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HIGH TEMPERATURE FERROELECTRIC MATERIALS

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TECHNICAL DOCUMENTARY REPORT No. ML-TDR 64-24

MARCH 1964

AF MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Project No. 7371, Task No. 737101
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300 - April 1964 - 162-36-711
FOREWORD

This report was prepared by R. W. Ohlwiler, 1st Lt, USAF, under Project No. 7371, "Exploratory Development in Electrical, Electronic, and Magnetic Materials," Task No. 737101, "Dielectric and Optical Maser Materials." The work was administered by the Materials Physics Division, AF Materials Laboratory, Research and Technology Division.
ABSTRACT

This report reviews published data on high temperature ferroelectric materials. Applicable terms are defined and general characteristics of this type of material are given. High temperature ferroelectric materials studied were: lead metaniobate, lithium tantalate, potassium niobate, lead titanate, sodium tantalate, and lead metatantalate. Other ferroelectric materials with less supporting data are discussed also.

This technical documentary report has been reviewed and is approved.

JULIS I. WITTEBORT, Chief
Thermal & Solid State Branch
Materials Physics Division
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INTRODUCTION

An attempt has been made to survey the field of ferroelectricity and to gather the published electrical, thermal, and elastic data on the known ferroelectric materials which have high Curie temperatures. By far the most studied ferroelectric material is barium titanate, which has a ferroelectric Curie temperature of 120°C. The materials of primary interest in this study are those which exhibit ferroelectricity at temperatures considerably above the barium titanate Curie temperature.

CRYSTAL PROPERTIES

Ferroelectric materials are crystalline and have the property that they are spontaneously polarized (a condition in which the center of positive charge does not coincide with the center of negative charge). This polarization can be reversed by applying a large enough electric field. Therefore, a sufficiently strong alternating field shows hysteresis. The electric-field, polarization hysteresis is very analogous to the magnetic-field, magnetization hysteresis characteristic of ferromagnetic materials. This is, in fact, how the word "ferroelectricity" was derived. On first sight the work is misleading, as it has nothing to do with the metal iron; ferroelectrics are dielectrics. A typical hysteresis loop is shown in Figure 1 which defines the terms "spontaneous polarization," \( P_s \), and "coercive field," \( E_c \).

The theory of ferroelectricity is not entirely understood especially for the more complex crystal structures. The answers lie in understanding the microscopic properties of the crystals such as the atomic size and packing, bonding character, ionic polarizability, etc. Most ferroelectrics have a Curie point, a temperature above which the spontaneous polarization is absent. The transition from the nonferroelectric state to the ferroelectric state is usually rather sharp. At the Curie point the electrical, elastic, optical, and thermal properties all experience an anomaly. The dielectric constant, for example, may increase by an order of magnitude within 5°C. The elastic compliance, refractive index, and specific heat anomalies are not as great and for instance are about 55, 2, and 35 percent respectively, for barium titanate.

In addition to the spontaneous polarization and coercive field, the properties of interest in this study are the dielectric constant and dissipative factor, the elastic properties (compliance and stiffness), and the piezoelectric modulus.

The dielectric constant of a material is defined as the ratio of the capacitances of a condenser with the dielectric material to the capacitance of the condenser with a vacuum between the plates. It is a complex quantity, and the ratio of the imaginary part to the real part of the dielectric constant is defined as the dielectric loss tangent or the dissipative factor.

Manuscript released by the author 1 January 1964 for publication as an RTD Technical Documentary Report.
Figure 1. Typical Ferroelectric Hysteresis Loop
The Piezoelectric modulus, $d$, is defined by the relationship $p = d \sigma$ where $p$ is the polarization and $\sigma$ the stress. The polarization is a vector and the stress a second rank tensor (9 components). It follows that the piezoelectric modulus is a third rank tensor with 27 components. Thus, the general statement of the above relationship is $P = d_{ij} \sigma_{jk}$.

In practice this is simplified by defining new symbols in which the piezoelectric modulus can be written as a three-by-six matrix, $P = d_{ij} \sigma$ where $i = 1, 2, 3$, and $j = 1, 2, \ldots, 6$. The piezoelectric modulus is always reported as elements of this matrix.

