Dielectric and X-Ray Studies of $Ca_xBa_{1-x}TiO_3$ and $Ca_xSr_{1-x}TiO_3$†

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Ceramics of $Ca_xBa_{1-x}TiO_3$ and $Ca_xSr_{1-x}TiO_3$ have been prepared and their dielectric and structural properties investigated. Firing conditions were adjusted to obtain sharp x-ray back reflections. The Curie point of $Ca_xBa_{1-x}TiO_3$ increases with Ca concentration up to 136°C for $x=0.08$, and then decreases. Both the tetragonal-orthorhombic and the orthorhombic-rhombohedral transition points of $Ca_xBa_{1-x}TiO_3$ decrease monotonically with increasing Ca concentration. $Ca_xSr_{1-x}TiO_3$ solid solutions with $0.01 \leqslant x \leqslant 0.10$ are ferroelectric at very low temperatures. $SrTiO_3$ assumes a tetragonal structure below about 80°K.

DIELECTRIC and structural properties of $Ca_x Ba_{1-x}TiO_3$ have been reported by several workers who found that Ca addition to $BaTiO_3$ causes a negligible change[1] or only a slight decrease of the Curie point.[2] This effect is somewhat puzzling, since in $Sr_xBa_{1-x}TiO_3$ increasing Sr concentration decreases the Curie point systematically to 90°K, as observed by others,[3] and to 8°K as measured in this laboratory. This action is usually ascribed to the small ionic size of Sr^{2+}. Any increase of Sr concentration causes a decrease of the unit cell volume, thereby lowering the Curie point in the same manner as the hydrostatic pressure.[4]

This reasoning, however, cannot be extended to $Pb_xBa_{1-x}TiO_3$. Although Pb^{2+} has a smaller ionic radius than Ba^{2+}, the Curie point of $(Pb,Ba)TiO_3$ increases with Pb concentration.[5] The usual explanation is that Pb^{2+} has a very much larger electronic polarizability than Ba^{2+} or Sr^{2+}; this polarizability intensifies the interactions between the Ti ions and thus raises the Curie point.

These explanations, however, encounter another contradiction for $Ca_xBa_{1-x}TiO_3$. Ca^{2+} has a smaller ionic radius and a smaller electronic polarizability than either Ba^{2+} or Sr^{2+}, but $Ca_xBa_{1-x}TiO_3$ has almost the same Curie point as pure $BaTiO_3$ up to about 25 mole % of Ca, above which an insolubility region extends to 90 mole % of $CaTiO_3$,[2] leading to the speculation that Ca ions are not uniformly distributed in the $(Ca,Ba)TiO_3$ solid solutions. In that case $(Ca,Ba)TiO_3$ might behave to some extent like a simple mixture of $CaTiO_3$ and $BaTiO_3$, resulting in a lowering of the dielectric peak at the Curie point and in a broadening of the x-ray back-reflection lines with increasing Ca concentration. In

fact, DeVries and Roy[2] reported very diffuse back-reflection lines for their solid solutions.

We have examined whether this broadening is inherent and studied the dielectric properties of these compounds over a wide temperature range. While Berlincourt and Kulesar[1] investigated the change of the second transition point (tetragonal-orthorhombic) in detail, there seem to be no published data on the behavior of the third transition point (orthorhombic-rhombohedral). The nonferroelectric phase transition of $SrTiO_3$ (around 80°K) discussed by Gränicher and Jakits[6] was also investigated.

EXPERIMENTAL PROCEDURE

Solid solutions were prepared from cp $CaTiO_3$, $BaTiO_3$, and $SrTiO_3$ powders (supplied by Titanium Alloy Division, National Lead Company).[7]

$CaTiO_3$ and $BaTiO_3$ were mixed with a small addition of alcohol, dried, pressed after drying into pellets, and heated in air in a Globar furnace. Firing between 1350° and 1400°C resulted in good ceramics of $Ca_xBa_{1-x}TiO_3$ for $0 \leqslant x \leqslant 0.08$. An additional firing cycle was required for greater Ca concentration $(0.12 \leqslant x \leqslant 0.24)$. The pellets were crushed, mixed and pressed again, and fired at 1450°C for 24 hr. Mixtures of $CaTiO_3$ and $SrTiO_3$ were prefired at 1300°C for 24 hr and then reground, pressed into pellets, and sintered at 1400°C for 24 hr. Carbowax was used to get dense ceramics.

