

Frequency and Temperature Response of the Polarization of Barium Titanate*

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The frequency and temperature response of the polarization of BaTiO₃ from 1 to 1000 cm⁻¹ and between 24 and 200°C has been determined by transmission and reflectivity measurements on polarized single crystals. A single absorption band located at 491 cm⁻¹ was observed in transmission, while in reflectivity a drop occurs from 10 to 80 cm⁻¹ and absorption bands are located near 175 and 470 cm⁻¹. These bands show temperature-dependent splittings caused by changes in crystal symmetry. Reflectivity analysis indicates that the dispersion of the polarization in single-domain BaTiO₃ consists of resonances at 12, 182, and 491 cm⁻¹. The 12-cm⁻¹ resonance is highly damped and exhibits an unusual dispersion. The integrated intensity of the 12-cm⁻¹ resonance is very large, and above the Curie point decreases rapidly with increasing temperature. Its frequency remains between 6 and 22 cm⁻¹ in the 24 to 200°C range.

INTRODUCTION

THE frequency and temperature responses of the dielectric constant of barium titanate have long been a subject of interest to those concerned with the ferroelectric state. Ferroelectricity in cubic BaTiO₃ arises when, at a critical temperature, the Ti and O atoms shift from their high-temperature equilibrium positions to stable new positions in the now distorted lattice.¹ This phenomenon is somewhat akin to the spontaneous alignment (Mosotti catastrophe) of rotating permanent dipoles treated by the Langevin theory.² For ferroelectricity to arise there must therefore be a coupling between the vibrational states of adjacent unit cells.³ The detailed nature and strength of this coupling are unknown. Cochran⁴ proposed a theory which links the cause of ferroelectricity in the perovskites to the existence of a temperature-dependent "soft" lattice vibrational mode, caused by the near cancellation of the long-range Coulomb binding forces by the short-range repulsive terms. That some type of group effect is present is apparent from the large difference between the low-frequency and the infrared dielectric constants; measurements of the high-frequency and temperature responses of the dielectric constant should therefore yield important information regarding the formation of the ferroelectric state.

Measurements of the temperature response of the dielectric constant of single-domain BaTiO₃ at high frequencies by microwave techniques show conflicting

results; they include those by Westphal⁵ (no dielectric dispersion up to 100 Mc/sec), Jaynes and Varenhorst⁶ (moderate dispersion at 4 kMc/sec), Benedict and Durand⁷ (no dispersion at 24 and 50 kMc/sec), Fousek⁸ (strong relaxation at 9 kMc/sec), and Stern and Lurio⁹ (no relaxation up to 2 kMc/sec). Several workers approached the region of interest from the infrared, which includes the absorption bands caused by the optically active lattice vibrations. The normal modes of the perovskite lattice were analyzed by Last,¹⁰ who predicted three triply degenerate, optically active vibrations for the cubic phase. He assigned the two higher frequencies (ω_1 and ω_2) to "stretching" and "bending" vibrations of the TiO₆ octahedra, and the lowest frequency (ω_3) to the cation-versus-TiO₃ vibration. From reflection and transmission measurements of single crystals and powder samples, he concluded that the frequencies of ω_1 and ω_2 were 495 and 400 cm⁻¹, respectively. He also observed the normal splitting of the 490-cm⁻¹ band as the symmetry of the crystal changed with temperature but was unable to find any behavior which might account for the ferroelectric state.

Recent workers extended the infrared measurements on BaTiO₃ and isomorphous materials to longer wavelengths, finding that a single far-infrared resonance is responsible for the high dc permittivity of the perovskites. Although no direct measurements of this resonance have been made for BaTiO₃, Barker and Tinkham¹¹ measured reflectivity at two different temperatures on single-crystal SrTiO₃ from 1 to 3000 cm⁻¹ and by means of a Kramers-Kronig analysis assigned normal-mode frequencies of 550 and 100 cm⁻¹, the 100-cm⁻¹ mode giving rise to the large dc permittivity.

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¹ For comprehensive surveys see A. von Hippel, *Molecular Science and Molecular Engineering* (The Technology Press and John Wiley & Sons, Inc., New York, 1959); W. Känzig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4, p. 1.

² J. C. Slater, *Phys. Rev.* **78**, 748 (1950).

³ A. von Hippel, *Dielectrics and Waves* (John Wiley & Sons, Inc., New York, 1954), p. 210.

⁴ W. Cochran, *Advan. Phys.* **9**, 387 (1960).

⁵ A. von Hippel and W. B. Westphal, MIT Technical Report No. 145, Insulation Research Laboratory, December, 1959 (unpublished).

⁶ E. T. Jaynes and V. Varenhorst, Microwave Laboratory Report No. 287 Stanford University, 1956 (unpublished).

⁷ T. S. Benedict and J. L. Durand, *Phys. Rev.* **109**, 1091 (1958).

⁸ J. Fousek, *Czech. J. Phys.* **9**, 172 (1959).

⁹ E. Stern and A. Lurio, *Phys. Rev.* **123**, 117 (1961).

¹⁰ J. T. Last, *Phys. Rev.* **105**, 1740 (1957).