The elastic properties of a crystal are described by Hooke’s Law, $e = s \sigma$, where $e$ is the strain, $\sigma$ the stress, and $s$ the elastic compliance (sometimes called the elastic modulus). The units of the compliance are area/force. The inverse of $s$ is denoted $c$ and is called the elastic stiffness (sometimes called the elastic constant or Young’s modulus). The units are, of course, force/area. The compliance and stiffness are fourth rank tensors. However, as for the piezoelectric modulus, symmetry allows these coefficients to be written as six-by-six matrices and Hooke’s Law becomes $e_{ij} = s_{ij} \sigma_{ij}$ where $i, j = 1, 2, \ldots, 6$. Thus, the compliance and stiffness of crystals are expressed as terms of this matrix.

Because of the symmetry of crystals the number of independent piezoelectric moduli and compliance (and stiffness) moduli are further reduced and many elements of the matrices are zero.

It is of interest in some applications to transform as much input electrical energy as possible in a piezoelectric crystal into mechanical energy. A measure of the efficiency of this conversion is the electromechanical coupling factor, $k$. This is defined as the square root of the ratio of the energy stored in mechanical form, for a given type of displacement, to the total input electrical energy. In terms of the piezoelectric modulus, $d$, the permittivity $\varepsilon$ and the compliance, $s$, the electromechanical coupling factor is:

$$k_{ij} = \frac{d_{ij}}{\left(\varepsilon_{ij}^s s_{ij}^s\right)^{1/2}}$$

For example, this factor is 0.095 for quartz, one of the more commonly used piezoelectric crystals (Reference 1).

MATERIALS

In general, there is very little information available on high temperature ferroelectrics. Many compounds such as the mixed bismuth oxides have only recently been discovered to possess this property. Even the materials which have for some time been known to be ferroelectric have realized only a small amount of research effort. Only lately has there been a great demand for electronic materials with high temperature application potential.

Ferroelectric crystals are usually classified into several groups, the primary ones being Rochelle salt and the associated isomorphus salts, crystals with hydrogen bonds where the motion of the hydrogen atoms is related to the ferroelectric properties, and ionic crystals (Reference 2). Included in the latter group are the perovskite and ilmenite...
crystal structures which possess the property of ferroelectricity at the high temperatures of interest in this study. Most of the research on ferroelectricity has been on crystals with the perovskite structure as it is the simplest crystal form to exhibit this property. Although perovskite is specifically the mineral CaTiO₃, it is used to denote all the compounds with the structure of the family AB₃, where A and B are metal ions, and the valence of A is less than or equal to B.

The majority of the information found in the literature is on the ceramic or polycrystalline form of the material. Single crystals of ferroelectrics are usually difficult to grow. However, some work has been done on the single crystal development of ferroelectric materials. This task is difficult and often a separate problem for each material. The resultant crystals are always very small and often have a high degree of impurity and imperfection. For this reason a range of values may be reported for, say, the dielectric constant of crystals prepared by different methods or even by the same method. For example, the dielectric constant of several samples of potassium niobate were measured and reported by Timofeeva and Popova (Reference 3). These values range from 9 to 437. The color of the crystals vary from light yellow to black. But, this is one of the rare papers which actually reports more than one measurement; most authors only report one measured value for a given property, leaving the reader to wonder if this was his only measurement, his best measurement, or an arbitrary determination derived from several measurements.

It became apparent during the study that there is only a relatively small number of known high temperature ferroelectrics. Those which have received the most attention, more or less in order, are: lead metanlobate (PbNb₂O₆), potassium niobate (KNbO₃), lead titanate (PbTiO₃), lead metatantalate (PbTa₂O₆), sodium tantalate (NaTaO₃), and lithium niobate (LiNbO₃). The available data for these are presented in Table 1. The status of single crystal development of these materials is also discussed.

There is also a section on the high temperature ferroelectrics on which there has been reported even less information. Some have only recently been discovered. With some, it is not even clear whether or not they are actually ferroelectrics. For example sodium vanadate exhibits a typical polarization electric field hysteresis but no large anomaly in the dielectric constant, temperature relationship. Some mixed bismuth oxides show a typical dielectric constant but apparently no hysteresis.

