

Dielectric Constant in Paraelectric Perovskites

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The relative dielectric constant of a series of perovskites such as CaTiO_3 , SrTiO_3 , BaTiO_3 , PbTiO_3 , and KTaO_3 has been measured at microwave frequencies over a wide range above the Curie temperature. It was found that a Curie-Weiss law of the form $\epsilon = \epsilon_L + C/(T - T_c)$ is accurately obeyed where ϵ_L is of the order of 50 and represents the dielectric constant in the limit of infinite temperature, and that T_c and C , the Curie temperature and Curie constant, increase monotonically with increasing cation mass. ϵ_L consists of contributions from the electronic polarizability, temperature-independent optically active lattice vibrations, and a dominant term stemming from the finite frequency of the temperature-dependent soft mode in the limit of infinite temperature. The limiting frequency of the "soft mode" at high temperatures is estimated.

I. INTRODUCTION

THE dielectric constant in perovskite structures has been the subject of many investigations, both experimental and theoretical. Some of these materials, like BaTiO_3 , are ferroelectric below a Curie temperature T_c . Above T_c , they are paraelectric, and the dielectric constant follows a Curie-Weiss law as a function of temperature T . This law is usually given in the form $\epsilon = C/(T - T_c)$ or $\epsilon = \epsilon_{op} + C/(T - T_c)$. C is the Curie constant and ϵ_{op} is the contribution of the electronic polarizability to the dielectric constant of the order of 5 to 6. Many of the determinations of the dielectric properties have been made with data over a rather limited temperature range. However, Gränicher and Jakits¹ have noted that the constant term is larger than should be expected from the optical index of refraction.

In this paper, we present an accurate determination of the dielectric constant at microwave frequencies over a wide temperature range up to 1000°K on a series of perovskites, (CaTiO_3 , SrTiO_3 , BaTiO_3 , PbTiO_3 , and KTaO_3) and their mixtures. Our results can be accurately described (with less than 1% deviation) by an equation of the form: $\epsilon = \epsilon_L + C/(T - T_c)$. ϵ_L is between 39 and 58 for all these substances and thus substantially exceeds the contribution of the electronic polarizability to the dielectric constant. The parameters T_c and C have been determined for these substances and show a monotonic dependence on the cation mass.

As proposed by Cochran² and verified by the experimental work of Barker and Tinkham,³ and Cowley,⁴ the temperature dependence of the dielectric constant for SrTiO_3 can be understood in terms of a temperature-dependent "soft mode," i.e., a low-lying transverse optically active lattice vibration where $\omega_T^2 = A(T - T_c)$. We would like to point out, however, that this relation is only a good approximation not too far above the

Curie temperature. It is immediately obvious, though, that the frequency of this lattice mode cannot increase indefinitely with temperature since it is determined by finite masses and finite force constants. The limiting frequency at infinite temperature $\omega_T(\infty)$ has been obtained from the experimental data and the temperature dependence of the frequency was found to be of the form $\omega_T^{-2} = \omega_T^{-2}(\infty) + [A(T - T_c)]^{-1}$. The significance of $\omega_T(\infty)$ may be seen in the fact that, at high temperatures, the effect of the long-range Coulomb interaction which is responsible for the ferroelectric behavior should become negligible. In all cases where optical data were available the frequency of the "soft mode," extrapolated to infinite temperature, exceeds the frequency of the next higher lying mode, at least at $k=0$.

In the course of this study, it has been established that CaTiO_3 is also a paraelectric material whose dielectric constant follows a Curie-Weiss law, but with a negative Curie temperature. This means that the frequency of the soft mode in this material never becomes small enough for a lattice instability to cause a ferroelectric transition as observed in some other perovskites.

