

III. FAR INFRARED SPECTROSCOPY

Prof. C. H. Perry

A. INFRARED STUDIES OF PEROVSKITE TITANATES

1. Introduction

Several infrared absorption studies¹⁻³ of perovskite and other titanates of the perovskite structure have been carried out to determine the frequencies of the normal modes of vibration of these important materials. Last¹ considered the vibrations of the cubic perovskites (for example, SrTiO₃) in terms of the modes of vibration of the TiO₆ octahedra and reached the conclusion that there should be three triply degenerate infrared-active vibrations. From his infrared studies he assigned the frequencies as follows: a Ti-O stretching mode, ν_1 , at 610 cm⁻¹; a Ti-O bending mode, ν_2 , at 395 cm⁻¹; and a cation-TiO₃ lattice vibration, ν_3 . The frequency ν_3 was beyond the range of his spectrometer.

More recently, Barker and Tinkham² and Spitzer and his co-workers³ have made thorough investigations of the infrared reflectivity of SrTiO₃. Both groups placed the highest frequency at approximately 550 cm⁻¹ and assigned it as a Ti-O stretching vibration. They also found evidence for two more frequencies near 178 cm⁻¹ and 90-100 cm⁻¹. The higher of these could be seen directly in the reflectivity curve and was assigned as a cation-TiO₃ vibration by Spitzer et al.,³ whereas the low frequency was obtained only from analysis of the reflection data by a Kramers-Kronig⁴ (K-K) and classical dispersion treatment. It was further interpreted as the chief contributor to the ferroelectric behavior of the crystal.

An investigation of the Raman spectrum of SrTiO₃, a substance that is not expected a priori to exhibit its fundamental frequencies therein, was reported by Narayanan and Vedam.⁵ Although the spectrum obtained was very weak and broad, it was interpreted by them as showing certain frequencies in reasonably close accord with the infrared values of Last.¹ They selected the frequencies 620, 335, and 90 cm⁻¹ as those corresponding to Last's ν_1 , ν_2 , and ν_3 . Also, they asserted that a normal mode rejected by Last as a "torsional motion of the unit cell" (that is, as an optically inactive motion of symmetry species F_{2u}) should in fact be included among the infrared-active modes, all of which are of symmetry species F_{1u}. They placed the frequency of this vibration at 441 cm⁻¹ on the basis of their Raman data, in agreement with the calculations of Rajagopal and Srinivasan,⁶ who also estimated the other frequencies as 517, 512, and 74 cm⁻¹. The agreement of the calculated and observed values is not expected to be very close in view of the simplifications required to make the computation tractable.

No band near 450 cm⁻¹ had been observed by previous workers in the infrared reflection spectra of SrTiO₃.¹⁻³ In this report we wish to point out experimental evidence

(III. FAR INFRARED SPECTROSCOPY)

for the nonexistence of a band at $\sim 450\text{ cm}^{-1}$ in SrTiO_3 , but additional bands of varying intensity are present in CaTiO_3 and in PbTiO_3 .

2. Experiment

The room-temperature reflectances of calcium, strontium, and lead titanates have been measured from 4000 cm^{-1} to 30 cm^{-1} relative to the reflectance of a reference mirror coated with aluminum. Transmission measurements over the same frequency range were made on finely divided powders of the three materials suspended in polyethylene and potassium bromide matrices.

Reflection and transmission data above 300 cm^{-1} were obtained on a Perkin-Elmer Model 112 double-pass instrument equipped with NaCl and CsBr prisms. The reflection spectra were recorded at an angle of incidence of approximately 45° on the sample. The transmission data were repeated on a Perkin-Elmer Model 521 double-beam spectrophotometer that scanned continuously from 4000 to 250 cm^{-1} . A reflection attachment that provided an angle of incidence of approximately 15° and required a sample of only $18 \times 2\text{ mm}$ area was used in the Perkin-Elmer 521 instrument to repeat the reflection data down to 250 cm^{-1} .

