Scholars' Mine

Masters Theses   Student Theses and Dissertations

1968

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

Harris C. Jones

Follow this and additional works at: https://scholarsmine.mst.edu/masters_theses

Part of the Physics Commons

Department:

Recommended Citation

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

BY

HARRIS C. JONES, 1944

_____

A

THESIS

submitted to the faculty of

THE UNIVERSITY OF MISSOURI AT ROLLA

in partial fulfillment of the requirements for the

Degree of

MASTER OF SCIENCE IN PHYSICS

Rolla, Missouri

1968

_____

Approved by

_____ (advisor) _____

_____

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% $BiFeO_3$ – 10% $PbTiO_3$ 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% $BiMnO_3$ – 60% $PbTiO_3$. 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

The author wishes to express his appreciation to Dr. R. Gerson for suggesting the problem and for his advice during the preparation of this thesis. He would also like to thank Mr. James Canner and Dr. J. Rivers for many helpful discussions and Mrs. Roberta Lamar for preparing the samples.

The financial assistance of the Atomic Energy Commission (project AT(11-1)1368) in the form of a research assistantship is gratefully acknowledged.

Finally, the author wishes to thank his wife, Jeannine, for her help in the preparation and typing of this thesis.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

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 ($850^{\circ}C$), 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.
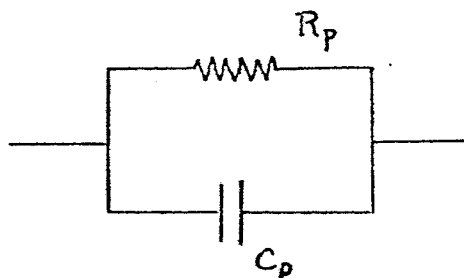
An excellent and straightforward method of measuring the dielectric constant at high frequencies (lower loss tangent) is to use a

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 minumum 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 ($400^\circ C$-$425^\circ C$).

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 $BiFeO_3$. This was done by extrapolating the Curie point of various solid solutions of $BiFeO_3-PbTiO_3$ to the case of 100% $BiFeO_3$.

There are necessary and sufficent 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 accoustical 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,

$$\epsilon = \frac{C}{T - T_c} \quad .$$

(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 M-K-S units the local field can be written

$$E_{LOCAL} = E_{APPLIED} + \gamma P,$$

(2)

where γ is purely a microscopic constant, analogous to a structure factor. The local field is not constant at each atomic site, thus γ 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 $\vec{p}$ be the dipole moment at the atom, $p = \alpha E$. Then:

$$P_{total} = \sum_i N_i \alpha_i E_{i\,LOCAL}$$
$$= \sum_i N_i \alpha_i [E + \gamma_i P_i]$$
$$= \sum_i N_i \alpha_i \left[1 + \frac{\gamma_i P_i}{E}\right] E,$$

(3)

Assume: $\sum_i \gamma_i \cdot P_i = \gamma P_{tot}$,

$$\frac{P_{tot}}{E} = \sum N_i \alpha_i \left(1 + \frac{\gamma P_{tot}}{E}\right)$$

(4)

$$= \frac{\sum N_i \alpha_i}{1 - \gamma \sum N_i \alpha_i}$$

Now the dielectric constant ϵ is defined

$$\epsilon = \frac{D}{E} = \frac{\epsilon_0 E + P}{E} = \epsilon_0 + \frac{P}{E} .$$

(5)

Substitution from equation (4)

$$\epsilon - \epsilon_0 = \epsilon \frac{\sum N_i \alpha_i}{1 - \gamma \sum N_i \alpha_i}$$

(6)

The dielectric constant becomes indeterminate as $\gamma \sum N_i \alpha_i$ approaches unity. Since $\epsilon = D/E$, 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 α_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

$$\gamma \sum N_i \alpha_i \approx 1 - C(T - T_c) .$$

(7)

Then

$$\epsilon - \epsilon_o = \frac{1}{\gamma} \left[\frac{1 - C(T - T_c)}{1 - 1 + C(T - T_c)} \right]$$

$$= \frac{1 - C(T - T_c)}{\gamma C(T - T_c)} \quad . \tag{8}$$

(2) THE DISSIPATION FACTOR

Suppose the applied field is periodic

$$E_{APPLIED} = E_o \cos(\omega t) \quad . \tag{9}$$

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 :

$$D = D_o \cos(\omega t - \delta)$$

$$= D_o \cos(\omega t) \cos(\delta) + D_o \sin(\omega t) \sin(\delta) . \tag{10}$$

Therefore: :

$$D = D_1 \cos(\omega t) + D_2 \sin(\omega t) \quad . \tag{11}$$

For homogeneous, isotropic samples

$$D = \epsilon_o (1 + \chi_E) E = K_E \epsilon_o E \quad . \tag{12}$$

One can introduce the relationships

$$D_1 = K_1(\omega)\,\epsilon_o\,E_o \quad , \quad D_2 = K_2(\omega)\,\epsilon_o\,E_o \qquad (13)$$

$$\frac{D_2}{D_1} = \frac{D_o\,\sin(\delta)}{D_o\,\cos(\delta)} = \frac{K_2(\omega)}{K_1(\omega)} = \tan\delta \; . \qquad (14)$$

$\text{Tan}\,\delta$ 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

$$V_{kk'} = Q_k\,Q_{k'}\,f(D_{kk'}) \; , \qquad (15)$$

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

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

$$= Q_k\,Q_{k'}\,f\left(D_{kk'}\left(1 + \frac{u_k - u_{k'}}{D_{kk'}}\right)\right) \qquad (16)$$

$$= Q_k\,Q_{k'}\,f_{kk'}\left(1 + \frac{u_k - u_{k'}}{D_{kk'}}\right)$$

Expanding this in a Taylor's series:

$$V\left(1 + \frac{u_K - u_{K'}}{D_{KK'}}\right) = Q_K Q_{K'} f_{KK'}^{(1)} + \frac{u_K - u_{K'}}{D_{KK'}} Q_K Q_{K'} f_{KK'}^{'(1)}$$

$$+ \left(\frac{u_K - u_{K'}}{D_{KK'}}\right)^2 Q_K Q_{K'} f_{KK'}^{''(1)} \ldots \ldots \quad (17)$$

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

$$F_{KK'} = C_{KK'} \frac{Q_K Q_{K'}}{D_{KK'}} (u_K - u_{K'}) , \quad (18)$$

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 $BiFeO_3$ and $BiMnO_3$. 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:

$$E = \frac{1}{2} m \dot{r}^2 + \frac{L^2}{2m r^2} - \frac{Q Q'}{r} . \quad (19)$$