All samples had densities >0.90 of the theoretical x-ray densities; and half-widths $<0.5°$ of 2θ for the $(422)\alpha_1$[8] x-ray reflection.

For dielectric investigations, circular disks (thickness ~1 mm, diameter ~6 mm) were cut with a diamond saw. A capacitance bridge served for the determination of the dielectric constant κ', and a Sawyer-Tower type circuit[9] for the observation of hysteresis loops. The x-ray measurements were carried out on a Norelco diffractometer with Cu $K\alpha$ radiation. Lattice parameters were

[1] D. A. Berlincourt and F. Kulesar, J. Acoust. Soc. Am. 24, 709 (1952).

[2] M. C. McQuarrie and F. W. Behnke, J. Am. Ceram. Soc. 37, 539 (1954); R. C. DeVries and R. Roy, *ibid.* 38, 142 (1955).

[3] W. Jackson and W. Redish, Nature 156, 717 (1945); D. F. Rushman and M. A. Strivens, Trans. Faraday Soc. 42A, 231 (1946); G. A. Smolenski and K. I. Rozgachev, J. Tech. Fiz. USSR 24, 1751 (1956); S. Kisaka, S. Ikegami, and H. Sasaki, J. Phys. Soc. Japan 14, 1680 (1959).

[4] W. J. Merz, Phys. Rev. 78, 52 (1950).

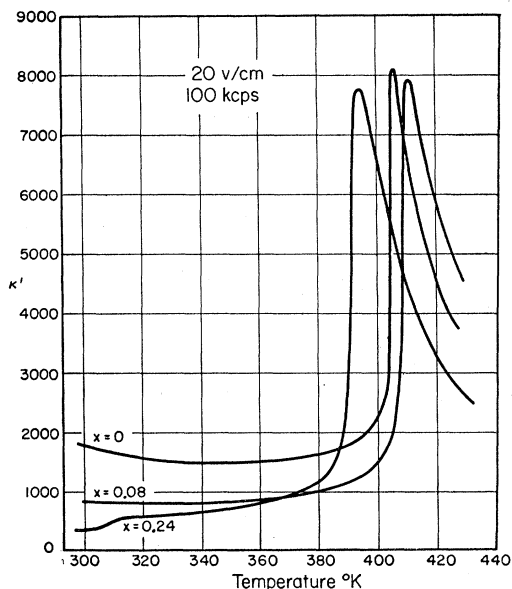[5] G. Shirane and K. Suzuki, J. Phys. Soc. Japan 6, 274 (1951).

[6] H. Gränicher and O. Jakits, Suppl. Nuovo cimento [9] 11, 480 (1954).

[7] Manufacturer's analysis lists as major impurities: 0.5% SiO_2 and 0.1–1% SrO in $CaTiO_3$; 0.1% SiO_2 and 0.1% Sr in $BaTiO_3$; and $<0.03\%$ SiO_2, 0.01% ZrO_2 and 0.01% BaO in $SrTiO_3$ (weight percent).

[8] The $(422)\alpha_1$ reflection appeared at $2\theta \cong 139° \leftrightarrow 145°$ for $Ca_xBa_{1-x}TiO_3$ and $150° \leftrightarrow 152°$ for $Ca_xSr_{1-x}TiO_3$ ceramics.

[9] C. B. Sawyer and C. H. Tower, Phys. Rev. 35, 269 (1930).

FIG. 1. Dielectric constants of $Ca_xBa_{1-x}TiO_3$ vs temperature (measured from low to high temperatures).

determined using $(422)\alpha_1$ and $(224)\alpha_1$ reflections. Instrumental errors in 2θ were corrected by referring to the $(444)\alpha_1$ and $(533)\alpha_1$ reflections of a silicon standard. The adapter of Calhoun and Abrahams[10] was used for low-temperature experiments.

$SrTiO_3$ single crystals (from Titanium Division, National Lead Company, major impurity $SiO_2 \approx 0.06$ weight percent) were also investigated.