A single-beam grating instrument originally constructed in this Laboratory by Lord and McCubbin,⁷ and recently modified to a vacuum instrument with more convenient sample optics⁸ was used from 500 cm^{-1} to 30 cm^{-1} . The angle of incidence was 15° . The two Perkin-Elmer instruments were flushed with evaporated liquid nitrogen to remove water vapor as much as possible. The complete removal of water vapor in the long-wave vacuum instrument provided smooth backgrounds so that more accurate transmission and reflection data could be obtained as compared with those obtained with a flushed instrument.

Reflection measurements at 5 cm^{-1} were made on all three materials by using a 2-mm carcinotron as a source at Lincoln Laboratory, M. I. T., and were found to be in good agreement with our far infrared results down to 30 cm^{-1} .

The specimen of SrTiO_3 consisted of a large, highly polished single crystal, 1 inch in diameter. Each of the calcium and lead titanate samples was made up of a mosaic of four polycrystalline samples cemented to an aluminum backing plate. The materials were ground and polished to a sample size of 1×1.25 inches so that full use could be made of the light beam with no vignetting.

Samples for transmission studies above 300 cm^{-1} were suspended in a KBr pellet by the usual techniques. Below 600 cm^{-1} polyethylene was found to be the most convenient matrix. The temperature of the press was brought up to approximately 120°C , and the samples were pressed at $25,000\text{ lb/sq in.}$ at this temperature for approximately 5 minutes.

3. Analysis of Data

The reflectivity data were transformed by using a Kramers-Kronig relation.⁴ The K-K relation used for the reflectivity R can be expressed as

$$\theta(\nu) = \frac{2\nu}{\pi} \int_0^{\infty} \frac{\ln[r(\nu')] d\nu'}{\nu^2 - \nu'^2}, \quad (1)$$

where $\theta(\nu)$ is the associated phase angle, which was obtained by using the IBM 7090 digital computer.

The reflectivity amplitude is characterized by $re^{i\theta}$, where $r = R^{1/2}$. This has been shown to be a good approximation, even at 45° .²

$$re^{-i\theta} = (n-ik-1)/(n-ik+1) \quad (2)$$

$$n = \frac{1 - r^2}{1 + r^2 - 2r \cos \theta} \quad (3)$$

$$k = \frac{2r \sin \theta}{1 + r^2 - 2r \cos \theta}, \quad (4)$$

where n is the refractive index, and k is the extinction coefficient.

The real and imaginary parts of the complex dielectric constant, ϵ' and ϵ'' , can be written

$$\epsilon' = n^2 - k^2 \quad (5)$$

$$\epsilon'' = 2nk, \quad (6)$$

and it is more revealing to show the results of the dispersion analysis in terms of the dielectric constant than in terms of n or k .

The infinite integral in Eq. 1 was evaluated by representing $\ln r(\nu')$ by straight-line segments between data points. The data were extrapolated to cover the infinite interval of Eq. 1. The reflectivity was assumed constant from 4000 cm^{-1} to infinity and from 30 cm^{-1} to zero. The justification of the extension of the data was confirmed by comparing the limiting values of R predicted from known values of the high- and low-frequency dielectric constants when these values were known. It is assumed that $k \ll n$ at these limiting frequencies so that

$$R = (\epsilon^{1/2} - 1)^2 / (\epsilon^{1/2} + 1)^2. \quad (7)$$

Each peak in the ϵ'' vs energy (frequency) plot provided by the K-K analysis represents a resonance. The frequency of a given resonance is the frequency at which the conductivity σ , $\sigma_j = \epsilon_j'' \nu/2$, is a maximum.⁹ The quantity ϵ_j'' is the contribution of the j^{th} resonance to ϵ'' .

(III. FAR INFRARED SPECTROSCOPY)

In the approximation $\gamma_j/\nu_j \ll 1$, the maximum of ϵ'' also occurs at ν_j , where γ is given by the frequency halfwidth of the ϵ'' peak.

4. Discussion

The reflectance and transmittance curves are shown in Figs. III-1 through III-3. Figures III-4 through III-6 show the real and imaginary parts of the dielectric constant for the three materials. Measurements below 400 cm^{-1} are estimated to be accurate to approximately ± 5 per cent for the reasons reported earlier.¹⁰

The reflectance curve shown here for SrTiO_3 resembles those reported by the earlier workers.¹⁻³ Last¹ was unable to work below 300 cm^{-1} and thus was unable to detect the minimum at approximately 175 cm^{-1} . Owing to the discrepancy between the results of Last and the other research groups with regard to a band at 400 cm^{-1} , we have studied carefully the region $500\text{-}300 \text{ cm}^{-1}$, using both a CsBr prism in the Perkin-Elmer 112 and the Perkin-Elmer 521, and a grating of 40 grooves/mm blazed at 360 cm^{-1} in our long-wave instrument. In the last case we used two reststrahlen plates of CaF_2 , which has a very sharp, short-wavelength cutoff at ~ 20 microns.