¹¹ A. S. Barker, Jr., and M. Tinkham, *Phys. Rev.* **125**, 1529 (1962).

Spitzer *et al.*¹² published room-temperature far-infrared reflection data on single crystals of BaTiO₃, SrTiO₃, and TiO₂, for wavelengths up to 120 μ (80 cm⁻¹). In BaTiO₃ they found bands at 491 and 183 cm⁻¹, but were prevented by the available frequency range from finding a lower frequency vibration. Their results on BaTiO₃ were confirmed by Ikegami *et al.*,¹³ who found bands at 500 and 180 cm⁻¹ by means of reflectivity measurements on single crystals to wavelengths as long as 200 μ . Ikegami also measured the 180-cm⁻¹ band for a possible temperature dependence, but found none.

The intent of the present work is to provide an accurate experimental determination of the temperature response of the polarization of single-domain BaTiO₃ from microwave to near-infrared frequencies, with special emphasis on the submillimeter region, where the measuring field ceases to see the ferroelectric state.

SAMPLE PREPARATION

The single-crystal BaTiO₃ used in this work consisted of large triangular "butterfly-wing" crystals ranging from 1 to 3 cm in length, and 50 to 1000 μ in thickness. All samples were first etched for at least a half hour at 150°C in concentrated phosphoric acid to remove the anomalous surface layer present on crystals grown by the Remeika process.¹⁴ Samples a few microns thick for transmission and waveguide measurements were prepared by continued etching using a refinement of Last's¹⁵ method, and final thickness was determined optically by measuring the width of laminar *a* domains. Before measurement the crystals were polarized to *c* domain plates using the method of Fang *et al.*,¹⁶ which consists of warming the glycerine-immersed crystal through the 0°C phase transition while bonding it in an orienting electric field. Trimming to size was accomplished after polarization using an air-abrasive unit.⁷ During measurement the samples were generally glued in place with a silicone-base adhesive, except for those measured on the vacuum grating spectrometer where an area of 3 cm² is required, and the samples were made of two "butterfly wings" butted together and cast into an epoxy resin block.

MEASUREMENT TECHNIQUES AND RESULTS

The spectrometers used to cover the broad frequency range are listed in Table I.

¹² W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, *Phys. Rev.* **126**, 1710 (1962).

¹³ S. Ikegami, I. Ueda, and S. Kisaka, *J. Phys. Soc. Japan* **17**, 1210 (1962).

¹⁴ J. P. Remeika, *J. Am. Chem. Soc.* **76**, 940 (1954); C. F. Pulvari, Proceedings of the Special Technical Conference, Solid-State Dielectric and Magnetic Devices, Paper No. 4, Catholic University of America, Washington, D. C., April 1957 (unpublished).

¹⁵ J. T. Last, *Rev. Sci. Instr.* **28**, 730 (1957).

¹⁶ P. H. Fang, S. Marzullo, and W. S. Brower, *Phys. Rev.* **108**, 242 (1957).

TABLE I. Spectrometers and their frequency ranges.

| Instrument | Frequency range (cm ⁻¹) | Wavelength (mm) |
|--|-------------------------------------|-----------------|
| Perkin-Elmer Model 521 ^a | 4000-250 | 0.0025-0.04 |
| Modified Perkin-Elmer Model 098 ^a | 600-50 | 0.014-0.2 |
| Vacuum grating spectrometer ^a | 340-35 | 0.03-0.3 |
| Submillimeter interferometer | 120-10 | 0.08-1.0 |
| Carcinotron system ^b | 10,5 | 1,2 |
| Microwave dielectrometer | 0.77 | 12 |

^a These infrared grating instruments were made available by the Spectroscopy Laboratory at M.I.T.

^b Made available by Division 82, Lincoln Laboratory, M.I.T.

Infrared Region

The reflectivity of single-domain BaTiO₃ was measured at room temperature in the 250- to 4000-cm⁻¹ region using the P-E 521 equipped with a P-E reflection attachment (angle of incidence 15 deg). The vacuum grating spectrometer, described by Perry,¹⁷ served to measure reflectivity at room temperature from 200 to 340 cm⁻¹ (angle of incidence 45 deg), and was used below 230 cm⁻¹ between 24 and 400°C (angles of incidence 10 and 45 deg). The averaged results of several runs on each of a number of crystals are given for the 200- to 4000-cm⁻¹ range in Fig. 1. No high-temperature measurements were made at frequencies above 230 cm⁻¹, because the careful study by Last¹⁰ revealed no change of the 490-cm⁻¹ band above the Curie point, and the author's measurements indicate at most a 2% difference between 24 and 150°C at 230 cm⁻¹.