RESULTS

Calcium-Barium Titanates

Figure 1 shows the dielectric constant of $Ca_xBa_{1-x}TiO_3$ for $x=0$, 0.08, and 0.24 at elevated temperatures. $Ca_{0.08}Ba_{0.92}TiO_3$ has the highest and $Ca_{0.24}Ba_{0.76}TiO_3$ the lowest Curie point of the compounds investigated (cf. also Fig. 3). Calcium addition causes a negligible change in peak height, but an increase in width. Measurements toward low temperatures (Fig. 2), taken with higher voltage in order to locate the transitions clearly, show that the two lower transition temperatures and peak heights are strongly affected by Ca addition.

Figure 3 shows the transition temperatures of $Ca_xBa_{1-x}TiO_3$ as functions of Ca concentration. The first transition point (cubic-tetragonal) (the Curie point) was previously reported[1,2] to be practically unaffected. In fact, the Curie point is not very sensitive to Ca concentration, but it does reach a maximum at 8 mole % of $CaTiO_3$, and then decreases. The transition, for rising temperature, lies at 130.7°C for pure $BaTiO_3$ and at 136.1°C for $Ca_{0.08}Ba_{0.92}TiO_3$.
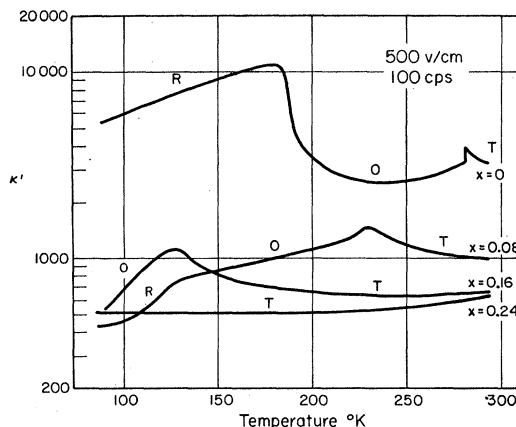
The lowering of the second transition (tetragonal-

orthorhombic) agrees well with the results obtained by Berlincourt and Kulesar.[1] The third transition point (orthorhombic-rhombohedral) similarly decreases monotonically with increasing Ca concentration.

Figure 4 gives the lattice parameters of $Ca_xBa_{1-x}TiO_3$ in the tetragonal phase at room temperature as functions of Ca concentration (experimental error $\leqslant 5 \times 10^{-4}$ A). For pure $BaTiO_3$, the values $a=3.992_5$ and $c=4.036_4$ A compare well with $a=3.994$ and $c=4.038$ A, as measured by Swanson and Fuyat.[11] Similar results have been reported elsewhere; the close spacing of our points, however, reveals a definite deviation from Vegard's law,[12] in contrast to the observation of McQuarrie and Behnke.[2] The straight line for Vegard's law is based on the parameters of $CaTiO_3$ reported by Kay and Bailey.[13]
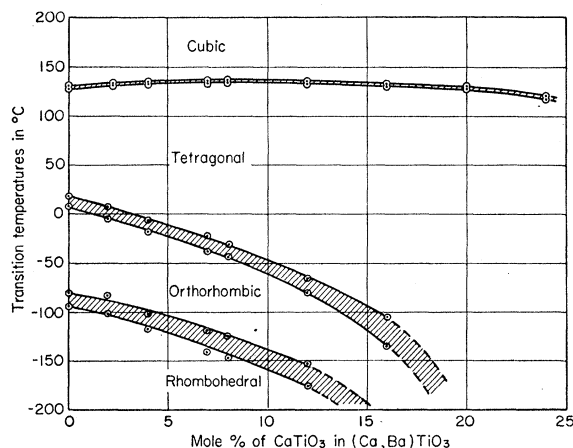

FIG. 2. Dielectric constants of $Ca_xBa_{1-x}TiO_3$ vs temperature (measured from high to low temperatures).

FIG. 3. Transition temperatures of $Ca_xBa_{1-x}TiO_3$ vs molar ratio x. (Shaded areas represent temperature hysteresis.)

[10] B. A. Calhoun and S. C. Abrahams, Rev. Sci. Instr. 24, 397 (1953).