The shell-core interaction is thus of the same form as the ion-ion interaction

$$F = C \frac{Q_c Q_s}{V_c} (u_c - u_s) .$$ (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

$$u_K = C_K e^{-i \omega t + i K k a} .$$

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:
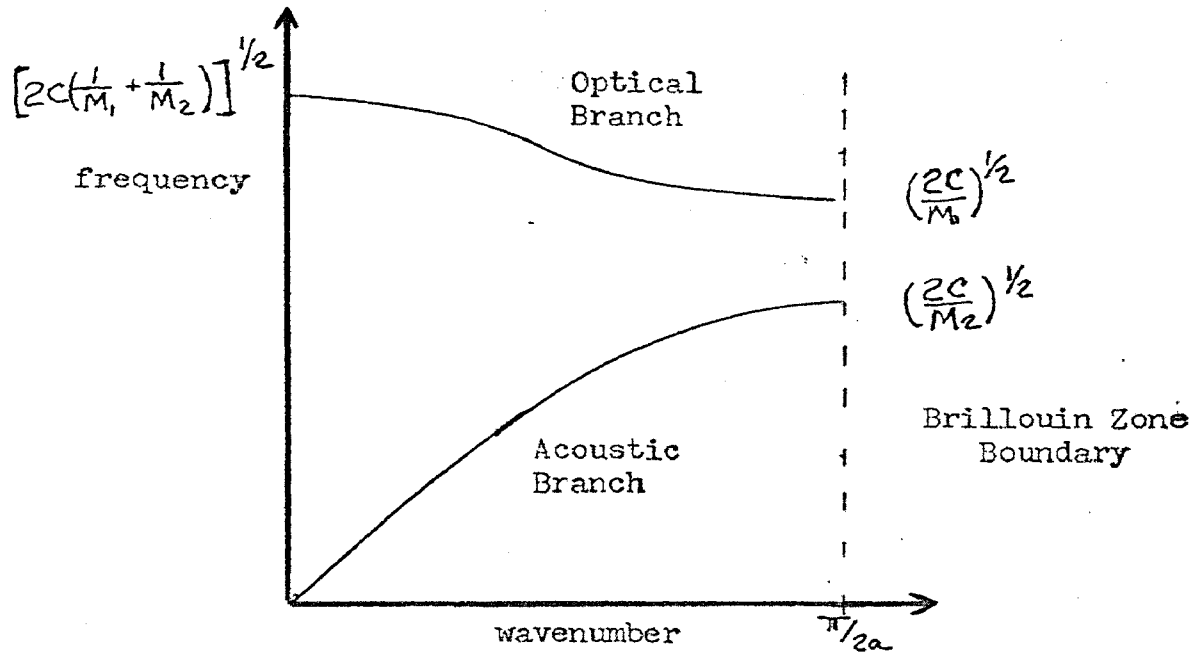
$$F_K = M_1 \frac{d^2 u_K}{dt^2} = C(u_{K+1} + u_{K-1} - 2u_K)$$ (22)

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

These may be solved simultaneously:

$$\omega^2 = C\left(\frac{1}{M_1} + \frac{1}{M_2}\right) \pm C\left[\left(\frac{1}{M_1} + \frac{1}{M_2}\right)^2 - \frac{4 \sin^2(k a)}{M_1 M_2}\right]^{1/2} .$$ (23)

Figure 1

$$\left[2c\left(\tfrac{1}{M_1}+\tfrac{1}{M_2}\right)\right]^{1/2}$$

frequency

Optical
Branch

$\left(\tfrac{2c}{M_b}\right)^{1/2}$

$\left(\tfrac{2c}{M_2}\right)^{1/2}$

Brillouin Zone
Boundary

Acoustic
Branch

wavenumber $\pi/2a$

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

frequency

Optical
Branch

Brillouin Zone
Boundary

Acoustic
Branch

wavenumber $\pi/2a$
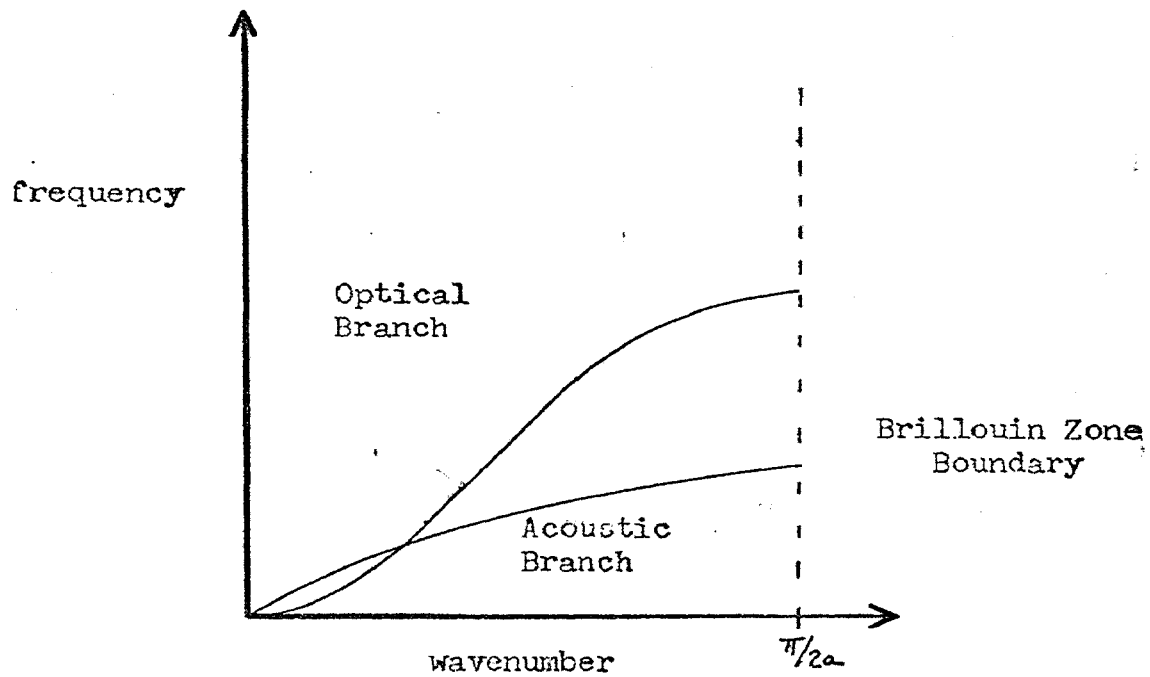
(b) Transverse phonons when the long and short
range forces cancel. (from Cochran)

The roots are, for $K \to 0$, $K = \frac{1}{\lambda}$:

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

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

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 $P_o(\vec{r})$ is a density function representing the full symmetry of the crystal in the point group $G_o(\vec{r})$ then $P_o(\vec{r})$ is an invariant. If the transition to another point group $G(\vec{r})$ lowers the symmetry, then $P(r) = P_o(r) - \Delta P(r)$. $P(r)$ is a subgroup of $P_o(r)$ and therefore cannot have symmetry operations not in $P_o(r)$.

