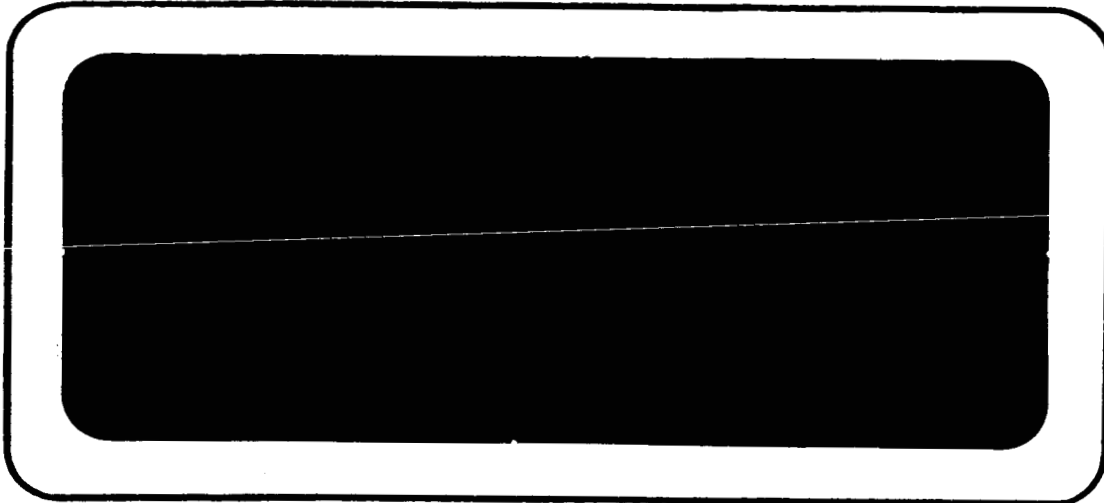


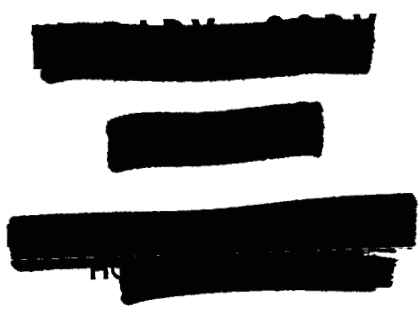
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STUDY
HIGH DIELECTRIC CONSTANT THIN FILM CAPACITOR MATERIALS
INTERIM REPORT

March 25, 1966

Prepared for
NASA MANNED SPACECRAFT CENTER
Houston, Texas

Under
Contract No. NAS 9-5592

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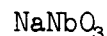
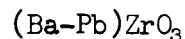
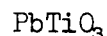
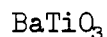
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I. INTRODUCTION AND SUMMARY

In fulfillment of the Phase I requirement on NASA Contract NAS 9-5592, a literature search has been conducted for the purpose of investigating the properties of numerous materials, generally of the ABO_3 type, with regard to their potential utilization in the preparation of high vacuum evaporated capacitors of high specific capacitance. The compounds investigated are those listed in "Exhibit A" of the contract. A detailed discussion of the physical and electrical properties of each of these materials is included in this Interim Report.

Since the phenomena of ferroelectricity, antiferroelectricity, and paraelectricity are intimately associated with the materials in question, a technical background discussion of these phenomena was considered essential for the correlation of the physical and electrical properties discussion and is included herein.

Subject to approval by NASA, the materials selected for further study in Phase II are:



Discussion of the bases upon which the above materials were selected is included in this report.

II. GENERAL PROPERTIES

A. Ferroelectric Materials (1, 24, 32, 57, 63, 90, 138, 142)

The study of dielectrics and their properties is generally concerned with the polarization or dielectric displacement that can be induced by application of an external electric field. For most dielectrics, the charge which may be induced is quite small for readily attainable field strengths. There is, however, a considerable body of materials whose polarization properties are quite different from the normal, or paraelectric, dielectrics. Not only do these materials exhibit high polarization effects, but also differ from normal dielectrics in that the polarization vs. electric field strength characteristic is not linear, and exhibits a hysteresis effect. These materials are generally classified as ferroelectric.

Historically, the term is derived as the electrical analog of ferromagnetism, although the chemical compounds are not identical. This is primarily as a result of the similarity of the polarization - electric field strength and magnetism-magnetic field strength hysteresis effects, although domain effects are also to be noted in each. These effects are to be noted only below certain transition temperatures known as Curie points. Above the Curie point the materials lose their ferroelectric properties and behave as normal, paraelectric dielectrics. Although some materials exhibit more than one Curie point (such as Rochelle salt: $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$), they are very much the exception. The temperature range of the Curie points for various materials of interest to us (type ABO_3) is quite broad: from approximately 13°K for KTaO_3 to 763°K for PbTiO_3 . These Curie points are generally discrete transition temperatures for any given material,

although some hysteresis effects may be noted depending upon the direction of temperature change. The Curie point may also be shifted significantly with additions of dopants, a valuable tool used in reducing temperature coefficients of capacitance. Typically, the maximum dielectric constant lies at the Curie point.

Above the Curie point, ferroelectric materials behave as normal, paraelectric dielectrics, and their dielectric constant may be related to temperature by the formula $\epsilon = \frac{C}{T - T_C}$, the Curie-Weiss law, where ϵ is the dielectric constant, C is the Curie constant, T is the temperature of the dielectric and T_C is the Curie temperature, not to be confused with the Curie point. (The Curie temperature is defined by the above equation and is generally slightly below the Curie point, the transition temperature of the crystal.)

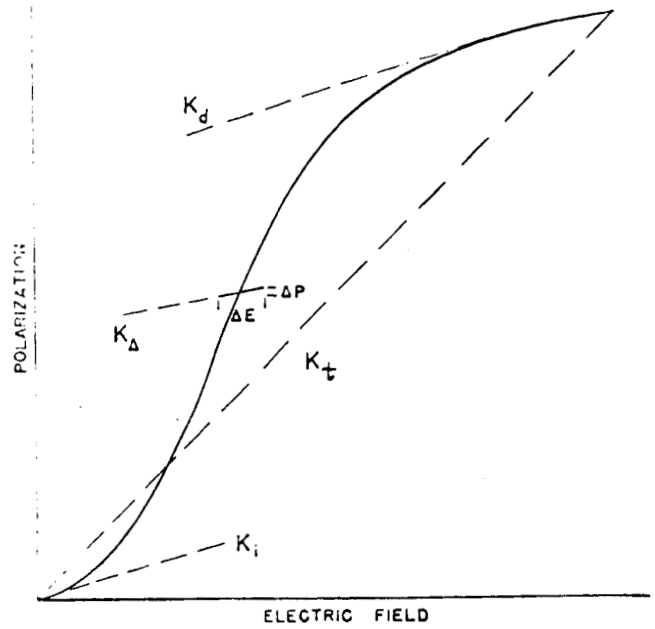
The hysteresis and non-linearity of polarization-field strength effects may generally be explained by consideration of the crystal structure. The materials of interest to this Contract are of the general form ABO_3 and are of ionic character. Below the Curie point of these crystals, there exists a net dipole moment caused by a displacement or distortion of the ions in the unit cell. Because many materials possess a net dipole moment and do not exhibit ferroelectric properties, a necessary condition is that this net dipole moment may be reversed by obtainable electric field strengths.

The non-linear hysteresis effect may most simply be explained by considering the effect of an applied electric field on the crystal dipole moments. Initially, we may consider the crystal dipole moments to be randomly oriented: there is no net polarization in the crystal. With

application of a low electric field strength, some of the dipole moments are reversed, slightly increasing the net polarization of the material. Further increase of the field strength switches more and more of the dipole moments. Eventually, saturation is reached and the polarization approaches a linear dependance on field strength (see Figure 1 (⁹⁰)).

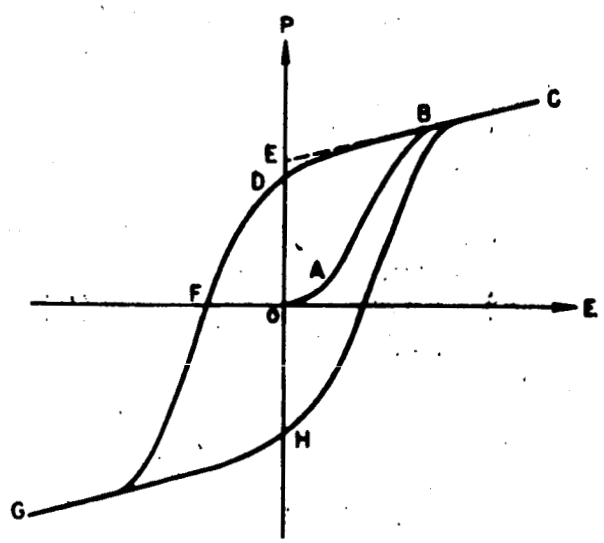
If the field strength is then decreased, many of the dipoles switch back to their initial position, although many will remain aligned with the electric field (see Figure 2 (²)). At zero field strength, the material will exhibit a net polarization called the remanent polarization (point D). Application of a reversed electric field will reduce the net polarization to a point where no polarization is present (point F). The field strength necessary to reduce the net polarization to zero is called the coercive field strength. Further increase of the reversed field will complete the polarization in the negative direction (point G). Reversal of this field strength will complete the hysteresis loop (point C).

An interesting and important phenomenon peculiar to ferroelectric materials is related to the remanent polarization. If a crystal or polycrystalline ceramic is polarized by an applied electric field at a temperature below its Curie point, it will retain a net polarization upon removal of the field (remanent polarization). If the crystal temperature is raised through the Curie point, the net polarization will suddenly decrease to zero at the Curie point (the pyroelectric effect). Assembling these phenomena, a ferroelectric crystal may be defined as "a pyroelectric crystal with reversible polarization."⁽¹⁾



Plot of polarization vs. applied field strength for a non-linear (ferroelectric) dielectric material illustrating the various dielectric permittivities.

Figure 1

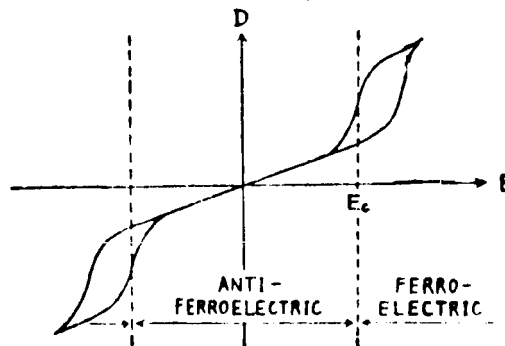


Ferroelectric hysteresis loop (schematic).

Figure 2

B. Antiferroelectricity (1,17,90)

Considerations of antiferroelectric materials basically involve the same phenomenon of spontaneous polarization of individual crystal cells. In the antiferroelectric case, however, application of an electric field realigns the dipole moments, but the alignment is antiparallel, cancelling the net polarization: the shift of one dipole moment is compensated by a similar, reverse shift of another dipole moment. An increase in the field strength eventually induces a net polarization and the material behaves as a ferroelectric (Figure 3 (17)). Antiferroelectric materials also exhibit changes in structure and dielectric constant with temperature analogous to those of ferroelectric materials. It is therefore possible to change from an antiferroelectric state to a paraelectric state at the Curie point and to change from an antiferroelectric state to a ferroelectric state with application of sufficient electric field strength.



Tentative explanation of the anomalous hysteresis loops of PbZrO_3 at 30 kv/cm.

Figure 3

III. MATERIALS

A. Bulk Properties

1. Titanates

a. Barium Titanate

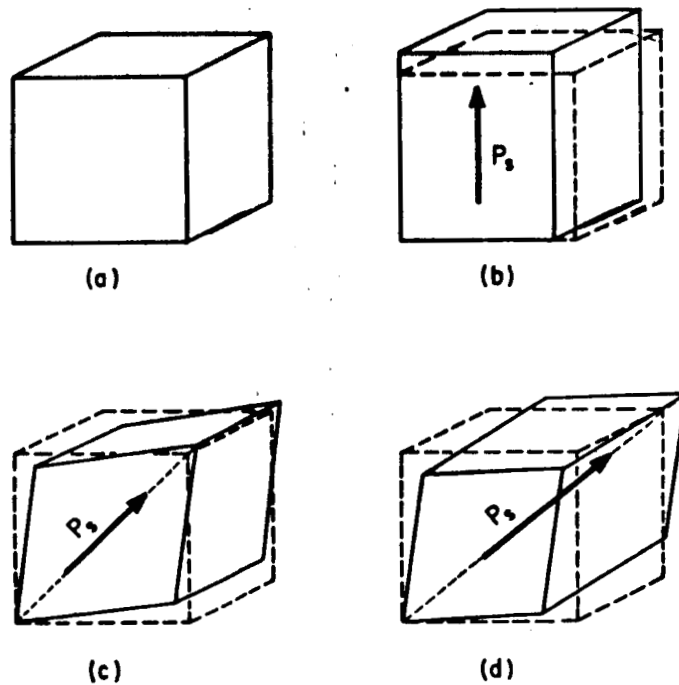
(1) Pure Material

Historically, barium titanate is perhaps the best understood and most extensively investigated of all the ferroelectric materials. The discovery of the ferroelectric properties of the ceramic material in 1943 was apparently made independently by several investigators. Since that time, and especially since 1954 when single crystal BaTiO_3 became available, investigations of the material in both single crystal and polycrystalline ceramic forms have increased.

BaTiO_3 is quite interesting in that its crystal structures are simple, it is quite stable at room temperature, and the ferroelectric state may be readily investigated at room temperature. Of greatest interest to us are its characteristics in ceramic form, although the characteristics of single crystal BaTiO_3 are usually more easily understood and are generally applicable to the polycrystalline case.

The Curie point of the pure BaTiO_3 is 120°C . Above that temperature, the unit cell structure is cubic (Figure 4a (90°)); below 120°C , the unit cell becomes tetragonal (Figure 4b (90°)) and is ferroelectric. One of the cube edges elongates to become the crystal c axis and the other two are compressed and become the tetragonal a axes. The tetragonal structure is stable to the next transition temperature of

5°C, when the unit cell shifts to an orthorhombic phase (Figure 4c⁽⁹⁾). The crystal remains ferroelectric through this phase; in fact, it remains ferroelectric down to approximately 2°K.⁽⁹⁾ This phase is stable to about -90°C when the cell structure shifts to a rhombohedral phase (Figure 4d⁽⁹⁾). In Figures 4a through 4d, the dotted lines represent the original cubic cell, and the heavy, dark arrow (P_s) indicates the direction of the spontaneous polarization of each phase.



Unit cells of the four phases of BaTiO_3 .

- (a) Cubic, stable above 120 °C.
- (b) Tetragonal, stable between 120 °C and 5 °C.
- (c) Orthorhombic, stable between 5 °C and -90 °C.
- (d) Rhombohedral, stable below -90 °C.

The dotted lines in (b), (c) and (d) delineate the original cubic cell. The heavy arrows indicate the direction of the spontaneous polarization P_s in each phase.

Figure 4

The variations of the crystal lattice parameters are shown in Figure 5 (primed letters refer to the pseudocubic cell axes when this is not the true cell).⁽⁹⁰⁾ The lattice constants have been thoroughly investigated from -160°C ⁽²⁰⁾ through room temperature,^(4,30) up to 1372°C .⁽²⁰⁾ The crystal structures and lattice constants shown were compiled from these works.

Production of BaTiO_3 is reasonably straightforward, generally starting with a stoichiometric mixture of either BaO and TiO_2 or BaCO_3 and TiO_2 . These materials are sintered at temperatures ranging from 1350°C to 1450°C ,^(5,125) yielding crystals of tetragonal structure at room temperature. Temperatures above 1460°C are to be avoided due to the transition of the cubic phase to a hexagonal phase at that temperature. The hexagonal phase of BaTiO_3 is not ferroelectric.⁽¹⁾

Perhaps the most successful technique for growing single crystal BaTiO_3 is that developed by Remeika⁽³⁾ utilizing a potassium fluoride flux which is decanted after firing. This process produces crystal plates which are nearly single domain. Addition of a Fe_2O_3 dopant to the flux decreases the BaTiO_3 crystal conductivity, probably by supplying oxygen to the BaTiO_3 . The Curie point is, however, also lowered by this addition.

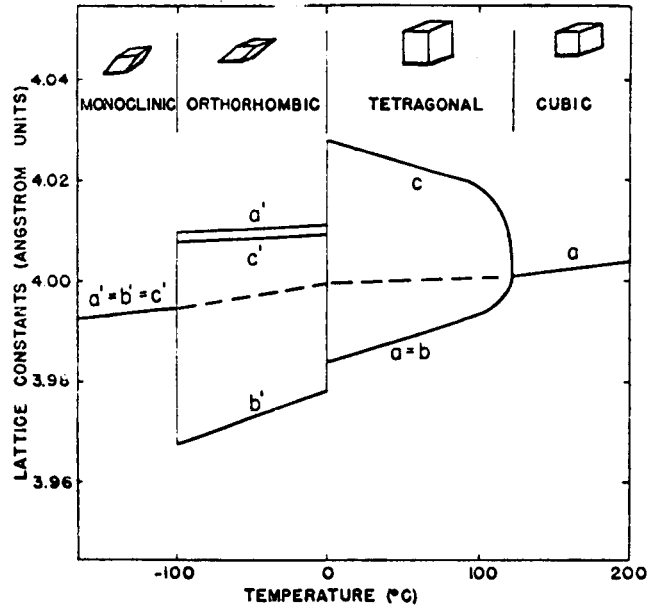
The electrical properties of BaTiO_3 crystals and ceramics are, of course, of primary concern. Although the crystallographic transitions below 5°C and above 120°C are of considerable academic interest, the tetragonal form remains the most important, as it is stable at room temperature. Figure 6⁽¹³⁾ shows the dielectric constant of single crystal BaTiO_3 vs. temperature. The notations ϵ_a and ϵ_c , respectively, refer to the values of the dielectric constant parallel to and perpendicular to the

polar axis of the crystal domain in the tetragonal phase. The dielectric constant vs. temperature characteristics of ceramic BaTiO₃ are shown in Figure 7.⁽¹⁴²⁾ The curve anomalies closely agree with those noted for single domain crystals. The published value of the dielectric constant of polycrystalline BaTiO₃ is approximately 1400 - 1500 at room temperature^(2, 25, 90) although there is considerable disparity in the reported values, depending upon the electric field strength, test frequency, chemical purity and crystallite size of the ceramic, etc.