Transmission measurements on thin single crystals, also made from 250 to 4000 cm⁻¹ on the P-E 521, revealed a great deal of structure at shorter wavelengths, previously unreported, due to residual traces of phosphoric acid from the etching bath. The transmission curve for the best crystal, corrected for absorptions due to traces of acid etch, for stray radiation in the instrument, and for radiation passed around the edges of the crystal (incomplete masking), is shown in Fig. 1. The curve is normalized to 100% transmission at 4000 cm⁻¹ because an adjustable blind had to be used in the reference beam to compensate for the vignetting of the sample holder. In reality the reflection loss will reduce the transmission at shorter wavelengths to about 70%.¹⁰

Reflectivity in the 450- to 520-cm⁻¹ region containing the highest frequency band was measured at 77°K (angle of incidence 10 deg) on the modified P-E 098¹⁸ to ascertain whether the splittings found by Last¹⁰ in transmission would also be observed in the reflectivity (Fig. 2). The absolute values of Fig. 2 are in error, as the Dewar sample holder used had to be disassembled to interchange mirror and sample, making it impossible to

¹⁷ C. H. Perry, Laboratory for Electronics Research, Massachusetts Institute of Technology, Quarterly Progress Report No. 70, July 1963, p. 19 (unpublished).

¹⁸ R. C. Lord and T. K. McCubbin, Jr., *J. Opt. Soc. Am.* **47**, 689 (1957).

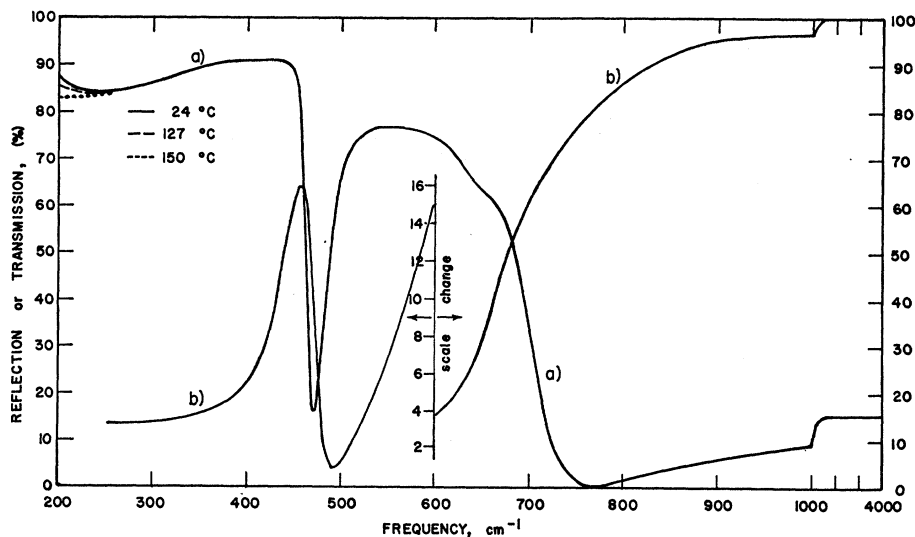


FIG. 1. Reflectivity and transmission of single-crystal BaTiO₃: (a) reflectivity of single-domain crystal; (b) transmission of 3- μ -thick crystal.

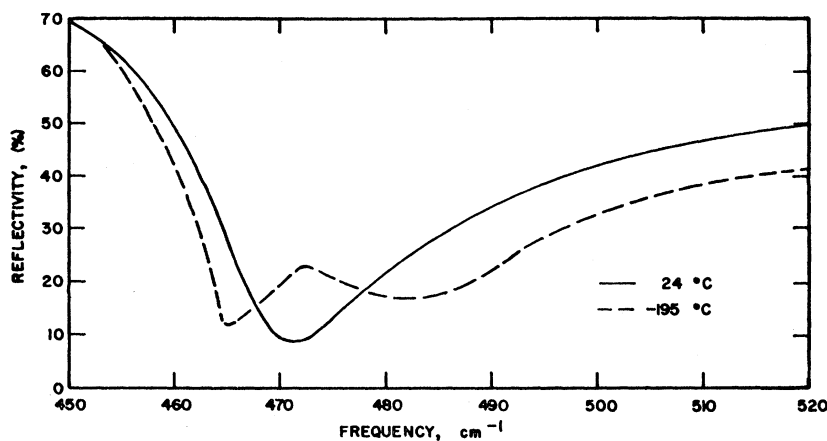


FIG. 2. Low-temperature reflectivity of unpolarized BaTiO₃ single crystal.

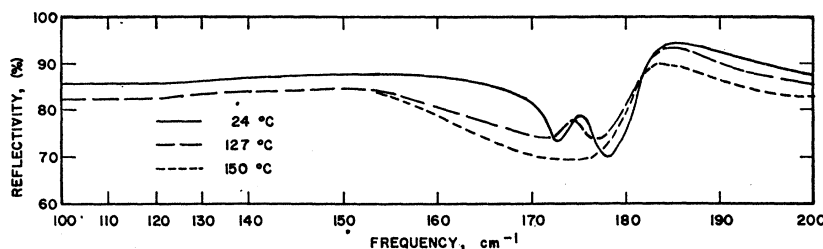


FIG. 3. Reflectivity of single-domain BaTiO₃ from 100 to 200 cm⁻¹.

insert them in precisely the same position in the beam. The shape of the curve is correct, however, and clearly shows the splitting required by the change in crystal symmetry from tetragonal to rhombohedral.¹⁰

The 100- to 200-cm⁻¹ region contains the lattice band first discovered by Spitzer *et al.*¹² Temperature-dependent reflectivity measurements taken in this region on the vacuum grating spectrometer (angle of incidence 45 deg) are shown in Fig. 3. This instrument was also used to measure reflectivity versus temperature in the 35- to 100-cm⁻¹ region. The results here did not meet

the desired accuracy ($\pm 1\%$) and therefore served only as a check on the interferometer data.