II. EXPERIMENTAL TECHNIQUE AND RESULTS

In order to measure the relative dielectric constant of a number of perovskites in the paraelectric region over a wide range of temperatures it was found to be of definite advantage to use microwave techniques. With increasing temperatures the electrical conductivity of these materials increases rapidly. Since the contribution of the conductivity σ to the loss tangent is frequency dependent and behaves as $\sigma/\epsilon\omega$, accurate measurements can be extended to much higher temperatures at microwave frequencies than in the commonly used audio range. Among the materials investigated were CaTiO_3 , SrTiO_3 , BaTiO_3 , PbTiO_3 , and KTaO_3 , and various mixtures of Ca-Sr and Sr-Ba titanates. Because of the somewhat large loss tangent in PbTiO_3 , poor results were obtained with this material.

The dielectric constant of the material under investigation was obtained with a relatively high accuracy

¹ H. Gränicher and O. Jakits, *Nuovo Cimento Suppl.* **11**, 480 (1954).

² W. Cochran, *Advances in Physics*, edited by N. C. Mott (Taylor & Francis, Ltd., London, 1960), Vol. 9, p. 387.

³ A. S. Barker, Jr., and M. Tinkham, *Phys. Rev.* **125**, 1527 (1962).

⁴ R. A. Cowley, *Phys. Rev. Letters* **9**, 38 (1962).

(≈0.5%) by observing a dielectric resonance in a spherical sample. Since the relative dielectric constant ϵ of these materials is large, the wavelength within the material is small compared to the free-space wavelength λ_0 . In a sphere, the lowest order dielectric resonance occurs when $\lambda_0/\epsilon^{1/2} \approx d$, where d is the diameter of the sphere. This problem has been treated by a number of authors.⁵⁻⁸

The value of ϵ is obtained from a solution of the transcendental equation for transverse electric solutions of Maxwell's equations

$$[\epsilon^{1/2}\xi j_n(\epsilon^{1/2}\xi)]'/j_n(\epsilon^{1/2}\xi) = [\xi h_n^{(1)}(\xi)]'/h_n^{(1)}(\xi), \quad (1)$$

where $j_n(x)$ and $h_n^{(1)}(x)$ are spherical Bessel and Hankel functions of the order n . $\xi = \omega a/c$, where ω is the radial frequency, a is the radius of the sphere, and c is the velocity of light. The prime indicates differentiation with respect to the argument $\epsilon^{1/2}\xi$ or ξ . It has been assumed that outside the sphere the relative dielectric constant is 1 and the permeability inside and outside is that of free space.

Assuming that $\epsilon \gg 1$ and $|\xi| < 1$, then to a very good approximation

$$\epsilon = (Z_{nm}/\pi)^2 (\lambda_0/d)^2, \quad (2)$$

where Z_{mn} is the m th root of the equation

$$j_{n-1}(Z) = 0.$$

The exact solution of Eq. (1) was used to evaluate the dielectric constant in several cases, but only when $\epsilon \leq 100$ was the difference between the exact solution and approximate solution as great as 1%.

Figure 1 is a simplified block diagram of the microwave apparatus used for the measurements. Power from a swept frequency microwave source is incident on a "magic" or "hybrid" tee. The power is divided so that one-half goes to the arm with a slide screw tuner and a load, and the other half to the sample arm. The slide screw tuner is adjusted to introduce a reflection with the right phase and amplitude so as to cancel any reflections from the sample arm if the sample is off resonance. When the frequency is changed so that the sample is resonant, the bridge circuit is unbalanced and a signal is observed at the detector. The reflection can be displayed on an oscilloscope as a function of frequency. The resonant frequency is then measured with an absorption wavemeter. The width of the resonance is proportional to the dielectric loss tangent.⁸

The dielectric samples were spheres with diameters between 2 and 3 mm. Care was taken to ensure that the samples were spherical to within 0.2%. The samples were supported on a quartz or sapphire rod in the center of a section of stainless-steel X-band waveguide