The second condition is that $\Delta P(r)$ is an irreducible

representation leaving $P_o(r)$ 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]

$$\phi(x) = \phi_o + \alpha x^2 + \beta x^4 + \gamma' x^6 + \dots \quad (24)$$

Goldrich and Berman [15] imploy 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_o. It is invariant under inner
products of the type $\langle \phi/\theta \rangle$. One assumes that G_1 is a subgroup of
G_o and G_1' is a subgroup of G_1. In other words, G_1 can contain
only symmetry operations that G_o contains. If it contains all the
symmetry operations it is a trivial subgroup (just the group G_o).
G_1' can contain only symmetry operations in G_1. If a density
function $P(1)$ 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_o to G_1 to G_1', where G_o 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_o 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

$$G = G_0 + \frac{1}{2}\alpha\left(P_x^2 + P_y^2 + P_z^2\right)$$
$$+ \frac{1}{2}\beta\left(P_x^4 + P_y^4 + P_z^4\right) \tag{25}$$
$$+ \frac{1}{4}\gamma\left(P_x^2 P_y^2 + P_y^2 P_z^2 + P_z^2 P_x^2\right) + \ldots$$

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

$$G = G_0 + \frac{1}{2}\alpha P^2 + \frac{1}{4}\gamma P^4 + \frac{1}{6}\delta P^6 + \ldots \tag{26}$$

It is assumed that α and δ are always positive, while γ may be positive or negative. If γ is negative the transition is first order, and if it is positive it is second order.[19] The electric field is given by

$$E = \frac{\partial G}{\partial P} = \alpha P + \gamma P^3 + \delta P^5 + \ldots \tag{27}$$

If this is equated to zero, then the spontaneous polarization is [20]

$$P_s = \mp \left\{ -\frac{\gamma}{2S} \left[\left(1 - \frac{4S\alpha}{\gamma^2}\right)^{1/2} + 1 \right] \right\}^{1/2}, \quad \gamma < 0 ;$$

$$P_s = \mp \left\{ \frac{\gamma}{2S} \left[\left(1 - \frac{4S\alpha}{\gamma^2}\right)^{1/2} - 1 \right] \right\}^{1/2}, \quad \gamma > 0 .$$

The Gibbs free energy is not as simple a function as it at first seems. The Gibbs free energy, or the potential ϕ 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: $G \rightarrow G(x, \chi, E, P, H, M)$. 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 $\hat{a}$, $\hat{b}$, $\hat{c}$ in the cubic crystal. In general, the crystal cannot be anistropic. Following the paper by G.A. Smolenskii [22] the expansion of Gibbs energy is

$$G(M,P) = G_0 + \alpha P^2 + \frac{\beta}{2} P^4 - PE$$
$$+ \alpha' M^2 + \frac{\beta'}{2} M^4 - MH + \gamma P^2 M^2 . \tag{28}$$

The solution is at an extremum (equilibrium condition) when

$$\left(\frac{\partial G}{\partial P}\right)_M = 0, \quad \left(\frac{\partial G}{\partial M}\right)_P = 0 . \tag{29}$$

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

$$\frac{\partial^2 G}{\partial P^2} > 0, \quad \frac{\partial^2 G}{\partial M^2} > 0, \quad \begin{vmatrix} \dfrac{\partial^2 G}{\partial P^2} & \dfrac{\partial^2 G}{\partial P \partial M} \\ \dfrac{\partial^2 G}{\partial P \partial M} & \dfrac{\partial^2 G}{\partial M^2} \end{vmatrix} > 0 . \tag{30}$$

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

$$\left[\alpha + \beta P^2 + \gamma M^2 \right] P = 0, \tag{31}$$

$$\left[\alpha' + \beta' M^2 + \gamma P^2 \right] M = 0 .$$

If the trivial solutions $P = O$, $M = O$ are ignored, these equations may be solved

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

$$M^2 = \frac{-\alpha' - \delta' P^2}{\beta'}.$$

(32)

There are three regions of interest, namely

$$T < \Theta_M < \Theta_c, \quad \Theta_M < T < \Theta_c, \quad \Theta_M < \Theta_c < T.$$

(Smolenskii assumes that $\Theta_c < \Theta_M$ but this is not the case with $BiFeO_3$)

For $\Theta_M < T < \Theta_c$, $M = O$, $P \neq O$:

$$G = G_o + \alpha P^2 + \frac{\beta^2}{2} P^4 + \cdots,$$

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

$$P^2 = \frac{-\alpha}{\beta}.$$

(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, $BaTiO_3$. Barium titanate has the cubic perovskite structure above the Curie point (120°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.

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

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 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 Cation

B Cation

Oxygen Anion
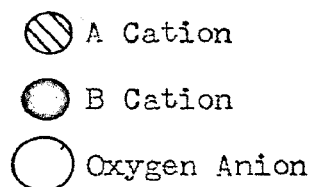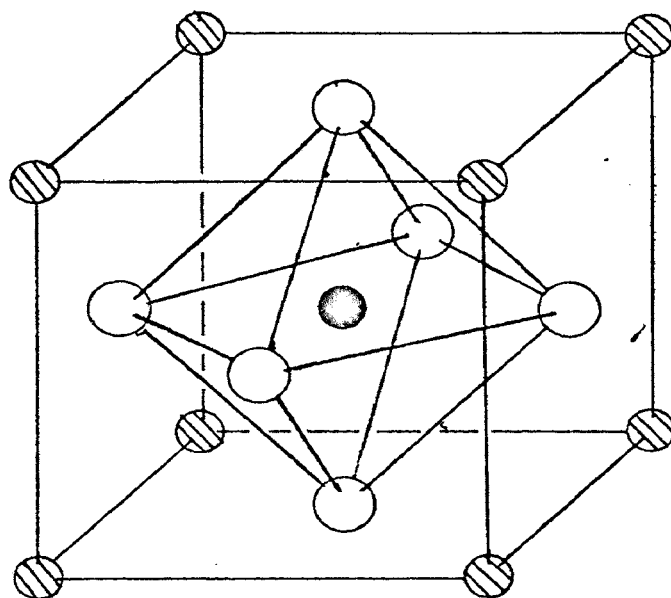
(a)   B Cation at Body Center Site
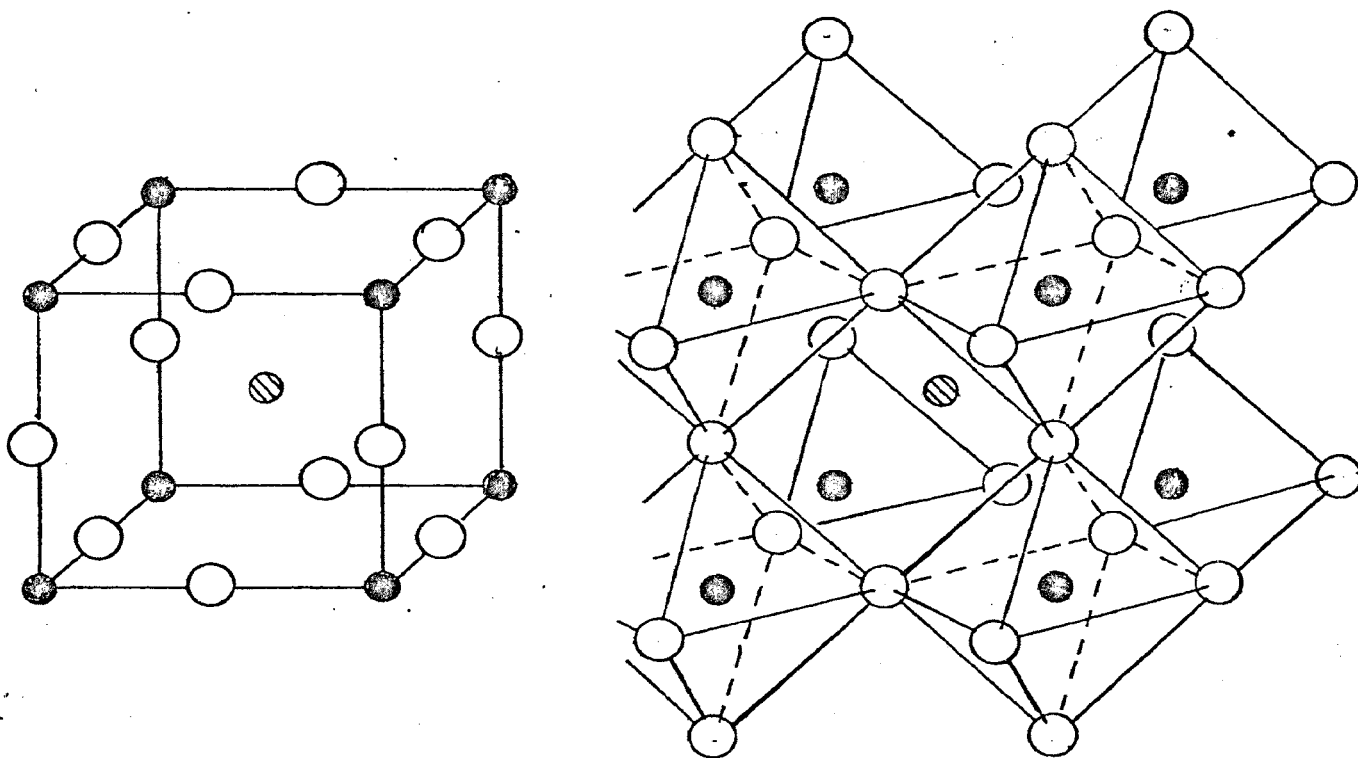
(b)   A Cation at Body Center Site

