A study of bismuth ferrate and bismuth manganate in solid solution with lead titanate

Harris C. Jones

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A STUDY OF BISMUTH FERRATE AND
BISMUTH MANGANESE IN SOLID SOLUTION
WITH LEAD TITANATE

BY

HARRIS C. JONES, 1964

A
THESIS
submitted to the faculty of
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ABSTRACT

A new sample holder for measuring the high frequency dielectric constant of ferroelectrics at high temperature was constructed. The new sample holder eliminated discontinuities in the slotted line and improved the electrical contact between the ceramic and brass components.

Measurements of the high frequency dielectric constant of an aged sample of 90% BiFeO₃ - 10% PbTiO₃ were made as a function of temperature using the slotted line technique. The dissipation function for the aged sample was found to have a more normal behavior near the Curie point than the virgin samples previously measured.

Resistivity measurements were made as a function of temperature and voltage on the solid solution of 40% BiMnO₃ - 60% PbTiO₃. These measurements showed that the conduction is primarily N-type and the contacts are ohmic.

A discussion is presented which indicates that for magnetic ions the Jahn-Teller effect may affect the short range forces in the crystal which determine ferroelectric parameters.
ACKNOWLEDGEMENTS

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I. INTRODUCTION

High temperature measurements of the dielectric constant may present a problem because of the very large conduction losses in the sample. The conductivity tends to dominate the dielectric behavior so that the true dielectric polarization cannot be measured except at high frequency. Because of the high conduction losses of solid solutions with a high BiFeO$_3$ content, the dielectric behavior of these samples could only be inferred from x-ray data on the phase transitions prior to the work by R.T. Smith in this laboratory.

The resistivity of solid solution of high BiFeO$_3$ content is of the order of $10^6$ ohm-cm. at room temperature and decreases rapidly with rising temperature. At the Curie point (850°C), the resistivity of these solid solutions may be as low as 10 ohm-cm. The equivalent circuit of the sample may be considered as a resistor in parallel with a capacitor (see sketch). Using this model for the sample, the dissipation factor (loss tangent) is inversely proportional to the frequency.

![Equivalent circuit diagram](image)

An excellent and straightforward method of measuring the dielectric constant at high frequencies (lower loss tangent) is to use a
coaxial wave guide and a slotted line. The sample is used as a termination and is compared to standard short and open terminations. There are many corrections that must be made to account for the discontinuities in the sample holder, the attenuation of the sample holder, and the size and shape of the sample. These corrections can be made using a computer.

However, it is very difficult to use even the slotted line technique with excessively high loss samples because the voltage minimum in the standing wave becomes excessively broad. It is because of this that the dielectric constant of pure BiFeO$_3$ cannot be directly measured. Therefore another high frequency method is proposed in this thesis which measures the phase of the forward and reflected power directly. This method may prove to be more satisfactory with high loss samples.

The work presented below includes high frequency dielectric measurements made on an aged sample of 90\% BiFeO$_3$ - 10\% PbTiO$_3$ as a function of temperature, using an improved sample holder. The value of the dielectric constant at the transition temperature is much lower on the aged sample and the dissipation function on the aged sample has a more normal behavior.

The projected studies of the solid solution series BiMnO$_3$-PbTiO$_3$ to determine dielectric transitions could not be made because of the high conductivity of these samples. Instead, resistivity measurements were made on a solid solution of 40\% BiMnO$_3$-60\% PbTiO$_3$. There were no anomalies in the region of the transition temperature (400°C-425°C).
II. LITERATURE REVIEW

A. GENERAL PROPERTIES OF FERROELECTRIC CRYSTALS

A ferroelectric crystal is defined as a crystal which has a spontaneous electric dipole moment. Also, in parallel to the ferromagnetic case, the ferroelectric crystal has a characteristic transition temperature, or Curie point above which the ferroelectric properties do not exist. It has been shown by Smith et al. (1) that the Curie point is about 850°C for BiFeO₃. This was done by extrapolating the Curie point of various solid solutions of BiFeO₃-PbTiO₃ to the case of 100% BiFeO₃.

There are necessary and sufficient conditions for the phenomenon of ferroelectricity (2),(3),(4). A necessary condition is that the crystal belongs to a pyroelectric point group. Of the thirty-two point groups, twenty do not have a center of symmetry. Of these twenty, ten are polar or pyroelectric. The ferroelectric crystals are a subgroup of the pyroelectric group. According to modern theories of degenerate acoustical and optical phonon modes, there may be no significant difference between a pyroelectric and ferroelectric crystal.

A sufficient condition for a ferroelectric crystal is that it exhibit a dielectric hysteresis loop.