In the cubic phase (above 150°C) of both single crystal and polycrystalline BaTiO₃, the dielectric constant varies in accordance with the Curie-Weiss law. For ceramic barium titanate, the Curie constant (C) is 1.54×10^5 °C and the Curie Temperature (T_c) is 118°C,⁽¹⁵⁾ with only slight differences for single crystals.⁽³³⁾

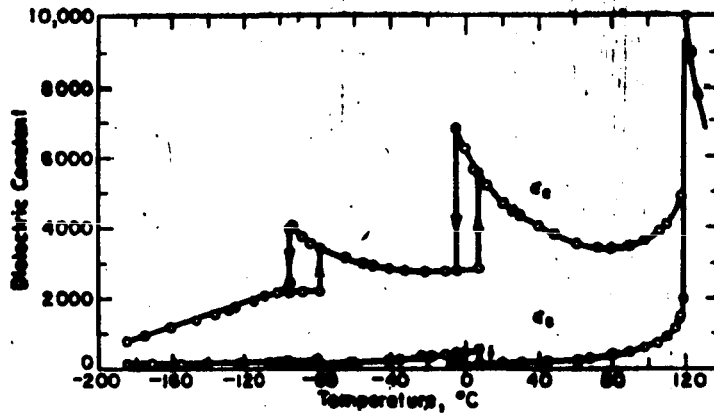
At the Curie point, the dielectric constant reaches a sharp maximum, corresponding to the 120°C transition of the crystal from the tetragonal to the cubic phase. Other dielectric constant maxima are noted at the other crystallographic transitions.

Experimental data on loss characteristics of ceramic BaTiO₃ show remarkable anomalies which do not coincide exactly with the crystallographic transitions. The dielectric constant and loss tangent over the temperature range 25°C to 350°C were reported by Roberts⁽¹⁵⁾ and are listed in Table I below. (Note the considerable decrease above the Curie point.)



Temperature variation of the lattice parameters of barium titanate, showing the various crystallographic transformations. (For the sake of clarity, the deviations from the cubic form have been exaggerated in the illustrations.)

Figure 5



Dielectric constants of BaTiO₃ as functions of temperature. The values of ϵ_s and ϵ_o in the tetragonal phase refer to single-domain crystals

Figure 6

DIELECTRIC PROPERTIES OF TICON B BaTiO₃

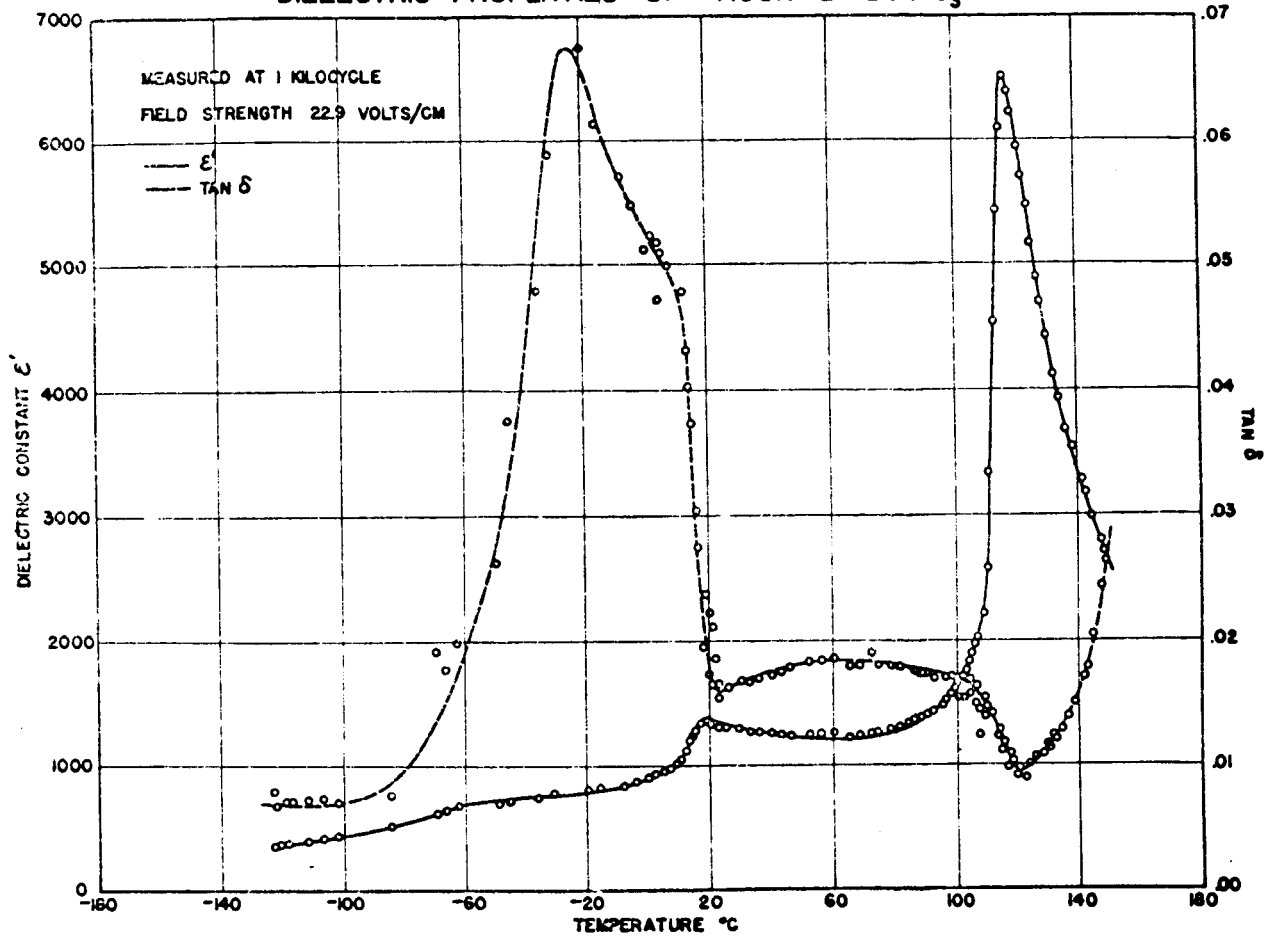
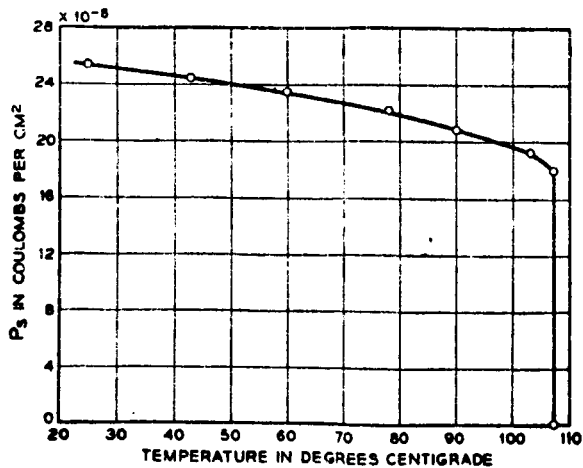


Figure 7

TABLE I

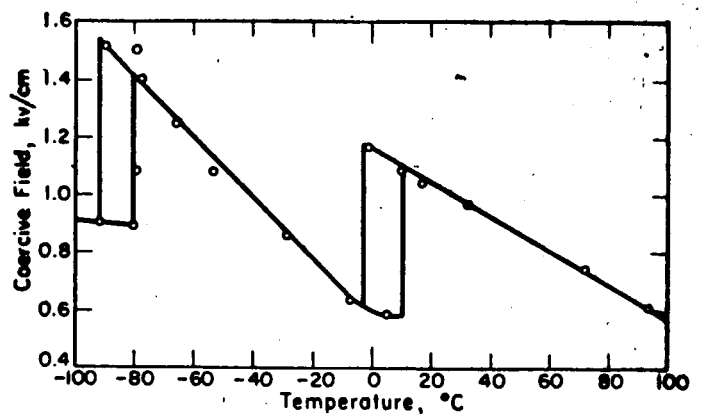
Temperature °C	K	$\tan \delta$	Temperature °C	K	$\tan \delta$
25	1525	0.009	150	2450	0.002
50	1413	0.011	175	1610	0.001
75	1440	0.010	200	1190	0.001
100	1750	0.014	225	993	0.002
110	2450	0.016	250	761	0.002
115	5070	0.013	275	656	0.007
120	5070	0.009	300	572	0.016
125	4430	0.006	325	506	0.040
130	3820	0.004	350	457	0.087
140	2970	0.003			

If the charge vs. an alternating applied field on a BaTiO₃ ferroelectric capacitor is displayed on an oscilloscope (technique of Sawyer and Tower⁽¹⁰⁸⁾), a typical hysteresis loop will be obtained (see Figure 2). As noted previously, the appearance of the hysteresis effect is due to the properties of the crystal dipole moments. Application of an increasing field tends to align the dipole moments. When the field decreases some of the aligned moments do not return to their original unaligned position, yielding remanent charge or polarization. It will be seen, therefore, that application of a field in the opposite direction will eventually cancel the effects of the alignment by providing sufficient energy to allow them to return to their initial state. This field, necessary to return the polarization to zero, is known as the coercive field. Measurements of the spontaneous polarization show the drop anticipated at the Curie point (Figure 8⁽³³⁾) due to the transition from the tetragonal, polarized state to the cubic, unpolarized state. The ceramic material used in the investigation had a Curie point of approximately 107.5°C at zero voltage. Measurements of the coercive field are in some disagreement, again probably due to crystalline imperfections and impurities. Values of the coercive field at room temperature generally range from 500⁽³³⁾ to 2000 V/cm.⁽¹⁾ The effect of temperature on the coercive field is well demonstrated in Figure 9.⁽¹⁾



Spontaneous electrical polarization P_s versus temperature T .

Figure 8



Coercive field of BaTiO₃ as a function of temperature

Figure 9

An important consideration regarding these dielectrics is the effect of field strength on the dielectric constant as well as the effect on the Curie point itself.

The effect of D. C. field strength on the dielectric constant is, of course, related directly to the polarization hysteresis loop. Technically, the dielectric constant is the slope of the dielectric displacement vs. the electric field strength curve, although in this case, due to the high value of the dielectric constant, there is little difference between polarization and the dielectric displacement.^(86,90) A typical curve of the effect of field strength (60 cps) on the dielectric constant is shown in Figure 10⁽¹³⁸⁾ The difference between the two curves is due to the hysteresis effects.

A very interesting investigation of the effect of electric field strength on the Curie point was published by Merz.⁽³³⁾ With application of a biasing field, the Curie point shifts to higher temperatures. This shift has been measured and is shown in Figure 11.⁽³³⁾ Merz used this information to test the behavior of ferroelectric BaTiO₃ single crystals near the Curie point and to derive information relating to the free energy of the crystal.

The aging characteristics of the dielectric constant is of great importance when one wishes to construct a usable capacitor. Partington, et. al.,⁽⁷³⁾ have noted that the dielectric constant of BaTiO₃ took considerable time to stabilize after a sudden change of the biasing voltage. Since this effect is only temporary, it is not of as great importance as the aging of the dielectric constant. Figure 12⁽¹⁴⁾ shows a plot of the dielectric constant for two different materials against time. The curve apparently remains linear on a semi-log plot, as measurements have been

taken for one year. This effect is apparently due to a loss of permanent polarization from the ceramic and is possibly due to domain wall shifts.⁽⁹⁴⁾ Interestingly, the initial, high dielectric constant may be reinstated by heating the ceramic through its Curie point and then cooling to the test temperature, where the aging begins once again. Thus, the aging phenomena is a reversible characteristic. There is some evidence⁽⁹⁴⁾ to show that the aging characteristics of a material may be modified by additions of dopants (Figure 13⁽⁹⁴⁾).

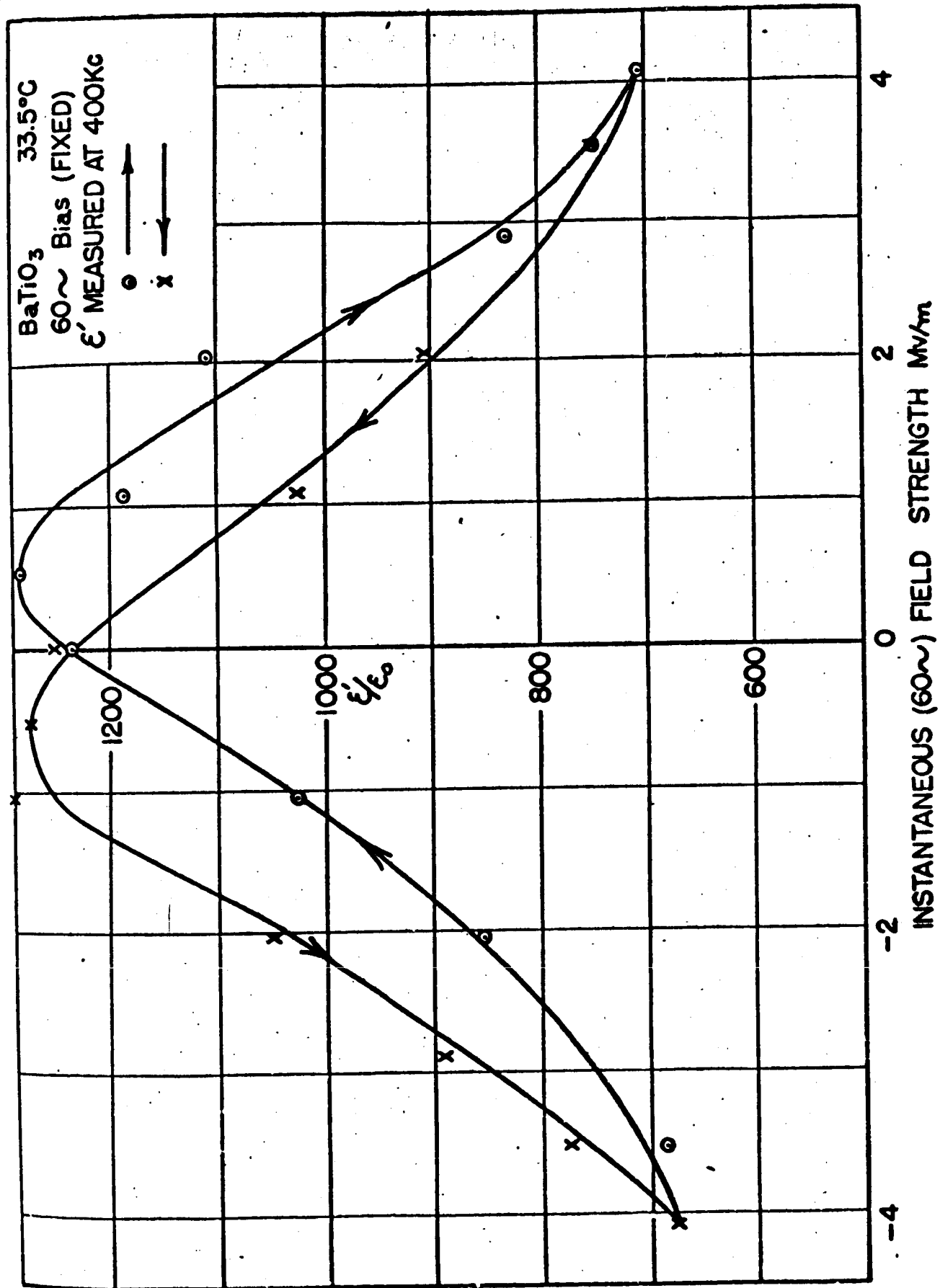
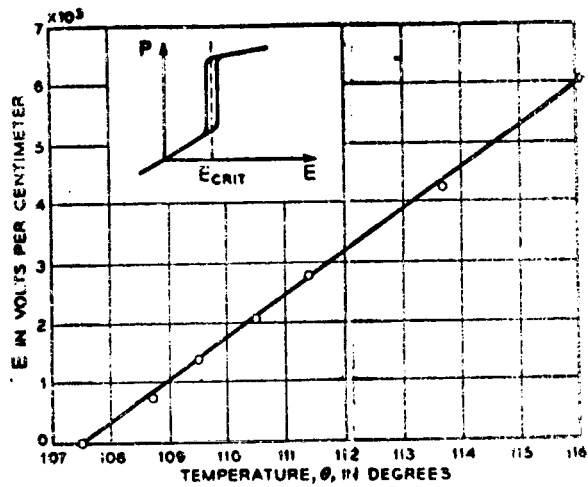
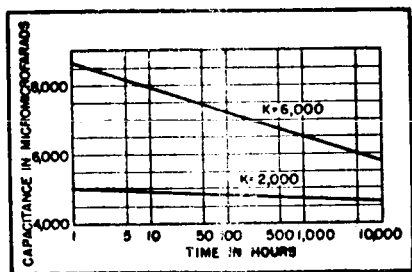


Figure 10



Shift of Curie temperature θ versus applied field E .

