

IV. FAR INFRARED SPECTROSCOPY

Prof. C. H. Perry
Jeanne H. Fertel

D. J. McCarthy
E. C. Reifenstein III
J. P. Stampfel, Jr.

H. D. Wactlar
E. F. Young

A. DIELECTRIC BEHAVIOR OF BaTiO_3 SINGLE CRYSTALS IN THE INFRARED REGION

An investigation of the temperature and frequency dependence of the dielectric constant of BaTiO_3 single crystals was extended to the infrared region by means of transmission and reflectivity measurements made with the aid of instrumentation in the Spectroscopy Laboratory, M. I. T. *

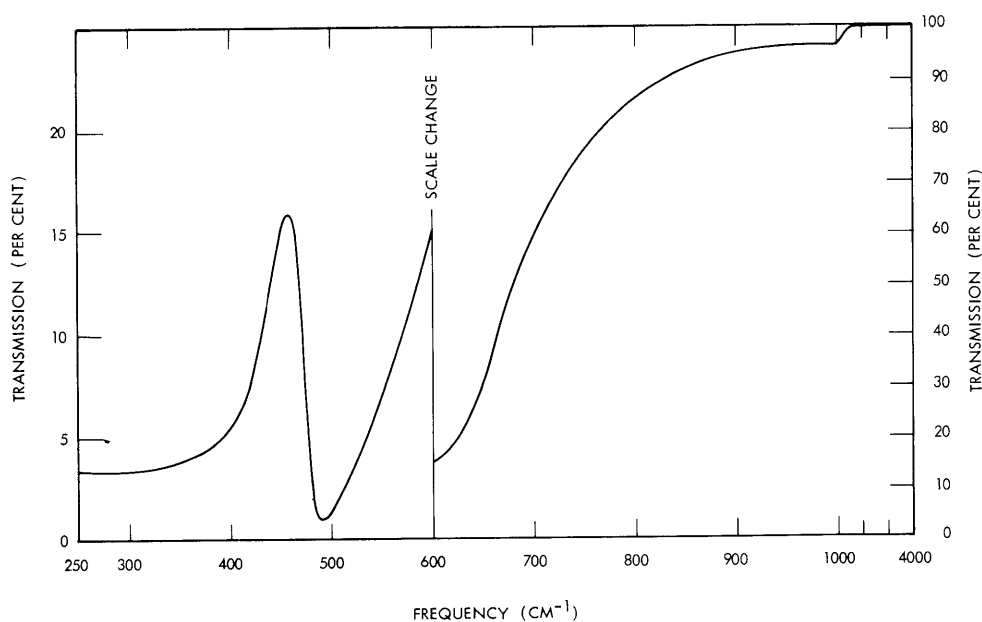


Fig. IV-1. Infrared transmission of 3- μ thick BaTiO_3 single crystal.

Transmission measurements in the frequency range $4000\text{-}250\text{ cm}^{-1}$ in the infrared were made in order to resolve the conflict between Last's¹ work and the recent papers of Barker and Tinkham,² and Spitzer, Miller, Kleinman, and Howarth³ in the matter of lattice-vibration frequencies. Several thin crystals were prepared by Last's techniques and measured in transmission with Perkin-Elmer 421 and 521 double-beam spectrophotometers. The transmission curve for the best crystal, corrected for absorptions that were due to traces of the phosphoric acid etch and for the effects of

* The work of this laboratory is supported in part by the National Science Foundation (Grant G-19637).