Ferroelectric crystals exhibit a Curie point, above which the dielectric constant follows a Curie-Weiss behavior,

\[ \varepsilon = \frac{C}{T - T_c}. \] (1)
C is the Curie constant, \( T_c \) is the Curie temperature, and \( T \) is the temperature. This relationship is found to hold to within a few degrees of the Curie point.

(1) THE POLARIZATION CATASTROPHE

The occurrence of ferroelectricity can be described by the polarization catastrophe, which occurs when the local field becomes infinite. This implies that there is a net polarization without an applied field. In K-K-3 units the local field can be written

\[
E_{\text{local}} = E_{\text{app}} + \gamma P,
\]

where \( \gamma \) is purely a microscopic constant, analogous to a structure factor. The local field is not constant at each atomic site, thus \( \gamma \) can have different values at different atomic sites. By using the same argument, even though the mean value of the polarization (and local field) is zero over the unit cell, this does not imply that the local field is zero at each atomic site.\(^5\)(6) Let \( \tilde{p} \) be the dipole moment at the atom, \( \tilde{p} = \alpha E \). Then:

\[
P_{\text{total}} = \sum_c N_c \alpha_c E_{c,\text{local}} \\
= \sum_c N_c \alpha_c \left[ E + \gamma \tilde{p} \right] \\
= \sum_c N_c \alpha_c \left[ 1 + \frac{\gamma \tilde{p}}{E} \right] E,
\]
Assume: \[ \sum \gamma_i \cdot P_i = \frac{D_{tot}}{E} \]

\[ \frac{D_{tot}}{E} = \sum N_i \alpha_i (1 + \frac{\chi_{tot}}{E}) \]

\[ = \frac{\sum N_i \alpha_i}{1 - \frac{\chi_{tot}}{E}} \]

Now the dielectric constant \( \varepsilon \) is defined

\[ \varepsilon = \frac{D}{E} = \frac{\varepsilon_0 \varepsilon_0 + P}{E} = \varepsilon_0 + \frac{P}{E} \]  \hspace{1cm} (5)

Substitution from equation (4)

\[ \varepsilon - \varepsilon_0 = \frac{\sum N_i \alpha_i}{1 - \frac{\chi_{tot}}{E}} \]  \hspace{1cm} (6)

The dielectric constant becomes indeterminate as \( \gamma \sum N_i \alpha_i \) approaches unity. Since \( \varepsilon = \frac{D}{E} \), an infinite value of the dielectric constant implies a net polarization. Experimentally, the dielectric constant becomes very large, but not infinite.

Slater (7) proposes that the reason for the polarization catastrophe is that \( \alpha_i \) is a slowly decreasing function with temperature. He assumes that it has a value greater than unity below the Curie point. In other words, \( \gamma \sum N_i \alpha_i \) would be of the form

\[ \gamma \sum N_i \alpha_i \approx 1 - C(T - T_C) \]  \hspace{1cm} (7)
Then

\[ \varepsilon - \varepsilon_\infty = \frac{1}{\delta} \left[ \frac{1 - C(T-T_c)}{1 - 1 + C(T-T_c)} \right] \]

\[ = \frac{1 - C(T-T_c)}{\delta C(T-T_c)} \] \hspace{2cm} (8)

(2) THE DISSIPATION FACTOR

Suppose the applied field is periodic

\[ E_{\text{applied}} = E_0 \cos(\omega t) \] \hspace{2cm} (9)

If the field has been applied for a sufficiently long time, then one can assume that the displacement vector is also periodic in time, but not necessarily in phase with \( E \):

\[ D = D_0 \cos(\omega t - \delta) \]

\[ = D_0 \cos(\omega t) \cos(\delta) + D_0 \sin(\omega t) \sin(\delta) \] \hspace{2cm} (10)

Therefore:

\[ D = D_1 \cos(\omega t) + D_2 \sin(\omega t) \] \hspace{2cm} (11)

For homogeneous, isotropic samples

\[ D = \varepsilon_0 (1 + \kappa_E) E = \kappa_E \varepsilon_0 E \] \hspace{2cm} (12)
One can introduce the relationships

\[ D_1 = \kappa_1(\omega) \varepsilon_0 E_0, \quad D_2 = \kappa_2(\omega) \varepsilon_0 E_0 \]  

\[ \frac{D_2}{D_1} = \frac{D_0 \sin(s)}{D_0 \cos(s)} = \frac{\kappa_2(\omega)}{\kappa_1(\omega)} = \tan S. \]  

\( \tan S \) is called the loss tangent, and is associated with the power dissipated by the sample. (8)