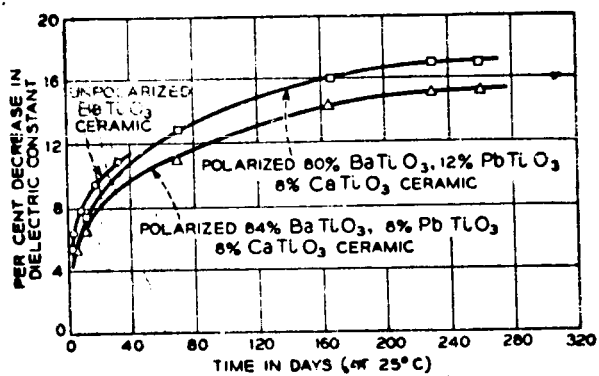
Figure 11



Aging curve of two Group-C materials, at a test frequency of 1,000 cps

Figure 12

DIELECTRIC AGING CURVES AT ROOM TEMPERATURE FOR SEVERAL CERAMIC COMPOSITIONS



Aging of the dielectric constants of polarized and unpolarized ceramics.

Figure 13

(2) Effect of Dopants and Impurities

The effect on the dielectric constant of departures from stoichiometry are significant. A standard 1 to 1 ratio of BaO and TiO₂ yields the dielectric maximum and tan δ related in Figure 7. If the BaO content is reduced, the dielectric constant curve is flattened and lowered, and the curve of tan δ vs. temperature changes dramatically (Figure 14⁽¹⁴²⁾).

Conversely, if the BaO content is increased relative to the TiO₂ content, the maximum dielectric constant increases dramatically (Figure 15⁽¹⁴²⁾). Although the maximum dielectric constant behaves wildly with variations of the constituents, the location of this maximum (the Curie point) is remarkably stable. Unfortunately, an excess of either constituent yields a material which is not as chemically stable as stoichiometric BaTiO₃, an important consideration in vacuum deposited thin film capacitors.

The effect of addition of either Silica (SiO₂) or Alumina (Al₂O₃) on BaTiO₃ is that of reducing and flattening the dielectric constant vs. temperature characteristic (Figure 16^(e3)). Although other impurities doubtless have a considerable effect on the characteristics of the BaTiO₃, the reports on their effect have not been found.

The addition of certain desired materials to BaTiO₃ as dopants may modify the crystal characteristics significantly.

One of the most studied of these additives is SrTiO₃. The material is not ferroelectric (its dielectric constant behaves according to the Curie-Weiss law, however) and has a room temperature dielectric constant of approximately 200,⁽⁹⁰⁾ and forms a complete range of solid

solutions with BaTiO_3 . The addition of SrTiO_3 causes a downward shift of the Curie point of BaTiO_3 and is almost linear (Figure 17⁽⁹¹⁾). Figure 17 also depicts the unit crystal cell dimensions with varying amounts of SrTiO_3 . The dependence of ϵ on temperature for various SrTiO_3 concentrations is shown in Figure 18⁽¹⁴¹⁾ (The notations on each curve signify the amount of SrTiO_3 in the solid solution: S-30 signifies a mixture of 30% SrTiO_3 , 70% BaTiO_3 .) Figure 19⁽¹⁴¹⁾ shows the thermal characteristics of ϵ and $\tan \delta$ for a 10% SrTiO_3 , 90% BaTiO_3 mixture.

The addition of PbTiO_3 in appreciable quantities to BaTiO_3 has an effect opposite to that of SrTiO_3 : The Curie point increases with increasing PbTiO_3 concentration (Figure 20).⁽¹⁰⁴⁾ The maximum dielectric constant at the Curie point is also considerably reduced with addition of PbTiO_3 (Figure 21),⁽⁷⁶⁾ and this propensity may be helpful in producing less erratic dielectric constant vs. temperature characteristics. This latter effect may more than compensate for the decreased dielectric constant. In Figure 22,⁽⁷⁷⁾ the stability of $\tan \delta$ is shown for an 80% BaTiO_3 , 20% PbTiO_3 mixture. The addition of PbTiO_3 to BaTiO_3 decreased the resistivity of the solid solution with increasing PbTiO_3 concentrations.⁽⁷⁹⁾

The interaction of CaTiO_3 with BaTiO_3 is much more limited than for PbTiO_3 and SrTiO_3 . Generally, the addition of CaTiO_3 to BaTiO_3 decreases the dielectric constant and the power factor of the solid solution at any temperature (Figures 23 through 25⁽⁸³⁾), but does not change the 120°C transition temperature of BaTiO_3 , although the 5°C transition temperature is shifted to lower temperatures.⁽⁹⁰⁾ The addition of CaTiO_3 to BaTiO_3 may also have the beneficial affect of reducing the thermal instability of both the dielectric constant and the power factor.

DIELECTRIC PROPERTIES OF DUPONT 2BaO·3TiO₂

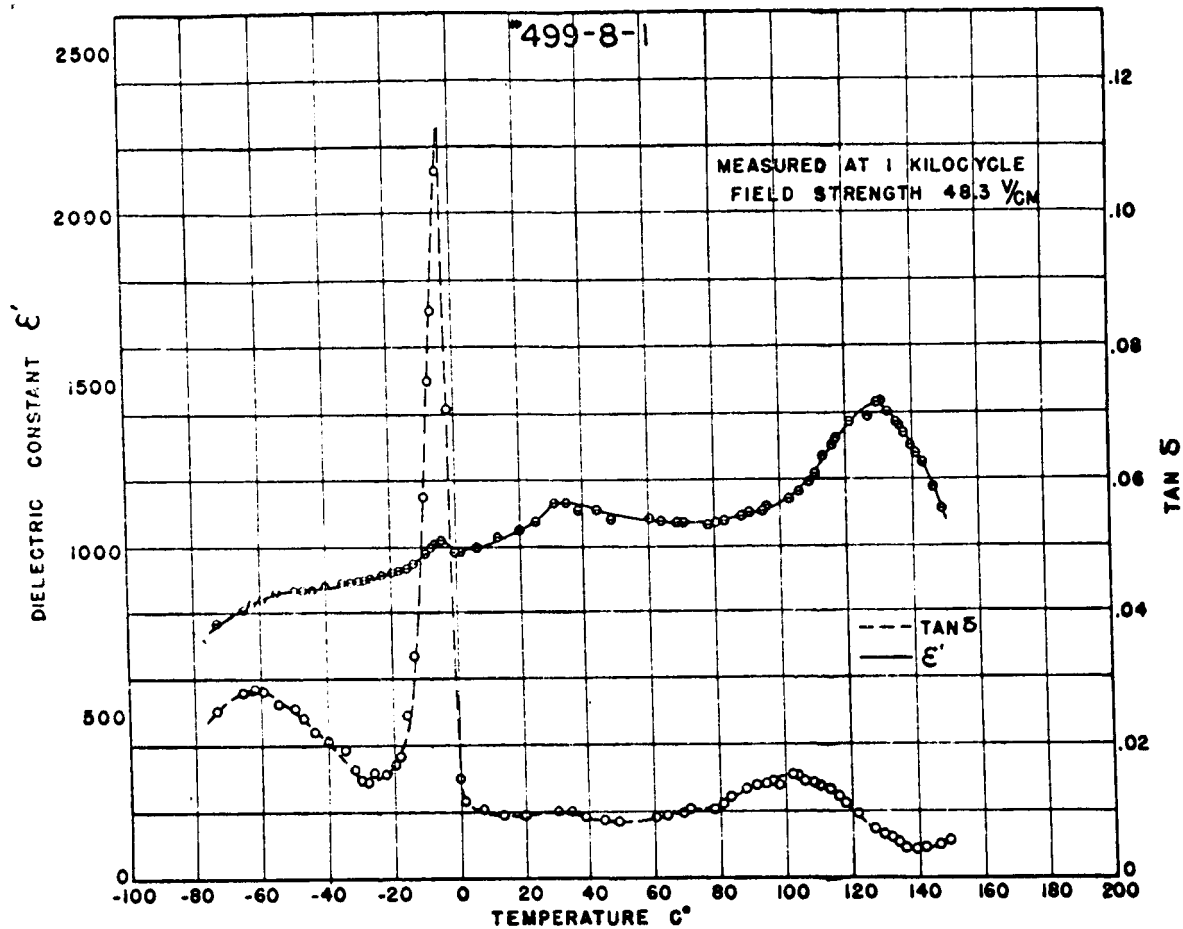


Figure 14

DIELECTRIC PROPERTIES OF DU PONT #499-18-2 65.95%BaO+33.8%TiO₂

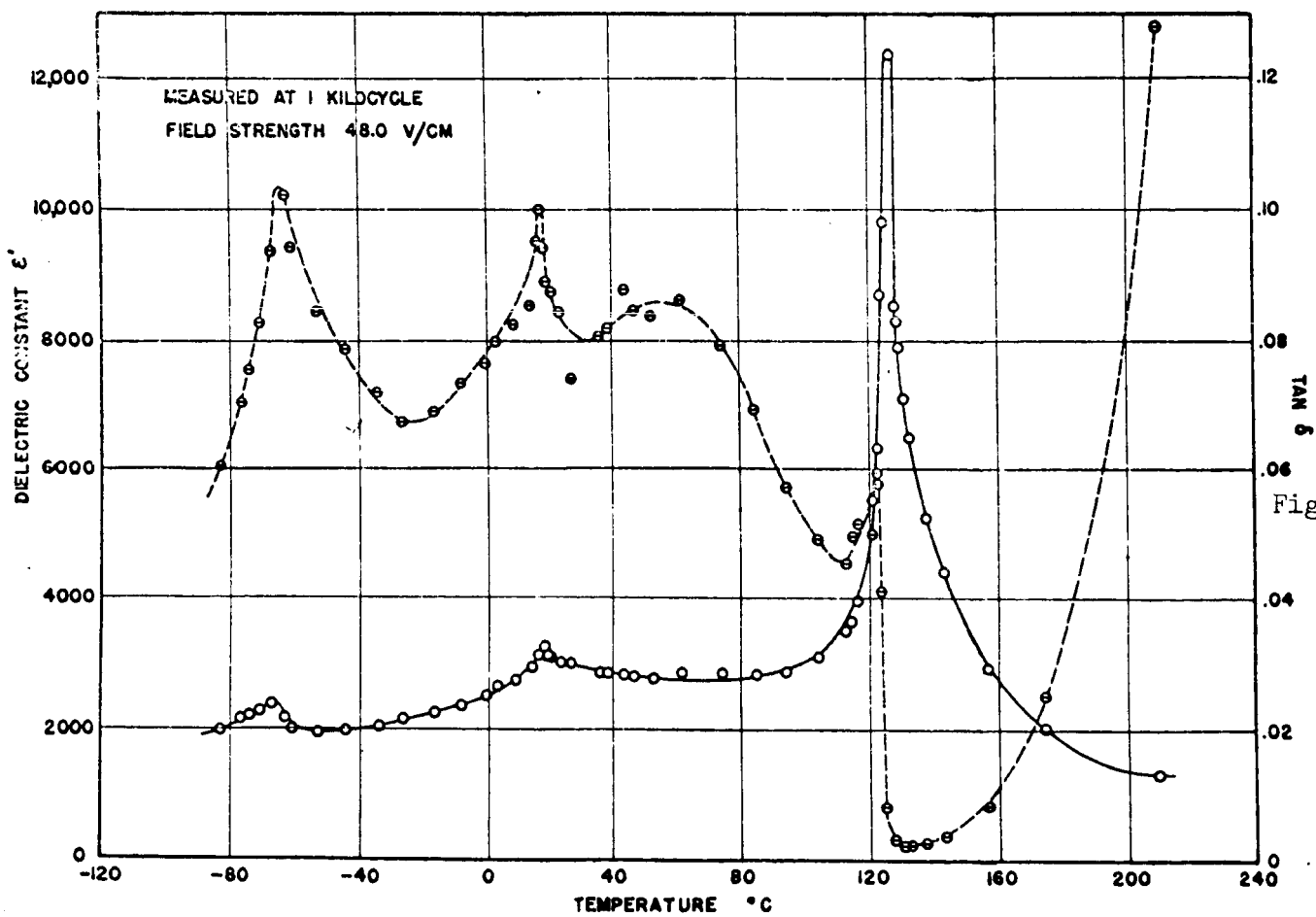


Figure 15

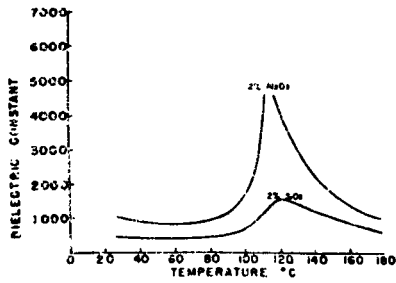


Figure 16

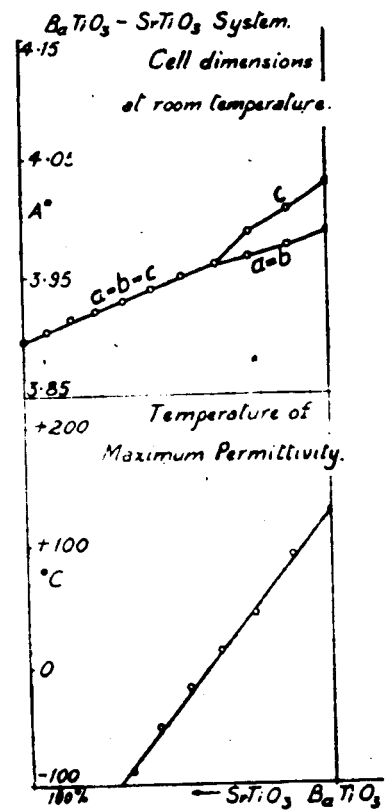
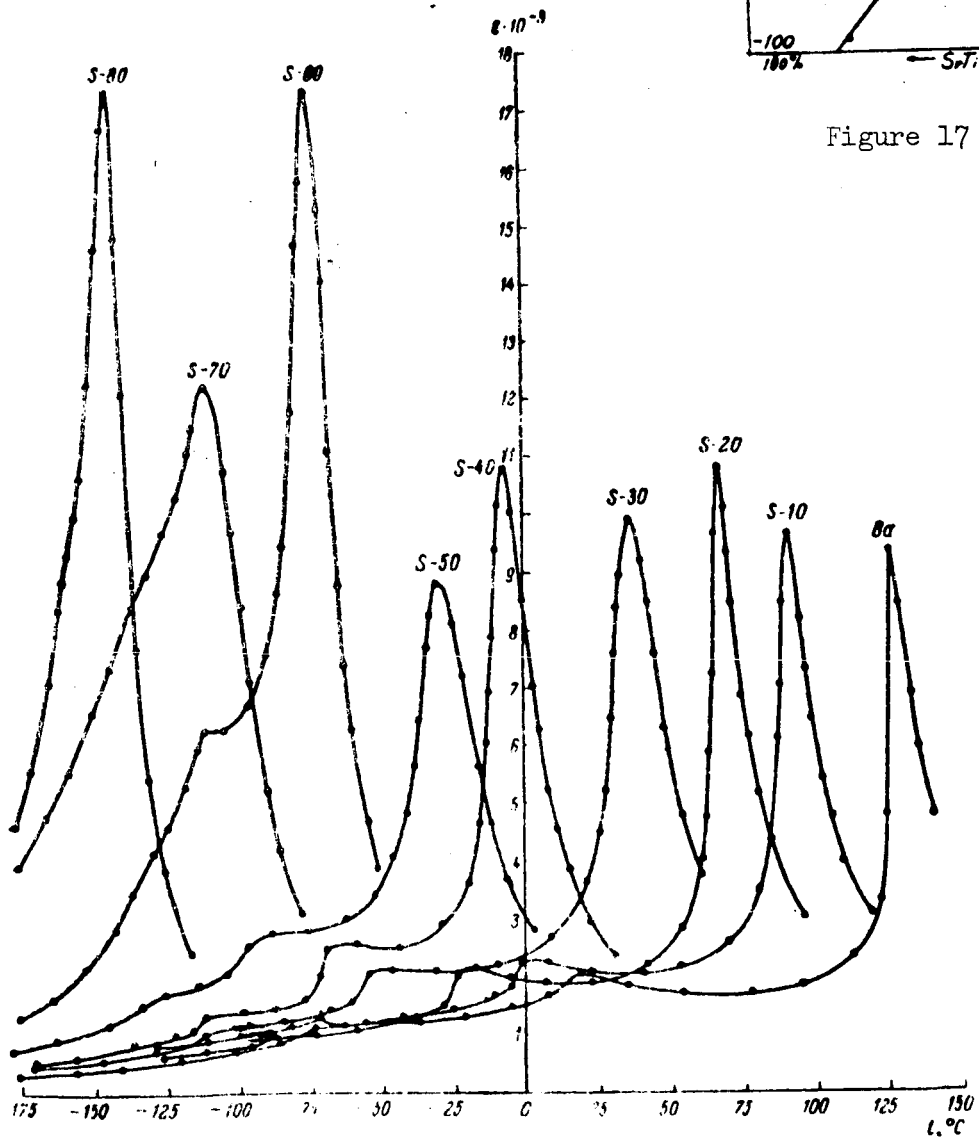
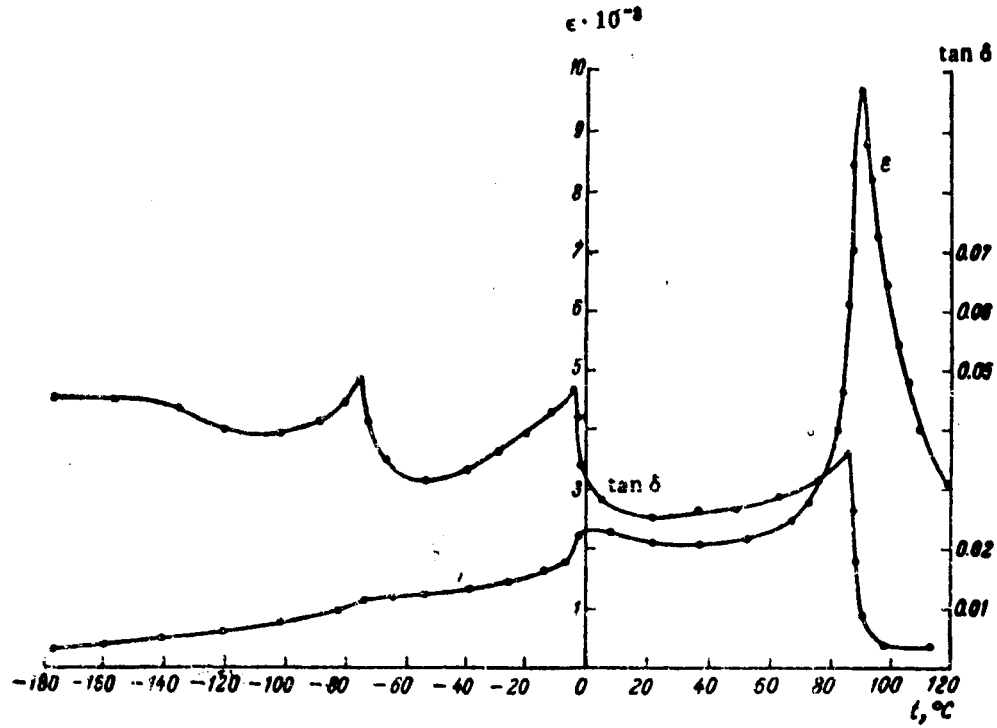


Figure 17



Dependence of the permittivity of solid solutions of (Ba, Sr)TiO₃ on temperature.