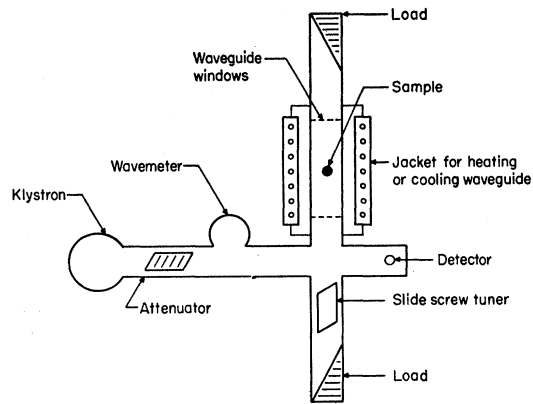


FIG. 1. Experimental apparatus for the measurement of the dielectric constant as a function of temperature.

which was surrounded by either a heating or cooling jacket. The waveguide section was flushed with nitrogen to prevent oxidation at the highest temperatures. Dielectric measurements were made from 77 to 1000°K at frequencies from 8.2 to 12.4 kMc/sec. The temperature of the sample was measured by a thermocouple in contact with the waveguide wall nearest the sample. The temperature of a resonance at constant frequency as measured by the thermocouple with slowly increasing and decreasing temperature varied by less than two degrees. A thermocouple in direct contact with the sample gave the same reading as that of the thermocouple on the waveguide.

Figure 2 shows typical experimental data for a single-crystalline KTaO_3 sphere of 2.059 mm diam taken between -190 and 30°C. The frequency for a dielectric

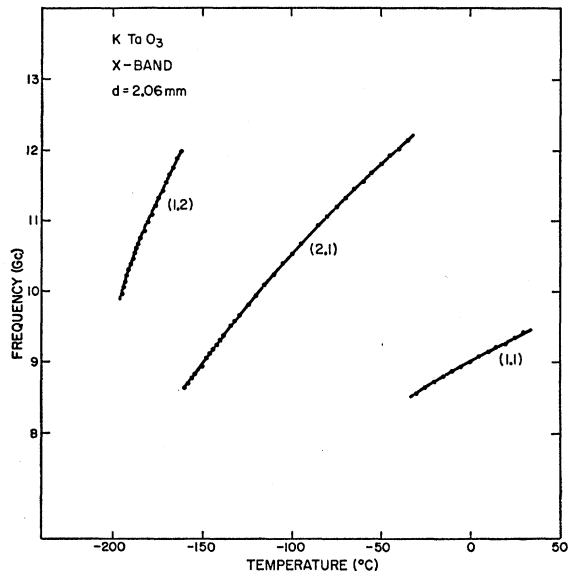


FIG. 2. Frequency of dielectric resonances in single crystalline KTaO_3 sphere as a function of temperature. The three different modes used are indicated.

⁵ P. Debye, Ann. Phys. **30**, 57 (1909).
⁶ R. D. Richtmeyer, J. Appl. Phys. **10**, 391 (1939).
⁷ J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill Book Company, Inc., New York, 1941), p. 554.
⁸ R. O. Bell and G. Rupprecht, Trans. IRE **MTT-9**, 239 (1961).

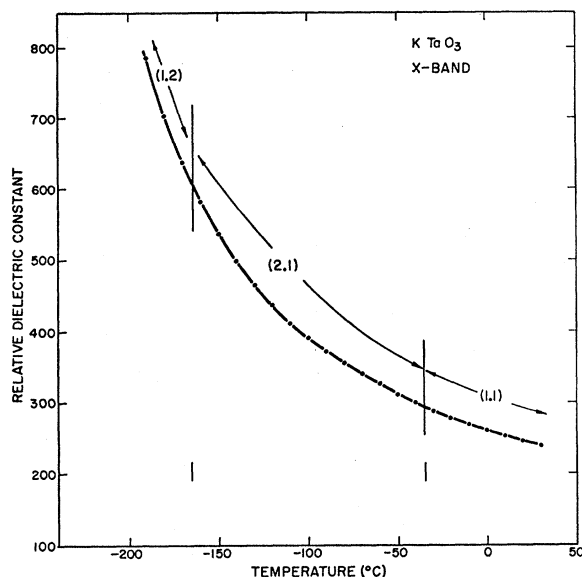


FIG. 3. Relative dielectric constant of KTaO_3 as a function of temperature.

resonance is plotted as a function of temperature. Because of the large change in the dielectric constant, it was necessary to use three different modes.