Reflection measurements over the same range were repeated at two different angles of incidence and also at liquid-nitrogen temperatures. No subsidiary maximum in the region of 450 cm^{-1} was found before the reflectance curve rose to a maximum at approximately 360 cm^{-1} .

Transmission measurements in this region showed a broad minimum at $\sim 400 \text{ cm}^{-1}$, in agreement with Last¹ and with Barker and Tinkham.² Barker and Tinkham, however, found that this minimum is sensitive to powder density and suggested that it might be a scattering effect. Only in CaTiO_3 and PbTiO_3 was a band observed in reflection around 450 cm^{-1} which had not been reported previously.

The curves also show a maximum at approximately 600 cm^{-1} with a slight shoulder near 700 cm^{-1} , as well as a low-frequency minimum in reflection around $150\text{-}200 \text{ cm}^{-1}$. These results are substantiated by the transmission data, which show minima in the region of reflection maxima and vice versa. As can be seen from the transmittance curves, several different concentrations of the sample were put in KBr and in polyethylene, and no appreciable shift in the frequencies of the minima was observed.

The maximum in reflectance at 605 cm^{-1} in SrTiO_3 is in good agreement with Last, Spitzer and his co-workers, and Barker and Tinkham (before K-K analysis of the data). This band has been assigned to the Ti-O stretching vibration by all of the previous workers.¹⁻³ But an ambiguity appears to exist as to whether an "internal vibration" or the cation- TiO_3 vibration is responsible for the ferroelectric behavior of these materials below their Curie points. In SrTiO_3 the ν_3 band has been interpreted as an internal vibration, and the ν_2 band as the cation- TiO_3 vibration by Spitzer et al., whereas the opposite view is held by others.

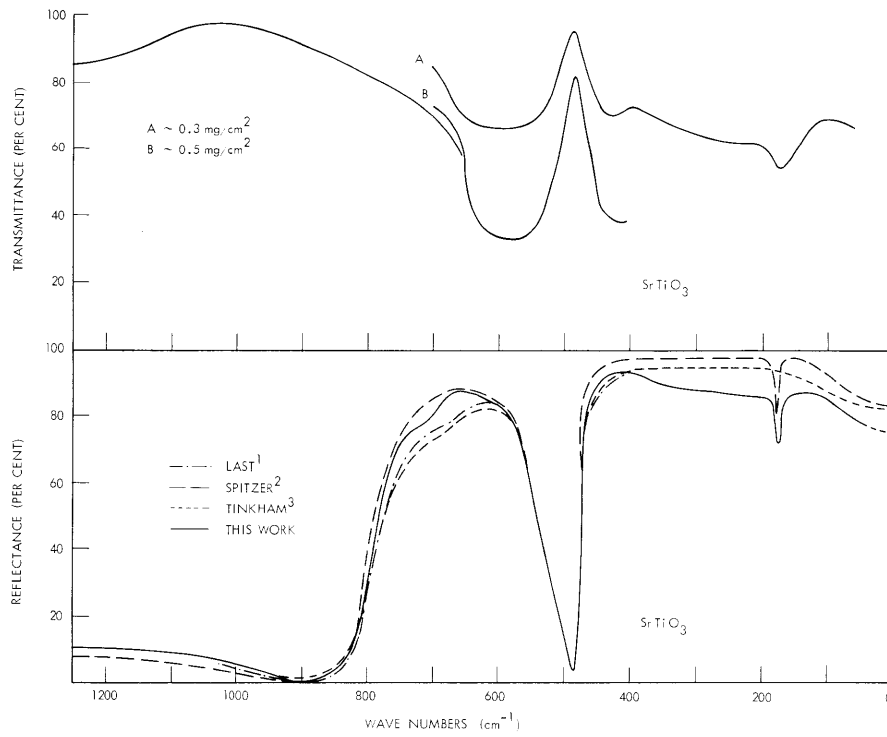


Fig. III-1. Infrared transmittance and reflectance spectra of SrTiO₃ from 1250 to 50 cm⁻¹.