III. APPARATUS

The apparatus for the high frequency dielectric measurements is basically the same as that described by R.T. Smith.[24] 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 $\pm 3db$ points of the sample with the positions and $\pm 3db$ 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 primarly 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 .089 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 MV-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.
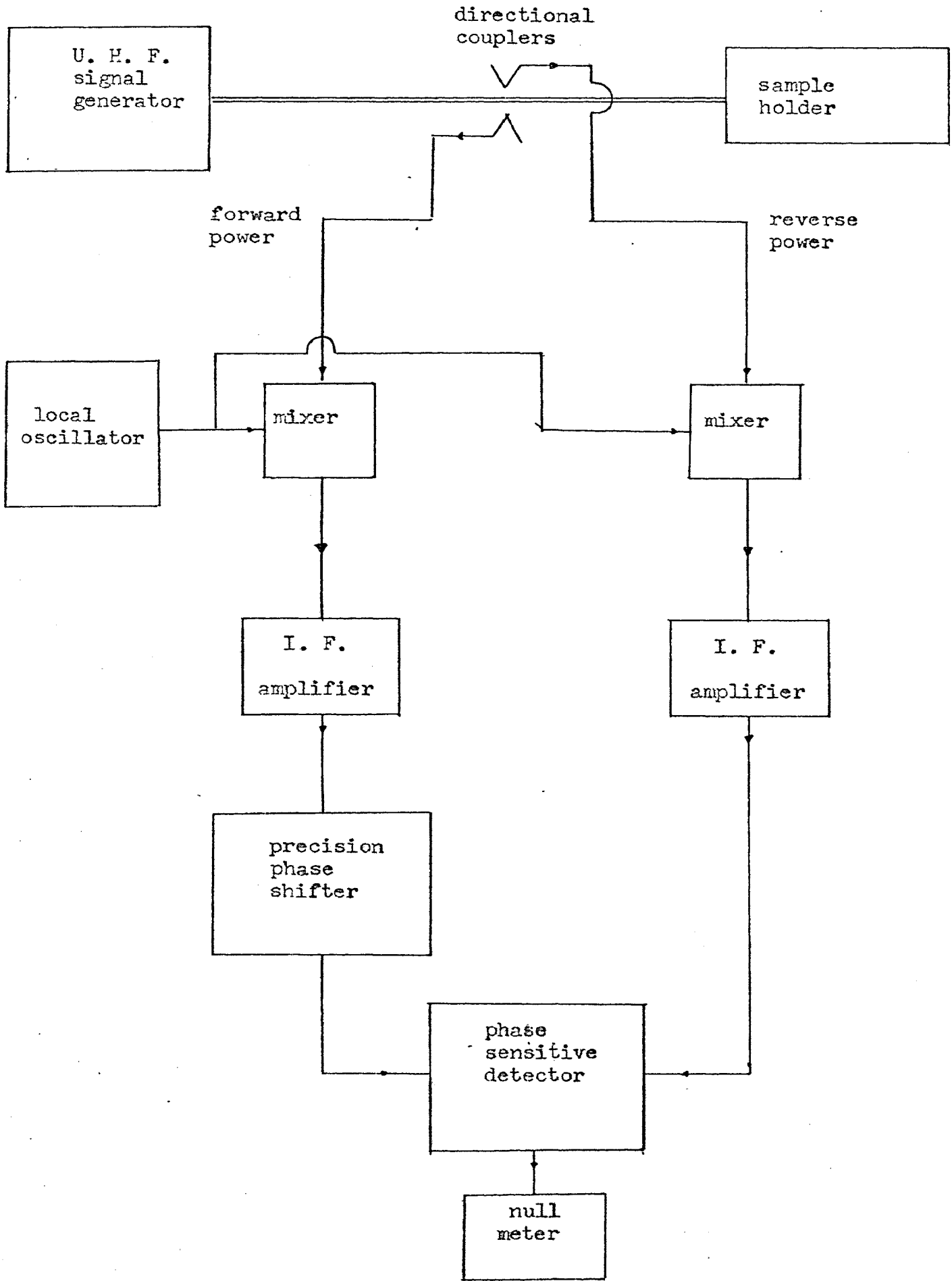
Block diagrams of the slotted line circuit and the phase comparison circuit are shown in figures 4 and 5.