Submillimeter and Millimeter Region

A lamellar-grating submillimeter interferometer^{19,20} was used to cover the spectral region from 10 to 120

¹⁹ J. M. Ballantyne, MIT Technical Report No. 188, Insulation Research Laboratory, March, 1964 (unpublished).

²⁰ S. J. Allen, Jr., MIT Progress Report No. XXXI, Insulation Research Laboratory, July, 1962 (unpublished) *ibid.*, p. 74; S. J. Allen, Jr. and J. M. Ballantyne, *ibid.*, No. XXXIII, July, 1963, p. 72.

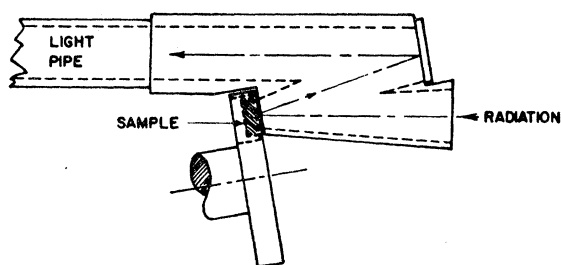


FIG. 4. Ray diagram of conical light-pipe optics for submillimeter reflection.

cm^{-1} . The conical lightpipe reflection optics used in this instrument had a principal angle of incidence of 10 deg (Fig. 4). Most of the measurements on the interferometer were taken with a spectral resolution of 5 cm^{-1} , since no additional structure was resolved on either the interferometer or the vacuum grating spectrometer with a resolution of 1 cm^{-1} .

The noise level of the interferometer in the important 10- to 20-cm^{-1} range was such that for any single run a $\pm 10\%$ uncertainty was present in the reflectivity. A method of averaging was therefore developed, by making use of a long series of mirror-sample-mirror-sample, etc., runs. The mirror runs were then averaged, as were the sample runs, and the transforms of the averaged interferograms computed. Each measurement thus constitutes an average of about 16 separate runs on a crystal, and each curve in Fig. 5 is the average of several such measurements on different crystals. The absolute values and shapes of these curves are believed to be accurate to $\pm 1\%$, except between 10 and 30 cm^{-1} , where deviations as great as $\pm 2\%$ may exist.

Reflectivity was measured at 10 cm^{-1} using a system composed of a modulated carcinotron source, a rotating-vane attenuator serving as an isolator, the reflection

optics of Fig. 4, and a bolometer detector with amplifier. The results are given in Fig. 6 along with reflectivity values calculated from the microwave measurement of κ^* at 24 kMc/sec . The same millimeter system was used to measure reflectivity at 5 cm^{-1} by substituting a different carcinotron. The results show the same temperature behavior as Fig. 6, but are of dubious accuracy since the pipe at the sample surface is only three wavelengths in diameter at 5 cm^{-1} , and standing-wave effects could not be avoided. It was therefore assumed that no structure was present in the reflectivity between 1 and 10 cm^{-1} .

Microwave Region

Because of discrepancies between previous microwave measurements of single-domain BaTiO_3 , κ' and κ'' were remeasured at 24 kMc/sec . The method used involves measuring the standing-wave ratio in front of a thin crystal plate spaced a quarter wavelength from the shorted end of a waveguide.²¹ A quarter-wavelength thick quartz spacer was ground to fit the broached guide with a clearance of 0.0002 in. , the previously prepared BaTiO_3 plate being then cemented to its face and its edges trimmed with the air-abrasive technique. After insertion of the crystal-spacer sandwich in the sample holder, any spaces between the crystal edges and the waveguide wall were filled with silver paint. The crystal selected had a final thickness of 31μ , since it seemed impossible to prepare a plate of sufficient area in the $10\text{-}\mu$ thickness desired. The dielectric constant could therefore not be measured above the Curie point, since here κ^* was so high as to bring the crystal thickness very close to a quarter wavelength, thus decreasing the precision of measuring the distance between the crystal surface and the first electric field node. The results (accuracy about $\pm 20\%$) of the microwave measurement are given in Fig. 7.

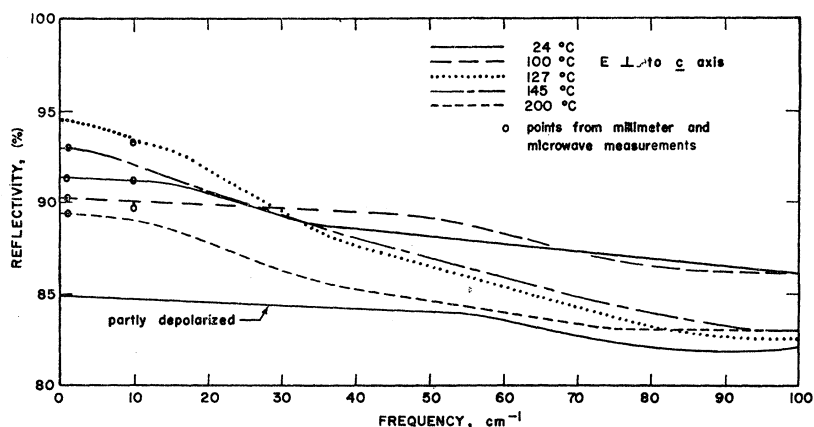


FIG. 5. Reflectivity of single-domain BaTiO_3 from 1 to 100 cm^{-1} .