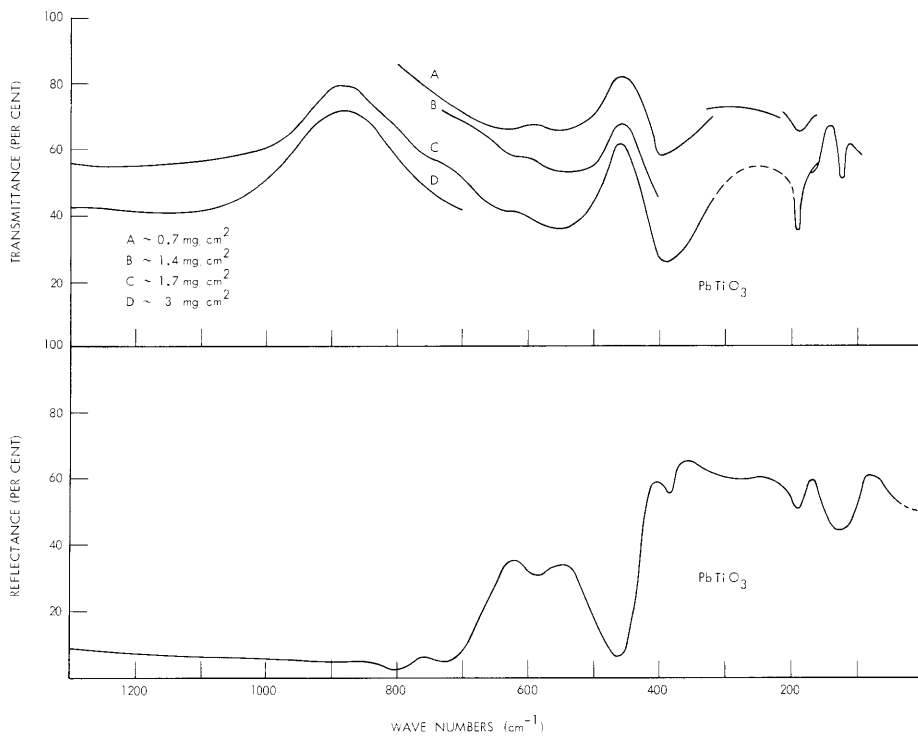


Fig. III-2. Infrared transmittance and reflectance spectra of PbTiO₃ from 1250 to 5 cm⁻¹.