Figure 3

Block Diagram of Slotted Line Apparatus

Figure 4

24
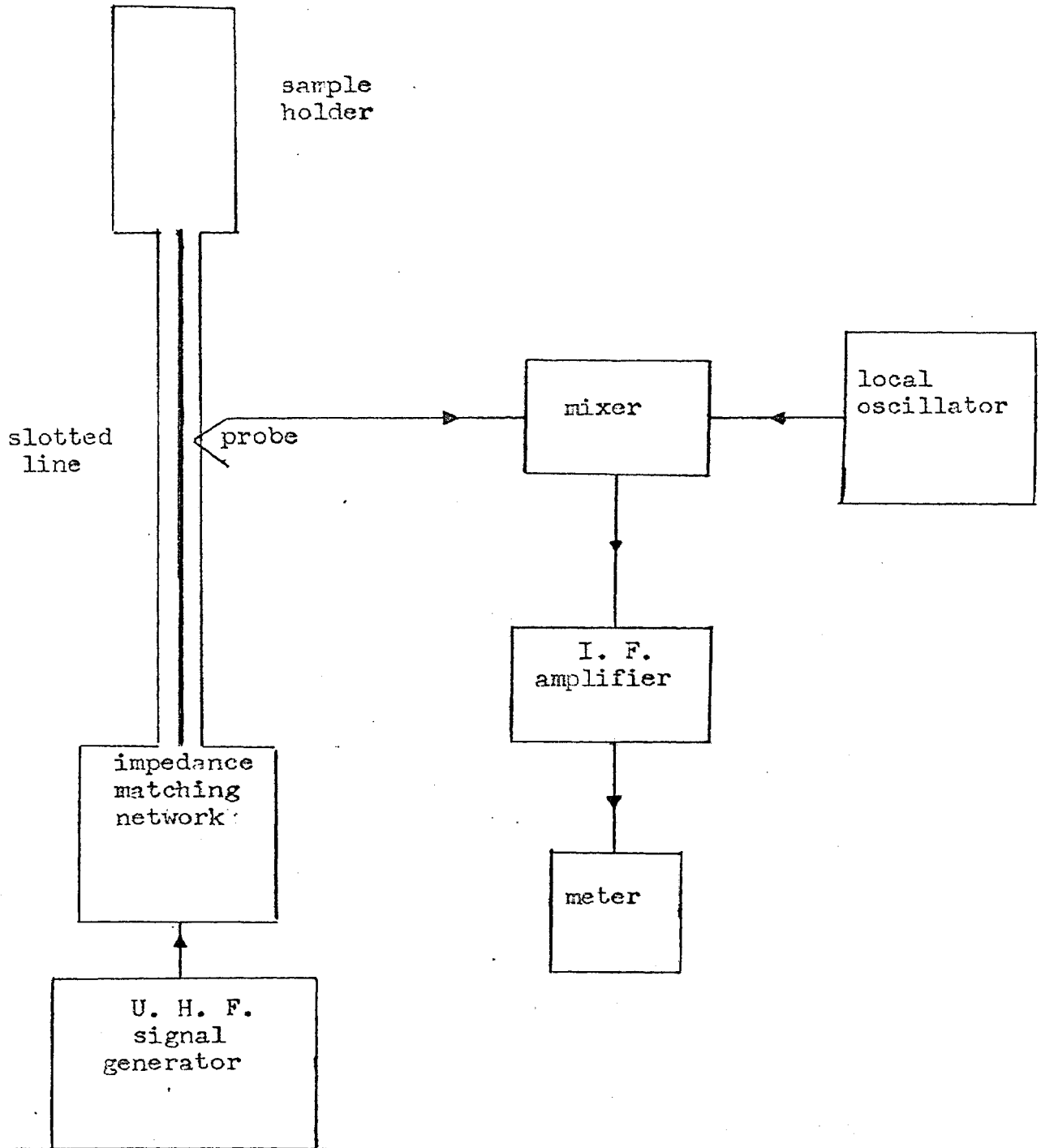
Block Diagram of Proposed Phase Comparison Apparatus

IV. EXPERIMENTAL RESULTS AND CONCLUSIONS

A. $BiFeO_3-PbTiO_3$

Measurements on the $BiFeO_3-PbTiO_3$ 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% $BiFeO_3$ 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 Fe^{3+} ion (see figure 6).

B. $BiMnO_3-PbTiO_3$

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% $BiMnO_3-$ 60% $PbTiO_3$. 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% $PbTiO_3$

$\triangle$ New Sample (after Smith)
O Aged Sample

Figure 6
Relative Dielectric Constant
New Sample and Aged Sample
90% BiFeO$_3$–10% PbTiO$_3$

