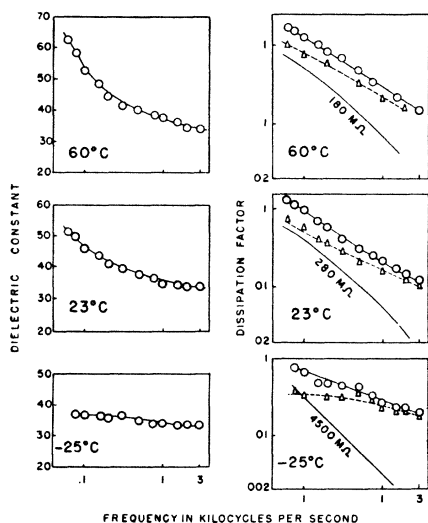


FIG. 4. Dielectric constant and dissipation factor as a function of frequency of a single crystal, No. 3S, at three different temperatures. The circles are measured data points. The line without data points shows computed loss due to the indicated dc resistances, which were measured in a separate experiment. The triangles are total loss minus computed dc loss.

was computed from the estimated values of dc resistance and subtracted from the measured loss to give the "net ac" loss as marked by triangles in Figs. 2 and 4. Typical of results at room temperature, the "net ac" loss curve in Fig. 2 still rises appreciably toward decreasing frequency.

Measurements over the low frequency region from 60 cycles to 3 kc were also made at several temperatures on single crystal No. 3S. Results are shown in Fig. 4 for -25°C , $+23^\circ\text{C}$, and $+60^\circ\text{C}$. At -25°C there was no appreciable change in κ and the "net ac" loss as a function of frequency. At 60°C the changes were more pronounced than at room temperature.

Qualitatively, the audio frequency behavior might be explained in terms of a dispersion peak below 60 cycles, caused by pairs of lattice defects.¹¹ It might also be due to the formation on the surfaces of a very thin layer of $\text{Ba}(\text{OH})_2$ having a much lower conductivity than the BaO . The equivalent circuit representing such a $\text{BaO}-\text{Ba}(\text{OH})_2$ combination behaves like the actual samples.

The applied voltage with the different instruments could be varied from 0 up to about 150 volts. No

TABLE II. κ as calculated from (2) versus crystal thickness.

Thickness in cm	κ	Electrode contact
0.082	32	Fig. 1(b)
0.071	31.5	1(b)
0.054	32	1(b)
0.050	31.5	1(b)
0.042	30	1(b)
0.019	31.5	1(c)

changes in κ and D were observed which were greater than expected random variations.

IV. SUMMARY

The low frequency dielectric constant of barium oxide was measured on single crystals while taking substantial precautions to prevent conversion of this substance to barium hydroxide. This value was found to be 34 and remained constant from about 2 kc to 60 Mc, the end of our measuring range. An apparent rise in the dielectric constant accompanied by a rise in the ac loss was observed from 2 kc down to 60 cycles at room temperature, which disappeared upon lowering the temperature to -25°C . A unique explanation for this behavior has not as yet been found.

The authors wish to express their appreciation for the assistance of Professor H. S. Sack, Mr. W. C. Dash, and Mr. S. S. Stevens.

APPENDIX

By means of conformal mapping it is possible to obtain an approximate expression for the capacitance of a condenser such as

¹¹ R. G. Breckenridge, J. Chem. Phys. **16**, 959 (1948); **18**, 913 (1950).

shown in Figs. 1(b) and (c) with air rather than BaO between the electrodes.¹² In electrostatic units

$$C = (r^2/4t) + (r/2\pi)(1 - \ln 2); \quad (t/r) \ll 1,$$

where r is the electrode radius and t is the thickness of the air-gap. The first term is the familiar major term, the second is an end correction term from the charge collected on the flat surface near the intersection of the cylindrical and flat circular surfaces. The end correction from charge on the cylindrical surfaces cannot be correctly obtained by conformal mapping (since this method strictly applies to two-dimensional problems only), and it is omitted here for the following reason: if one introduces a slab of BaO instead of air, its periphery being shaped like the outermost line of force from charge on the intersection between the cylindrical and flat circular surfaces, then the field in the surrounding air remains undistorted. Hence, the difference between the BaO