Figure 3 shows a plot of the dielectric constant versus temperature as calculated from the data in Fig. 2. A least-square fit was made to the data using the equation:

$$\epsilon = A + B/(T - T_c),$$

with the result that $A = 39.32$, $B = 5.989 \times 10^4 \text{ }^\circ\text{C}$, $T_c = -270.35^\circ\text{C}$.

Figure 4 is a plot of the measured value of the relative dielectric constant minus the calculated value. The greatest deviation is approximately 0.7 or 0.2%. The temperatures where a change from one mode to another was made are indicated in the figure. Close examination of the data shows that the discontinuity when switching from mode to mode is less than 0.2%.

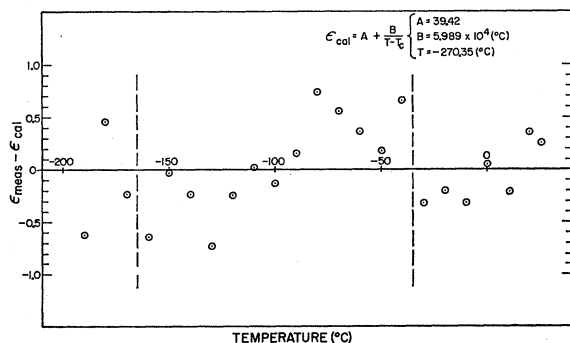


FIG. 4. Difference between the calculated and measured value of the relative dielectric constant. The calculated values were obtained from a least-square fit of the data. The mode change is indicated.

This slight discontinuity probably occurs because of deviations from sphericity. Data obtained on CaTiO_3 , $\text{Ca}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$, SrTiO_3 , $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$, and BaTiO_3 were just as good. For SrTiO_3 measurements were made on three different spheres with diameters from approximately 1 to 3 mm which gave agreement of the dielectric constant within experimental error. The measurements on the PbTiO_3 , however, showed a scatter of 5% because the high dielectric loss made it difficult to accurately measure the resonant frequency of the dielectric cavity.

Figure 5 shows the reciprocal of the relative dielectric constant for SrTiO_3 as a function of temperature from 140°K up to 1080°K. If the dielectric constant followed a Curie-Weiss law of the form $\epsilon = C/(T - T_c)$, the data would fall on a straight line. However, it is obvious that this is not the case.

The measurements on the BaTiO_3 were made from 320°K up to 850°K since BaTiO_3 has a high loss tangent at microwave frequencies around the Curie temperature T_c . For this reason, it was necessary to raise the temperature 200°K above T_c before the losses were low enough to obtain a sharply-defined resonance.

Although a Curie-Weiss law of the form $\epsilon = C/(T - T_c)$ is not obeyed for these perovskites, it is obvious (Fig. 6) that the measured data can be represented to a high degree of accuracy by a modified Curie-Weiss law as

$$\epsilon = \epsilon_L + C/(T - T_c). \tag{3}$$

ϵ_L is the dielectric constant extrapolated to infinite temperature and has a value of the order of 50 for all the perovskites under investigation. The slopes in Fig. 6 are interpreted as the respective Curie constants. The results for T_c and C are given in Table I. It can be seen that both the Curie temperature and the Curie constant of the titanates are monotonic functions of the cation