B. PHONONS IN FERROELECTRIC CRYSTALS

Suppose that the ions in a lattice undergo only small displacements. If \( Q_k \) is the charge on ion \( K \) and \( Q_k' \) is the charge on ion \( K' \) then a potential between the ions may be written

\[ V_{kk'} = Q_k Q_k' f(D_{kk'}), \]  

where \( D_{kk'} \) is the distance between lattice sites, and \( f \) is any function of \( D_{kk'} \). If ion \( K \) is displaced a distance \( u_k \) from the lattice site, and ion \( K' \) is displaced \( u_{k'} \) then the potential is of the form

\[ V = Q_k Q_k' f(D_{kk'} + u_k - u_{k'}), \]

\[ = Q_k Q_k' f(D_{kk'})(1 + \frac{u_k - u_{k'}}{D_{kk'}}), \]  

\[ = Q_k Q_k' f_{kk'}(1 + \frac{u_k - u_{k'}}{D_{kk'}}). \]  

(16)
Expanding this in a Taylor's series:

\[ V(l + \frac{u_k - u_k'}{D_{kk'}}) = \sum_{n=0}^{\infty} \frac{(u_k - u_k')^n}{n!} \left( \frac{\partial^n V}{\partial l^n} \right) \]

The force between the ions is the first derivative in the expansion:

\[ F_{kk'} = c_{kk'} \frac{Q_k Q_{k'}}{D_{kk'}} (u_k - u_{k'}) \]  

This is the harmonic oscillator approximation.

Cochran (9) assumes that there is an harmonic oscillator interaction between the ions, and between the outer shells of the ions. Thus there are three types of interactions: core-core, core-shell, and shell-shell. He further assumes that only the outer shells of the negative ions interact as a separate unit.

This is equivalent to saying that the positive ions have a noble gas configuration and the outer shell is tightly bound to the nucleus. This is not true for the perovskites BiFeO₃ and BiMnO₃.

The adiabatic or Born-Oppenheimer approximation is assumed to hold: the Hamiltonian can be split into a nuclear and electronic Hamiltonian. The outer shell of the negative ion is assumed to have an effective mass, reducing the interaction between the negative ion shell and the negative ion core to a problem which is the same type as the classical hydrogen atom:

\[ E = \frac{1}{2} m v'^2 + \frac{L^2}{2m v'z} - \frac{Q' \phi'}{r} \]
The shell-core interaction is thus of the same form as the ion-ion interaction

\[ F = C \frac{Q_e Q_s}{r_0} (u_e - u_s). \]  

(20)

Although this approach does not have any anharmonic terms, it treats the outer shell as a separate particle, and gives the same answer as an approach using energy perturbation and dipole moments. (10)

Summing over all the atoms in the crystal

\[ F_K = \sum_{K \neq K'} C_K \frac{Q_K Q_{K'}}{D_{KK'}} (u_K - u_{K'}). \]  

(21)

One assumes a solution of the form

\[ u_K = C_K e^{-i \omega t + i n k a}. \]

As an example suppose that there are two atoms per unit cell of mass $M_1$ and $M_2$ and only nearest neighbor interactions are considered:

\[ F_K = M_1 \frac{d^2 u_K}{dt^2} = C (u_{K+1} + u_{K-1} - 2u_K) \]  

(22)

\[ F_{K'} = M_2 \frac{d^2 u_{K'}}{dt^2} = C (u_{K+2} + u_{K-2} - 2u_{K+1}) \]

These may be solved simultaneously:

\[ \omega^2 = C \left( \frac{1}{M_1} + \frac{1}{M_2} \right) \pm C \left[ \left( \frac{1}{M_1} + \frac{1}{M_2} \right)^2 - \frac{4 \sin^2 \left( \frac{32 \pi}{M_1 M_2} \right)}{M_1 M_2} \right]^{1/2}. \]  

(23)
(a) Transverse phonons for a diatomic lattice (from Kittel)

(b) Transverse phonons when the long and short range forces cancel. (from Cochran)
The roots are, for $K \rightarrow 0$, $K = \frac{1}{2\alpha}$:

$$\omega^2 = 2c \left( \frac{1}{M_1} + \frac{1}{M_2} \right), \quad \text{(optical branch)}$$

$$\omega^2 = \frac{2c}{M_1 + M_2} K^2 a^2. \quad \text{(acoustical branch)}$$

This is the linear chain solution, which appears in Kittel (11).

However, if both long range and short range forces are considered, it is possible for the long and short range forces to cancel for a particular phonon mode. Cochran asserts that this instability is the cause of ferroelectric behavior. Some of the assumptions of this argument are that the phonons are pure transverse and pure longitudinal and that the wave vector is in a symmetry direction. There are $3n$ possible phonons, where $n$ is the number of atoms in the unit cell, 3 acoustical phonons and $3n - 3$ optical phonons. Since the perovskite structure has 5 atoms per unit cell, this implies 15 phonon modes. However, below the Curie point there are two oxygen ions with identical environments so there are only twelve non-degenerate phonon modes. Above the Curie point all oxygen ions are identical, so there are only nine non-degenerate phonon modes. For BaTiO$_3$ the oxygen octahedra appears to be undistorted in the transition. (12) This implies that there is strong covalent bonding between the oxygen ions since there are different effective fields at the type 1 oxygen ions and type 11 oxygen ions.