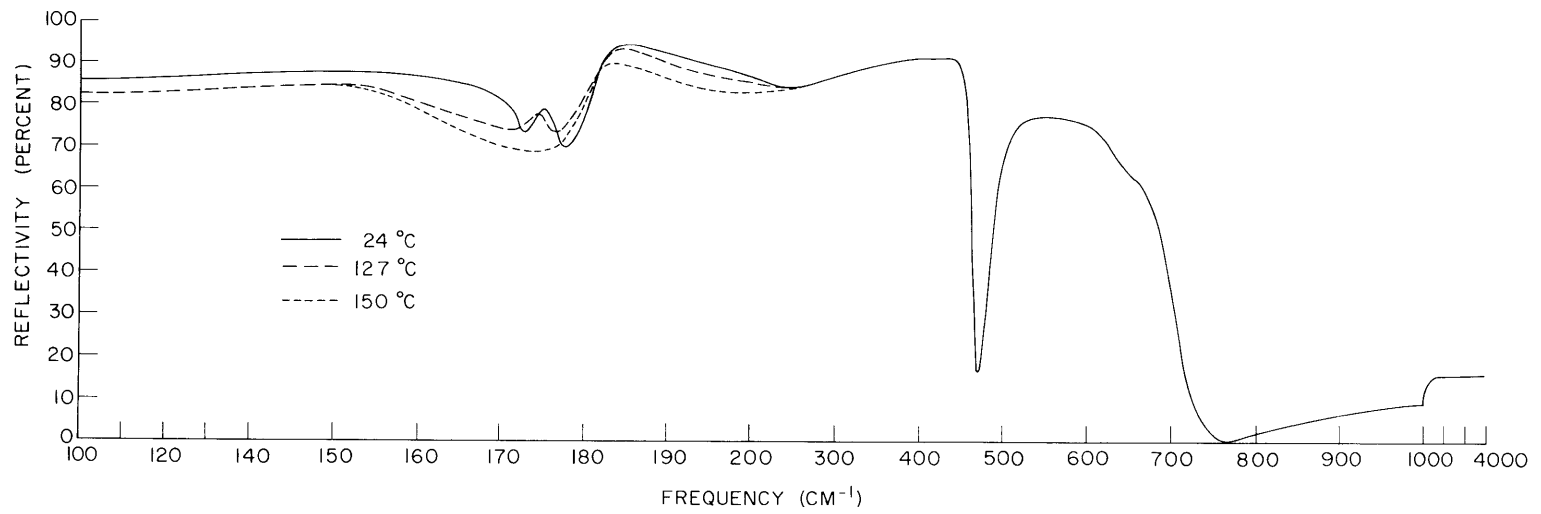


Fig. IV-2. Infrared reflection of single-domain BaTiO₃ crystals.

(IV. FAR INFRARED SPECTROSCOPY)

stray radiation in the instrument, is shown in Fig. IV-1. Contrary to Last's results, there is no rise in transmission in the $400\text{-}250\text{ cm}^{-1}$ region; this shows that the second band reported by him at 340 cm^{-1} is actually at the lower frequency 183 cm^{-1} , as found by Spitzer et al.³ and the present writer.

The reflectivity of polarized BaTiO_3 single crystals was measured in the region from 1000 cm^{-1} to 35 cm^{-1} with the facilities described previously.⁴ Samples were prepared by etching large "butterfly" crystals in hot phosphoric acid to remove the surface layer, and then polarizing them to c-domain plates.⁵ To obtain a sufficiently large area, two polarized crystals were butted together and then cast into an epoxy resin block so as to maintain the plane surface.

The composite reflectivity curve measured for many samples on a variety of instruments and at three temperatures is given in Fig. IV-2. The angle of incidence is 45° from 100 cm^{-1} to 250 cm^{-1} , and 10° at higher frequencies. Resonances are observed at 491 and 182 cm^{-1} .

The lattice band at 180 cm^{-1} occurs at about the same place as that reported by Spitzer et al.³ It has a slight temperature dependence which is easily explainable by ordinary broadening with increase in temperature and by the change in lattice symmetry above and below the Curie point. No anomalous change in the frequency or intensity of this band is observed as one traverses the Curie point.

Accurate measurements⁶ in the submillimeter and millimeter regions indicate a third resonance at approximately 12 cm^{-1} which is responsible for the ferroelectric state in BaTiO_3 .

J. M. Ballantyne

(Dr. Joseph M. Ballantyne, Research Associate in the Department of Electrical Engineering, has been using the equipment of our group in the Spectroscopy Laboratory, M. I. T.)

References

1. J. T. Last, *Phys. Rev.* 105, 1740 (1957).
2. A. S. Barker and M. Tinkham, *Phys. Rev.* 125, 1529 (1962).
3. W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, *Phys. Rev.* 126, 1710 (1962).
4. C. H. Perry, Quarterly Progress Report No. 70, Research Laboratory of Electronics, M. I. T., July 15, 1963, p. 19.
5. J. M. Ballantyne, Quarterly Progress Report No. XXXII, Laboratory for Insulation Research, M. I. T., 1963, p. 5.
6. J. M. Ballantyne, Ph. D. Thesis, Department of Electrical Engineering, M. I. T., February 1964.