[11] H. E. Swanson and R. K. Fuyat, National Bureau of Standards, Circular 539, 1954, Vol. 3, p. 45.
[12] L. Vegard, Z. Physik 5, 17 (1921).
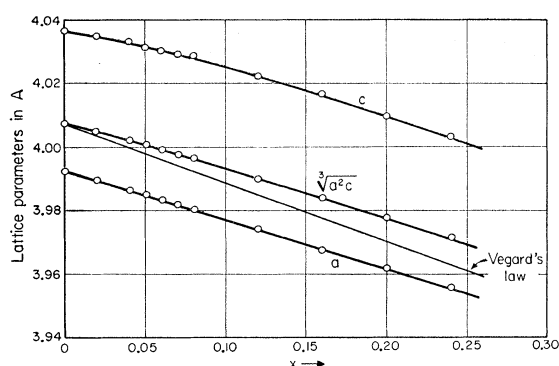[13] H. F. Kay and P. C. Bailey, Acta Cryst. 10, 219 (1957).

Fig. 4. Lattice parameters of $Ca_xBa_{1-x}TiO_3$ vs molar ratio x (room temperature).

Calcium-Strontium Titanates

Dielectric-constant measurements of $Ca_xSr_{1-x}TiO_3$ compounds as function of temperature are shown in Fig. 5. Gränicher and Jakits[6] reported a dielectric anomaly for $Ca_{0.20}Sr_{0.80}TiO_3$ near 116°K; it appears in the lowest curve near 120°K. This anomaly becomes more pronounced with decreasing Ca concentration. The peak dielectric constant of $Ca_{0.04}Sr_{0.96}TiO_3$ is as high as that of $BaTiO_3$ at its Curie point (cf. Fig. 1). The dielectric constant of pure $SrTiO_3$ ceramic increases monotonically down to 4.3°K, as previously reported.[14]

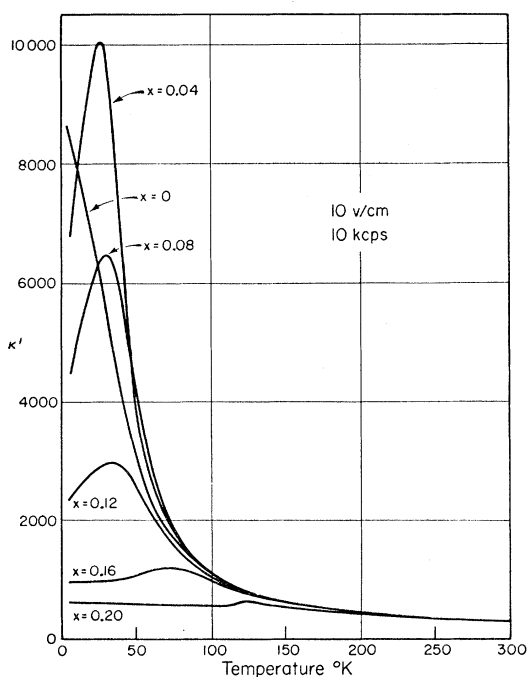At 4.3°K, $Ca_xSr_{1-x}TiO_3$ ceramics with $0.01 \leqslant x \leqslant 0.10$ exhibit a hysteresis loop (Fig. 6) characteristic for

Fig. 5. Dielectric constants of $Ca_xSr_{1-x}TiO_3$ ceramics as functions of temperature (measured with decreasing temperature).

ferroelectric ceramics.[15] With increasing temperature the remanence polarization decreases (Fig. 7), but the loop does not disappear at the temperature where the dielectric constant reaches its maximum. The observed remanence polarization depends on ac field strength. For an applied field of 1.7 kv/cm, the loop of $Ca_{0.04}Sr_{0.96}TiO_3$ disappears near 37°K, but the polarization-vs-field $(P-E)$ characteristic is still nonlinear at 40°K. The curvature of $P-E$ is convex for increasing field strength, as in rochelle salt or TGS just above the Curie point, suggesting that dc bias decreases the dielectric constant. Figure 8 proves this to be so and shows that the effect of the biasing field is much more pronounced than in the case of $BaTiO_3$. With the bias of 6 kv/cm, the shift of dielectric peak temperature is 21°K for $Ca_{0.04}Sr_{0.96}TiO_3$ and 2.9°K for $BaTiO_3$.