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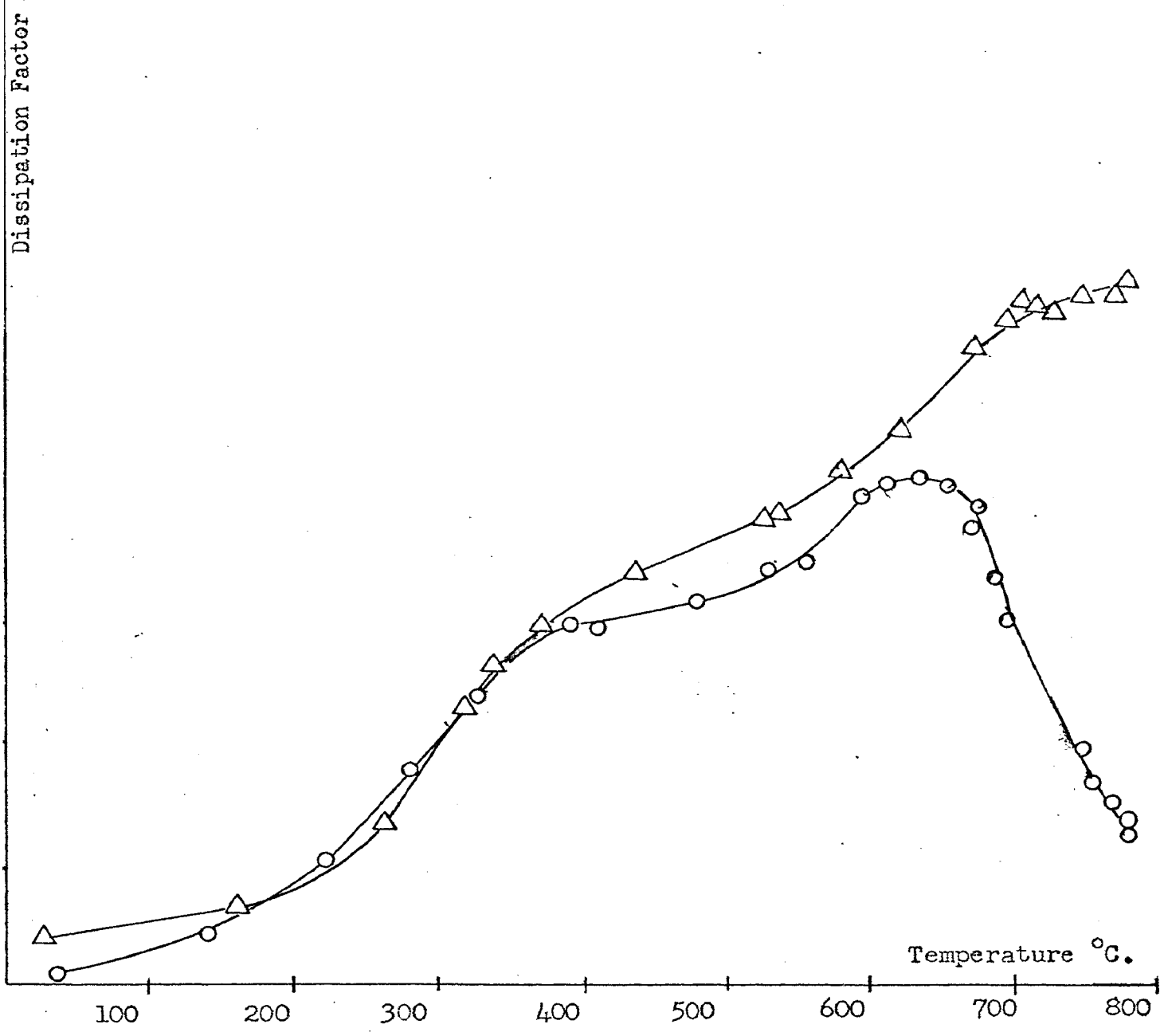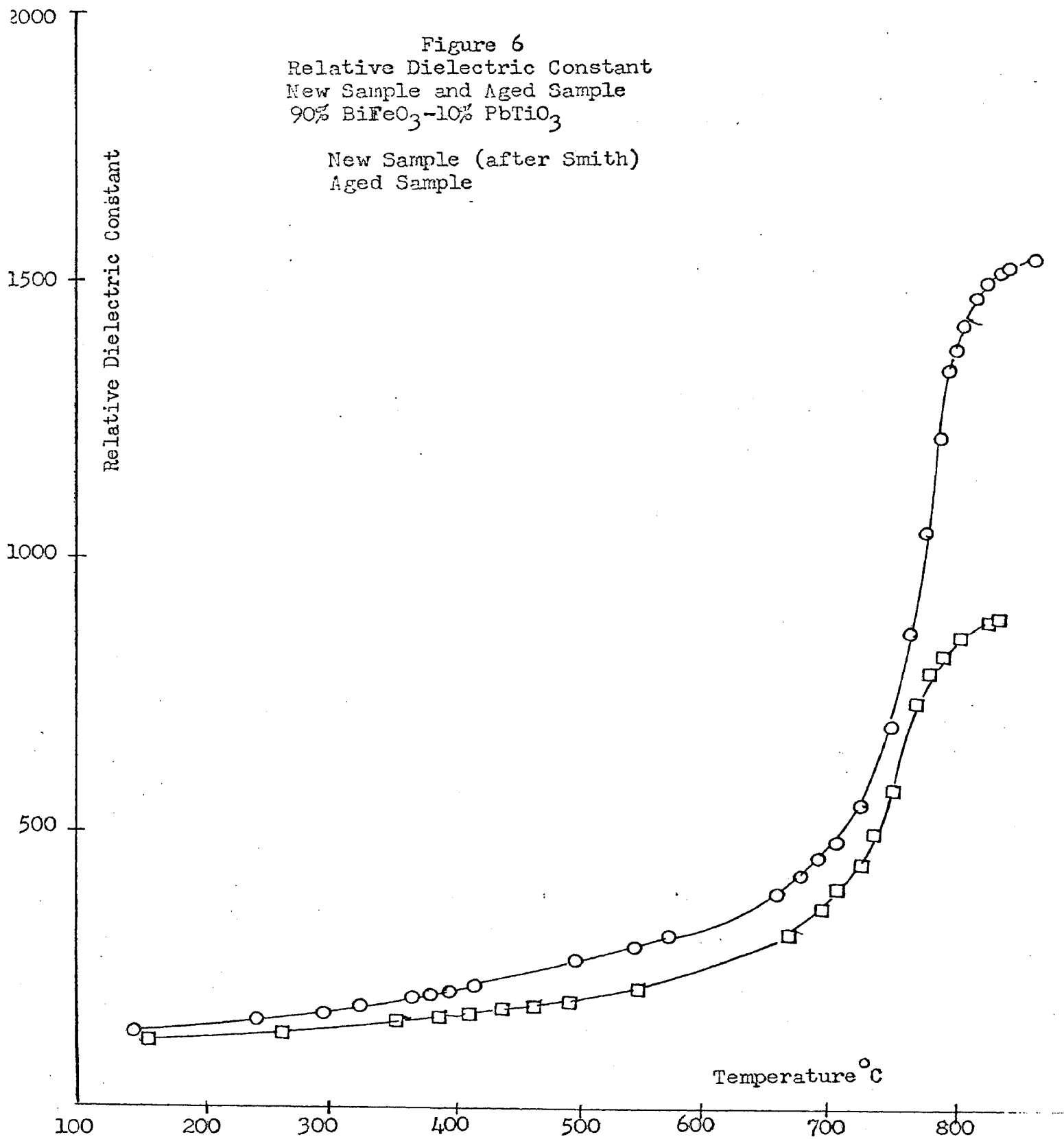
primarily N-type. The sample showed no anomalies near or above the transition temperature. The contacts are ohmic, even when a pointed 5 mil tungsten wire is used as a contact. Graphs of resistance as a function of temperature and applied voltage are shown in figures 7, 8, and 9.

The $BiMnO_3$-$PbTiO_3$ binary system is described in a paper by Bokov et al.[27] According to them, in the region from 55%-100% $PbTiO_3$ the system is tetragonal below the Curie temperature, isomorphic with pure $PbTiO_3$. In the region of 35%-55% the system is cubic and in the region from 15%-35% $PbTiO_3$, the system is orthorhombic.

They were unable to make single phase solutions with compositions above 85% $BiMnO_3$. In the samples prepared at the UMR Materials Research Center, it was found that the contaminant is $Bi_2Mn_4O_{10}$. 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 $BiMnO_3$, by comparison with other phase diagrams of perovskites. Secondly, $BiMnO_3$ may have a very high transition temperature, in the region of 900°C, higher than the transition temperature of $BiFeO_3$. 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 $BiMnO_3$. Both Bokov et al.[28] and Sugawara et al.[29] agree that the distance between the manganese