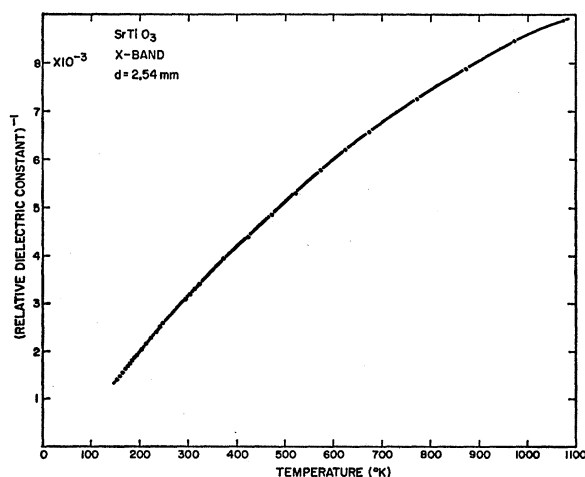


FIG. 5. Reciprocal of the relative dielectric constant of SrTiO_3 as a function of temperature.

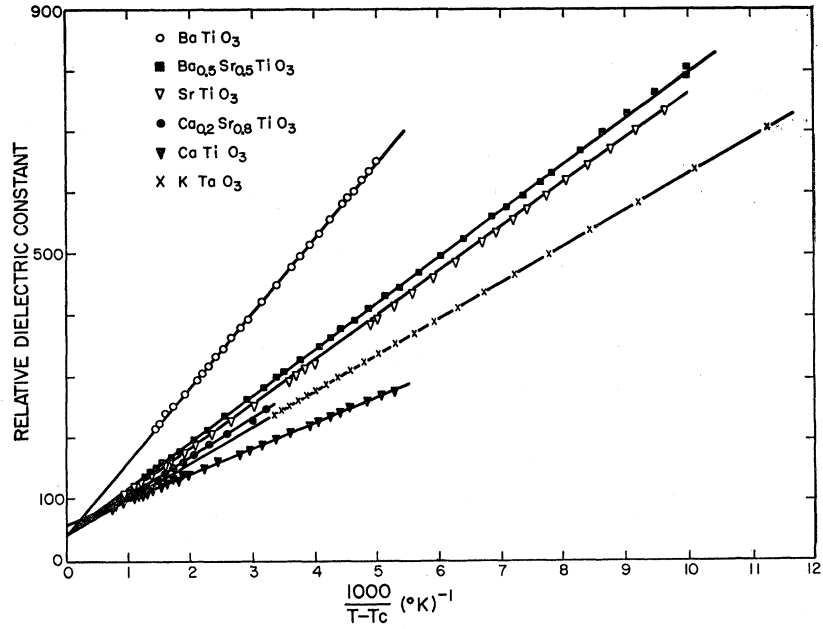


FIG. 6. $1/(T-T_c)$ versus the dielectric constant for a number of paraelectric perovskites.

mass. It also is apparent that CaTiO_3 and $\text{Sr}_{0.8}\text{Ca}_{0.2}\text{TiO}_3$ are materials which formally obey a Curie-Weiss law, but with a negative Curie temperature.

III. DISCUSSION

It has been shown in the previous section that the temperature dependence of the dielectric constant ϵ of the perovskites under investigation can be accurately described by Eq. (3).

According to dispersion theory, the dielectric constant ϵ is given as a function of temperature T and frequency ω without damping by

$$\epsilon(T, \omega) = \epsilon_{op} + \sum_{i=1}^n \frac{f_i}{\omega_{Ti}^2 - \omega^2}, \quad (4)$$

where ϵ_{op} is the high-frequency dielectric constant, ω_{Ti} is the frequency of the i th transverse optical lattice vibration, and f_i is the oscillator strength. The sum is extended over all the optically active vibrations. At microwave frequencies where $\omega^2 \ll \omega_{Ti}^2$, ϵ can be expressed in the form:

$$\epsilon(T, 0) = \epsilon_{op} + \sum_{i=1}^n \frac{f_i}{\omega_{Ti}^2}. \quad (5)$$