C. THERMODYNAMIC THEORIES OF FERROELECTRICITY

There are several thermodynamic theories of ferroelectricity.
based on the second order phase transition. Classically, the second order phase transition is characterized by a discontinuity in the second derivative of the Gibbs free energy while the first order transition is discontinuous in the first derivative of the Gibbs free energy. Ferroelectric transitions may be of either the first or second order. (Ferromagnetic transitions are second order.) However, there is a real question as to whether there is any sharp delineation between first and second order transitions, or whether it is just a case of the relative magnitudes of the important factors.

A second order phase transition implies a gradual change between phases. It is a transition in which there is a continuum of phases between the initial and final phase.

C. Haas(13) enumerates the symmetry conditions above and below the transition temperature necessary for a transition to be second order.

The first condition is that the less symmetric point group is a subgroup of the more symmetric point group. If \( P_0(\vec{r}) \) is a density function representing the full symmetry of the crystal in the point group \( G_0(\vec{r}) \) then \( P_0(\vec{r}) \) is an invariant. If the transition to another point group \( G(\vec{r}) \) lowers the symmetry, then \( P(\vec{r}) = P_0(\vec{r}) - \Delta P(\vec{r}) \). \( P(\vec{r}) \) is a subgroup of \( P_0(\vec{r}) \) and therefore cannot have symmetry operations not in \( P_0(\vec{r}) \).

The second condition is that \( \Delta P(\vec{r}) \) is an irreducible
representation leaving \( P_0(r) \) invariant.

The third condition (due to Landau) is that all odd powers vanish in an expansion of the free energy of crystal. If the free energy is expanded in terms of some variable it is of the form (14)

\[
\phi(x) = \phi_0 + \alpha x^2 + \beta x^4 + \gamma x^6 + \ldots
\]  

Goldrich and Berman \(^{(15)}\) employ the idea of Haas in connection with the perovskite structure. Using the Gibbs function as an appropriate density function they state that it must span the higher energy symmetry group \( G_0 \). It is invariant under inner products of the type \( \langle \phi/\Theta \rangle \). One assumes that \( G_1 \) is a subgroup of \( G_0 \) and \( G_1' \) is a subgroup of \( G_1 \). In other words, \( G_1 \) can contain only symmetry operations that \( G_0 \) contains. If it contains all the symmetry operations it is a trivial subgroup (just the group \( G_0 \)). \( G_1' \) can contain only symmetry operations in \( G_1 \). If a density function \( P(l) \) is invariant under a group it must also be invariant under a subgroup. If a second order transition does imply a gradual change between phases then the transition would go from \( G_0 \) to \( G_1 \) to \( G_1' \), where \( G_0 \) and \( G_1' \) are (stable) space groups. Because the Gibbs free energy is a scalar invariant in a transition (it must be equal in both phases at the transition temperature), the transition will gradually go from the group \( G_0 \) to the largest subgroup, \( G_1 \) and will be stable. It will not go to \( G_1' \). Thus
Goldrich and Berman are able to list the possible transitions from any given space group by considering only the largest subgroups.

The best known theory of ferroelectricity is that by Devonshire (16),(17),(18). He assumes that the Gibbs free energy can be expanded using the polarization as a variable. If the transition is second order, then the coefficients for the odd powers are zero and

\[ G = G_0 + \frac{1}{2} \alpha (P_x^2 + P_y^2 + P_z^2) + \frac{1}{2} \beta (P_x^4 + P_y^4 + P_z^4) + \frac{1}{4} \gamma (P_x^2 P_y^2 + P_y^2 P_z^2 + P_z^2 P_x^2) + \ldots \]  

By assuming that the spontaneous polarization is in only one direction, then the equation reduces to

\[ G = G_0 + \frac{1}{2} \alpha P^2 + \frac{1}{4} \gamma P^4 + \frac{1}{\epsilon} \delta P^6 + \ldots \]  

It is assumed that \( \alpha \) and \( \delta \) are always positive, while \( \gamma \) may be positive or negative. If \( \gamma \) is negative the transition is first order, and if it is positive it is second order. (19)