Although a clear-cut hysteresis loop was not observed in $SrTiO_3$ ceramics, a loop similar to that of Fig. 6 was observed in single crystals, as reported by Gränicher.[16] The temperature dependence of the remanence polarization is shown in Fig. 7. With increasing temperature the loop collapsed, but a nonlinear $P-E$ relation, similar to
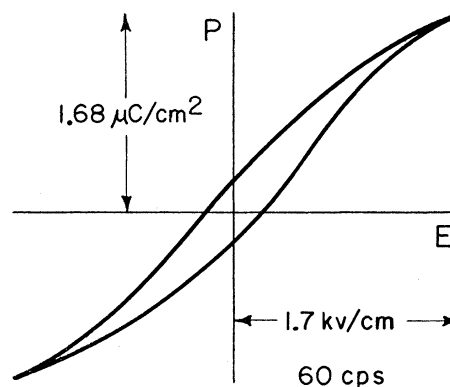

Fig. 6. Hysteresis loop of $Ca_{0.04}Sr_{0.96}TiO_3$ ceramics at 4.3°K.

that just discussed, was maintained over a temperature range. The remanence polarization depends on ac field strength (Fig. 9). The hysteresis loop was observed for a field as low as 150 v/cm. Its shape was definitely not elliptical.

The dielectric peaks of Fig. 5 prove the existence of a ferroelectric phase transition in $Ca_xSr_{1-x}TiO_3$ at a low temperature. An additional phase transition without dielectric anomaly is described below.

Figure 10 summarizes lattice parameters of (Ca,Sr)-TiO_3 at room temperature (296°K) and near 110°K, the lowest temperature at which our equipment allowed systematic x-ray measurements (experimental errors $\leqslant 5 \times 10^{-4}$ A at 296°K and $\leqslant 10^{-3}$ at 110°K). The lattice constant of pure $SrTiO_3$, 3.905_0 A at room temperature, agrees with Swanson and Fuyat's value.[11] At 296°K,

14 J. K. Hulm, Proc. Phys. Soc. (London) B63, 1184 (1950).

15 A. von Hippel et al., Ind. Eng. Chem. 38, 1097 (1946); A. von Hippel, Revs. Modern Phys. 22, 221 (1950).
16 H. Gränicher, Helv. Phys. Acta 29, 210 (1956).

$Ca_xSr_{1-x}TiO_3$ is cubic up to $x=0.10$ and tetragonal for larger values of x in the composition range investigated. The existence of this tetragonal phase was already reported by Gränicher and Jakits[6] and by McQuarrie.[17] Our phase boundary agrees better with that found by the former authors. No superlattice lines were seen in x-ray powder patterns of these tetragonal compounds, and no ferroelectric effect could be observed above liquid-nitrogen temperature. There is again a deviation from Vegard's law (cf. Fig. 10).

X-ray powder patterns of $Ca_{0.20}Sr_{0.80}TiO_3$ revealed that it changed from tetragonal to a different structure near 110°K. This low-temperature phase seems to be the "nearly cubic" one reported by Gränicher and Jakits.[6]

Figure 10 shows that the high-temperature cubic-tetragonal phase boundary is lowered from 296°K for $x=0.10$ to 110°K for $x=0.01$, suggesting that pure $SrTiO_3$ becomes tetragonal near liquid-nitrogen temperature. Linz[18] of our Laboratory observed a laminar structure of fine cracks in $SrTiO_3$ after dipping the
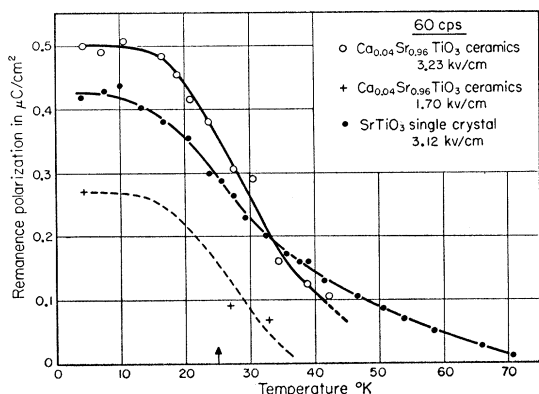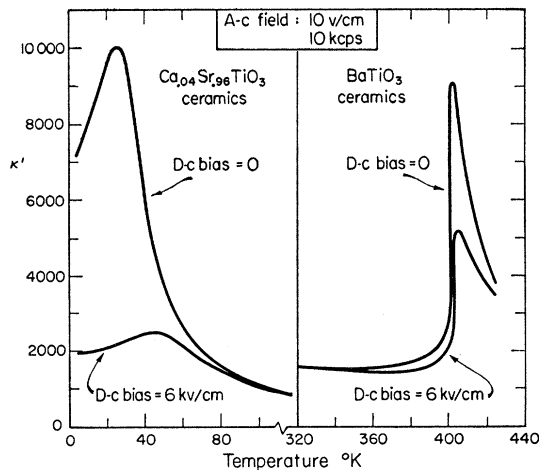

FIG. 8. Effect of a dc bias field on κ' of $Ca_{0.04}Sr_{0.96}TiO_3$ compared with that of $BaTiO_3$ (measured from high to low temperatures).