²¹ S. Roberts and A. von Hippel, Phys. Rev. **57**, 1056 (1940); J. Appl. Phys. **17**, 610 (1946); A. von Hippel, *Dielectrics and Waves* (John Wiley & Sons Inc., New York, 1954), p. 73.

DISCUSSION

Nonexistence of 400-cm⁻¹ Band

Recent discussion has centered on the existence or nonexistence of the band at 400 cm⁻¹ reported by Last¹⁰ in the perovskite titanates. Evidence for the existence of this band came from transmission measurements of powders pressed in alkali-halide matrices. To resolve this controversy, single-crystal transmission measurements were made in the infrared. An examination of Fig. 1 reveals, in contrast to the powder measurements of Last, that for single crystals there is no rise in transmission in the 400- to 250-cm⁻¹ region. As noted by Spitzer *et al.*,¹² the transmission curve of Fig. 1 is that expected from a single lattice vibration at 492 cm⁻¹ and leads to the conclusion that the band at 400 cm⁻¹ does not exist in single-crystal BaTiO₃.

The anomalous nature of this band is exposed by other considerations: Recent workers could not find it in single crystals either in reflection or transmission^{11,12}; it occurs at the same frequency¹⁰ in SrTiO₃, PbTiO₃, and BaTiO₃, while the 491-cm⁻¹ band and others discovered since^{11,12,22} occur at different frequencies in these materials; it shows no temperature dependence¹⁰ over a range of 300°K, while the 491- and 180-cm⁻¹ bands do show temperature-dependent splittings (see Figs. 2 and 3); it exhibits a marked dependence on powder density¹¹; and its frequency is affected much more by the refractive index of the matrix material than is the frequency of the 491-cm⁻¹ band.¹⁰ We conclude that it is caused by a scattering phenomenon.

Infrared Reflectivity

The infrared reflectivity of Figs. 1 and 3 agrees substantially with that observed by other workers on single-crystal BaTiO₃. In the 190- to 600-cm⁻¹ region, the curve is very close to that of Ikegami *et al.*,¹³ the reflectivity from 200 to 400 cm⁻¹ being less than that reported by Spitzer *et al.*¹² The observed reflectivity near the 182-cm⁻¹ band lies between the values of Ikegami and Spitzer, agreeing well with the former on the high-frequency, and with the latter on the low-frequency side. A splitting of the 182-cm⁻¹ band was observed at room temperature (cf. Fig. 3) but disappeared on heating above the Curie point. This splitting can be accounted for by the change in crystal symmetry from cubic, above the Curie point, to tetragonal below this temperature, the symmetry of the vibration changing from a triply degenerate *F*_{1u} mode in the cubic phase to a doubly degenerate *E* plus a single *A* mode in the tetragonal phase.¹⁰ At normal incidence, only the *E* mode should be observed, as the crystals were polarized with the *c* axis perpendicular to the surface and would thus appear isotropic to the incident wave. Measurements in the 182-cm⁻¹ region were taken

²² C. H. Perry, MIT Quarterly Progress Report No. 71, Electronics Research Laboratory, October, 1963 (unpublished), p. 23.

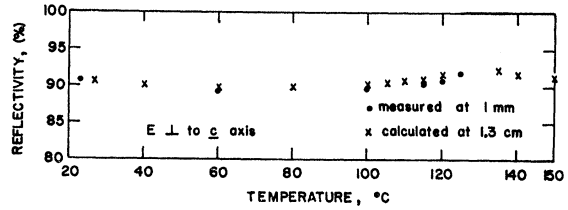


FIG. 6. Reflectivity of single-domain BaTiO₃ at $\lambda = 1$ mm and 1.3 cm.

with a 45-deg angle of incidence, however, and thus both modes should be observed in the tetragonal phase. That such a splitting can be observed in reflectivity is attested by Fig. 2.

Submillimeter, Millimeter, and Microwave Reflectivity

Reflectivity of single-crystal BaTiO₃ has not been previously measured from 1.6 to 100 cm⁻¹. The resolved structure in this range is limited to a broad drop in reflectivity from 10 to 80 cm⁻¹. Points taken at 0.77 and 10 cm⁻¹ agree well with the lowest frequency interferometer data (cf. Fig. 5).

The complex permittivity measured at 0.77 cm⁻¹ (Fig. 7) is in agreement with the values of Benedict and Durand,⁷ showing the results reported by Fousek⁸ at 9 kMc/sec to be in error. The measured permittivities are about half those observed at audio frequencies, the decrease resulting from the clamping of the mechanical vibrations above the piezoelectric resonance and not from the disappearance of the ferroelectric state. The same conclusion was reached by Benedict and Durand and is substantiated by Westphal,⁵ who found *c*-axis permittivities of about 4000 below and 2000 above the piezoelectric resonance of a single-domain crystal. Reflectivities calculated on the basis of Fig. 7 are accurate to better than $\pm 1\%$.