There was hope of finding more information than was found on the piezoelectric properties of these high temperature ferroelectrics, but this data is extremely scarce.
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<td>2.4 (POLYCRYST) (9) (SEE PARA b)</td>
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<td>0.7 TO 1.2 (S₁, 150°C, SINGLE CRYSTAL) (63)</td>
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<td>Perovskite</td>
<td>Perovskite</td>
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<td>0.17 (100(^\circ)C, 10K/sec, Single Crystal) (14)</td>
<td>0.08 (30(^\circ)C, 10(^{16})cps) (16) (See Par. g)</td>
<td>0.02 (20(^\circ)C, 1K/sec, Poly (26)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2 (355(^\circ)C, 10K/sec, Single Crystal) (14) (See Par. e)</td>
<td>2.65 (17)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Supporting Data for Table

(a) Ferroelectricity of Lead Metaniobate

Lead metaniobate (PbNb$_2$O$_6$) is reported as being ferroelectric with a Curie temperature at about 570°C. However, this material is polymorphic and exists as two phases below about 1150°C: the ferroelectric phase is metastable while the non-ferroelectric rhombohedral phase is the stable form. The ferroelectric phase can be obtained however, by annealing at temperatures above 1150°C at which temperatures a phase transformation from rhombohedral to tetragonal transpires. On cooling to 570°C the tetragonal phase transforms reversibly to the ferroelectric orthorhombic phase (References 8, 27).

(b) Dielectric Constant and Loss of Lead Metaniobate

Lead metaniobate (PbNb$_2$O$_6$) is an example of a "two-dimensional" ferroelectric material, since spontaneous polarization can occur in two directions, identified with the a and b axes of the orthorhombic unit cell. The permittivity along each axis is reported by Francombe and Lewis (Reference 8). This property was found by measuring the capacitance of a crystal in the three crystalline directions at 159 or 500 kc/sec. The results show that along the c-axis the permittivity is almost independent of temperature. However, along either of the other two axes the dielectric constant rises sharply from about 1000 at 500°C to about 24,000 at 560°C.

(c) Piezoelectric Modulus of Lead Metaniobate

It was noted by Gurevich and Rez (Reference 28) that lead metaniobate has a tendency to lose its piezoelectric activity at temperatures that are sometimes substantially lower than the Curie temperature. This is probably due to an increase of the electrical conductivity at temperatures above 250° to 300°C. Gurevich and Rez attempted to find a dopant which would reduce the high temperature conductivity while maintaining the piezoelectric properties. Although they were able to control the conductivity the doped ceramics did not exhibit piezoelectricity. However, Smazhevskaya and Podol'ner (Reference 29) continued the work and found that polycrystalline PbNb$_2$O$_6$ specimens containing 4 to 5 mole percent Nb$_2$O$_5$ have a piezoelectric constant $d_3 = 0.6 \times 10^{-6}$ stearcoulombs/dyne, a dielectric constant of the order of 500, and a Curie point above 450°C.

(d) Spontaneous Polarization, Coercive Field, and Dielectric Constant of Lithium Tantalate

Single crystals of lithium tantalate were found to be strongly ferroelectric by Matthias and Remeika (References 7, 11) but no mention was made of the Curie point. Curves of dielectric constant, spontaneous polarization, and the coercive field are reported as a function of temperature, and it is evident that the ferroelectric properties are radically different from those of other ferroelectric materials. The coercive field strength, the spontaneous polarization, and dielectric constant increase with temperature up to and apparently beyond 450°C. At room temperature the values of these properties are 6000 volts/cm, 1 microcoulomb/cm$^2$, and 50, respectively. The coercive field is constant to 220°C where it rises linearly and is 10,000 volts/cm at 320°C. The spontaneous polarization begins to rise at 200°C and has almost leveled off again at 450°C where it is about 23 microcoulomb/cm$^2$. The dielectric constant also begins to rise at 200°C and is still going up at 450°C where it has the value of about 330. Matthias and Remeika also state that LiTaO$_3$ crystals are piezoelectric, but no data are given (Reference 11).
(e) Dielectric Constant and Piezoelectric Modulus of Potassium Niobate

Measurements made and reported by Timofeeva and Popova in 1961 (Reference 3) on the dielectric and piezoelectric properties of single crystals of potassium niobate resulted in a wide variation of the data. The piezoelectric modulus ranges between 0.2 to $6 \times 10^{-8}$ statcoulombs/dyne for different samples and the dielectric constant from 9 to 437. An experimental relationship is given for the piezoelectric moduli, $d_{33}$, and temperature for a typical crystal. It goes up linearly from about $4.25 \times 10^{-1}$ at room temperature to about $5.8 \times 10^{-1}$ statcoulombs/dyne at 230°C. At that point it drops off slowly with temperature. A typical dielectric constant curve begins at about 83 at room temperature and rises to about 240 at 260°C then drops off slowly with temperature.

The plot of temperature versus dielectric constant would lead us to believe that the Curie point is at about 260°C even though the behavior is not quite typical there. Earlier reporters (References 12, 14), have indicated that there is a genuine ferroelectric transition at 435°C. This would have undoubtedly been observed by the above authors had they continued up the temperature scale.