40% BiMnO$_3$ – 60% PbTiO$_3$
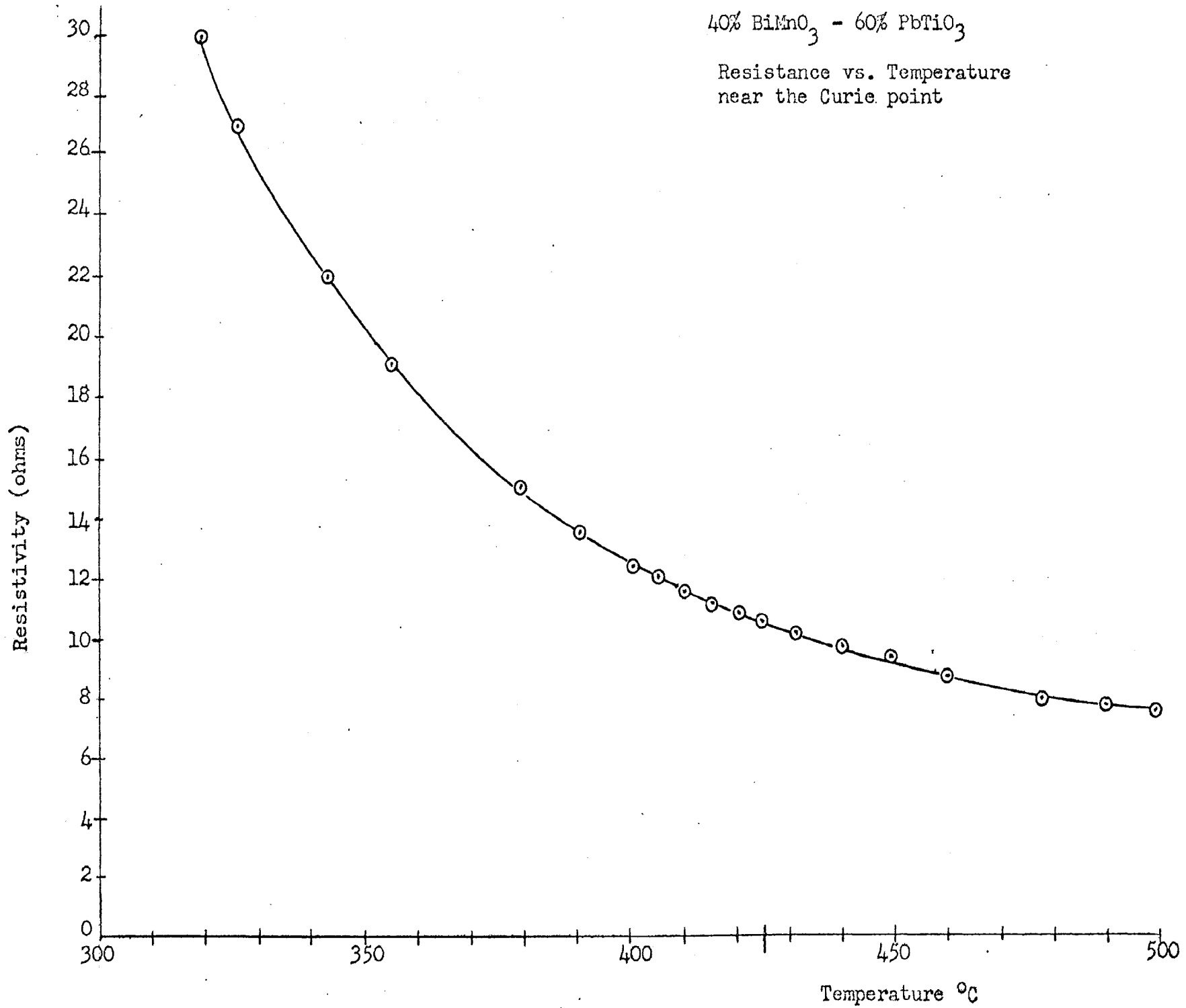
Resistance vs. Temperature
near the Curie point