Reflectivity Analysis

Values of the real (κ') and imaginary (κ'') parts of the relative permittivity in the 1- to 1000-cm⁻¹ range were

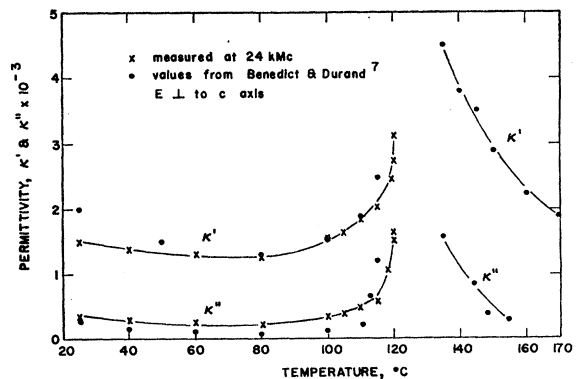


FIG. 7. Permittivity of single-domain BaTiO₃ at 24 kMc/sec.

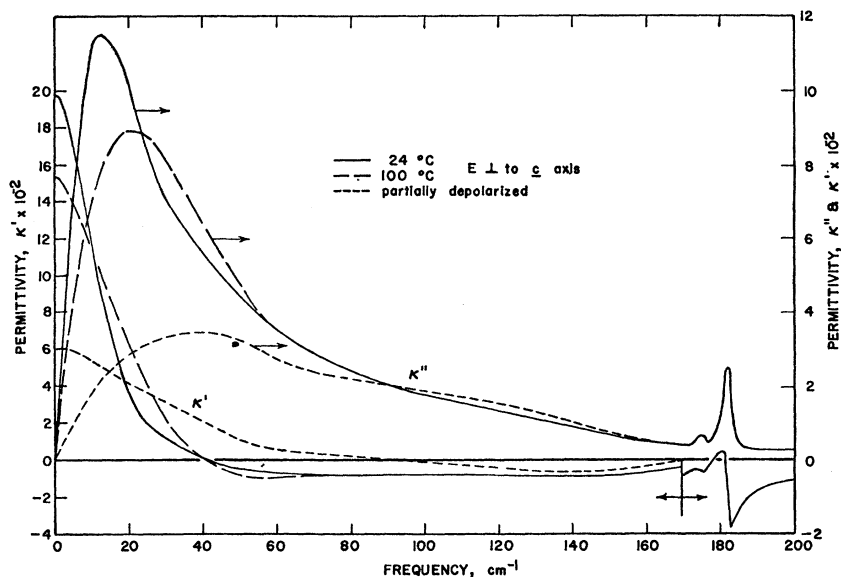


FIG. 8. Permittivity of single-domain BaTiO_3 from 1 to 200 cm^{-1} .

calculated on a digital computer from the composite reflectivity data (Figs. 1, 3, and 5) by means of a Kramers-Kronig analysis and the Fresnel equations for normal incidence (cf. Refs. 11 and 12). In this computation, the reflectivity was assumed to be constant at the 4000- cm^{-1} value to infinite frequency because

there is no structure in the reflectivity above 4000 cm^{-1} caused by the physical processes in question, and the localized nature of the analysis permits negligible contributions from the high-frequency spectrum.

The computed curves of κ' and κ'' for single-crystal BaTiO_3 between 24 and 200°C are given in Figs. 8 to