In comparing potassium niobate with other piezoelectric substances, the efficiency
\[
K = \frac{d_{33}}{\varepsilon_{11}} \times 10^8
\]
of quartz, lithium sulfate, Rochelle salt, and KNbO$_3$ is 3.24, 14.2, 26.2, and 87 esu respectively. The KNbO$_3$ was assumed polarized. The efficiency is 46 for the unpolarized crystal. (Reference 3)

In a review article Sonin (Reference 30) states that Timofeeva and Popova found that polarization of KNbO$_3$ single crystals at 200°C in silicone oil causes the piezoelectric constant to double.

(f) Dielectric Loss of Potassium Niobate

The dielectric loss tangent is considerably lower on increasing temperature than it is on decreasing temperatures, between room temperature and the Curie point. The maximum difference occurs at 240°C where the loss is 0.25 on increasing and 0.37 on decreasing the temperature. At 420°C, just prior to the Curie point, the loss tangent values are 0.29 and 0.33, respectively (Reference 14).

(g) Dielectric Constant and Loss of Lead Titanate

Fesenko et al. (Reference 16) obtained single crystals of lead titanate by three different methods which are briefly described under "Single Crystals" and compared their properties, primarily their dielectric and loss properties. There is a wide variation in these properties with the three methods of growing the single crystals as observed in Figure 2. Note that the frequency of measurement is $10^7$ cps for method one and $10^6$ cps for methods two and three. What this might be expected to contribute to the resultant curves is not mentioned. It is stated, however, that the single crystals had different appearance, being dark brown for method one and transparent for method two. The appearance of those crystals produced by method three were not reported. There is also disagreement in the measured temperature-conductivity relationship of the first two methods. The variation in the properties is presumably due to a difference in the number and type of impurities present at different levels in the crystals produced by the three methods.
Figure 2. Dielectric Constant and Loss Tangent of Lead Titanate Single Crystals
Curie Point and Dielectric Constant of Sodium Tantalate

Sodium tantalate has been reported as being ferroelectric with a Curie point of 475°C by Matthias in 1949 (Reference 18). However, Smolenskii et al. (Reference 21) of the USSR states that no anomalies are found in the variations of the coefficient of linear expansion over the temperature range of -180°C to 510°C. They also report finding no variations in the dielectric constant with temperature. Extrapolation of a plot of the dielectric constant versus temperature for solid sodium tantalate concentration led Smolenskii to the conclusion that sodium tantalate is not a ferroelectric material.

As far as can be determined, no future work has been done on this material that would clear up the above uncertainty, so it is presently unknown whether or not sodium tantalate is ferroelectric.

Dielectric Constant and Loss of Lead Metatantalate

Single crystals of lead metatantalate were prepared by Subbarao et al. (Reference 23). The dielectric constant was measured parallel and perpendicular to the c-axis. At room temperature the dielectric constant along this axis is about 150 while the values obtained perpendicular to the c-axis are either 300 or 700. After measurements of spontaneous polarization, birefringence, as well as the dielectric constant with temperature, it was concluded that PbTa$_2$O$_6$ crystals are unidirectionally ferroelectric, i.e., ferroelectric along one axis perpendicular to the c-axis. Along this axis the dielectric constant is reported to be 300 at room temperature and about 4200 at 265°C (at 10 kc).

Leak metatantalate in the polycrystalline form was reported as being ferroelectric by Isupov (Reference 26) with a dielectric constant of 250 at room temperature and 1050 at 260°C (at 1 kc). This seems to be about what one would expect for the net effect of a random distribution of the ferroelectric axes.

The dielectric properties of polycrystalline PbTa$_2$O$_6$ were also reported by Coats and Kay (Reference 25), and no ferroelectric anomaly was observed. They suggested a possible antiferroelectric transition at 70°C. This is in disagreement with other reporters.

STATUS OF SINGLE CRYSTAL DEVELOPMENT

Lead Metaniobate

Needles of lead metaniobate measuring 1 mm long and 0.1 mm cross section have been grown by Goodman (Reference 6) by slow cooling of the molten material in platinum.

Francombe and Lewis (Reference 8) grew small crystals of orthorhombic PbNb$_2$O$_6$ from the melt in a platinum boat or crucible. The crystals were pale yellow to yellow-green in color. Plate-like crystals were occasionally obtained with the large faces measuring as much as 3 mm across.