Figure 18



Dependence of ϵ and $\tan \delta$ on temperature for a specimen of the solid solution S-10.

Figure 19

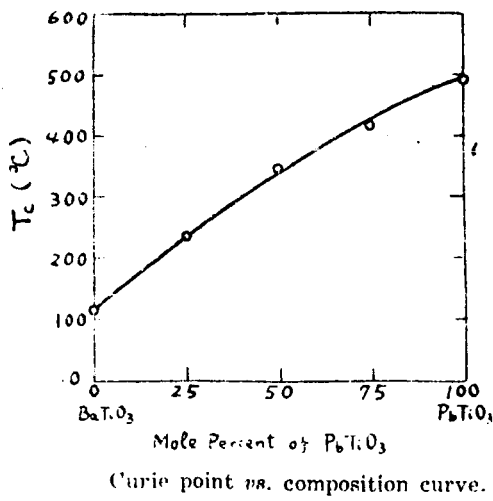
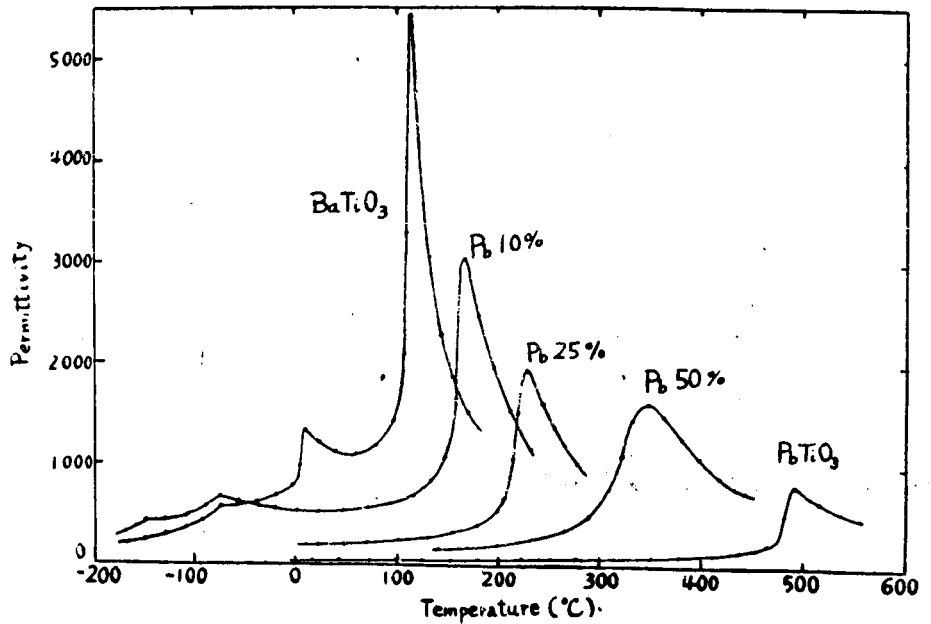


Figure 20



Dielectric constants of $(Ba-Pb)TiO_3$ as a function of temperature.

Figure 21

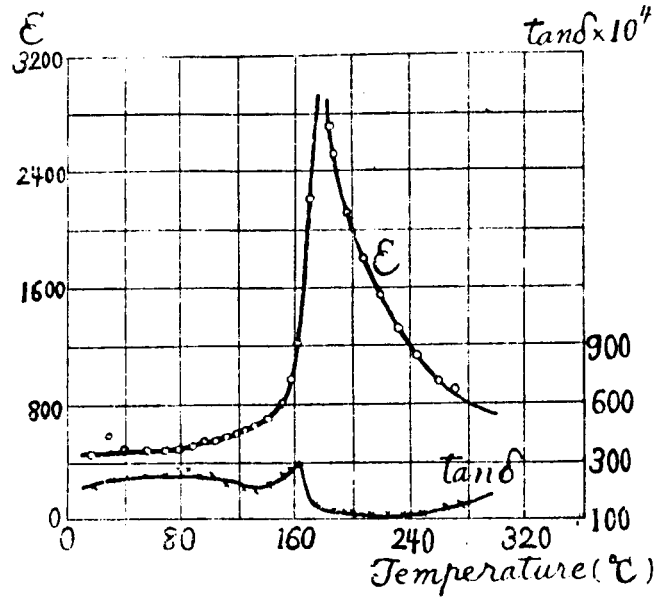
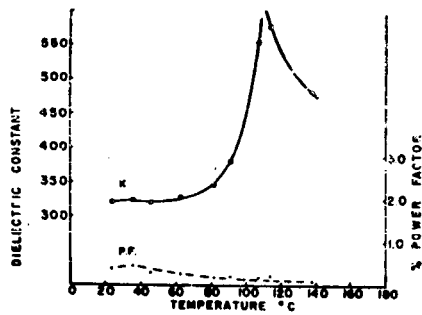
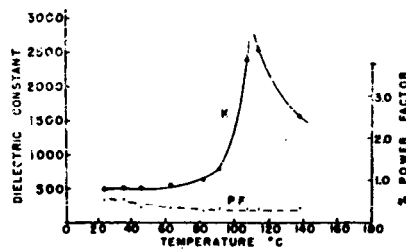


Figure 22



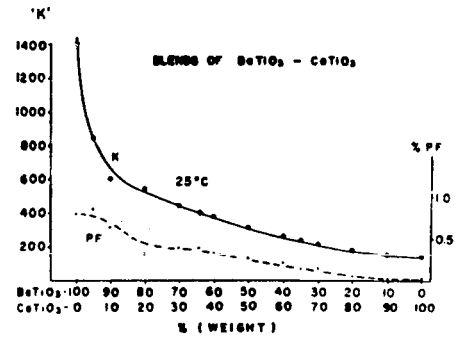
Temperature Characteristics of Dielectric Properties of 50% BaTiO₃, 50% CaTiO₃

Figure 23



Temperature Characteristics of Dielectric Properties of 75% BaTiO₃, 25% CaTiO₃

Figure 24



Dielectric Properties at 25°C. of BaTiO₃-CaTiO₃ Blends

Figure 25

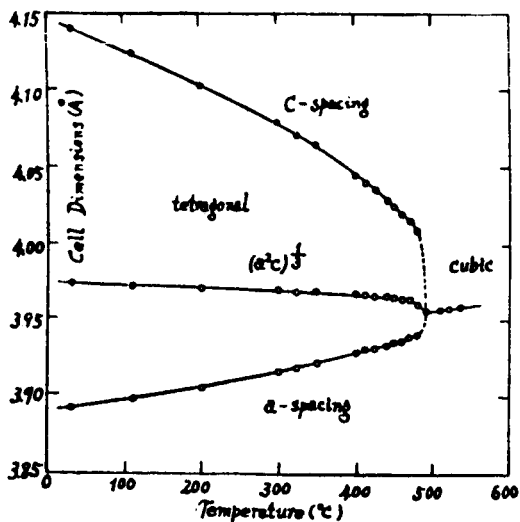
b. Lead Titanate

The crystal structure of lead titanate, PbTiO_3 , is quite similar to that of BaTiO_3 : cubic above the Curie point (490°C) and tetragonal below it. The lattice constants of the unit cell through the temperature range 0°C to 600°C are shown in Figure 26.⁽¹³¹⁾ The dielectric constant varies with temperature as shown in Figure 27.⁽¹³¹⁾

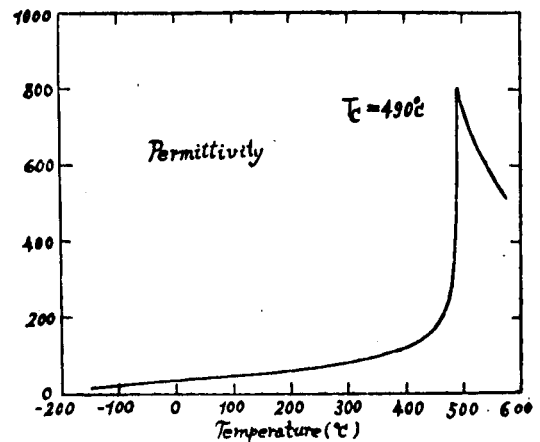
Above the Curie point, the dielectric constant is governed by the Curie-Weiss law, with $C = 1.1 \times 10^5$ and $T_c = 420^\circ\text{C}$.

Except for the transition at 490°C , no other crystallographic transitions have been observed down to -170°C .⁽³⁰⁾ One interesting phenomenon is the apparent decrease in unit cell volume near (and below) the Curie point. Apparently, the ferroelectric unit cell volume is larger than the paraelectric cubic cell. This phenomenon is not detectable in its relative, BaTiO_3 .

A discussion of the effects of the addition of PbTiO_3 to BaTiO_3 ceramic has already been noted.



Lattice spacing as a function of temperature.



Permittivity as a function of temperature.

c. Strontium Titanate

SrTiO_3 has been reported as both ferroelectric and as paraelectric by various authors.^(1, 42, 102, 142, 143) One reason given to substantiate the claim to ferroelectric behavior is based on the behavior of the dielectric constant with changing temperatures. Most observers agree that the dielectric constant closely follows the Curie-Weiss law down to about 50°K, with $C = 8.3 \times 10^4$ °K and $T_c = 38$ °K. The crystal structure apparently experiences a crystallographic transition at 40°K, the unit cell being tetragonal below this point and cubic perovskite above it.

The dielectric constant of SrTiO_3 at room temperature is approximately 220, and gradually increases to approximately 20,000 at 20°K.⁽¹⁾ The behavior of the dielectric constant and $\tan \delta$ are shown over the temperature range -90°C to 130°C in Figure 28.⁽¹⁴²⁾

At temperatures below 50°K, the dielectric constant is lower than predicted by the Curie-Weiss law, and tends toward a steady value of 1300 as absolute zero is approached.⁽¹⁴³⁾ This lack of hysteresis effect below 50°K is in opposition to the findings of F. Jona and G. Shirane.⁽¹⁾

The primary interest in SrTiO_3 appears to be in its use as a dopant for BaTiO_3 .

d. Calcium Titanate

Calcium titanate (CaTiO_3) has given its mineral name to the structural type of compound devoted to ABO_3 : the mineral perovskite. The unit crystal cell structure changes from the room temperature orthorhombic

form to a tetragonal form at about 600°C and to a cubic form at about 1000°C. The dielectric constant and $\tan \delta$ for a ceramic specimen of CaTiO_3 , are plotted vs. temperature in Figure 29.⁽¹⁴²⁾ The material is not ferroelectric and its main use is as a dopant for BaTiO_3 , as noted previously.