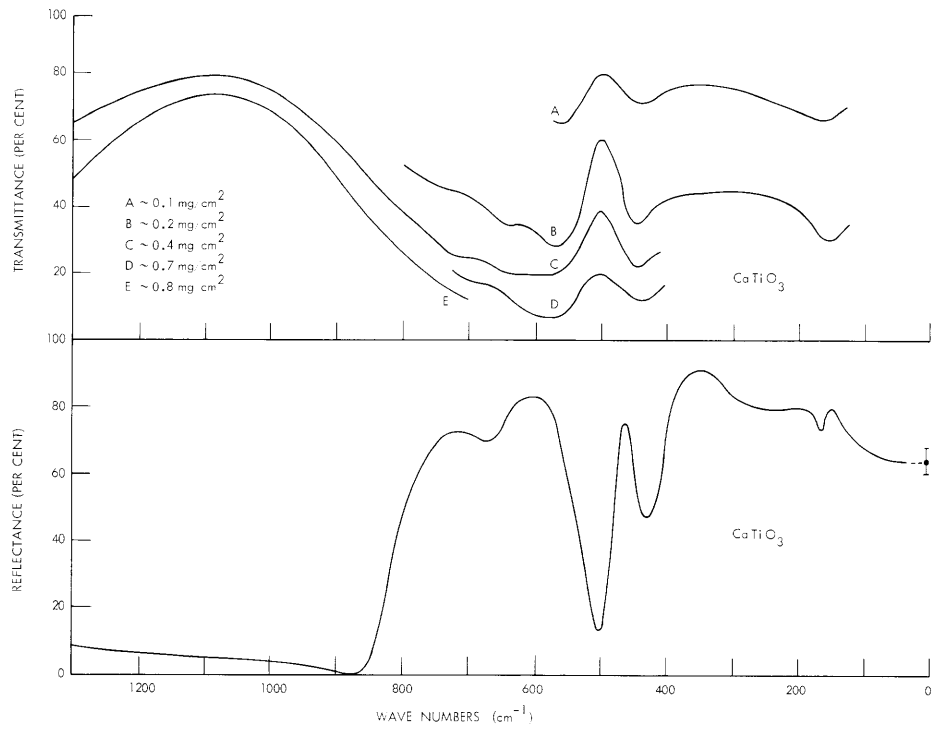


Fig. III-3. Infrared transmittance and reflectance spectra of CaTiO₃ from 1250 to 5 cm⁻¹.

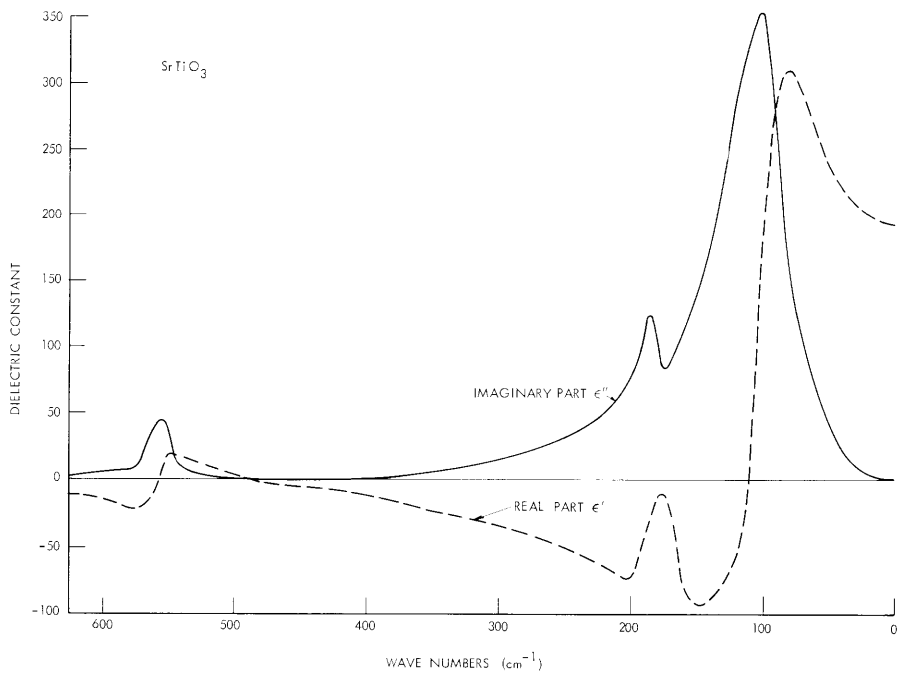


Fig. III-4. Real and imaginary parts of the dielectric constant of SrTiO₃ obtained from the reflectivity data in Fig. III-1.

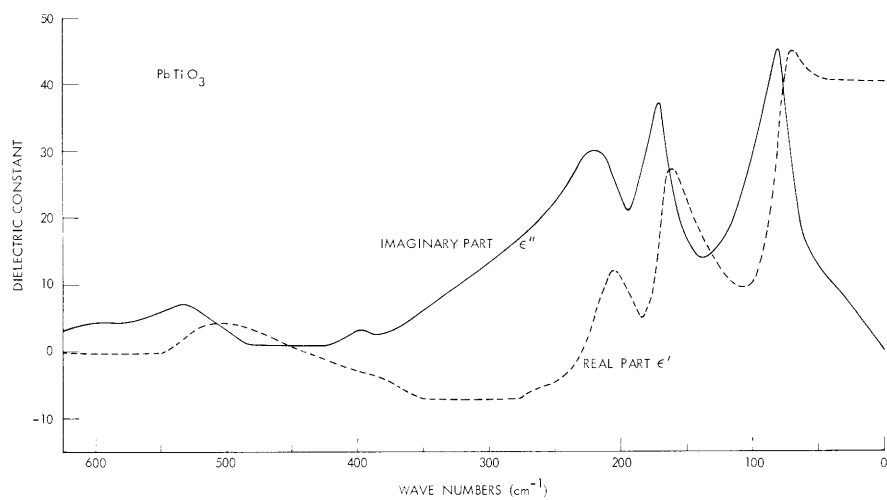


Fig. III-5. Real and imaginary parts of the dielectric constant of PbTiO₃ obtained from the reflectivity data in Fig. III-2.