Small single crystals were obtained from solution by Khodakov and Sholokhovitch (Reference 27). They used an equimolar mixture of PbO and Nb$_2$O$_5$ in an equimolar mixture of PbO and B$_2$O$_3$ heated to 1050°C to 1100°C and cooled at a rate of 20°C per hour. Annealing of the crystals at temperatures above 1250°C caused them to become opaque, presumably as a result of being in the orthorhombic (ferroelectric) phase.
The phase diagram of the PbO-Nb$_2$O$_5$ system was investigated by Roth (Reference 31).

**Lithium Tantalate**

Small single crystals were used by Matthias and Remeika (Reference 11) for measuring certain properties of lithium tantalate. However, how these crystals were obtained was not stated.

**Potassium Niobate**

Potassium niobate crystals were originally grown by Wood (Reference 32) from a mixture of 3.20 grams of K$_2$CO$_3$ and 5.34 grams of Nb$_2$O$_5$ held at 1000°C in a platinum crucible for 30 hours. At the end of this period the furnace was turned off and cooled at the rate of approximately 100°C per hour. The crystals were cube-shaped, water-clear, and about 1 to 2 mm on an edge.

Later Miller (Reference 33) was able to grow large flawless single crystals up to one inch on a side. The method involves the use of a K$_2$CO$_3$ - Nb$_2$O$_5$ mixture with excess K$_2$CO$_3$ acting as a flux. After seeding the molten mixture with a small crystal seed the seed growth was activated by lowering the temperature at the rate of 3°C per hour for about 8 hours. At the end of this time the newly grown crystal was removed from the solution and left suspended just above the surface of the solution. Then cooling to room temperature was continued at the original rate. Such slow cooling of the crystal almost completely eliminates cracking from thermal shock and eases the strain when cooling past the transition temperatures at 435°C and 230°C (Reference 14).

Timofeeva and Popova (Reference 3) pointed out some peculiarities of the single crystal growth of potassium niobate (and potassium tantalate). It was found that the seemingly simple K$_2$O - Nb$_2$O$_5$ in the temperature range 950°C to 1280°C gives five different forms of compounds (Reference 34): 3K$_2$O · Nb$_2$O$_5$, K$_2$O · 3Nb$_2$O$_5$, 2K$_2$O · 3Nb$_2$O$_5$, K$_2$O · 3Nb$_2$O$_5$, and 3K$_2$O · 2Nb$_2$O$_5$ with respective melting points 950°C, 1050°C, 1160°C, 1200°C, and 1280°C. The conditions of growth of potassium niobate were investigated by means of a method of differential thermal analysis of the system K$_2$O - Nb$_2$O$_5$ in the range from 900°C to 1400°C. Taking into consideration the results of the thermal analysis, single crystals of KNbO$_3$ were subsequently grown by the method of crystallization from solutions in a molten solvent. The above authors employed another method of preparing crystals of KNbO$_3$. This was based on growing the crystals with removal of the heat of crystallization. This amounted to keeping the system at a constant temperature for several days. Single crystals were obtained in the form of small cubes up to 1 cm$^3$ in various colors from pale yellow to black. Since chemical analysis gave the same formula, KNbO$_3$, the variations in color is believed to be related to the disturbance of the oxygen portion of the system. A darker color is usually associated with a longer period of growth of the crystals.

**Lead Titanate**

Lead titanate single crystals are noted for their difficulty to grow. Single crystals can be grown with flux methods but not easily, primarily because of the loss of PbO at higher temperatures. The first degree of success in the growth of PbTiO$_3$ single crystals was when Nomura and Sawada (Reference 35) used a PbCl$_2$ flux. About the same time, Rogers (Reference 36) obtained crystals of a few millimeters in size from binary melts in which PbO was used as the flux. Generally, these methods are convenient for growing large polycrystalline crystals but do not yield large crystals from simple twinning.
Fesenko et al. (Reference 16) compared the properties of PbTiO$_3$ single crystals prepared by three different methods: 1) crystallization from the ternary mixture V$_2$O$_5$ + PbO + TiO$_2$, (producing crystals of a dark brown color which contained an appreciable amount of impurities,) 2) slowly cooling a melt containing 80 percent Pb(BO$_3$)$_2$ and 20 percent PbTiO$_3$, from 900°C (forming crystals that were light green and transparent), and 3) slowly cooling a melt of 50 percent NaSiO$_3$ + 50 percent PbTiO$_3$, from 1100° to 850°C (from which crystals appeared about the same as those prepared by the second method).