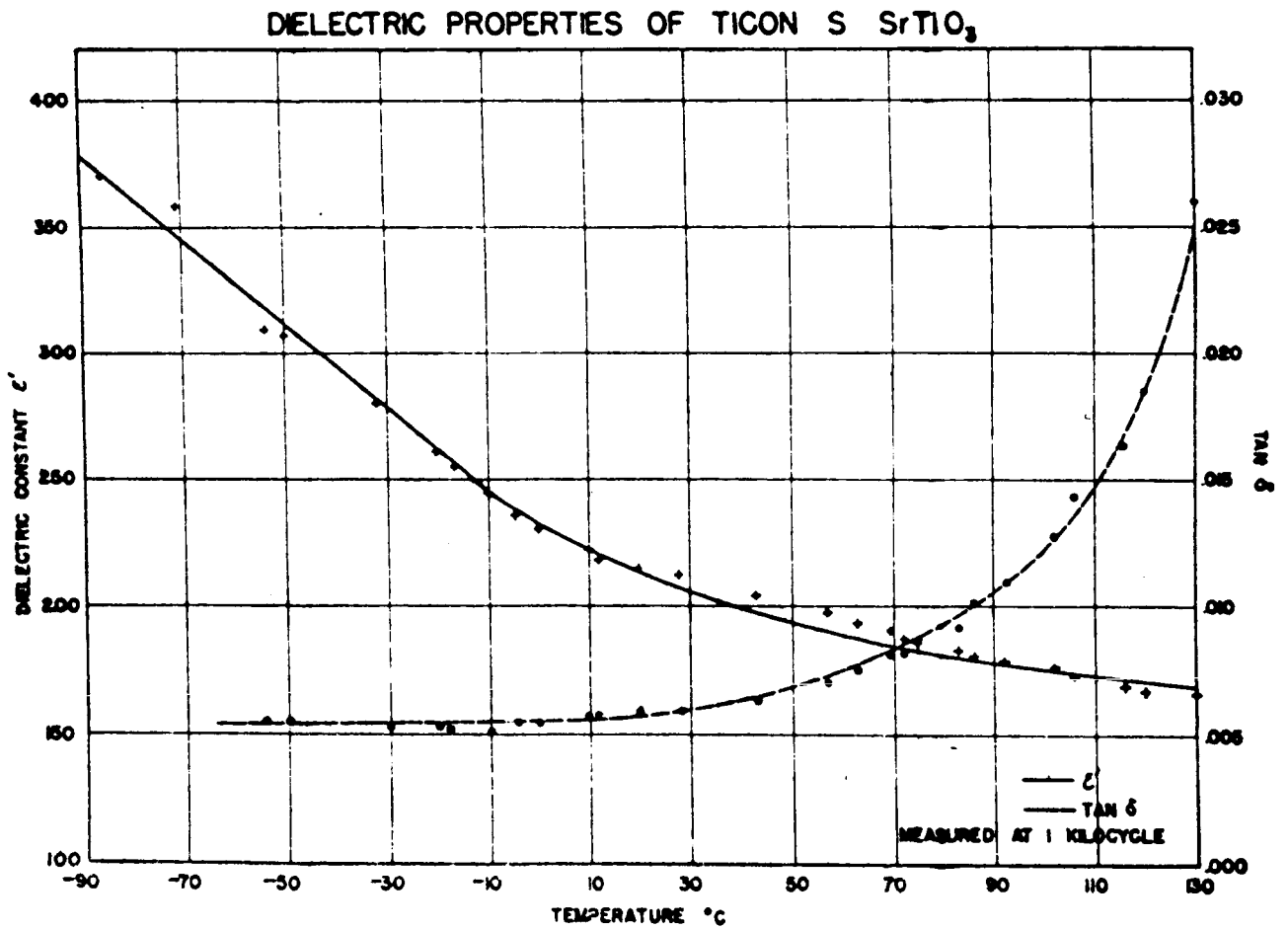


Figure 28

DIELECTRIC PROPERTIES OF TICON C CaTiO_3

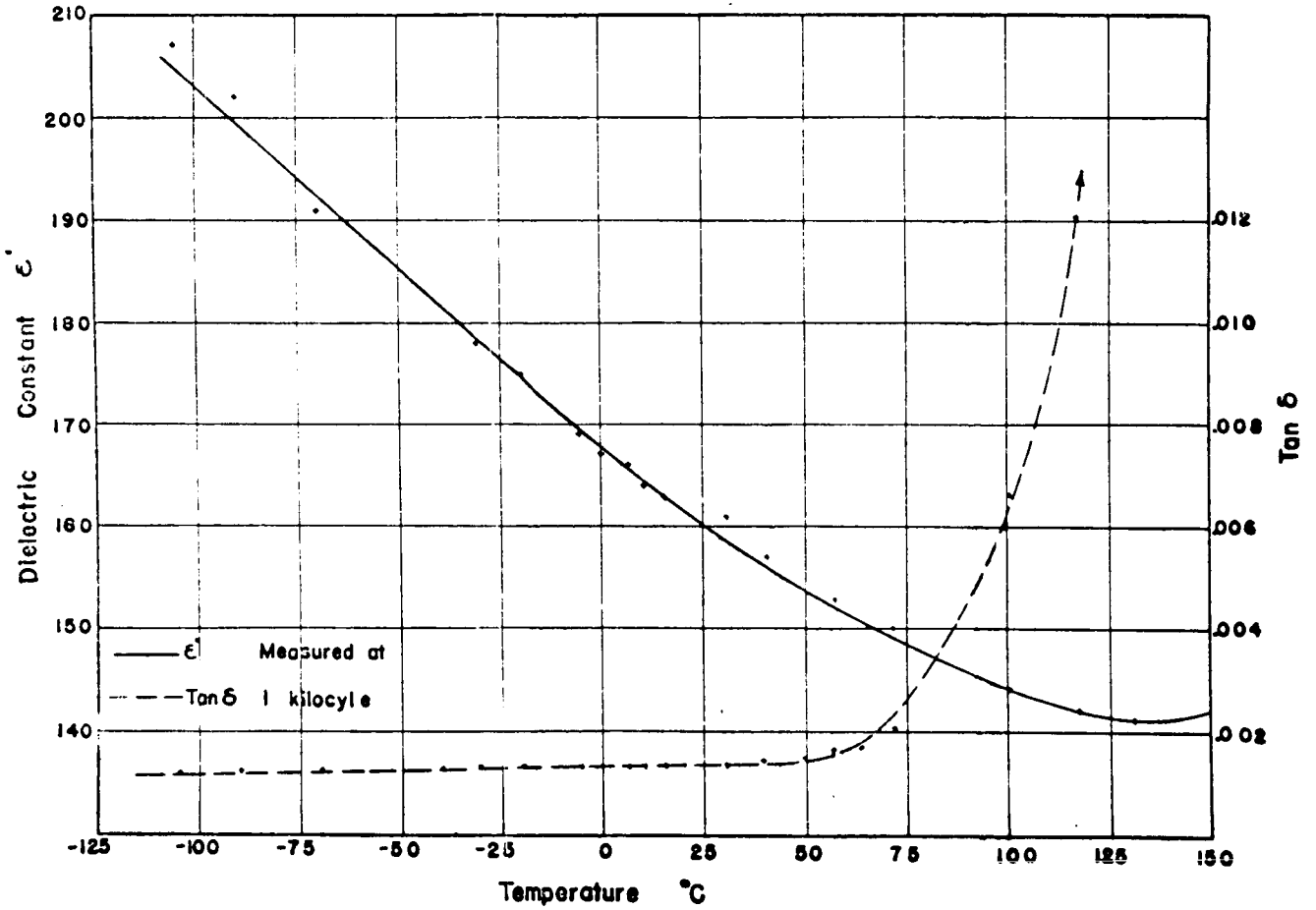


Figure 29

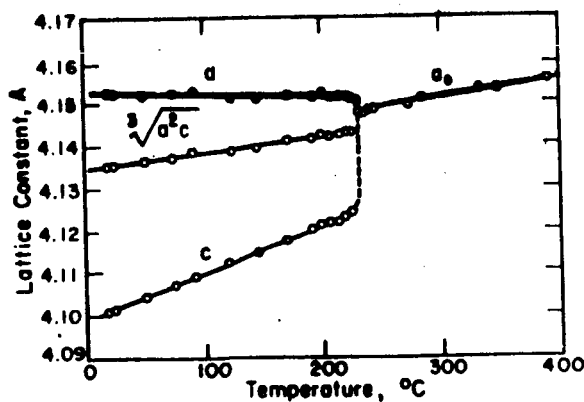
2. Zirconates

a. Lead Zirconate

(1) Pure Material

Lead zirconate has attracted considerable attention due to its dielectric properties: it is apparently an antiferroelectric material. Although considerable work was directed to measuring its dielectric properties, the first report was made by S. Roberts in 1950.⁽⁴¹⁾ Since that time, considerable interest in lead zirconate has been engendered, especially in Japan.^(12, 17, 33, 100, 132)

There are two known states of the crystal unit cell: cubic above 230°C and orthorhombic below,⁽¹²⁾ although the latter was earlier reported to be tetragonal.⁽²³⁾ The unit cell lattice constants vs. temperature are shown in Figure 30.⁽¹⁾ Also shown is the unit cell volume vs. temperature characteristic, which exhibits the anomalous volume change at the Curie point transition and which has been confirmed by other measurements.

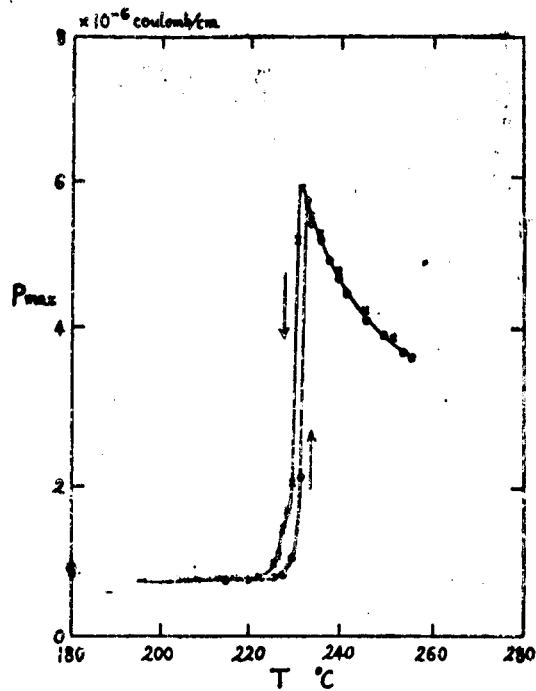


Temperature dependence of the lattice parameters of PbZrO_3 . The antiferroelectric phase is described in terms of pseudo-tetragonal axes a and c .
 a_0 = cubic parameter

Figure 30

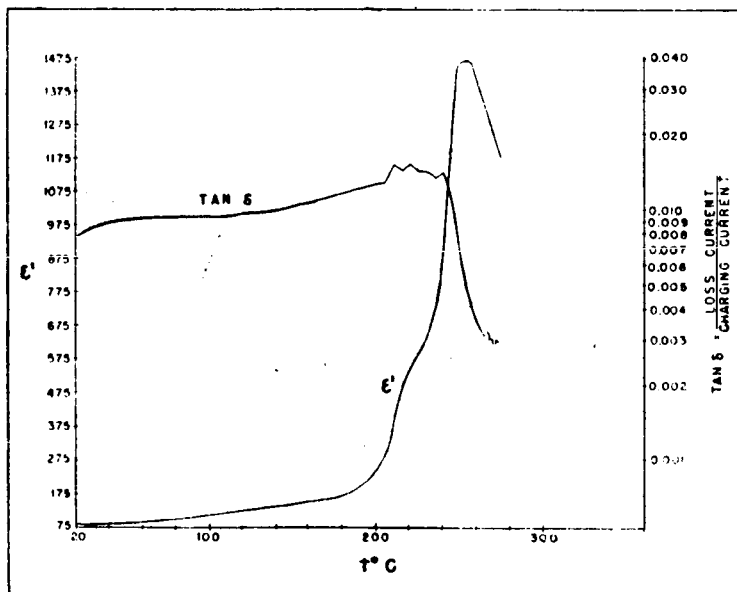
Of greater interest are the electrical properties of PbZrO_3 . Measurement of the polarization vs. electric field strength characteristics yield data as in Figure 3. At low field strength, the polarization varies linearly. At a certain critical field strength, labeled E_c , the characteristic becomes non-linear and a hysteresis loop develops which is similar to that observed for BaTiO_3 . Consequently, it is inferred that application of sufficient field strength (E_c) induces a ferroelectric state which is more stable than the antiferroelectric state. This phenomenon is due to the action of reversible, anti-parallel dipole moments, whose energies are eventually overcome to produce a net polarization in the crystal. In contrast with BaTiO_3 , an increase may be noted in the polarization at the Curie point (Figure 31⁽¹⁷⁾).

The increase in polarization corresponds directly to the increase in dielectric constant at the Curie point. Figure 32^(e9) shows the variations of both the dielectric constant and the loss tangent vs. temperature. Above the Curie point, the dielectric constant follows the Curie-Weiss law, with $C = 1.6 \times 10^{-5} \text{ }^\circ\text{C}$ and $T_c = 118^\circ\text{C}$. Although the dielectric constant vs. temperature slope is quite flat at room temperature, its low value will be immediately noted (≈ 100). Consequently, PbZrO_3 as a pure material is of very little interest to us. However, the dielectric characteristics of the material in solid solution with other materials is of considerable interest.



Maximum polarization as a function of varying temperature at $E_{max} = 20$ kV/cm.

Figure 31



Dielectric constant ϵ' and loss tangent as function of temperature for impure lead zirconate.

Figure 32

(2) Effect of Dopants (Solid Solution with PbZrO_3)

Addition of BaZrO_3 , even in small quantities, drastically changes the characteristics of PbZrO_3 . Figure 33⁽¹⁰⁶⁾ illustrates the phase diagram of the $(\text{Pb}, \text{Ba})\text{ZrO}_3$ system and the electrical characteristics of each phase. The antiferroelectric state may still be noted to approximate 5% BaZrO_3 concentration. As the Curie point is lowered still further by increasing additions of BaZrO_3 , a new ferroelectric phase appears. The effect of the addition of BaZrO_3 to PbZrO_3 on the behavior of the dielectric constant with temperature is well represented in Figure 34.⁽⁴¹⁾ The last figure exhibits the features of what appears to be a very desirable solid solution for use as a capacitor dielectric. At high concentrations of BaZrO_3 (approximately 40%), the dielectric constant - temperature characteristic is flattening, and the room temperature dielectric constant is high (approximately 2600).

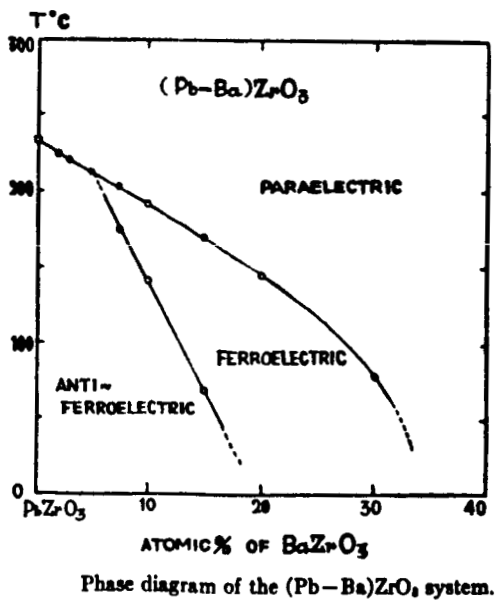


Figure 33

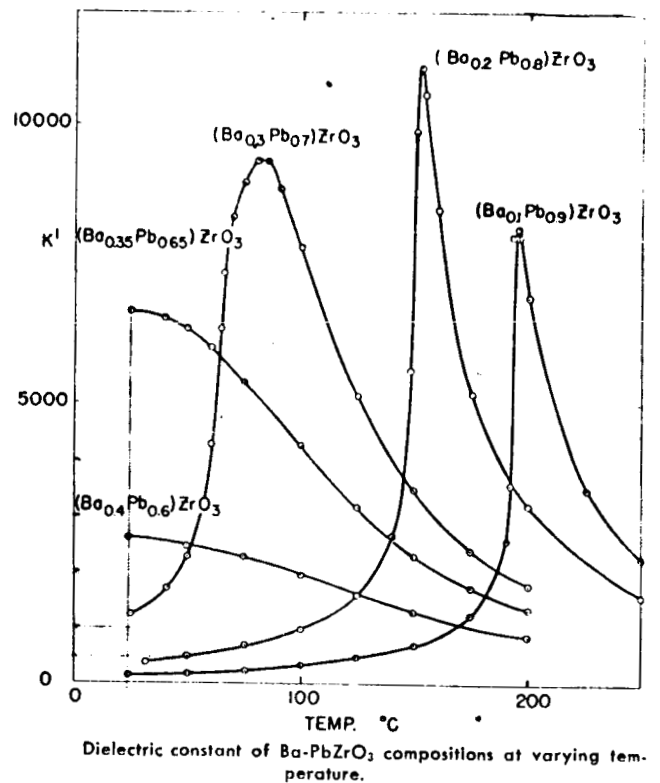


Figure 34

The measured dielectric constant and loss tangent are shown in Table II, below.

TABLE II

Table I. Dielectric Constant (K') and Dielectric Loss ($\tan \delta$) for Pure Lead Zirconate and Solid Solutions of Barium-Lead Zirconate

Temp. (°C.)	K'	$\tan \delta$	Temp. (°C.)	K'	$\tan \delta$
PbZrO₃			(Ba_{0.2}Pb_{0.8})ZrO₃		
23	110	0.0028	33	370	0.0238
50	111	0.0028	50	453	0.0285
100	133	0.0027	75	633	0.0317
150	162	0.0035	100	957	0.0311
200	218	0.0042	125	1580	0.0350
225	329	0.0054	140	2600	0.0455
230	453	0.0071	148	5600	0.0503
232	517	0.0081	150	9850	0.0347
234	1189	0.0070	152	11000	0.0250
236	3260	0.0040	154	10500	0.0174
238	3020	0.0020	160	8470	0.0105
240	2880	0.0022	175	5180	0.0053
250	2350	0.0017	200	3180	0.0035
275	1632	0.0021	250	1563	0.0020
300	1260	0.0030	300	950	0.0038
350	865	0.0072	(Ba_{0.3}Pb_{0.7})ZrO₃		
275	1632	0.0022	25	1227	0.0257
250	2340	0.0023	41	1690	0.0245
240	2830	0.0025	50	2240	0.0245
236	3130	0.0032	60	1270	0.0280
234	3340	0.0038	64	6320	0.0294
232	3480	0.0058	66	7320	0.0254
230	1905	0.0146	70	8340	0.0158
228	960	0.0096	75	8980	0.0180
226	671	0.0087	80	9330	0.0187
224	505	0.0074	85	9330	0.0157
220	366	0.0066	90	8820	0.0148
200	236	0.0051	100	7800	0.0107
(Ba_{0.4}Pb_{0.6})ZrO₃			125	5110	0.0064
25	143	0.0084	150	3430	0.0043
50	180	0.0093	175	2380	0.0026
75	212	0.0100	200	1750	0.0021
100	346	0.0240	(Ba_{0.5}Pb_{0.5})ZrO₃		
125	466	0.0329	25	6630	0.0329
150	670	0.0369	40	6530	0.0147
175	1188	0.0377	50	6350	0.0100
190	2510	0.0377	60	6000	0.0074
192	3530	0.0406	75	5400	0.0055
194	8000	0.0191	100	4250	0.0047
195	8150	0.0102	125	3140	0.0035
196	8000	0.0100	150	2290	0.0024
200	6900	0.0062	175	1705	0.0017
225	3450	0.0035	200	1310	0.0014
250	2280	0.0035	(Ba_{0.6}Pb_{0.4})ZrO₃		
275	1650	0.0046	24	2600	0.0081
300	1286	0.0060	50	2490	0.0070
			75	2245	0.0077
			100	1920	0.0086
			150	1255	0.0041
			200	820	0.0013

As in the case of BaTiO_3 , the dielectric constant is sensitive to the applied electric field strength (Figure 35⁽⁴¹⁾).

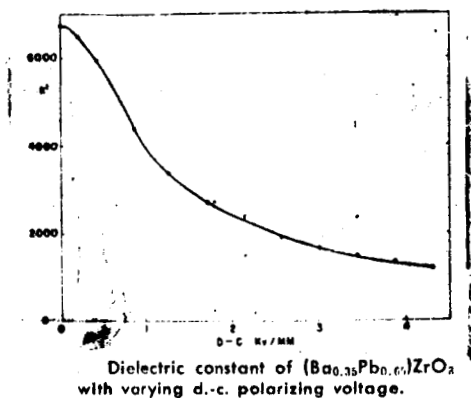


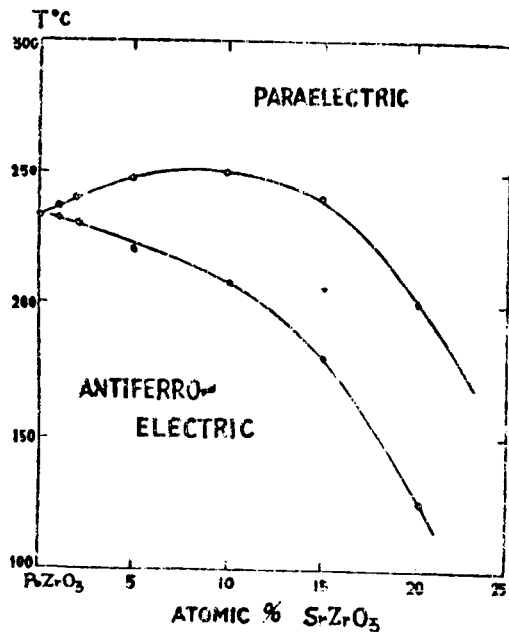
Figure 35

The effect of SrZrO_3 addition to PbZrO_3 is to decrease the dielectric constant of the solid solution. The crystal transition temperatures change with increasing SrZrO_3 concentration as shown in the phase diagram, Figure 36.⁽¹⁰⁶⁾ With only slight additions of SrZrO_3 , a new phase appears. Above the primary transition, the unit cell is cubic and paraelectric. The intermediate phase is antiferroelectric, and the unit cell is apparently tetragonal. The third phase again is antiferroelectric, but with an orthorhombic, pseudo-tetragonal unit cell. The effect of the SrZrO_3 addition to PbZrO_3 is well illustrated in Figure 37.⁽¹⁰⁶⁾ The low dielectric constant at room temperature makes this combination of zirconates of little interest to us.

The addition of CaZrO_3 to PbZrO_3 has been reported to yield an effect similar to that of the addition of SrZrO_3 noted above.