The electric field is given by

\[ E = \frac{\delta G}{\delta P} = \alpha P + \gamma P^3 + \delta P^5 + \ldots \]
If this is equated to zero, then the spontaneous polarization is

\[ P_s = \pm \left\{ \frac{\gamma}{2 \delta} \left[ \left(1 - \frac{4 \delta \epsilon}{\gamma^2} \right)^{1/2} + 1 \right] \right\}^{1/2}, \quad \gamma < 0; \]

\[ P_s = \pm \left\{ \frac{\gamma}{2 \delta} \left[ \left(1 - \frac{4 \delta \epsilon}{\gamma^2} \right)^{1/2} - 1 \right] \right\}^{1/2}, \quad \gamma > 0. \]

The Gibbs free energy is not as simple a function as it at first seems. The Gibbs free energy, or the potential \( \phi \) defined as the Gibbs free energy per mole, is much more complex. It is a function of the mechanical stress, mechanical strain, the electric field, and the polarization. Also to be considered are crystals which contain some type of magnetic ordering (ferromagnetic or antiferromagnetic) making the potential a function of the magnetic field and magnetization. Thus \( G \) is a function of at least six variables: \( G(x, \lambda, E, P, H, M) \). The first assumption is that there is no mechanical strain nor stress. This is not a trivial assumption since stress and strain are tensors and are a function of the fabrication of the crystal as well as the applied stresses. (21)

The assumption that the crystal may be expanded in even powers of the polarization and magnetization is the same as assuming the function is symmetric about the origin in P-M space:

\[ \phi(P, M) = \phi(-P, M) = \phi(P, -M) = \phi(-P, -M). \]
This assumption is only valid for those directions in the crystal which have mirror symmetry, for example along the three axes ̂a, ̂b, ̂c in the cubic crystal. In general, the crystal cannot be anisotropic. Following the paper by G.A. Smolenskii (22) the expansion of Gibbs energy is

\[ G(N, P) = G_0 + \alpha P^2 + \frac{\beta}{2} P^4 - P E + \alpha'M^2 + \frac{\beta'}{2} M^4 - M H + \gamma P^2 M^2. \]

(28)

The solution is at an extremum (equilibrium condition) when

\[ \left( \frac{\partial G}{\partial P} \right)_M = 0, \quad \left( \frac{\partial G}{\partial M} \right)_P = 0. \]

(29)

In order for this to be a minimum, the second derivatives must be greater than zero. (23)

\[ \frac{\partial^2 G}{\partial P^2} > 0, \quad \frac{\partial^2 G}{\partial M^2} > 0, \quad \begin{vmatrix} \frac{\partial^2 G}{\partial P^2} & \frac{\partial^2 G}{\partial P \partial M} \\ \frac{\partial^2 G}{\partial P \partial M} & \frac{\partial^2 G}{\partial M^2} \end{vmatrix} > 0. \]

(30)

Calculating the first derivatives (with no applied field) and setting them to zero yields

\[ \left[ \alpha + \beta P^2 + \gamma M^2 \right] P = 0, \]

(31)

\[ \left[ \alpha' + \beta' M^2 + \gamma P^2 \right] M = 0. \]
If the trivial solutions $P=0$, $M=0$ are ignored, these equations may be solved

$$P^2 = \frac{-\alpha - \gamma M^2}{\beta},$$

$$M^2 = \frac{-\alpha' - \gamma' P^2}{\beta'}.$$  \hspace{1cm} (32)

There are three regions of interest, namely

$$T < \Theta_m < \Theta_c, \quad \Theta_m < T < \Theta_c, \quad \Theta_m < \Theta_c < T.$$  \hspace{1cm} (Smolonskii assumes that $\Theta_c < \Theta_m$ but this is not the case with $\text{BiFeO}_3$)

For $\Theta_m < T < \Theta_c$, $M=0$, $P \neq 0$:

$$G = G_0 + \alpha P^2 + \frac{\beta^2}{2} P^4 + ...$$

which is the standard expansion for a ferroelectric crystal, and is the basis of the approach of Devonshire's treatment of barium titanate \((16),(17)\). The solution to the differential equations is

$$P^2 = \frac{-\alpha}{\beta}.$$  \hspace{1cm} (34)

For $T < \Theta_m < \Theta_c$, the result is equation (32).

D. THE PEROVSKITE STRUCTURE

An outstanding example of the perovskite-type ferroelectrics is barium titanate, $\text{BaTiO}_3$. Barium titanate has the cubic perovskite structure above the Curie point ($120^\circ\text{C}$) and tetragonal perovskite structure in the ferroelectric phase.
The theories of the previous two sections are very difficult to apply to anything but the simplest crystal structures because of summations of the form of equation (21), i. e.

\[ F_k = \sum_{k'} C_k \frac{Q_k Q_{k'}}{D_{kk'}} (\alpha_k - \alpha_{k'}) \]