FIG. 7. Remanence polarization of a $Ca_{0.04}Sr_{0.96}TiO_3$ ceramic and an a-cut $SrTiO_3$ crystal vs temperature. Arrow=dielectric peak temperature of $Ca_{0.04}Sr_{0.96}TiO_3$.

below about 80°K. The very gradual departure suggests that the cubic-tetragonal transition is of higher order. Weaver[19] has measurements to 1.4°K, also showing deviations which he suggests may be caused by quantum-mechanical effects at low temperatures, as discussed by Barrett[20] in extension of Slater's[21] theory. Recent measurements[22] in this laboratory on $KTaO_3$ crystals in the same temperature range have shown no deviation.

The phase diagram of the $Ca_xSr_{1-x}TiO_3$ solid solution is given in Fig. 12. The nonferroelectric dielectric peaks of $Ca_xSr_{1-x}TiO_3$ (cf. Fig. 5, the peaks for $x\geqslant0.12$) seem to appear at the boundary between the tetragonal and the nearly cubic phases. It is not certain whether or not a distinct boundary exists between the ferroelectric and the nearly cubic phases. The shaded area represents the extension of ferroelectricity observed in ceramics for the applied field of about 2 kv/cm.
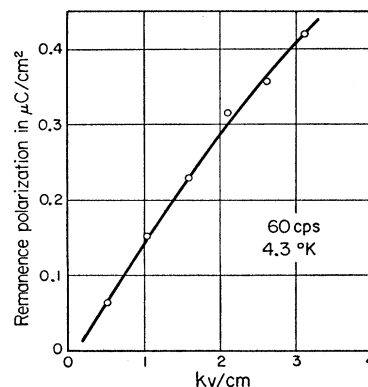
crystal into liquid nitrogen and warming to room temperature, a fact indicating the occurrence of a transition. We now have observed this transition optically. An a-cut crystal plate of 0.45 mm thickness was suspended in liquid nitrogen and inspected between crossed polaroids. A fine twin structure appeared with laminae parallel to the [011] direction of the cubic axes, similar in appearance to the 90° domain structure in tetragonal $BaTiO_3$. The width of the laminae was about 50 μ. After warming to room temperature, no cracks were observed in this case. Obviously, $SrTiO_3$ is tetragonal below about 80°K.

The dielectric constant κ' of $SrTiO_3$ does not show any anomaly at this temperature (Fig. 11),[15] but the deviation from the Curie-Weiss law becomes appreciable

FIG. 9. Remanence polarization of an a-cut $SrTiO_3$ crystal as a function of the ac field.

[17] M. McQuarrie, J. Am. Ceram. Soc. 38, 444 (1955).
[18] A. Linz, Jr. (private communication).

[19] H. E. Weaver, J. Phys. Chem. Solids 11, 274 (1959).
[20] J. H. Barrett, Phys. Rev. 86, 118 (1959).
[21] J. C. Slater, Phys. Rev. 78, 748 (1950).
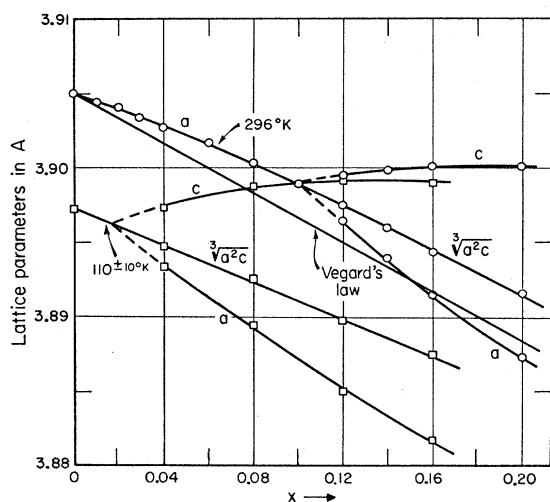[22] S. Wimple (private communication).