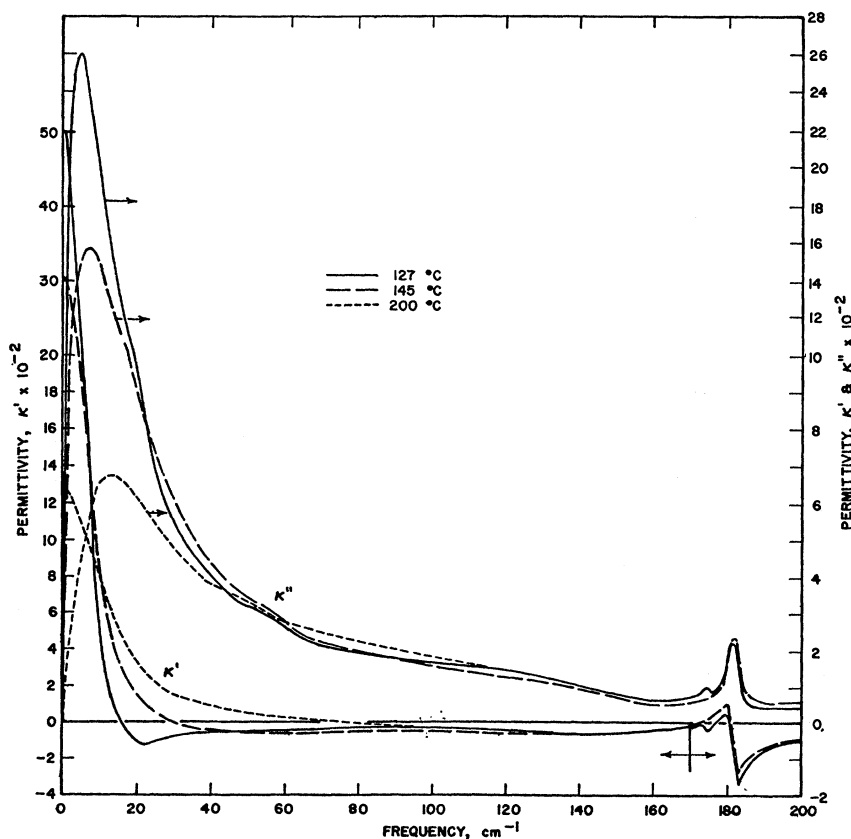


FIG. 9. Permittivity of single-crystal BaTiO_3 from 1 to 200 cm^{-1} .

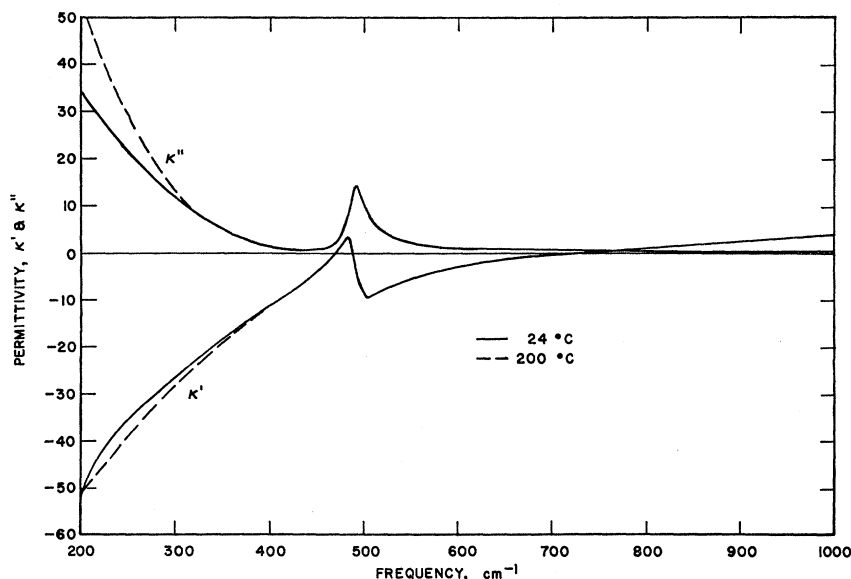


FIG. 10. Permittivity of single-crystal BaTiO₃ from 200 to 1000 cm⁻¹.

10. At low frequency, their main feature is a strong temperature-dependent maximum located below 20 cm⁻¹. Negative values of κ' (extending beyond 700 cm⁻¹) form a high-frequency tail of this peak and indicate that it is due to a resonance phenomenon (although an unusual one). Above 100 cm⁻¹, there is little temperature dependence in the κ' and κ'' curves, except for the splitting of the lattice band at 182 cm⁻¹. The lattice vibrations at 182 and 491 cm⁻¹ contribute the usual resonance dispersion to the κ' and κ'' curves. The frequencies of the three resonances observed are listed in Table II.

The accuracy of the reflectivity analysis depends on the validity of the assumption of a linear material response to the measuring field and of normal incidence for the radiation, on the accuracy of the measured reflectivity data, and on the precision with which the measured data are fed to the computer. The assumption of a linear material response is justified on the basis of the extremely small field strengths present in the infrared spectrometer beams. Barker and Tinkham¹¹ justified the normal incidence assumption for an angle of incidence of 45 deg. In the present work the approximation is even better, since the usual incident angle was only 10 deg. Errors introduced by the piecewise-linear

approximation of the reflectivity curves were minimized by sampling at frequency increments corresponding to 1% changes in the value of the reflectivity.

The main factor which determines the accuracy of the computed κ' and κ'' values is therefore the accuracy of the measured reflectivity, whose effect on the computed values of permittivity is greatest in the low-frequency region (Fig. 11). Values of permittivity were calculated for the room-temperature reflectivity and for curves representing the upper and lower limits of experimental error. The shapes of the κ' and κ'' curves are similar for all three calculations, but the peak in κ'' shifts by as much as 4 cm⁻¹ and the absolute magnitudes of κ' and

TABLE II. Frequencies of the peaks in κ'' for single-domain BaTiO₃.

| T(°C) | ω ₁ (cm ⁻¹) | ω ₂ (cm ⁻¹) | ω ₃ (cm ⁻¹) |
|------------------|------------------------------------|------------------------------------|------------------------------------|
| 24 | 12 ₋₂ ⁺⁴ | 174±1 | 182±1 491±1 |
| 100 | 22±10 | 174±1 | 182±1 491±1 |
| 127 | 6 ₋₁ ⁺⁷ | 174±1 | 182±1 491±1 |
| 145 | 8 ₋₂ ⁺⁶ | 174±1 | 182±1 491±1 |
| 200 | 13±4 | 174±1 | 182±1 491±1 |
| 115 ^a | 39±20 | 174±1 | 182±1 491±1 |

^a Partially depolarized.