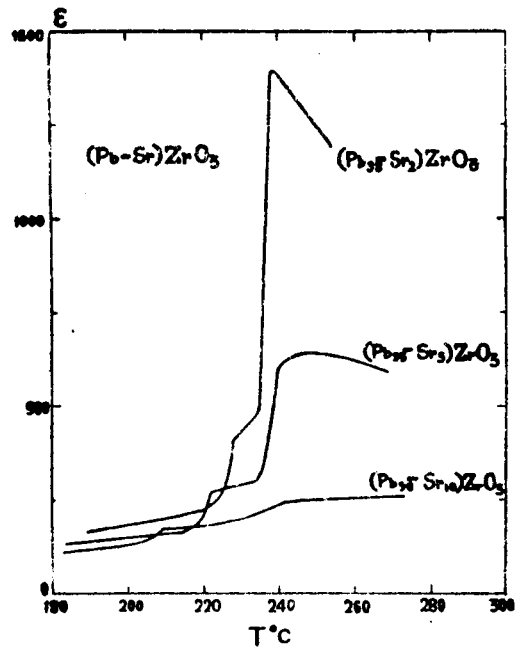
b. Barium, Strontium and Calcium Zirconates

In their "pure" form, the zirconates of barium, strontium and calcium hold very little promise for our work. The unit crystal cells of both barium and strontium zirconate are of cubic perovskite structure, while calcium zirconate is of orthorhombic form. None of the compounds show unusual dielectric properties and are apparently not ferroelectric. Their main use is in the preparation of solid solutions with PbZrO_3 , as noted previously.



Phase diagram of the $(\text{Pb}-\text{Sr})\text{ZrO}_3$ system.

Figure 36



Permittivity vs rising temperature curves of $(\text{Pb}-\text{Sr})\text{ZrO}_3$ compositions.

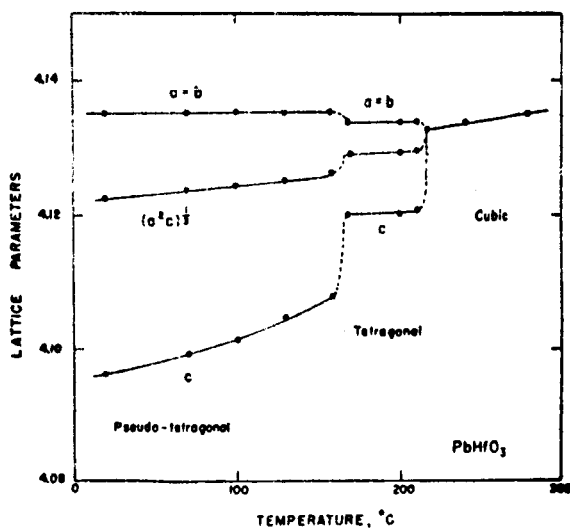
Figure 37

3. Hafnates

a. Lead Hafnate

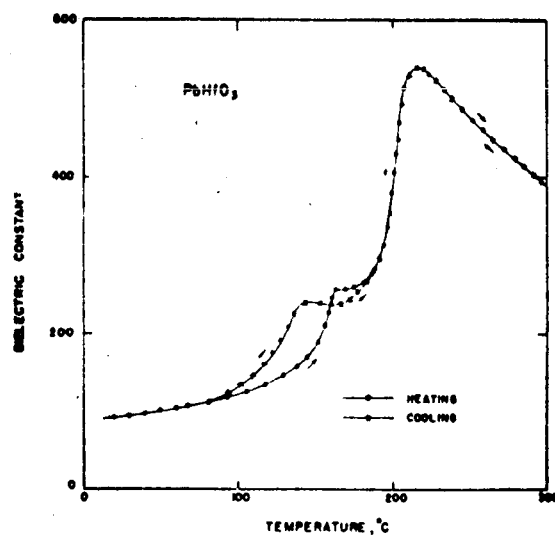
The characteristics of lead hafnate have been investigated by Shirane and Pepinsky.⁽³⁷⁾ Samples for testing were produced from PbCO_3 and HfO_2 and fired at 1200°C , with special precautions taken to retard the evaporation of PbO . The crystalline structure of the ceramic was determined to be tetragonal at room temperature. The unit cell lattice parameter variations with temperature are shown in Figure 38.⁽³⁷⁾

The dielectric properties of PbHfO_3 were evaluated: the variation of dielectric constant with temperature is shown in Figure 39.⁽³⁷⁾ The material exhibits paraelectric properties above the Curie point at 215°C and the dielectric constant is closely described by the Curie-Weiss law, with $C = .095 \times 10^5^\circ\text{C}$ and $T_c = 50^\circ\text{C}$. Between the transition point at 165°C and the Curie point at 215°C , the crystal is apparently tetragonal and antiferroelectric. Below 165°C , the crystal structure is distorted tetragonal and is antiferroelectric. The low dielectric constant at room temperature makes this compound of little interest.



Lattice spacing vs temperature for PbHfO_3 .

Figure 38



Dielectric constant vs temperature for PbHfO_3 , at 10 kc/sec.

Figure 39

b. Other Hafnates

The crystal structure of the hafnates of strontium and barium are apparently cubic and their behavior paraelectric at room temperature. No discussions of the dielectric properties were found and it is assumed that they are comparable to those of the zirconates.

4. Stannates

The dielectric properties of stannates, as a group, have apparently not been thoroughly investigated. Only one general report was found which treated the dielectric and chemical properties of the stannates.⁽⁴⁴⁾ In general, the dielectric constant and power factors are quite low (Table III below), and none appear to have ferroelectric properties. The anomalously high dielectric constant noted for NiSnO₃ is questionable in light of the poor power factor and the high temperature coefficient of the dielectric constant.

TABLE III

MATERIAL	At 25°C	1 KC	Temp. Coeff. of K, ppm/°C (25°C - 85°C, 1 KC)	D. F. at 85°C, 1 KC
	K	P.F.		
BaSnO ₃	17	0.0004	0 ± 200	0.0022
CaSnO ₃	17	0.0004	0 ± 200	0.0006
SrSnO ₃	15	0.0006	0 ± 200	0.0006
MgSnO ₃	62	0.0760	+ 6,300 ± 500	0.1500
Bi ₂ (SnO ₃) ₃	34	0.0050	+ 500 ± 200	0.0167
PbSnO ₃	16	0.0300	+ 1,800 ± 500	0.0390
CoSnO ₃	16	0.0110	+10,400 ± 1000	0.1960
NiSnO ₃	235	0.2670	+19,700 ± 1000	0.3270

There is apparently some interest in the utilization of the stannates in solid solution with their respective titanates to modify the titanate Curie points and to stabilize the reduction of the titanate bodies during firing.

5. Niobates

a. Potassium Niobate

The ferroelectric behavior of single crystal KNbO_3 was reported by Matthias as early as 1949.⁽¹⁰⁾ In the same article, he also reports the addition of NaNbO_3 , KTaO_3 and NaTaO_3 to the list of materials with ferroelectric properties.

Potassium niobate appears to pass through three crystal modifications in the temperature range of 0°C to 500°C . The unit cell is apparently orthorhombic below 224°C , tetragonal above 225°C and below 435°C , and cubic above the 435°C Curie point (see Figure 40⁽²¹⁾). The tetragonal and orthorhombic phases are ferroelectric, the cubic cell is paraelectric.

The variation of the dielectric constant and loss tangent with temperature are shown in Figure 41.⁽⁹⁹⁾ The dielectric constant remains at essentially the same value from 100°C down to about -190°C . The dielectric constant at room temperature is approximately 500. The dielectric constant anomalies correspond closely with the crystal structural transition.

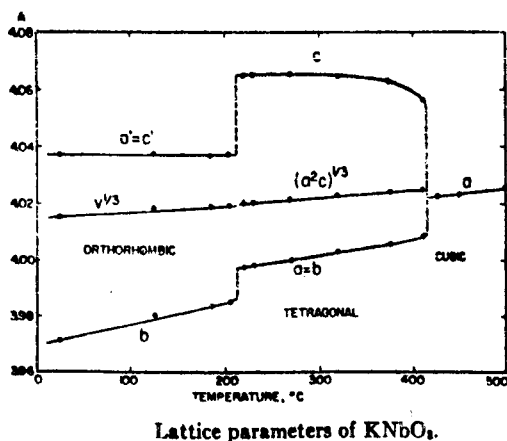


Figure 40

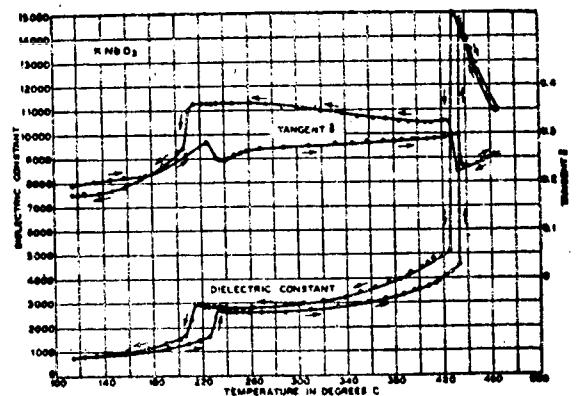


Figure 41

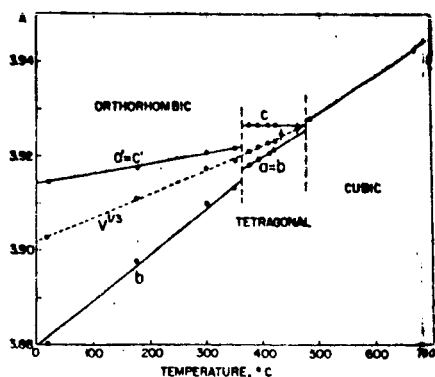
There has been some discussion of the validity of the claim of ferroelectric behavior of KNbO_3 . Shirane, Newnham and Pepinsky⁽²¹⁾ have, however, noted a large discharge current from a polarized single crystal as it was heated through the transition points of 225°C and 435°C .

Above the Curie point, the dielectric constant is governed by the Curie-Weiss law, with $C = 1-2 \times 10^5$ $^\circ\text{C}$ and $T_c = 300^\circ\text{C}$.

b. Sodium Niobate

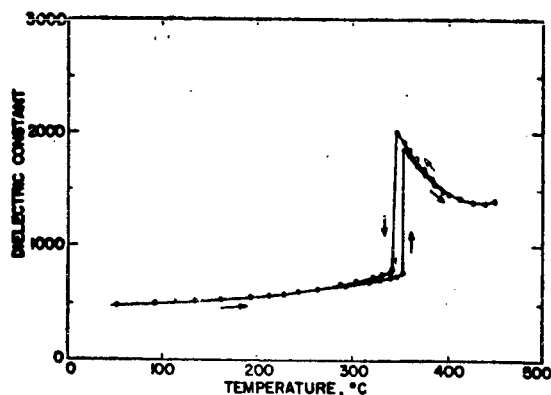
As noted in the previous section, the first report of the ferroelectric behavior of NaNbO_3 was that of Matthias.⁽¹⁰⁾ As with KNbO_3 , the unit crystal cell experiences two transitions: above 480°C the cell is cubic, below 480°C and above 360°C the cell is tetragonal, and below 360°C the cell is orthorhombic.⁽²¹⁾ The effect of temperature on the lattice parameters is shown in Figure 42.⁽²¹⁾

Although several researchers report hysteresis effects for NaNbO_3 at room temperature and below,^(21, 45, 99, 115) most feel that the material is antiferroelectric in behavior. The effect of temperature on the dielectric constant over the temperature range of 0°C to 500°C is shown in Figure 43.⁽²¹⁾ No dielectric anomalies have been reported between room temperature and -185°C . Most importantly, no pyroelectric effect was noted upon heating a polarized sample of NaNbO_3 . The dielectric constant also remains stable under field strengths up to 8 KV/cm. Therefore, the reports noted show no evidence of ferroelectricity but are consistent with the findings of Vousden,⁽⁴⁶⁾ who postulated antiparallel domains and antiferroelectric characteristics.



Lattice parameters of NaNbO_3 .

Figure 42



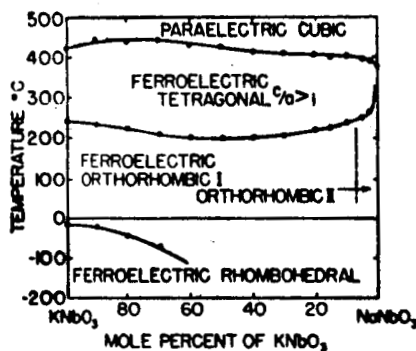
Dielectric constant of NaNbO_3 single crystal.

Figure 43

c. Mixtures of Sodium and Potassium Niobates

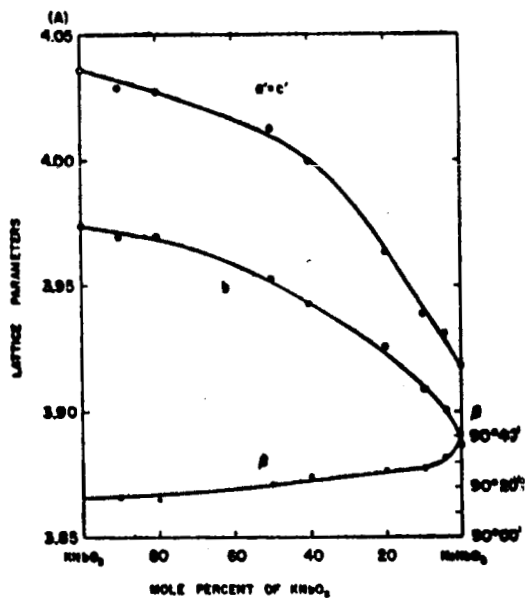
The mixture of NaNbO_3 and KNbO_3 has been studied extensively, both for its piezoelectric response and its high dielectric constant.⁽²¹⁾ The phase diagram for the $(\text{Na}, \text{K})\text{NbO}_3$ solid solution is shown in Figure 44.⁽²¹⁾ The lattice parameters of the crystal unit cell vs. the composition of the solid solution are shown in Figure 45.⁽²¹⁾

An interesting anomaly in the dielectric constant develops at 200°C (Figure 46⁽²¹⁾). This anomaly appears with only small additions of KNbO_3 to NaNbO_3 . In any case, the dielectric constant at room temperature appears to be lower than 500. The separate examination of potassium and sodium niobates appears to hold more promise for our purpose.



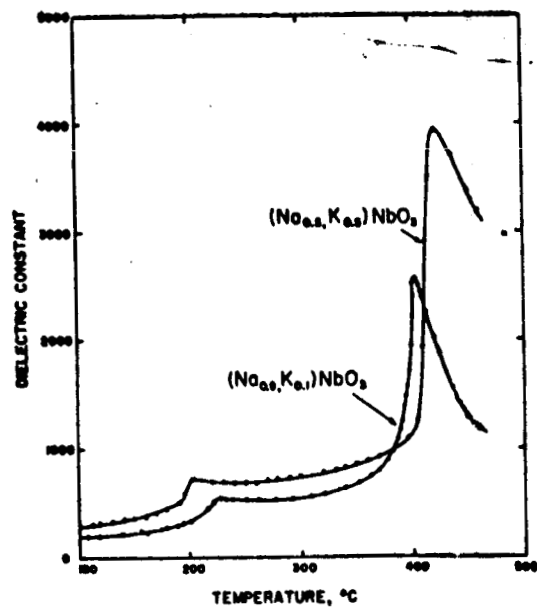
Phase diagram of NaNbO_3 - KNbO_3 system.

Figure 44



Lattice parameters of $(\text{Na}, \text{K})\text{NbO}_3$ system.

Figure 45



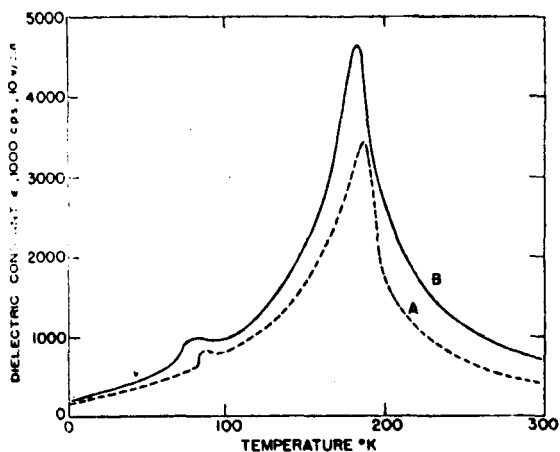
Dielectric constant of $(\text{Na}, \text{K})\text{NbO}_3$ solid solution.

Figure 46

d. Cadmium Niobate

The investigation of $\text{Cd}_2\text{Nb}_2\text{O}_7$ has been carried out by three investigators, (^sA, ^sB, 11) with some promising results. The unit cell structure has been reported to be strictly cubic, but with a low temperature Curie point transition (170°K), with an orthorhombic structure below the transition point.

The dielectric constant at room temperature has been reported as approximately 320 to 500 (Figure 47(^sB)). The dielectric constant above the Curie point closely follows the Curie-Weiss law, with $C = 4.6 \times 10^4 \text{ }^\circ\text{K}$ and $T_c = 150^\circ\text{C}$.