FIG. 10. Lattice parameters of $Ca_xSr_{1-x}TiO_3$ at 296° and at $\sim$110°K.

DISCUSSION

Calcium-Barium Titanate

Sharp x-ray back reflections were obtained for $Ca_xBa_{1-x}TiO_3$ up to $x=0.24$. The half-width of the $(422)\alpha_1$ reflection was $<0.4°$ for $x=0.20, 0.16$, and 0.24; that of pure $BaTiO_3$ was $0.28°$. The increase of the half-width due to Ca addition is therefore of the order of $0.1°$ for our best ceramics. The very diffuse x-ray back-reflection lines observed by DeVries and Roy[2] are thus not characteristic of $Ca_xBa_{1-x}TiO_3$ as such, but apparently caused by incomplete reaction or too small grain size. The sharpness of the dielectric peaks near the Curie point (cf. Fig. 1) also supports this conclusion.

In a lattice of the perovskite type, each Ba or Ca is coordinated to twelve oxygens. Since Ca^{2+} has a smaller ionic radius than Ba^{2+}, the space available to Ca^{2+} in $Ca_xBa_{1-x}TiO_3$ solid solution must be larger than in
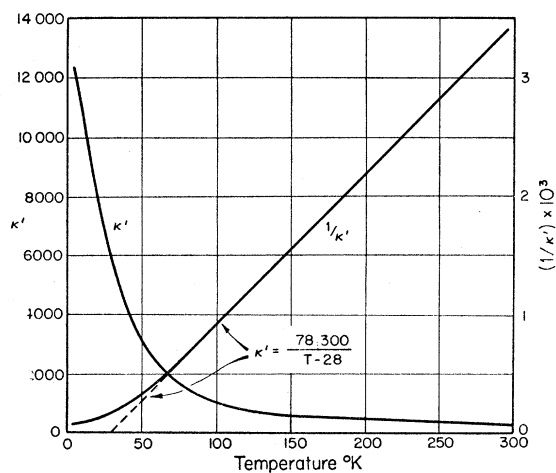

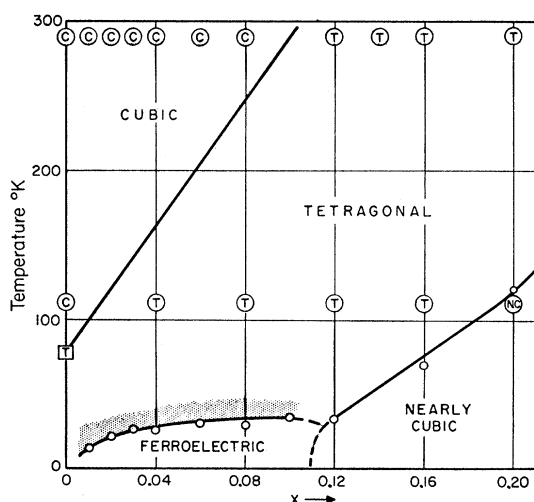FIG. 11. Dielectric constant of an a-cut $SrTiO_3$ crystal as function of temperature.

FIG. 12. Phase diagram of $Ca_xSr_{1-x}TiO_3$. o = dielectric peak temperature; C = cubic, T = tetragonal, and NC = nearly cubic, as determined by x rays; T enclosed in a square indicates tetragonal as determined optically.

$CaTiO_3$, and that for Ba^{2+} smaller than in $BaTiO_3$. The observed deviation from Vegard's law (cf. Fig. 4) proves that a compromise is made in favor of the $BaTiO_3$ lattice, i.e., the space for Ca^{2+} is increased beyond that of an ideal solid solution. In $Ca_xBa_{1-x}TiO_3$ the Ca ion therefore seems to have greater atomic polarizability. The Curie point of $Pb_xBa_{1-x}TiO_3$ increases with the Pb concentration,[5] presumably because of the large electronic polarizability of Pb^{2+}. Similarly, the increased atomic polarizability of Ca^{2+} might raise the Curie point initially, but the marked shrinkage of the unit-cell volume of $Ca_xBa_{1-x}TiO_3$ due to Ca addition later lowers the Curie point, as hydrostatic pressure would.[4] The behavior of the Curie point in Fig. 3 seems to be a compromise between these two effects.