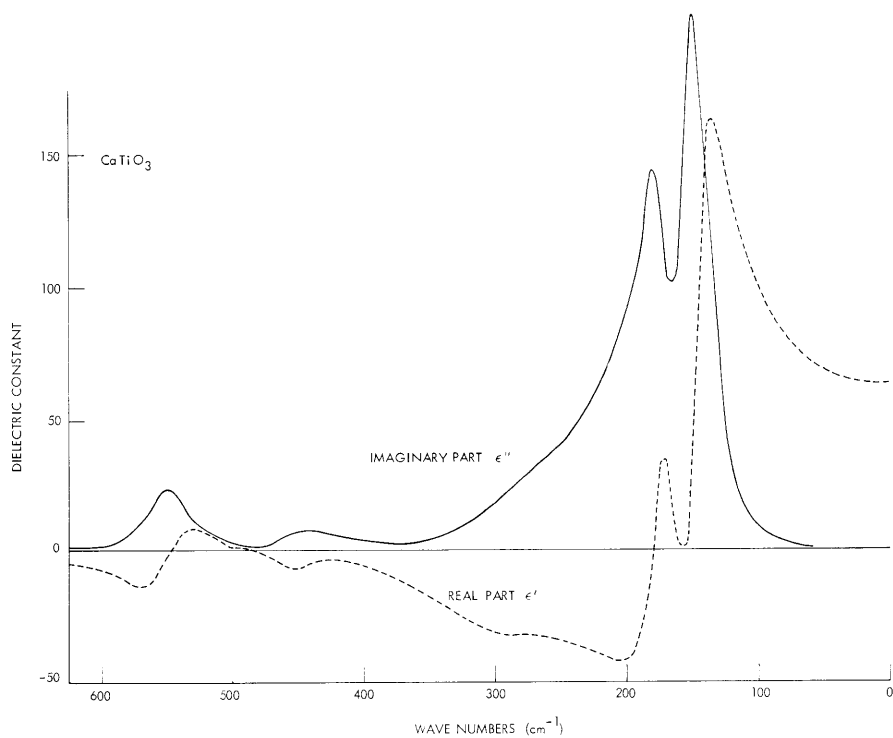


Fig. III-6. Real and imaginary parts of the dielectric constant of CaTiO₃ obtained from the reflectivity data in Fig. III-3.

Table III-1. Infrared and Raman frequencies in SrTiO₃ (cm⁻¹).

Modes	This work	Last ¹	Tinkham ²	Spitzer ³	Rupprecht ¹² using Spitzer's results	Raman (Obs.) Narayanan and Vedam ⁵	Calculated Rajagopal and Srinivasan ⁶
ν_1 (stretch)	555 ±5	610 ^a	550	544 ^b	544	620	517
ν_2 (bend)	185 ±5	395 ^a	~175 no assignment given	88 ^b	178	335	512
ν_3 (Sr-TiO ₃)	100 ±5	—	100	178	88	90	74
ν_4 (bend?)	—	—	—	—	—	441	445

^aFrequency maximum observed in reflectivity without K-K analysis of the data.

^bSpitzer does not make it clear whether or not ν_1 and ν_2 should be interchanged.

(III. FAR INFRARED SPECTROSCOPY)

Table III-1 shows the frequencies of the normal modes for SrTiO₃ reported by previous researchers, and comparison can be made with our results after a K-K analysis of our reflection studies.