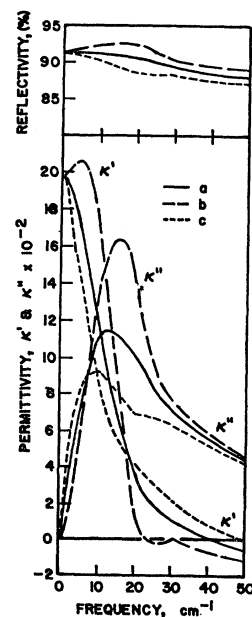


FIG. 11. Influence of the experimental uncertainties in reflectivity on the computed permittivity at 24°C: (a) measured curve, (b) upper limit of error, (c) lower limit of error.

TABLE III. Physical constants of BaTiO₃.

| j | $(\omega_l)_j$ | $(\omega_l)_j$ (Ref. 23) | $\epsilon(\infty)$ (Ref. 24) | C^b |
|-----|----------------|-----------------------------|---------------------------------|------------------|
| | | | 5.29 | 11×10^4 |
| 2 | | 180 | | |
| 3 | 182 | ^a | | |
| 4 | ^a | 463 | | |
| 5 | 491 | 735 | | |

^a $(\omega_l)_4$ and $(\omega_l)_3$ are degenerate.

^b Computed from the data of Benedict and Durand (Ref. 7).

κ'' are appreciably affected. A similar precision holds for the curves of Figs. 8 and 9.

Comparison with Cochran's Theory

The results of the preceding analysis may be compared with the crystal behavior predicted on the basis of Cochran's theory,⁴ according to which the frequency of the first lattice vibration shifts with temperature and may be calculated from the relations

$$\epsilon(0)/\epsilon(\infty) = \prod_{j=2}^n (\omega_l)_j^2 / (\omega_t)_j^2 \quad (1)$$

and

$$\epsilon(0, T) = C/T - T_C, \quad (2)$$

where C is the Curie constant and T_C the Curie temperature. Equation (1) is derived by Cochran and gives the static dielectric constant $\epsilon(0)$ for the perovskite titanates in terms of the optical dielectric constant $\epsilon(\infty)$ and the transverse (ω_t) and longitudinal (ω_l) lattice-vibrational frequencies (at $k=0$); the product is taken over all normal modes of the lattice except the acoustic mode ($j=1$). Above the Curie point the static dielectric constant obeys the Curie law [Eq. (2)]. The temperature dependence of the frequency $(\omega_l)_2$ is given explicitly by solving Eqs. (1) and (2):

$$\omega_{l2}^2(T) = 23(T - T_C), \quad (3)$$

when the physical constants for BaTiO₃ listed in Table III are substituted. Frequencies predicted on the basis of Eq. (3) for ω_{l2} are shown in Table IV. The frequency shifts of the lowest frequency peak in the κ'' curve (Fig. 9 and Table II) calculated from the experimental data are much smaller than required by Cochran's theory, even allowing for experimental error. Quantitative disagreement is expected, however, since Cochran assumed slightly damped lattice vibrations in the derivation of Eq. (1), while our measurement shows the low-frequency mode to be highly damped. This low-

²³ W. Cochran and R. A. Cowley, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. 1, p. 59.

²⁴ G. Busch, H. Flury, and W. Merz, *Helv. Phys. Acta* **21**, 212 (1948).

TABLE IV. Predicted frequency of the lowest transverse optic mode in BaTiO₃.

| Temperature (°C above T_C) | Frequency (cm ⁻¹) |
|----------------------------------|----------------------------------|
| 0 | 0 |
| 20 | 21 |
| 30 | 26 |
| 50 | 34 |
| 80 | 43 |

frequency band may be the envelope of a series of resonances of "dipolar distortion modes," as suggested by von Hippel²⁵ for the disappearance of the ferroelectric response beyond the microwave region. This interpretation is being investigated in more detail.

CONCLUSIONS

The dispersion of the polarization in single-domain BaTiO₃ from 1 to 1000 cm⁻¹ consists of resonances located at 12, 182, and 491 cm⁻¹. A resonance previously reported¹⁰ near 400 cm⁻¹ does not exist in single-crystal BaTiO₃. The 12-cm⁻¹ resonance is responsible for the ferroelectric state in this material and exhibits an unusual dispersion characteristic, being very broad and possessing an extended high-frequency tail. Because its frequency is near 12 cm⁻¹, no relaxation in the dielectric constant of single-domain BaTiO₃ occurs in the microwave region (0.8 cm⁻¹); such relaxation should not become pronounced until frequencies of 5 cm⁻¹ are exceeded. The frequency of the 12-cm⁻¹ resonance remains between the limits of 6 and 22 cm⁻¹ from 24 to 200°C. Above the Curie point, the strength of this resonance decreases rapidly with increasing temperature.

The 182- and 491-cm⁻¹ bands show typical resonance dispersions and are due to lattice vibrations. A splitting of the 182-cm⁻¹ vibration is caused by the change in crystal symmetry from cubic to tetragonal at the Curie point.

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²⁵ A. von Hippel *et al.*, MIT Technical Report No. 178, Insulation Research Laboratory, March, 1963 (unpublished), p. 31.