Thus Cochran's theory can only be easily applied to the (cubic) perovskite structure, the simplest ferroelectric structure. The formula for the perovskite structure is \( \text{ABO}_3 \), where A and B are transition metals. The A ion is the larger ion and occupies the corners of the cubic unit cell. The B ion is in the center of the cube, and the oxygen ions occupy the faces of the cube. If the lattice is displaced so that the A ion is at the center of the cube, then the B ion is at the corners, and the oxygen ions are at the center of the twelve cube edges. The perovskite structure is shown in Figure 2.
Figure 2
The Perovskite Structure

(a) B Cation at Body Center Site

(b) A Cation at Body Center Site
III. APPARATUS

The apparatus for the high frequency dielectric measurements is basically the same as that described by R.T. Smith. The apparatus consists of a vertically mounted slotted line terminated with a ceramic coaxial sample holder. The signal sensed by the probe of the slotted line is mixed with a local oscillator signal, producing a 30 megahertz beat frequency signal which is amplified on an I-f strip. By comparing the position of the minimum and the \( \pm \frac{\lambda}{2} \) points of the sample with the positions and the \( \pm \frac{\lambda}{4} \) points of the open and short circuit terminations, the impedance of the sample can be determined. By using a computer program, the real and imaginary dielectric constants are determined as a function of temperature.

Important corrections are due to the attenuation of the sample holder and discontinuities between the sample holder and the slotted line. The attenuation corrections are due primarily to the resistance of the fire-on platinum-gold conductive paste on the ceramic holder. However there were discontinuities in the old sample holder due to the differences in diameters of the outer and inner conductors. The outer conductor of the sample holder was 0.039 cm. larger than that of the slotted line. This caused additional reflections. Also, the old sample holder was extruded and not machined, so that the surface was rough. A new sample holder was made using precision ground Mullite MW-30 ceramic
inner and outer conductors (by McDanel) and precision brass tubing from General Radio Co. All parts of the sample holder were milled to within .001". All brass parts were silver plated prior to final assembly to improve conductivity. The new sample holder resulted in the following improvements:

1. Elimination of discontinuities due to a change in diameter of outer and inner conductors and non-uniformities caused by surface imperfections in the extruded ceramic.

2. Improved electrical contact between the ceramic center conductor and brass center conductor.

3. Improved design of the termination which allowed the thermocouple to be placed within 0.3 inches from the sample.

A practical improvement was that large fins were milled into the outer conductor for more efficient cooling outside the furnace.

Using the slotted line technique it is very difficult to get accurate data when the sample is very lossy (as in the case of bismuth ferrate). The reason is that it is difficult to measure precisely the position of the voltage minimum. In the error analysis by R.T. Smith (25) the maximum error in the dielectric constant was 20% and in the dissipation factor 25%. The residual standing wave ratio of his sample holder was

\[ R = 1.09. \]

The residual standing wave ratio of the improved sample holder is

\[ R = 1.02. \]

The residual standing wave ratio of an ideal sample holder is

\[ R = 1. \]
The sample may be considered as a capacitor either in series or in parallel with a resistor. Thus any geometrical change of the sample would at most add a capacitor in series with the sample and would not improve the problem of the conduction loss term masking the dielectric constant.

Another method is to use a phase comparison method which measures the change of phase directly. This may require going to higher frequencies than are now used, but this method may be the only solution to the measurement of high loss samples. The method consists of measuring the phase of the forward power and comparing it to the phase of the reflected power. The phase change is compared to that of the open circuit and short circuit terminations.

Block diagrams of the slotted line circuit and the phase comparison circuit are shown in figures 4 and 5.
Block Diagram of Slotted Line Apparatus

- Slotted line
- Probe
- Sample holder
- Impedance matching network
- U.H.F. signal generator
- Local oscillator
- I.F. amplifier
- Meter
- Mixer
Figure 4

Block Diagram of Proposed Phase Comparison Apparatus

- U.H.F. signal generator
- directional couplers
- sample holder
- forward power
- reverse power
- local oscillator
- mixer
- mixer
- I.F. amplifier
- I.F. amplifier
- precision phase shifter
- phase sensitive detector
- null meter
IV. EXPERIMENTAL RESULTS AND CONCLUSIONS

A. BiFeO₃-PbTiO₃

Measurements on the BiFeO₃-PbTiO₃ binary system were made with an improved sample holder on samples aged about six months. In the measurements by R.T. Smith (26) on the 90% BiFeO₃ sample, the imaginary part of the dielectric constant increased uniformly in the region 700°C-800°C while the real part approached a maximum. The total absorbed energy is usually nearly constant as a function of temperature for a small range in temperature. Thus one would expect that for a large increase in the real part of the dielectric constant there would be a corresponding decrease in the imaginary component. In the measurement on the aged sample the expected drop in the dissipation function occurs (see figure 5). The relative dielectric constant at the Curie point is 900 for the aged sample compared to 1700 for the virgin sample. This may be due to a valency change in the Fe³⁺ ion (see figure 6).