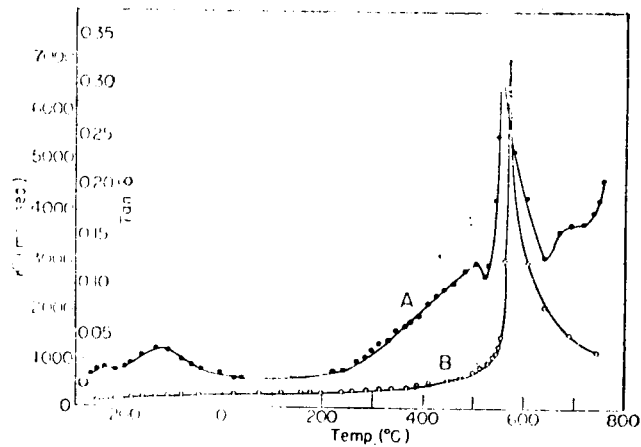


Temperature variation of dielectric constant for specimens of cadmium niobate fired at 1180°C (A) and at 1260°C (B).

Figure 47

e. Lead Niobate

The investigators of $\text{Cd}_2\text{Nb}_2\text{O}_7$ have also examined the characteristics of the related material $\text{Pb}(\text{NbO}_3)_2$. The results indicate a ferroelectric material with a dielectric constant of 280 at room temperature. The variations of dielectric constant and loss tangent with temperature are shown in Figure 48.⁽⁵⁾ Because of its relatively low dielectric constant at room temperature and the chemical instability of the material, the material is not felt to hold much promise for thin film applications.



Dielectric constant and loss tangent vs. temperature for lead niobate ceramic. Curve (A) $\tan \delta$; (B) k' (corrected for porosity). Note: 25° to 750°C., $\text{Pb}(\text{NbO}_3)_2$; -263° to 25°C., 98.63 $\text{Pb}(\text{NbO}_3)_2$, 1.37% ZrO_2 .

Figure 48

6. Tantalates

a. Potassium Tantalate

The investigation of KTaO_3 has yielded a very interesting and very low Curie point: approximately 13°K .⁽²²⁾ This is the lowest Curie point found in the literature and is apparently legitimate, as the crystals displayed typical hysteresis effects below that temperature. The variation of the dielectric constant with temperature is shown in Figure 49.⁽²²⁾ Unfortunately, no data have been found on the dielectric constant of KTaO_3 at room temperature, although extrapolation of the curve would indicate that it is probably below 500.

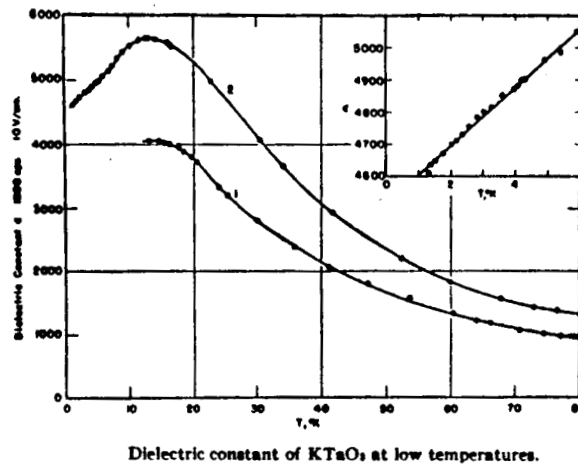


Figure 49

b. Sodium Tantalate

Investigation of NaTaO_3 has also been reported,⁽¹⁰⁾ and it apparently displays ferroelectric phenomena up to the Curie point of 475°C . Unfortunately, no data are given regarding the dielectric constant.

7. Other Materials

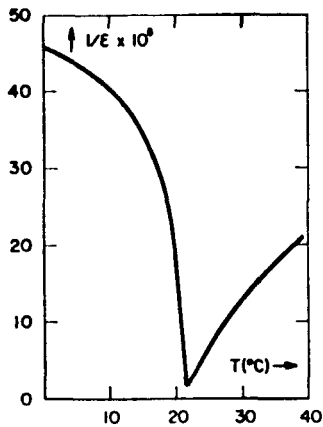
a. Tungsten Trioxide

Sawada, Ando and Nomura⁽⁹⁸⁾ have investigated the behavior of WO_3 in order to determine whether or not the material is ferroelectric. Their investigation extended the temperature range to the Curie point at about $710^\circ C$. Although generally high dielectric constants are alluded to, there are none offered. Extreme difficulty has been noted in the production of non-conducting samples, which will therefore significantly limit its use as a dielectric.

b. Antimony Sulfur Iodide

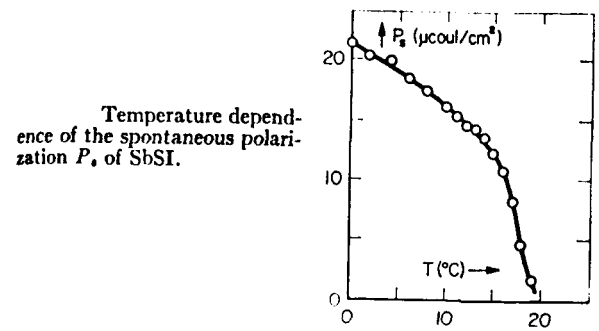
The electrical properties of SbSI have been recently investigated^(122,123) and it has been found to be both photoconductive and ferroelectric. The dielectric properties are quite interesting: the dielectric constant attains a value of 50,000 parallel to the needle crystal axis, but is only 25 perpendicular to the axis. The dielectric constant perpendicular to the needle axis is frequency independent over the range of 1 KC to 100 KC/sec. Figure 50⁽¹²²⁾ shows the behavior of the inverse of the "parallel" dielectric constant with temperature. The minimum in the curve represents the dielectric constant anomaly at $22^\circ C$. The behavior of the "parallel" spontaneous polarization of the crystal with temperature is typical for a ferroelectric and is shown in Figure 51.⁽¹²²⁾

Although the material possesses a fantastic dielectric constant, it has only been measured on single crystals and is high in



Temperature dependence of $1/\epsilon$ below and above the Curie point.

Figure 50



Temperature dependence of the spontaneous polarization P_s of SbSI.

Figure 51

only one axis. Consequently, the dielectric constant of a polycrystalline material is in some doubt. Considering also the magnitude of the temperature anomaly near the projected operating temperature of a capacitor (22°C) the value of the pure material as something other than a scientific curiosity is questionable. Doubtless the dielectric constant - temperature characteristics could be modified by suitable dopants or variations in stoichiometry, but the magnitude of such a project is considerably beyond the scope of our work.

B. Thin Film Properties

The production of thin films of BaTiO_3 for use as capacitor dielectrics is of considerable interest. Not only are achievable packing densities considerably higher than is possible with bulk material (due to the smaller thickness), but vacuum deposition has the added advantage of compatibility with integrated microcircuitry techniques.

Consequently, two different approaches to the production of thin BaTiO_3 films have been noted. One technique, reported by Bursian and Smirnova⁽⁵⁵⁾ is perhaps the most straightforward: the fusing of BaTiO_3 powder on a heated (platinum) substrate. Unfortunately, the film thicknesses obtainable are within the range of 5μ to 50μ , and the required firing temperature is of the order of 1600°C to 1700°C . Both are severe limitations to the value of such materials as capacitor dielectrics, even though dielectric constants in the order of 4000 to 6000 were achieved and ferroelectric behavior was noted.

The second method is more applicable to the technology of integrated microcircuitry: vacuum deposition. Several investigators have reported varying degrees of success using this technique,^(50, 51, 53, 54, 56, 60, 61, 70, 92) although Feldman appears to be the earliest to report his findings.

A major problem relating to the deposition of BaTiO_3 (or any other ABO_3 compound) is in the propensity of the compound to dissociate into its component parts upon heating in a vacuum. This decomposition results in the production of BaO and TiO_2 (which may be further reduced). Unfortunately, the components do not have equal vapor pressures, and the result is a nonuniform evaporation rate of the components. (BaO has a

vapor pressure considerably above that of TiO_2 or its reduced oxide or metal.) Consequently, the deposition and post-deposition treatment techniques must not only compensate for the disparity of vapor pressures, but also must react the components to form the perovskite structure, with its attendant desirable dielectric properties.

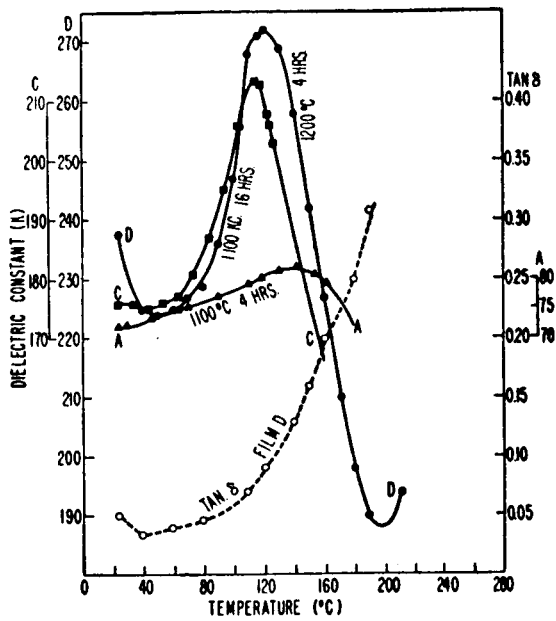
Feldman^(55, 58) approached the decomposition problem by attempting to completely evaporate a charge of stoichiometric BaTiO_3 powder from a tungsten filament and then recombine the separated components on the substrate. Although there has been some controversy over this technique due to the probability of an alloying reaction between the evaporant and the filament, Feldman did report tetragonal structure and ferroelectric behavior for his films. The films not only showed the typical hysteresis effects, but also displayed a dielectric constant peak at the bulk Curie point of approximately 120°C (see Figure 52⁽⁵⁴⁾) on a plot of dielectric constant vs. temperature. (The three curves are labeled with the post-deposition baking procedure used.) The dielectric constant of the films also obeys the Curie-Weiss law above 120°C (Figure 53⁽⁵⁴⁾), although the values of C and T_c differed from those of the bulk material and were not reported. The saturation polarization was 4×10^{-7} coulomb/cm², the remanent polarization 2×10^{-7} coulomb/cm², and the coercive force 7×10^6 Volts/cm., all lower than the bulk material values.

The material was deposited on a platinum substrate and subsequently baked in air at temperatures up to 1200°C . This heat treatment sharpened the Curie point transition, developing the crystallite size to approximately 1000\AA to 5000\AA for films approximately $1 - 2\mu$ thick.

Feldman also reports⁽⁵⁸⁾ the unfortunate instability of the dielectric constant with time under an applied alternating field less than the coercive field. Figure 54⁽⁵⁸⁾ illustrates the percent decrease in dielectric constant with time at various temperatures. When the field is removed, the value of the dielectric constant rises to approximately its initial value in a short time, indicating that there is no permanent film damage. This phenomenon is apparently due to a change in the polarization of the crystallites.

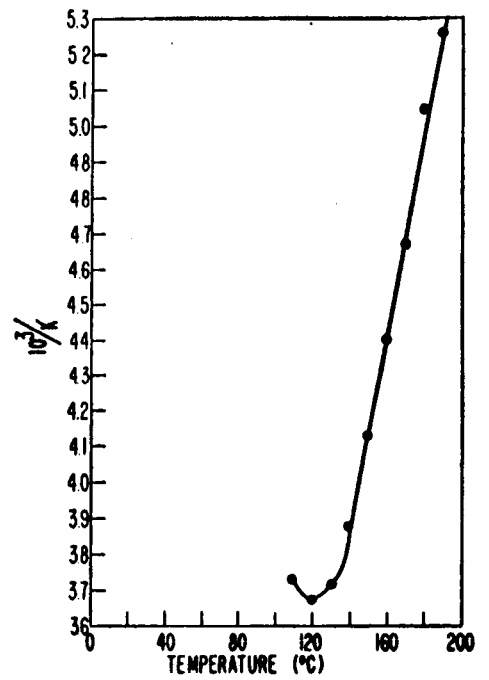
Moll⁽⁵¹⁾ has reported the successful deposition of ferroelectric films of a mixture of (73% Ba, 27% Sr)TiO₃, with the dielectric constant and loss tangent characteristics shown in Figure 55⁽⁵¹⁾ Moll, however, deposited his films by two methods: flash evaporation of a powder from a heated beryllium oxide coated filament, and evaporation of a mixture of BaTiO₃, SrTiO₃, and TiO₂ from an SrO coated tungsten filament. The films were also deposited in the presence of an electric field of up to 8 KV/cm at substrate temperatures of approximately 200°C. Dielectric constants up to 9000 at 1000 megacycles were reported.

Green⁽⁵²⁾ approaches the decomposition problem by alternately evaporating reduced BaCO₃ and TiO₂ films from tungsten filaments and then relies on an air heat treatment to recombine the components into stoichiometric, hopefully tetragonal, BaTiO₃. The heat cycle consisted of baking the film (deposited on platinum substrates). The substrate temperature is at room ambient during deposition. Green does not report the dielectric constant but does report that hysteresis was obtained.



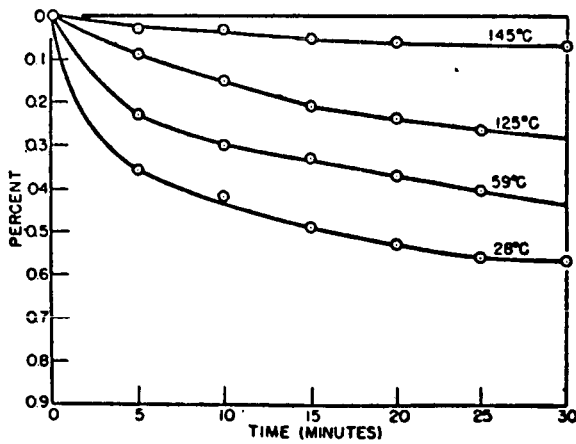
Approximate dielectric constant of evaporated BaTiO₃ films 1.5 μ thick as a function of temperature for three baking conditions. Measured at 1 kc and 3000 v/cm.

Figure 52



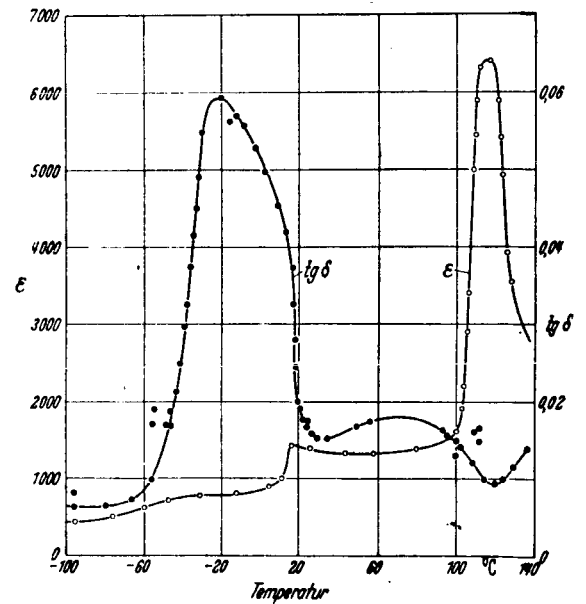
Confirmation of Curie-Weiss type of relation for BaTiO₃ film.

Figure 53



Typical time change curves at various temperatures measured at 1 kc and 700 volts rms/cm showing percent decrease of dielectric constant as a function of time (Sample #33B, 2.8 μ thick).

Figure 54



DK und tg δ einer BaTiO₃-Keramik, gemessen bei 1 kHz und einer Feldstärke von 2,29 V/cm.

Figure 55

Sekine and Toyoda⁽⁵³⁾ reported deposition of (Ba, Sr)TiO₃ by two techniques. One involved the constant feeding of a stoichiometric powder onto a heated filament. The other method, and the least successful in achieving high dielectric constant films, was rapid evaporation of a powder charge from a tungsten ribbon filament which was rapidly heated from ambient to 2200°C (5 seconds).

The powder used was obtained from BaTiO₃ crystals grown by the technique of Remeika,⁽³⁾ or from a mixture of (Ba, Sr)TiO₃. The substrates used were platinum, nickel, slide glass, fused quartz, mica and Al₂O₃ ceramic plates. During deposition, the substrate temperature ranged from 200°C to 1200°C. Post-deposition baking in pure oxygen lasted approximately ½ to 4 hours at temperatures of 200°C to 1200°C. The density of the films obtained was approximately 5.1 g/cc for film thicknesses of 1 - 3μ.

An interesting display of the visual appearance of films prepared by the rapid vaporization of a charge (Method A) and flash evaporation of particles dropped onto a heated filament (Method B) is shown below in Table IV.⁽⁵³⁾ The "smoky" appearance of the films prepared by Method A is

TABLE IV

Method	"A"		"B"	
Substrate	Pt	Glass	Pt	Glass
Sub. Tem. (°C)				
200	Pale purple (S)	Pale purple (S)	Pale brown (T)	Pale brown (T)
300	Purplish green (S)	Purple (S)	Dark purple (T)	Pale brown (T)
400	Yellowish brown (S)	Pale brown (S)	Dark purple (T)	Pale brown (T)
500	Dark purple (S)	Dark gray (S)	Dark purple (T)	Pale brown (T)

(S) : Smoky. (T) : Transparent.

apparently due to the excess BaO, which may react with the atmospheric CO₂ to form BaCO₃ or with atmospheric water vapor to produce Ba(OH)₂ or Ba(OH)₂·8H₂O. With increasing baking temperatures, the color of the film gradually changes to a pale yellow above 500°C.

At 500°C baking temperature, there is an indication (x-ray diffractometer) of cubic BaTiO₃. In general, films prepared by the "B" method are more highly crystallized than those prepared by the "A" method. Figure 56⁽⁵³⁾ shows the measured variation in crystallite size vs. post-deposition baking temperature. The variations of dielectric constant vs. temperature for various strontium concentrations and processing procedures are shown in Figure 57⁽⁵³⁾. The dependence of the dielectric constant on the electrical field frequency is shown in Figure 58⁽⁵³⁾. The dielectric field strength at breakdown is reported to be in excess of 10⁵ V/cm. A typical ferroelectric hysteresis loop was obtained with the films, but the remanent polarization is considerably lower than that obtained with ceramic specimens.