¹² This problem is similar to finding the magnetic field between the magnetic poles of a cyclotron, as discussed by M. E. Rose, *Phys. Rev.* **53**, 715 (1938).

and air condenser capacitance is

$$\Delta C = (\kappa - 1)[(r^2/4t) + (r/2\pi)(1 - \ln 2)], \quad (1)$$

where κ is the dielectric constant of BaO. By using only the major term,

$$\Delta C = (\kappa - 1)(r^2/4t), \quad (2)$$

the calculated κ for a 0.051-cm thick slab of BaO, 0.478 cm in diameter, is 4 percent too high; for a 0.0255-cm thick slab it is 2 percent too high.

Since the shape of the actual periphery of the slab of BaO was far from the ideal, the edge effect was also investigated experimentally. A series of measurements on polycrystalline sample No. 5P of diameter 0.0470 cm gave the results shown in Table II. Electrode contact as in Fig. 1(c) had to be used for thin samples. For these, sufficient pressure to obtain good electrical contact could not be applied with the aluminum foil without shorting the electrodes. The data indicate that random errors in measurement make end effect corrections quite insignificant.

Photoconductivity and Photoelectric Emission of Barium Oxide

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(Received December 26, 1950)

Barium oxide, in the form of a sprayed coating on a nickel base, was investigated by means of studies of photoconductivity, photoemission, and absorption measurements and the variation of these with temperature. Changes occurring during activation of the oxide were observed. The results are discussed in terms of an energy level structure for barium oxide.

I. INTRODUCTION

THE literature on the oxide cathode is replete with investigations undertaken to establish constants on which to set up a picture of the electron energy band structure for the (Ba, Sr)O emissive coating.¹ Very few of these studies have been concerned with the individual components of these coatings. One of the earliest of these is reported by Nishibori *et al.*,² wherein studies of the conductivity and thermionic and photoelectric emissions were combined to derive values for the electron affinity and Fermi level for BaO and SrO, as well as for the combined form.

More recently, Tyler,³ working with barium oxide single crystals prepared by Sproull, as well as with evaporated films, has studied the optical absorption and photoconductivity. The location of the absorption edge (~ 3.8 ev) reported by Tyler has been confirmed by Taft and Dickey⁴ on the basis of studies of photoelectric

emission from thin metallic layers deposited on a base of barium oxide. Apker, Taft, and Dickey⁵ have reported studies of the photoelectric emission from BaO which indicate an energy for the top of the filled band 5.0–5.2 ev below vacuum potential.

In the work reported here, photoconductivity, photoelectric emission, and optical reflectivity measurements have been made on barium oxide, as formed, and have been followed through the activation process in order to obtain further information concerning the energy level structure.

II. EXPERIMENTAL

Figure 1 shows the form of the tubes used in this work. Barium carbonate (Mallinckrodt Ultra Pure), dispersed in a nitrocellulose binder, was sprayed on a cathode sleeve of N-81 (pure) nickel to give a coating weight of 10–15 mg/cm². A probe wire of pure platinum, 0.001 in. diameter, was wound over this coating, and a second thin coating of the carbonate was sprayed over the probe wire, primarily to seal it in place. The anode cylinder, also of N-81 nickel, was provided with longitudinal slots to permit irradiation and observation of the oxide surface. The electrode assembly was sealed into an envelope having a fused quartz section sur-

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¹ A. S. Eisenstein, *Advances in Electronics* **1**, 1–64 (1948); J. P. Blewett, *J. Appl. Phys.* **10**, 668 (1939); **10**, 831 (1939); **17**, 643 (1946).

² E. Nishibori and H. Kawamura, *Proc. Phys.-Math. Soc. Japan* **22**, 378 (1940); Nishibori, Kawamura, and Hirano, *Proc. Phys.-Math. Soc. Japan* **23**, 37 (1941).

³ W. W. Tyler, *Phys. Rev.* **76**, 179(A) (1949); **76**, 1887 (1949); dissertation, Cornell University, Ithaca, New York (1949).

⁴ E. A. Taft and J. E. Dickey, *Phys. Rev.* **78**, 625 (1950).

⁵ Apker, Taft, and Dickey, *Phys. Rev.* **76**, 453(T) (1949).