B. BiMnO₃-PbTiO₃

The original intention was to measure the Curie points of this system at high frequency using the slotted line technique. The sample was found to be too conductive. Therefore resistivity measurements were made on a solid solution of 40% BiMnO₃- 60% PbTiO₃. The sample was two phase, containing both the cubic and tetragonal phases. By determining the direction of the thermoelectric effect (sign of the Seebeck coefficient), the conduction was found to be
Figure 5

Dissipation Function For
New Sample and Aged Sample
90% BiFeO$_3$ - 10% PbTiO$_3$

△ New Sample (after Smith)
○ Aged Sample
Figure 6
Relative Dielectric Constant
New Sample and Aged Sample
90% BiFeO$_3$-10% PbTiO$_3$

New Sample (after Smith)
Aged Sample
primarily N-type. The sample showed no anomalies near or above the transition temperature. The contacts are ohmic, even when a pointed 5 mil tungsten wire is used as a contact. Graphs of resistance as a function of temperature and applied voltage are shown in figures 7, 8, and 9.

The BiMnO₃-PbTiO₃ binary system is described in a paper by Bokov et al. (27) According to them, in the region from 55%–100% PbTiO₃ the system is tetragonal below the Curie temperature, isomorphic with pure PbTiO₃. In the region of 35%–55% the system is cubic and in the region from 15%–35% PbTiO₃, the system is orthorhombic.

They were unable to make single phase solutions with compositions above 85% BiMnO₃. In the samples prepared at the UMR Materials Research Center, it was found that the contaminant is Bi₂Mn₄O₁₀. No method for removing the contaminant has yet been found.

From the data of Bokov, several conclusions may be tentatively drawn. First, the orthorhombic phase may be isomorphic with pure BiMnO₃, by comparison with other phase diagrams of perovskites. Secondly, BiMnO₃ may have a very high transition temperature, in the region of 900°C, higher than the transition temperature of BiFeO₃. However, from the samples prepared at UMR Materials Research Center, there is indication that the region that Bokov considers orthorhombic may actually be two phase.

There has been some work on pure BiMnO₃. Both Bokov et al. (28) and Sugawara et al. (29) agree that the distance between the manganese
40% BiMnO$_3$ - 60% PbTiO$_3$

Resistance vs. Temperature near the Curie point
Figure 8
RESISTANCE AS A FUNCTION OF RECIPROCAL TEMPERATURE
(40% BiMnO3 - 60% PbTiO3)
Figure 9

(a) CONDUCTIVITY AT ROOM TEMPERATURE

(b) RECTIFYING CONTACT EFFECT

○ forward current
△ reverse current
**Figure 10**

**a)**

**PHASE DIAGRAM OF BiMnO$_3$-PbTiO$_3**

(After Bokov)

**b)**

**Pure BiMnO$_3$ lattice parameters**

<table>
<thead>
<tr>
<th></th>
<th>Sugawara et al. (triclinic)</th>
<th>Bokov et al. (triclinic)</th>
<th>Bokov et al. (monoclinic*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a = c$</td>
<td>$3.93 \text{Å}$</td>
<td>$7.86 \text{Å}$</td>
<td>$10.93 \text{Å}$</td>
</tr>
<tr>
<td>$b$</td>
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<td>$7.98 \text{Å}$</td>
<td>$11.31 \text{Å}$</td>
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<tr>
<td>$\alpha = \gamma$</td>
<td>$91°25'$</td>
<td>$91°40'$</td>
<td>$92°24'$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$90°55'$</td>
<td>$90°58'$</td>
<td>$92°24'$</td>
</tr>
</tbody>
</table>

* Not necessarily in agreement with triclinic data.
ions is $3.93\AA$ in the $\hat{a}$ direction and $3.98\AA$ in the $\hat{b}$ direction. They both report that the unit cell is triclinic. Sugawara assigned fifteen lines of his x-ray analysis to the $(1,1,1)$, $(2,0,0)$, $(2,1,1)$, and $(2,2,0)$ peaks of the triclinic structure. However, due to the complexity of the triclinic structure it is doubtful whether fifteen lines are sufficient to conclude that the structure is actually triclinic, or even if the sample is single phase. Roth (30) indicates in his paper that by using the hard sphere model the structure would probably be of the Ti$_2$O$_3$ form and not single phase. Bokóv indicates that BiMnO$_3$ has a multiple unit cell, while Sugawara states that the superstructure is negligible. Sugawara assumes that the space group is monoclinic and by the extinction rules eliminates all but three possible space groups, Cn$_2$, C$_2$, C$_5$. Two of these are non-centrosymmetric and one is centrosymmetric.