Muller, Nicholson and Francombe⁽⁵⁰⁾ attacked the problem of BaTiO₃ decomposition in a slightly different method than those reported above. Their technique involved simple flash evaporation of the stoichiometric powder. The philosophy of the flash deposition technique has been approached from two different directions: complete evaporation of individual grains before the arrival of another grain, and evaporation from a liquid pool of evaporant (BaTiO₃) which is maintained at constant size by the regulated addition of BaTiO₃ powder. The second method takes advantage of the relatively lower source temperature required for melting BaTiO₃, as compared with that required for flash evaporation.

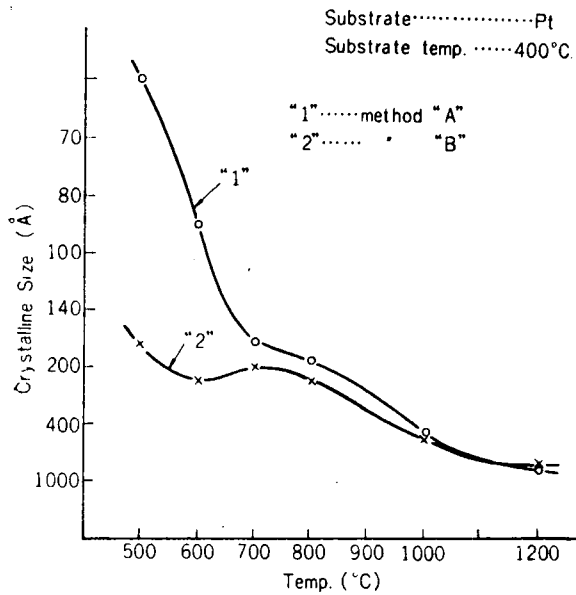
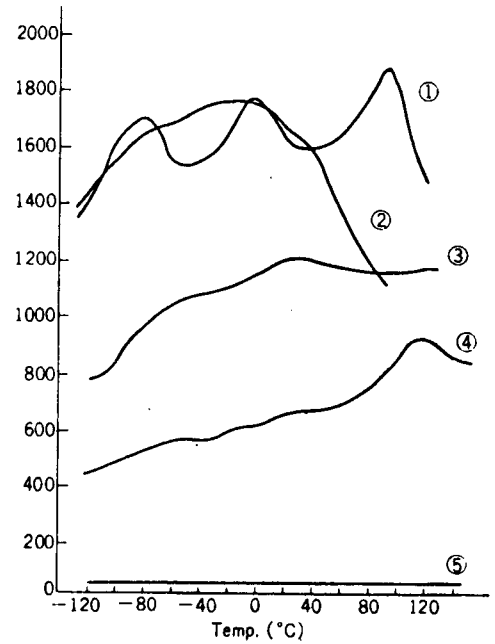
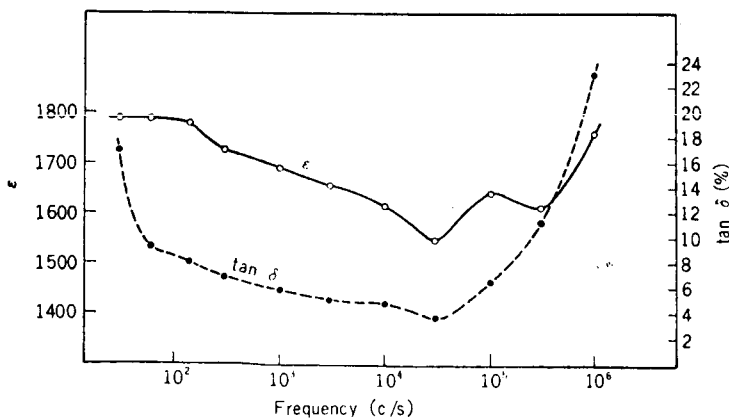


Figure 56



Sr	Thickness	S.T.	B.T.	Time	Freq.	E.	
1	5%	2.4 μ	500° C	1200° C	2 hr	30 kc	8.3 kV/cm
2	20%	2.3 μ	1200° C	1200° C	1 hr	10 kc	8.7 kV/cm
3	0%	2.7 μ	700° C	1200° C	4 hr	10 kc	7.5 kV/cm
4	2%	3 μ	300° C	1200° C	0.5 hr	10 kc	7 kV/cm
5	0%	2.7 μ	300° C	1000° C	2 hr	10 kc	7.5 kV/cm

Temperature dependence of the dielectric constant of (Ba-Sr)TiO₃ films.



Frequency dependence of dielectric constant and $\tan \delta$ of a (Ba_{0.8}Sr_{0.2})TiO₃ film.

Figure 58

Figure 57

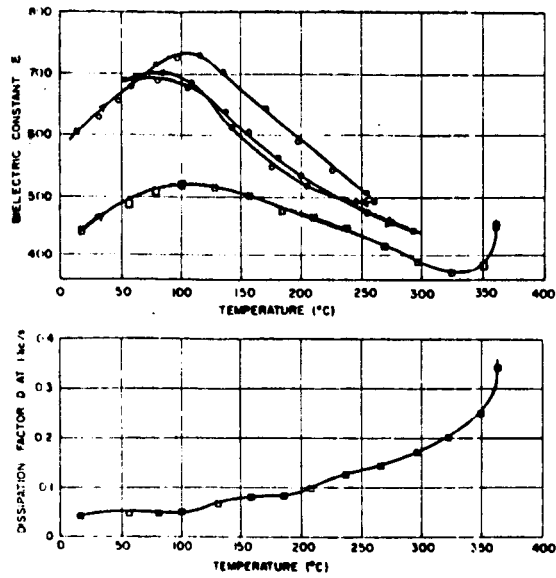
Selection of the filament was based primarily on the vapor pressure at 2300°C (the temperature slightly greater than that required for vaporization of BaTiO₃) and reactivity with the evaporant. Eventually, iridium was chosen and film contamination by the source was reduced to as low as 2%. (Tungsten may contribute up to 10 - 20% contamination of BaTiO₃ films.)

Films deposited by the latter method (boat at 2300°C) were amorphous when the substrate was at ambient temperature during deposition. Post-deposition heating to between 400°C and 500°C with an electron beam transformed the structure to that of cubic perovskite BaTiO₃. Upon heating to a temperature of 600°C, crystallites of approximately 2000Å size were measured. Similar results were noted for films deposited using the "constant pool size" technique, with crystallite size approximately 1000Å to 3000Å.

Test capacitors were produced utilizing metal substrates as the base electrode and evaporated aluminum counter-electrodes, and the dielectric constants of the dielectrics were measured using the circuit of Sawyer and Tower.⁽¹⁰⁸⁾ The temperature dependence of the BaTiO₃ dielectric constant and the dissipation factor are shown in Figure 59.⁽⁶⁰⁾ The importance of post-deposition baking temperature is shown in Figure 60⁽⁶⁰⁾ for two different film thicknesses.

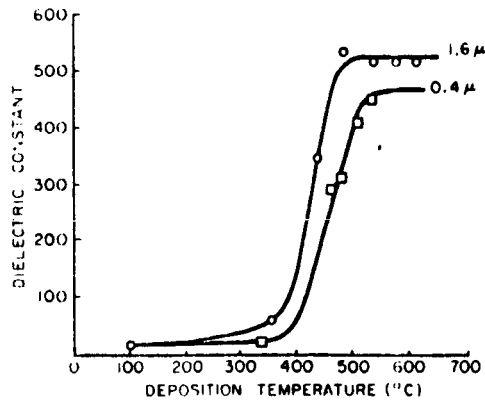
The authors postulated that the results of Moll⁽⁵¹⁾ were due to tungsten contamination of the dielectric and that the observed high dielectric constant arises from surface boundary polarization.

The results of this paper⁽⁶⁰⁾ were compared with those obtained by Feldman,^(54, 58) with the suggestion that the two works were equivalent



Temperature dependence of dielectric constant and dissipation factor: \circ , $1\mu\text{ BaTiO}_3$ film; \square , $0.5\mu\text{ BaTiO}_3$ film.

Figure 59



Dependence of dielectric constant on deposition temperature.

Figure 60

if one postulates that the crystal structure obtained by 500°C baking would be cubic and paraelectric and that heat treatment to a temperature of 1100°C would produce results similar to those of Feldman.

The investigations of BaTiO₃ and PbTiO₃ being carried out by Hagenlocher, Feuersanger, et al^(56, 61, 70) incorporate a slightly different philosophy than those presented heretofore in that the deposition technique utilizes an electron beam as an energy source for the evaporation of the bulk material. BaTiO₃ component materials were evaporated in their separate form: from BaO and TiO₂ rods. Their conclusions were that BaTiO₃ could be produced with dielectric constants greater than 200, but that the dissipation factor usually exceeded 10%. A substrate temperature in excess of 900°C was felt to be necessary for deposition of BaTiO₃ and that this precluded its use in Silicon integrated microcircuitry. Their investigation of BaTiO₃ was therefore terminated in favor of an investigation of PbTiO₃.

Their reasons for interest in PbTiO₃ as a dielectric are as follows:

1. PbTiO₃ films can be formed at considerably lower substrate temperatures than BaTiO₃.
2. Only the desired compound PbTiO₃ can be formed from the constituents PbO and TiO₂.
3. Excess BaO in a film of BaTiO₃ produces an atmospheric instability in the film; PbO is considerably less reactive.
4. The Curie point of PbTiO₃ is considerably higher than that of BaTiO₃.

5. The stoichiometric Pb:Ti ratio can be controlled more easily than the corresponding Ba:Ti ratio.

The fact that the bulk PbTiO_3 dielectric constant is lower than that of BaTiO_3 has had no bearing on the thin film properties: the dielectric constants observed are comparable.

Substrate temperature during deposition was held at 680°C , sufficiently moderate to allow its use on Silicon substrates. Films with dielectric constants of 200 to 450 were produced using PbTiO_3 .

IV. MATERIALS SELECTED FOR PHASE II STUDY

Table V summarizes several of the pertinent facets of the numerous materials investigated in the Phase I literature survey. Inspection of the table reveals that most of the materials are eliminated from consideration for investigation in Phase II by virtue of having bulk dielectric constants of less than 500.

Subject to NASA approval, the following materials have been selected for further investigation in the Phase II effort of the contract on the basis of predicted potential success as high dielectric constant dielectrics in vacuum evaporated thin film capacitors.

1. BaTiO_3
2. PbTiO_3
3. $(\text{Ba}, \text{Pb})\text{ZrO}_3$
4. KNbO_3
5. NaNbO_3

A detailed discussion of each of these materials was presented in Sections II and III. The following brief reiteration will merely attempt to relate the above-listed materials to each other and to enumerate some of the envisioned advantages and disadvantages of each.

BaTiO_3 : It is readily apparent from the bibliography and from the preceding text that a great deal of investigation of this material has already been performed. The basic problem is that of dissociation when evaporation in a vacuum is attempted, and this is expected to be common to all the ABO_3 materials. Despite this propensity for partial fractionation and change of stoichiometric ratio between source and condensed film, successful vacuum deposition of the material has been accomplished. However, as a

result of having a multiplicity of transition points within the nominal temperature spectrum of operation of a capacitor, the material is prone to extremely erratic variations of dielectric constant and hence, capacitance, with temperature. In addition, relatively high processing temperatures are required, either during deposition or in a post-deposition anneal, or both, and this aspect seriously limits its ultimate usefulness in thin film and compatible microcircuitry applications. Charles Feldman of Melpar, Inc. suggested in a personal telecommunication that the addition of a suitable flux, such as PbO, to the evaporated film of BaTiO₃ might increase the mobility and thus enhance the probability of reaction of the constituents. He postulated that this flux could later be re-evaporated.

PbTiO₃: This material exhibits a conveniently high Curie point and is uncomplicated by numerous additional transition points, thus alleviating the problem of erratic temperature-capacitance behavior noted above. In addition, the substrate temperature requirements necessary for appropriate recombination of the constituents are less stringent than those for BaTiO₃, thus making it more attractive from the standpoint of versatility in practical application. Also, even though dissociation is expected to present a problem, only PbTiO₃ can be formed from the constituents PbO and TiO₂, whereas numerous compounds can be formed from the constituents BaO and TiO₂. The above-noted advantages may well more than compensate for its lower dielectric constant.

(Ba, Pb)ZrO₃: Casual inspection of Table V reveals that neither BaZrO₃ nor PbZrO₃ taken alone appear to hold any interest for Phase II study.

The combination of the two materials in solid solution, however, presents a highly interesting profile. The temperature of maximum dielectric constant can be conveniently shifted by varying the relative proportions, as can the magnitude of the dielectric constant at any given temperature. The extremely high room temperature dielectric constants reported (2600 for a 40% BaZrO₃, 60% PbZrO₃ mixture) makes a combination of the two materials an extremely interesting prospect for Phase II study. The primary problem envisioned in attempting to adapt the material(s) to high vacuum deposition techniques will be the fact that the addition of yet another material will make the attainment of proper stoichiometric ratios an even more complicated task than would be the case with a single ABO₃ compound.

KNbO₃: This material has the advantage of having a reasonably high dielectric constant over a wide temperature range. In addition, the dielectric constant vs. temperature curve is quite flat over the anticipated temperature operating range of a capacitor. Since no known work has been performed on the material with respect to adapting it to high vacuum deposition techniques, the processing temperatures which will be required in order to obtain satisfactory dielectric properties are unknown at the present time.

NaNbO₃: Sodium niobate, like potassium niobate, has a reasonably high dielectric constant over a wide temperature range, and exhibits a flat dielectric constant vs. temperature curve over an even greater temperature span. As is the case with potassium niobate, no known attempts to utilize the material in high vacuum deposition techniques are reported.

Despite the fact that antimony sulfur iodide is reported to exhibit a phenominally high dielectric constant under certain conditions, it is not considered to be a likely candidate for further investigation in Phase II.

The problems associated with not only obtaining single crystallinity in a vacuum deposition thin film, but also achieving highly critical orientation of the crystal axes, are felt to present acute disadvantages above and beyond those exhibited by the other materials selected. In addition, the constituent parts, which will most certainly display a gross tendency toward partial fractionation, are not considered to be compatible with high vacuum techniques and equipment.

All of the above materials were discussed with A. von Hippel of the Naval Research Laboratories and Charles Feldman of Melpar, Inc. Conversations with both of the above were general in nature and dealt primarily with the envisioned problems which would be faced in attempting to utilize vacuum deposition techniques (fractionation, high processing temperatures, lack of proper stoichiometry, etc.), all of which have been covered in some detail in this report. Both expressed interest in our selection of materials for further study, and neither knew of any vacuum deposition work being performed on $(\text{Ba}, \text{Pb})\text{ZrO}_3$, KNbO_3 , or NaNbO_3 .

TABLE V

MATERIAL	ROOM TEMPERATURE CRYSTAL STRUCTURE	ELECTRICAL PROPERTIES	CURIE POINT	DIELECTRIC CONSTANT	TEST CONDITIONS		COMMENTS
					TEMP.	FREQ.	
BaTiO ₃	Tetragonal	Ferroelectric	120°C	1400	25°C	1KC	Thin film form
PbTiO ₃	Tetragonal	Ferroelectric	490°C	450	25°C	1KC	
SrTiO ₃	Cubic	Ferroelectric	~40°K	250	25°C	50 cps	
CaTiO ₃	Orthorhombic	Paraelectric	N/A	143	25°C	50KC	
CdTiO ₃	Orthorhombic	Ferroelectric	-218°C	250	25°C	---	
PbZrO ₃	Orthorhombic	Antiferroelectric	233°C	~100	25°C	---	
BaZrO ₃	Cubic	Paraelectric	N/A	low	---	---	
(Ba _{0.4} Pb _{0.6})ZrO ₃	---	Paraelectric	N/A	2600	25°C	1KC	
SrZrO ₃	Cubic	Paraelectric	N/A	low	---	---	
CaZrO ₃	Orthorhombic	Paraelectric	N/A	low	---	---	
PbHfO ₃	Tetragonal	Antiferroelectric	215°C	90	25°C	10KC	
SrHfO ₃	---	Paraelectric	N/A	low	---	---	
BaHfO ₃	---	Paraelectric	N/A	low	---	---	
BaSnO ₃	Cubic	Paraelectric	N/A	17	25°C	1KC	
SrSnO ₃	Cubic	Paraelectric	N/A	17	25°C	1KC	
CaSnO ₃	Orthorhombic	Paraelectric	N/A	15	25°C	1KC	
MgSnO ₃	---	---	---	62	25°C	1KC	
Bi ₂ (SnO ₃) ₂	---	---	---	34	25°C	1KC	
PbSnO ₃	---	---	---	16	25°C	1KC	
CaSnO ₃	---	---	---	16	25°C	1KC	
NiSnO ₃	---	---	---	235	25°C	1KC	
KNbO ₃	Orthorhombic	Ferroelectric	434°C	~500	25°C	1KC	
NaNbO ₃	Orthorhombic	Antiferroelectric	355°C	575	25°C	1KC	
Cd ₂ Nb ₂ O ₇	---	---	170°K	320/500	25°C	---	
Pb(NbO ₃) ₂	---	---	575°C	300	25°C	---	
KTaO ₃	Cubic	Ferroelectric	~13°K	Below 500	25°C	---	
NaTaO ₃	Orthorhombic	Paraelectric	475°C	---	---	---	
WO ₃	Monoclinic	Antiferroelectric	-50°C	---	---	---	
SbSI	Monoclinic	Ferroelectric	22°C	50,000	22°C	---	

--- No information available

N/A Not applicable

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