Kobayashi (Reference 37) employed KF as a flux and followed the general procedure developed by Remeika (Reference 38) for BaTiO$_3$. To begin with, small crystals (about 1 mm on a side) are prepared by the PbCl$_2$ flux method. A mixture of PbTiO$_3$ and PbO powder is placed in a platinum crucible and then covered with KF and put in a furnace at 920°C. After 15 hours it is cooled to 600°C at the constant rate of 60°C per hour. From this point it is cooled at a slower rate. The best crystals are very thin, transparent, and light yellow in color. The larger ones are on the order of 9 x 5 x .05 mm.

Sodium Tantalate

An account is given by Vousden (Reference 20) of methods of preparation of NaTaO$_3$ (as well as KTaO$_3$, KNbO$_3$, and NaNbO$_3$) in a polycrystalline state for the purpose of investigating the structure of these materials. Single crystals were less than 0.1 mm on a side.

Matthias (Reference 18) simply states that clear cubic-shaped single crystals of NaTaO$_3$ (as well as KTaO$_3$, NaNbO$_3$, and KNbO$_3$) have been obtained up to 1 to 2 mm on a side. Nothing is said about the method used nor the quality of the crystals.

In attempting to grow this crystal Kay (Reference 39) obtained the best results with Na$_2$CO$_3$, Na$_2$B$_4$O$_7$, and Ta$_2$O$_5$ in the respective ratios 7, 1, and 4 heated at 1250°C for 12 hours and cooled over a period of six hours. The crystals obtained were 1 to 2 mm on a side.

Lead Metatantalate

Single crystals of ferroelectric lead metatantalate were grown by Subbarao et al. (Reference 23) using Pb$_5$V$_4$O$_9$ as a flux. A mixture of PbO, Ta$_2$O$_5$ in the molar ratio 3:1:1 was heated in a platinum crucible at the rate of 250° to 1400°C per hour, then cooled at the rate of 40°C per hour. The flux was dissolved in dilute nitric acid. This resulted in crystals of about 10 microns in size. These small crystals were then mixed with sufficient PbO and V$_2$O$_5$ to give an equimolar mixture of PbTa$_4$O$_9$ and Pb$_5$V$_4$O$_9$, and then heated and cooled as before. This yielded crystals that were 1 x 1 x 4 mm in size which were generally elongated along the c-axis.

OTHER HIGH TEMPERATURE FERROELECTRICS

Lithium Niobate (LiNbO$_3$)

Lithium niobate is reported to be ferroelectric with a Curie point of 650°C (Reference 40). The crystal structure is related to that of ilmenite but with certain very significant differences which reflect its unusual properties (References 7, 41). Although the structure of LiNbO$_3$ is polar, it is not clear (due to its structure) how there can be a reversal of the
direction of the polar axis as in other ferroelectrics. However, this is based on room temperature data. Theoretical models have been postulated to account for the ferroelectricity but more experimental data is needed.

It was suggested by Megaw (Reference 41) that ferroelectricity in LiNbO₃ represents a transition from one polar rhombohedral structure, through ideal perovskite, to the rhombohedral structure of reversed direction.

In a popular paper by Allen (Reference 42) the ferroelectric properties of several materials were listed. This list indicates that lithium niobate has a Curie point above 450°C, a spontaneous polarization of 26.0 microcoulombs/cm², and a coercive field of 6,000 volts/cm up to 220°C. No reference is given, however. There is some question of the validity of this data as this corresponds exactly to the information reported on lithium tantalate by Matthias and Remeika (Reference 11). It seems probable that Allen meant LiTaO₃ rather than LiNbO₃ in his paper.

Small (1 mm) crystals have been made by Kay (Reference 39) by grinding and mixing stoichiometrically equal portions of Li₂CO₃ and Na₂CO₃. This is then sealed in platinum at 1150°C for 24 hours.

Rubidium Tantalate (RuTaO₃)

Rubidium tantalate (RuTaO₃) is reported to be ferroelectric with a Curie temperature of 247°C by Smolenskii et al. (Reference 43) and Allen (Reference 42). It has a tetragonal structure at room temperature.

Aluminum Metaniobate (Al₂Nb₂O₇)

The dielectric properties of ceramic aluminum metaniobate (density, 3.81 gm/cm³) were measured by Coats and Kay (Reference 25). It is reported to be ferroelectric with a Curie temperature of 220°C. The dielectric constant and loss tangent at 50 cps and room temperature are 170 and 0.01, respectively. The dielectric constant rises to about 220 at 220°C. The dielectric constant, temperature relationship is also reported for higher frequencies (0.1 mc/sec, 1 mc/sec, and 5 mc/sec). It decreases with increasing frequency, and the maximum at 5 mc/sec is about 120.