C. THE JAHN-TELLER EFFECT

The Jahn-Teller effect is the slight displacement of the potential minimum of an ion from the lattice site due to a lack of symmetry of the electronic wave function. There is a possibility that the Jahn-Teller effect may play an important role in the perovskites BiFeO$_3$ and BiMnO$_3$. An ion like Ti$^{4+}$ with a noble gas electron configuration has a potential well of the form:

$$V(x) = V_0 + A x^2 + B x^4 + C x^6 + \ldots$$ \hspace{1cm} (35)

However, for a ion like Fe$^{3+}$ with a non-symmetric electron structure.
the nuclear coordinates for a potential minimum may not be in the center of the oxygen octahedra. The potential well for Fe\textsuperscript{3+} or In\textsuperscript{3+} will probably be distorted and may have a barrier in the center.

The theory of Cochran is that the long range and short range forces cancel for a particular optical phonon mode, causing a ferroelectric transition. The salient point of this theory is that the ferroelectric transition is definitely a coupled behavior. Above the transition temperature the spontaneous polarization is zero, and below that temperature the spontaneous polarization is a finite number.

For the Jahn-Teller effect, the ferroelectric transition would be an uncoupled behavior. As the temperature (energy) increases, the Fe\textsuperscript{3+} or In\textsuperscript{3+} ion would jump between states. At a sufficiently high temperature the maximum probability of \( \hat{x} \) would be at the center of the well. Thus one would expect to see a washing out of the polarization as the temperature is increased. Since the transition would not be complete until the spontaneous polarization is zero, a very broad peak in the dielectric constant would be expected. For any appreciable barrier the probability of observing the nucleus would not be a maximum at the center except for very high temperatures.

Thus two experimental criteria for a Jahn-Teller ferroelectric transition are:

1. The peak should be very broad, since the polarization is a monotonically decreasing function.

2. The transition temperature should be very high so that \( Pr(\hat{x}) \) is a maximum at the center of the well.

These criteria are fulfilled by solid solutions of BiFeO\textsubscript{3}. From the data
Figure 11

(a) The Proposed One-Dimensional Jahn-Teller Potential

(b) Polarization From Cochran's Theory

(c) Polarization due to Jahn-Teller effect
Figure 12
BiFeO₃–PbTiO₃ Binary System
Relative Dielectric Constant
As a Function of Temperature
(after Smith)
by Smith\(^{(32),(33)}\) (see figure 12), the Curie point for pure BiFeO\(_3\) extrapolates to 850°C. The peak for solid solutions becomes much broader as the mole-percent content of BiFeO\(_3\) is increased. The 80% BiFeO\(_3\)-20%PbTiO\(_3\) and 90%BiFeO\(_3\)-10%PbTiO\(_3\) curves indicate a very diffuse peak. Thus the first criterion is also fulfilled.

The Jahn-Teller effect implies much more complex short range forces than proposed in the theory by Cochran. The relative importance of the Jahn-Teller effect in the ferroelectric transition of BiFeO\(_3\) can be determined by infrared spectroscopy or by the Mossbauer effect. If there is a soft phonon mode, then one should expect the resonant absorption peak of the Mossbauer effect to decrease as the phonon frequency lowers.\(^{(34)}\) If there is no soft phonon mode, then the effect would decrease as \(e^{-\frac{\Theta}{kT}}\) where \(\Theta\) is the Debye temperature.

E.N. Havinga\(^{(35)}\) has also proposed the Jahn-Teller effect for Mn\(^{3+}\). However, he claims that the Jahn-Teller effect distorts the oxygen octahedra and is a cooperative effect. He also states that the Jahn-Teller effect is very unfavorable to ferroelectricity. In contrast, the theory presented here has the assumption that the wave function for the outer electrons of the Fe\(^{3+}\) or Mn\(^{3+}\) may not assume the symmetry required by the oxygen octahedra, whose bonds to the central ion are assumed to be partially covalent in character and therefore rather rigid. This means that the least energy configuration for the Fe\(^{3+}\) or Mn\(^{3+}\) ion would be slightly displaced from the center, which leads to the Jahn-Teller effect. The Jahn-Teller effect is uncoupled, and changes the nature of the short range forces in the crystal.
V. BIBLIOGRAPHY


5. Burfoot op. cit., p. 82. (1967).


VITA

The author was born in Boston, Massachusetts on April 24, 1944. He received his primary education in St. Louis, Missouri and Hudson, New Hampshire. He graduated Salutatorian from Alvirne High School in Hudson, New Hampshire. He received a Bachelor of Arts degree in physics from Dartmouth College in June, 1966. He was a National Science Foundation Undergraduate Research Participant for three summers and one school year at Dartmouth College.

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