Calcium-Strontium Titanates

The above arguments hold also for the $Ca_xSr_{1-x}TiO_3$ system. The ferroelectric phase produced by the small Ca addition could be ascribed to the enlarged atomic polarizability of Ca^{2+} in the compound.

The hysteresis loop in $Ca_xSr_{1-x}TiO_3$ did not disappear at the temperature corresponding to the peak of dielectric constant but persisted over a wider temperature range (cf. Figs. 7 and 12). (The remanence polarization of $BaTiO_3$ drops sharply at the Curie point and survives only within 2 or 3°K above the Curie point.) Sawaguchi and Charters[23] observed an extended ferroelectricity in $Ca_{0.50}Pb_{0.50}TiO_3$ above its Curie point (303°K). The dielectric peak of their specimen was, however, rather low ($\kappa'=3000$ at 303°K) and nonuniform distribution of the Ca^{2+} ions may be, at least in part, responsible for the extended range of ferroelectricity. This explanation does

[23] E. Sawaguchi and M. L. Charters, J. Am. Ceram. Soc. **42**, 157 (1959).

not fit here since even pure $SrTiO_3$ crystals exhibit remanent polarization up to about 70°K, a temperature slightly below the cubic-tetragonal transition point ($\sim$80°K).

The dielectric properties of $SrTiO_3$ reported by other authors[16,19,24] have the same trend as ours, except for those of Smolenskii,[25] who observed a dielectric constant peak between 20° and 30°K on ceramic $SrTiO_3$. One possible explanation for this conflict seems to be that his sample was not very pure. Figures 5 and 12 show that a

[24] A. Linz, Jr., Phys. Rev. **91**, 753 (1953).
[25] G. A. Smolenskii, Izvest. Akad. Nauk S.S.S.R., Ser. Fiz. **20**, 149 (1956).

small addition of Ca^{2+} (for example) can change the dielectric properties of $SrTiO_3$ drastically.

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Spin Absorption of Solids*

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A study of the spin absorption lines of all orders was made. Rules for obtaining the absorption operator of any line were found. With magnetic dipole-dipole and exchange interactions taken into account, and with the assumption that the Zeeman energy is dominant, the zeroth and the second moments of the following four lines were evaluated for powders: (1) first Larmor line, parallel field, (2) second Larmor line, parallel field, (3) second Larmor line, perpendicular field, (4) low-frequency line, perpendicular field. The contribution of exchange to the second moment was found to be the same for the four cases treated, while the total intensity has the ratio 1:1:1:3/2. Agreement with existing experimental data is good.

I. INTRODUCTION

THE first Larmor line of a solid in a strong, constant, and perpendicular magnetic field, with the magnetic dipole-dipole and exchange interactions taken into account, was first studied by Van Vleck,[1] who calculated its shape function up to the fourth moment. Later, Wright[2] extended the moment method and applied it especially to low frequency lines. In recent years other satellite lines have also become of experimental interest.[3] Furthermore, in general, the Hamiltonian of a single molecule is not necessarily the Zeeman energy, and the method Wright developed cannot be applied directly. It is the purpose of this paper to cope with this situation. Rules will be given for obtaining moments of all lines, thus avoiding the elaborate derivation necessary in the previous method. The rules are

applicable to Hamiltonians of all kinds, provided that the perturbing part of the Hamiltonian is small enough for the perturbation method to be valid.

II. ABSORPTION OPERATOR

Let us assume that the Hamiltonian of a system is described by

$$\mathcal{3C}=\mathcal{3C}_0+\mathcal{3C}', \tag{1}$$

where $\mathcal{3C}'$ is the perturbing potential small compared with $\mathcal{3C}_0$.

Let us represent $\mathcal{3C}'$ as an integral over its spectrum,

$$\mathcal{3C}'=\int_{-\infty}^{\infty}\mathcal{3C}'(\omega)d\omega, \tag{2}$$

where

$$[\mathcal{3C}_0,\mathcal{3C}'(\omega)]=\hbar\omega\mathcal{3C}'(\omega). \tag{3}$$

Under an extremely small perturbing potential $\mathfrak{M}(t)$, $\mathfrak{M}(t)\ll\mathcal{3C}'$, the probability of transition from one state to another, both eigenstates of $\mathcal{3C}$ when $t=0$, is propor-

[1] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).
[2] A. Wright, Phys. Rev. **76**, 1826 (1949).
[3] A. G. Anderson, Phys. Rev. **115**, 863 (1959).