In SrTiO_3 it has been shown that the frequency of the lowest lying mode varies with temperature, whereas the frequencies of the other modes are essentially temperature-independent. Therefore,

$$\lim_{T \rightarrow \infty} \epsilon(T, 0) = \epsilon_L = \epsilon_{op} + \sum_{i=1}^{n-1} \frac{f_i}{\omega_{Ti}^2} + \frac{f_n}{\omega_{Tn}^2(T \rightarrow \infty)}. \quad (6)$$

Substituting Eqs. (5) and (6) into Eq. (3), leads to:

$$\frac{1}{\omega_{Tn}^2(T)} = \frac{1}{\omega_{Tn}^2(\infty)} + \frac{C}{f_n(T-T_c)}. \quad (7)$$

This result indicates that the frequency of the soft mode approaches a limiting value $\omega_{Tn}(\infty)$, a constant which appears in the description of the temperature dependence of $\omega_{Tn}(T)$. Equation (7) may be compared with the frequency quoted relation that

$$\omega_{Tn}^2 = A(T-T_c),$$

which will only be a good approximation in a limited temperature range above the Curie temperature. With increasing temperature ω_{Tn}^2 must be bounded because of the finite lattice forces and masses involved.

In materials such as KTaO_3 ,⁹ SrTiO_3 ,^{10,11} and CaTiO_3 ,¹¹ where optical data are available, $\omega_{Tn}(\infty)$ can be evaluated for the soft mode. If f_i/ω_{Ti}^2 is constant for the temperature-independent modes, one obtains from Eqs. (5) and (6)

$$\omega_{Tn}(\infty) = \omega_{Tn}(T) \left[\frac{f_n(\infty) \epsilon - \epsilon_1}{f_n(T) \epsilon_L - \epsilon_1} \right]^{1/2}, \quad (8)$$

where

$$\epsilon_1 = \epsilon_{op} + \sum_{i=1}^{n-1} f_i/\omega_{Ti}^2.$$

If in addition, f_n is temperature-independent, the

⁹ R. C. Miller and W. G. Spitzer, Phys. Rev. **129**, 94 (1963).
¹⁰ W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, Phys. Rev. **126**, 1710 (1962).
¹¹ C. H. Perry, B. N. Khanna, and G. Rupprecht, Phys. Rev. **135**, A408 (1964).

TABLE I. Dielectric constant of paraelectric perovskites at X band (8.2–12.4 kMc/sec). The dielectric constant is given by the expression $\epsilon = \epsilon_L + [C/(T - T_c)]$.

Material	Crystalline form	ϵ_L	T_c (°K)	C (°K)	Temperature range
PbTiO ₃	Polycrystal	...	763	15.4×10^4	900–1100°K
BaTiO ₃	Polycrystal	44	396	12.0×10^4	590–1120°K
Ba _{0.8} Sr _{0.2} TiO ₃	Polycrystal	46	227.2	7.8×10^4	270–1000°K
SrTiO ₃	Single crystal	43	44	7.1×10^4	60–1080°K
Sr _{0.8} Ca _{0.2} TiO ₃	Polycrystal	45	-12.5	4.25×10^4	80–300°K
CaTiO ₃	Polycrystal	58	-84	4.2×10^4	80–290°K
KTaO ₃	Single crystal	39	2.8	5.99×10^4	80–303°K

results in Table II are obtained. However, it should be kept in mind that only in the case of SrTiO₃ has the temperature dependence of the soft mode been demonstrated experimentally.^{3,4} In Eq. (6) ϵ_L has been identified as the value of $\epsilon(T, \omega)$ in the limit of high temperature at frequencies well below all the optically active lattice vibrations. A comparison of ϵ_1 and ϵ_L in Table II shows that the contribution of the soft mode to ϵ_L , $f_n/\omega_{T_n}^2(\infty) = (\epsilon_L - \epsilon_1)$, is larger than the combined contributions from all the other optically active modes and the electronic polarizability. Another possible contribution to ϵ_L could arise from electronic deformations as indicated by Silverman and Joseph,¹² but no estimate of the size of this contribution is available. It is apparent from Table II that $\omega_{T_3}(\infty)$ is larger than ω_{T_2} in every case. Thus at high temperatures, where the long-range Coulomb interaction is ineffective, the normal mode associated with the soft mode tends to a higher frequency than the next transverse optical mode.