Sodium Vanadate (NaVO₃)

Sawada and Nomura in 1950 (Reference 44) reported that sodium vanadate displays ferroelectric behavior with a Curie point at about 380°C. An electric field polarization-hysteresis loop was generated and is typical of the better ferroelectrics. However, measurements of the dielectric constant reveals only a slight hump at 380°C rather than the usual very large jump in the value of this property. Therefore it is not clear whether or not NaVO₃ is ferroelectric.

This work was done on plate-like single crystals of about 1 mm length. They were obtained by cooling the molten 1:1 mixture of V₂O₅ and Na₂CO₃. The crystals, which were yellowish brown, transparent, and hard, were observed to glitter.
Barium Titanate-Barium Hafnate (BaTiO$_3$-BaHfO$_3$) Single Crystals

It was discovered by Khodakov and Sholokhovich (Reference 45) that single crystals of a solid solution of BaTiO$_3$-BaHfO$_3$ containing small amounts of BaHfO$_3$ (1%) have a high piezoelectric modulus and are readily polarized. The crystals are in the form of triangular platelets with 0.5 cm sides on platelets in the form of trapezia. The thickness of the platelets varies from 60 to 700 microns and are yellow in color.

After polarizing with a field of 8 kv/cm at 50 cps the piezoelectric modulus $d_{33}$ is 50 to 110 x $10^{-6}$ statcoulomb/dyne units depending on the polarizing time (Note that for polycrystalline barium titanate, $d_{33}$ is between 5 and $6 \times 10^{-6}$ statcoulomb/dyne, (References 46, and 47).

Polycrystalline solid solutions of BaTiO$_3$-BaHfO$_3$ containing up to 2 percent BaHfO$_3$ gave values of $d_{33}$ up to $8 \times 10^{-6}$ statcoulomb/dyne units.

Nothing was said about the Curie point, but presumably it would be near that for BaTiO$_3$, 120°C.

Bismuth Ferrite (BiFeO$_3$)

Because bismuth has a high electrical conductivity, the Curie point cannot be determined by electrical measurements. It was determined by measuring the dielectric constant for the PbTiO$_3$-BiFeO$_3$ ceramic system and extrapolating from 85 to 100 percent BiFeO$_3$. The crystal structure of BiFeO$_3$ is rhombohedral below 850°C (Reference 48).

Mixed Bismuth Oxides

Subbarao (Reference 49) in 1960 reported work done on various mixed bismuth oxide ceramics which appear to be ferroelectrics. This work was motivated by the fact that the occurrence of ferroelectricity in oxides is favored when the crystal structure contains small, highly polarizable ions surrounded by oxygen octahedra, which are linked through corners. Several mixed bismuth oxides have this characteristic.

The Curie points of several of these materials were determined by dielectric constant measurements. The typical dielectric constants are about 200 at room temperature for PbBi$_4$Ti$_4$O$_{15}$ and BaBi$_4$Ti$_4$O$_{15}$ and 1500 and 5400 at their respective Curie points. The following compounds and their Curie points were reported:

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>CURIE TEMP. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbBi$_4$Nb$_8$O$_9$</td>
<td>550</td>
</tr>
<tr>
<td>PbBi$_4$Ta$_2$O$_9$</td>
<td>430</td>
</tr>
<tr>
<td>BaBi$_4$Ti$<em>9$NbO$</em>{19}$</td>
<td>270</td>
</tr>
<tr>
<td>PbBi$_4$Ti$<em>9$NbO$</em>{19}$</td>
<td>290</td>
</tr>
<tr>
<td>BaBi$_4$Ti$<em>4$O$</em>{15}$</td>
<td>395</td>
</tr>
<tr>
<td>PbBi$_4$Ti$<em>4$O$</em>{15}$</td>
<td>570</td>
</tr>
</tbody>
</table>

13
The Curie point of PbBi\textsubscript{2}Nb\textsubscript{2}O\textsubscript{9} is reported to be 526°C by Smolenskii et al. (Reference 50).

It is to be noted that at 250°C, with an applied field of 30 kv/cm, typical reasonably saturated D-E hysteresis loops were observed only with PbBi\textsubscript{2}Ta\textsubscript{2}O\textsubscript{9} ceramics. However, the ceramic discs poled at 200°C under a field of 20 to 50 kv/cm exhibit a piezoelectric response $d_{33} \sim 3 \times 10^{-7}$ statcoulomb/dyne.