SrTiO₃, PbTiO₃, and CaTiO₃ can be compared with reference to Table III-2. Only in CaTiO₃ and PbTiO₃ was a band around 450 cm⁻¹ observed, and the other additional band in PbTiO₃ also probably arises from systematic distortion from ideal cubic symmetry which would split degenerate modes to give more distinct resonances, although the splitting need not necessarily be observed in every case. However, strains in the crystal could result in the F_{2u} infrared-inactive mode becoming active; possibly this is the reason for an additional frequency in the Raman spectrum of SrTiO₃ reported by Narayanan and Vedam,⁵ since their interpretation of four infrared-active modes of F_{1u} symmetry for a cubic crystal appears to be incorrect on the basis of standard group theory.

Table III-2. Frequencies of the normal modes of SrTiO₃, PbTiO₃, and CaTiO₃ obtained from a K-K analysis of the reflection data.

Symmetry Point Group	SrTiO ₃ Cubic O _h	PbTiO ₃ Tetragonal C _{4v}	CaTiO ₃ Orthorhombic C _{2v}
ν_1 (stretch)	555 ± 5 (F _{1u})	530 ± 5 (E _u , A ₁) 400 ± 5	549 ± 3 (B ₁ , B ₂ , A ₁) 443 ± 3
ν_2 (bend)	185 ± 5 (F _{1u})	200 ± 3 (E _u , A ₁) 172 ± 2	179 ± 2 (B ₁ , B ₂ , A ₁)
ν_3 (cation-TiO ₃)	100 ± 5 (F _{1u})	83 ± 2 (E _u , A ₁)	148 ± 2 (B ₁ , B ₂ , A ₁)

From Table III-2 it can be seen that in all three titanates the ν_1 and ν_2 vibrations are essentially constant as the cation changes from Ca with a mass of 40 to Pb with a mass of 207; however, ν_3 depends sensitively on the nature of the cation. It is reasonable to associate the properties that remain nearly constant with the TiO₆ octahedron that is almost the same in all three materials. According to this reasoning, ν_1 and ν_2 should be vibrations associated with the TiO₆ octahedron, whereas ν_3 should depend on the cation mass (or the reduced mass of the cation and the TiO₆ octahedron), and it appears that the frequency of this vibration is lowered with increasing mass.

The authors wish to express thanks to Professor R. C. Lord for his advice and encouragement in this work; to Dr. G. R. Hunt of the Spectroscopy Laboratory, M. I. T.,

(III. FAR INFRARED SPECTROSCOPY)

for many helpful discussions of the K-K analysis; and to Mr. J. Ballentyne of the Insulation Laboratory, M. I. T., for the use of his program and for the reflection measurements taken at Lincoln Laboratory, M. I. T. We are much obliged to Dr. G. Wilkinson, King's College, London, for checking our dielectric constant results by using his K-K program on our reflectivity data. We would also like to express our thanks to Dr. G. Rupprecht, Tyco Laboratories, Inc., for supplying the samples.

C. H. Perry, B. N. Khanna

(Dr. B. N. Khanna is now at the Indian Institute of Technology, Department of Physics, Kanpur (U. P.), India.)

References

1. J. T. Last, Phys. Rev. 105, 1740 (1957).
2. A. S. Barker, Jr. and M. Tinkham, Phys. Rev. 125, 1527 (1962).
3. W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, Phys. Rev. 126, 1710 (1962).
4. T. S. Robinson, Proc. Phys. Soc. (London) B65, 910 (1952).
5. P. S. Narayanan and K. Vedam, Z. Physik 163, 158 (1961).
6. A. K. Rajagopal and R. Srinivasan, J. Phys. Chem. Solids 23, 633 (1962).
7. R. C. Lord and T. K. McCubbin, Jr., J. Opt. Soc. Am. 47, 689 (1957).
8. C. H. Perry, A technique of far infrared studies, Quarterly Progress Report No. 70, Research Laboratory of Electronics, M. I. T., July 15, 1963, pp. 19-31.
9. F. Seitz, Modern Theory of Solids (McGraw-Hill Book Company, Inc., New York, 1940), Chap. XVII, p. 635.
10. J. R. Durig, R. C. Lord, W. J. Gardner and L. H. Johnston, J. Opt. Soc. Am. 52, 1078 (1962).
11. A. Mitsuishi, Y. Yamada and H. Yoshinaga, J. Opt. Soc. Am. 52, 14 (1962).
12. G. Rupprecht, Private communication, 1963.