It is worthwhile to note that, as a result of this investigation, CaTiO₃ and mixtures with SrTiO₃ have been identified as paraelectric materials which obey a Curie-Weiss law with a negative Curie temperature. This can be interpreted in the following way: It is known² that at the Curie temperature the frequency of the temperature-dependent mode becomes low. Since the restoring forces for this vibration become small, the crystal lattice becomes unstable and assumes a new

TABLE II. Transverse optical frequencies for KTaO₃, CaTiO₃, and SrTiO₃. $\omega_{T_3}(\infty)$ was calculated with Eq. (8) using measured values of ϵ , ϵ_L , $\omega_{T_3}(T)$, and ϵ_1 . Because CaTiO₃ is orthorhombic ω_{T_1} is split into two modes.

Material	Ref.	ω_{T_1}	ω_{T_2}	ω_{T_3} (296°K)	ω_{T_3} (∞)	ϵ (296°K)	ϵ_L	ϵ_1	$f_n/\omega_{T_n}^2$ (∞)
KTaO ₃	9	549	199	85	272	292	39	11.7	27.3
CaTiO ₃	11	549 443	179	148	313	169	58	28	30
SrTiO ₃	10	544	178	88	272	323	43	10.7	32.3
	11	555	185	100	355			21.2	21.8

¹² B. D. Silverman and R. I. Joseph, Phys. Rev. **129**, 2062 (1963).

configuration. An example of this behavior is the well-known phase transition in perovskites from a cubic to a tetragonal lattice configuration. A negative Curie temperature is just another way of saying that the lattice instability caused by the temperature mode has not been reached at 0°K.

The identification of the normal modes in perovskite structures is still debated. The original proposal by Last¹³ was a mode assignment in which the soft mode is the vibration of the cation against the TiO₃ octahedron and the other modes are internal vibrations of the TiO₃ octahedron. The higher mode is a stretching vibration and the lower a bending vibration. Spitzer *et al.*,¹⁰ however, make the assignment of bending mode, cation TiO₃, and stretching mode with decreasing frequency. Perry *et al.*¹¹ arrive from infrared studies at an assignment similar to that of Last.

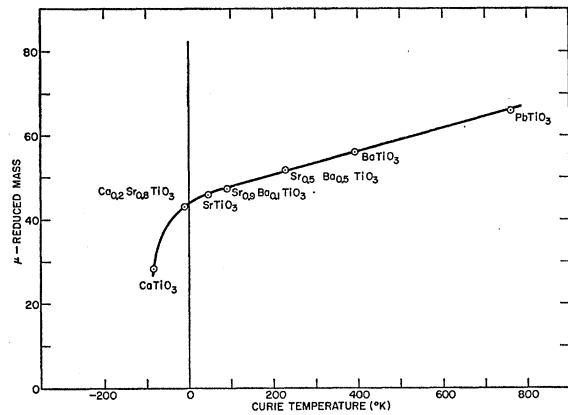


Fig. 7. Curie temperature as a function of reduced mass of the cation-TiO₃ complex for a number of perovskites.

Figure 7 shows a plot of Curie temperature versus the reduced mass of the cation TiO₃ configuration. All the materials are cubic above the Curie temperature except CaTiO₃ which is orthorhombic. The systematic variation of Curie temperature with reduced mass of the cation TiO₃ suggests that the soft mode is associated with a lattice vibration strongly involving the cation, although it may be an oversimplification to regard the vibrator of the TiO₃ octahedron as independent of the cation.

ACKNOWLEDGMENT

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¹³ J. T. Last, Phys. Rev. **105**, 1740 (1957).