Smolenskii et al. (Reference 51) reported that BiNaTiO\textsubscript{6} are ferroelectric with a perovskite structure and Curie points of 317°C and 377°C, respectively. Smolenskii (Reference 51) also reported CaBi\textsubscript{2}Nb\textsubscript{2}O\textsubscript{9}, CaBi\textsubscript{2}Ta\textsubscript{2}O\textsubscript{9}, and Bi\textsubscript{3}NbTiO\textsubscript{9} to have tetragonal symmetry with ferroelectric Curie points of about 625°C, 575°C, and 625°C, respectively.

Aurivillius and Fang (Reference 52) studied ferroelectricity in the compound Ba\textsubscript{2}Bi\textsubscript{4}Ti\textsubscript{12}O\textsubscript{21}. At room temperature the polarization is found to be about 2 microcoulomb/cm\textsuperscript{2} and the coercive field about 10 kv/cm. The dielectric constant is about 400 at room temperature and rises to about 850 at 329°C, which is the Curie point. The dielectric loss ($\varepsilon''$) is 22 at room temperature and is about 82 at the Curie temperature.

Bismuth titanate (Bi\textsubscript{4}Ti\textsubscript{12}O\textsubscript{21}) was found to be ferroelectric by Subbarao (Reference 53) and by Van Uitert and Egerton (Reference 54) in 1960. The former authors report properties on thin (2 to 4 mil) single crystals which were grown from a melt of Bi\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2}. The crystals are clear and slightly grayish in color. The dielectric constant and loss tangent at 1 kc were about 112 and 0.0029, respectively, at room temperature. The polarization is about 3.5 microcoulomb/cm\textsuperscript{2}. A phase transition was discovered at 643°C with birefringence measurements; this was presumed to be the ferroelectric Curie point. However, Subbarao (Reference 53) reported a maximum of about 570 in the dielectric constant at 675°C, measured at 100 kc/sec on a ceramic specimen. Fang et al. (Reference 55) observed a maximum in the dielectric constant $\varepsilon''$ of bismuth titanate grown from a melt at 685°C on raising the temperature, and at 670°C on cooling (40 mc/sec).

Jona and Shirane (Reference 4) list the following mixed bismuth oxide, strontium oxide compounds as being ferroelectric; SrBi\textsubscript{4}Nb\textsubscript{2}O\textsubscript{9} (440°C), SrBi\textsubscript{4}Ta\textsubscript{2}O\textsubscript{9} (335°C), SrBi\textsubscript{4}Ti\textsubscript{12}O\textsubscript{21} (345°C), and Sr\textsubscript{2}Bi\textsubscript{4}Ti\textsubscript{12}O\textsubscript{21} (285°C).

Lead Zirconate (PbZrO\textsubscript{3})

Lead zirconate was the first antiferroelectric to be discovered (Reference 56). Antiferroelectrics do not exhibit spontaneous polarization nor polarization-electric field hysteresis loops. However, the dielectric constants behave much like they do in the ferroelectrics. The dielectric constant of PbZrO\textsubscript{3} shows an anomaly at 230°C which is its antiferroelectric Curie point.

Crystals of PbZrO\textsubscript{3} are very difficult to grow primarily because of the severe evaporation of PbO at high temperatures. Small crystals were obtained by Jona, et al. (Reference 57) by using a method of binary melts. PbF\textsubscript{2} and also PbCl\textsubscript{2} were used as fluxes; the crystals are about 0.3 mm on an edge, light brown, and transparent. They are contaminated, however, by a small amount of the remaining flux material.
The dielectric constant of PbZrO₃ has been reported to be 100 (30°C, 1 mc/sec, ceramic) and about 3500 (230°C, 1 mc/sec, ceramic) (Reference 58). The compliance coefficient is 0.8 and 1.2 x 10⁻¹⁸ cm³/dyne at 30° and 230°C, respectively (Reference 59).

In an attempt to measure a piezoelectric effect in lead zirconate, Roberts (Reference 60) in 1950 found $d_{33} \sim 10^{-9}$ statcoulomb/dyne which is extremely small. However, this is expected because the antiferroelectric state is not piezoelectric (Reference 61).

Lead hafnate (Reference 62) and sodium niobate (Reference 12) are also antiferroelectric with Curie temperatures of 215° and 320°C, respectively.
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