Figure 7

Figure 8
RESISTANCE AS A FUNCTION
OF RECIPROCAL TEMPERATURE
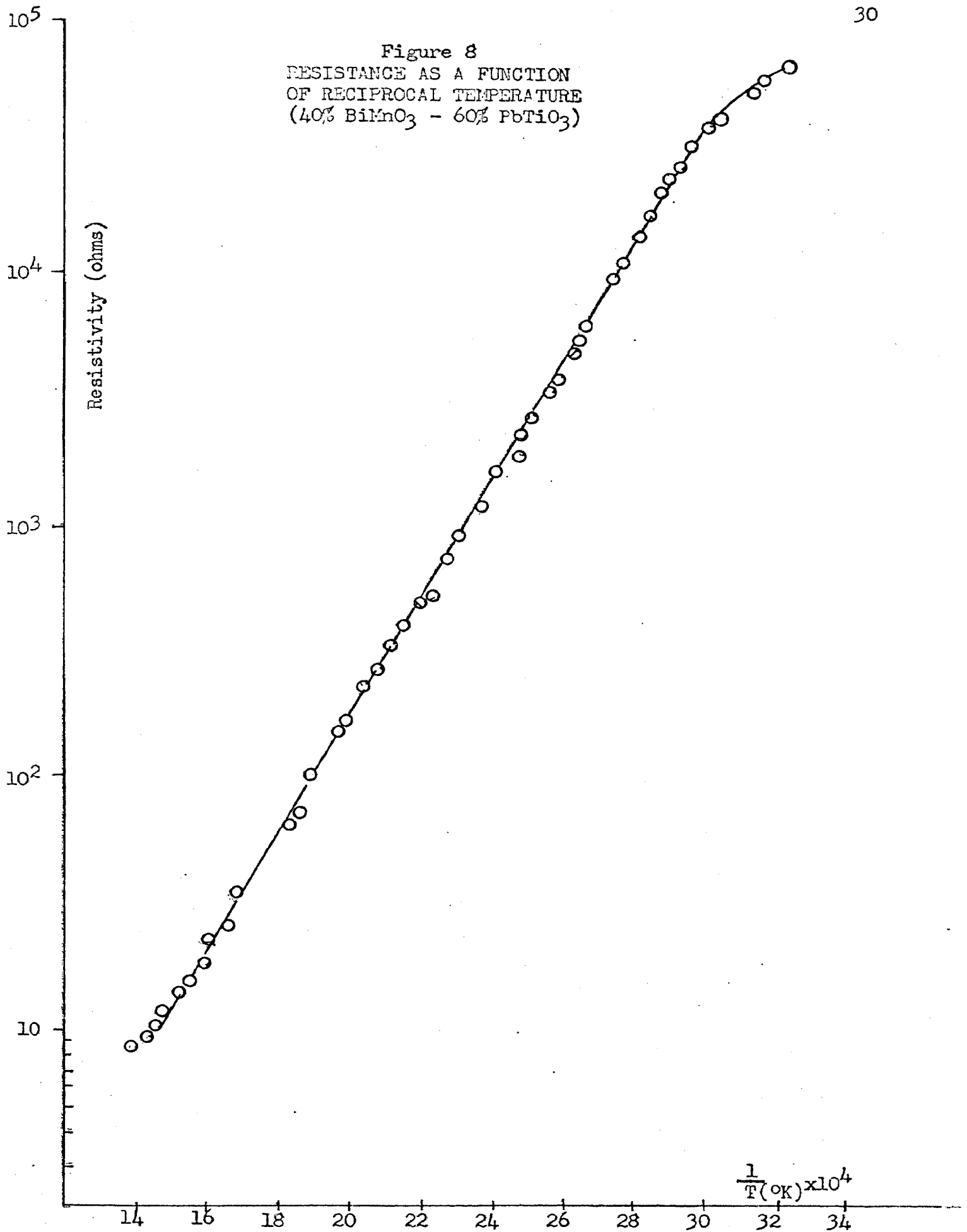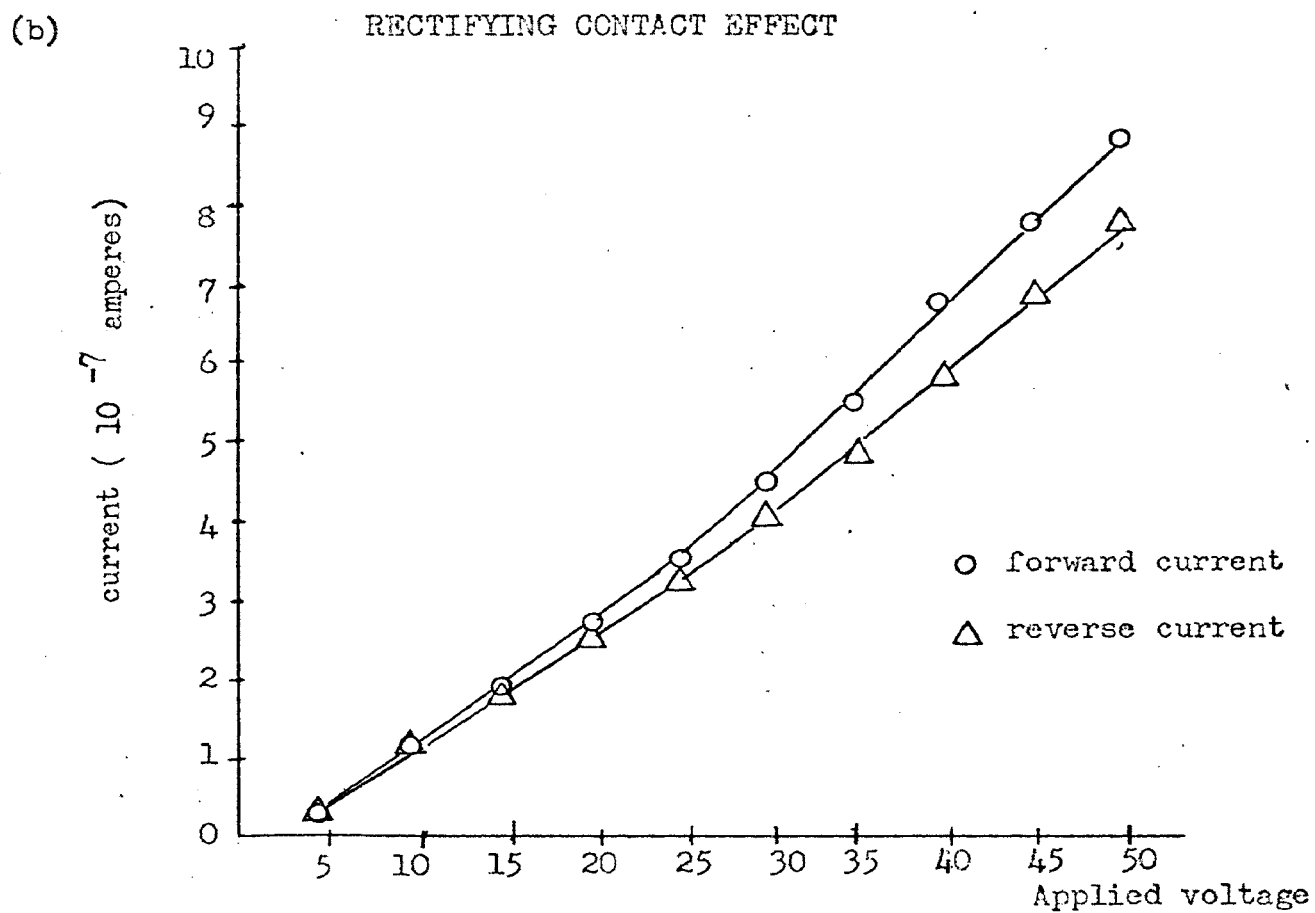$(40\% \; BiMnO_3 - 60\% \; PbTiO_3)$

Figure 9

(a)

CONDUCTIVITY AT ROOM TEMPERATURE

(b)

RECTIFYING CONTACT EFFECT

Figure 10

a)

PHASE DIAGRAM OF $BiMnO_3$-$PbTiO_3$
(After Bokov)
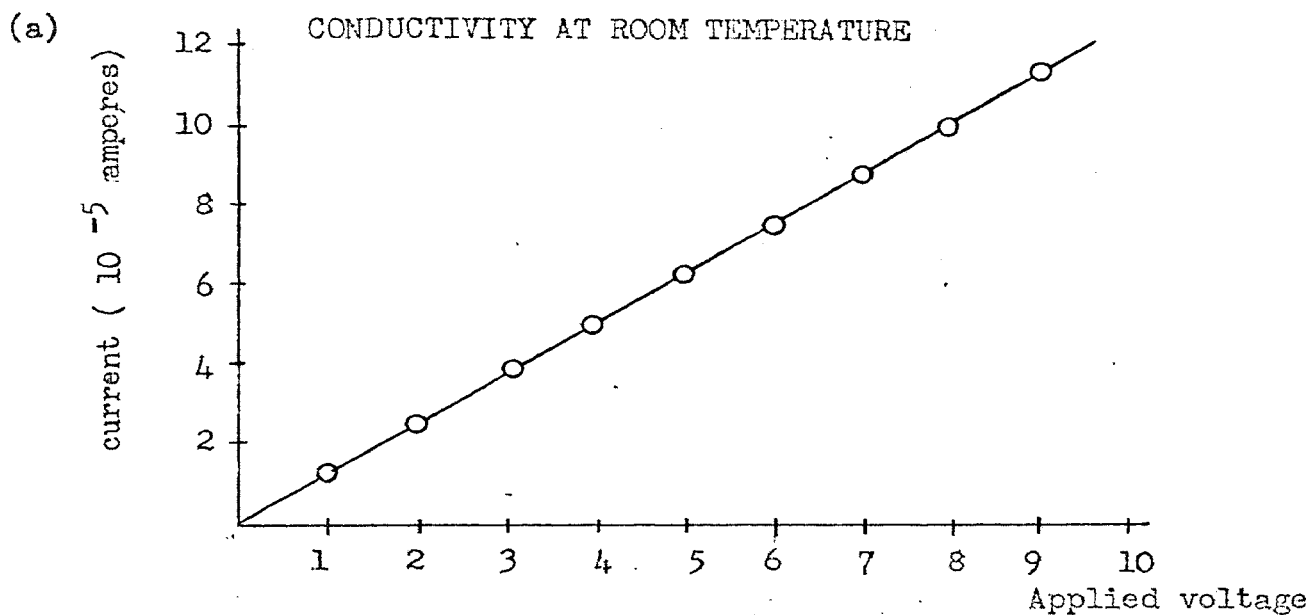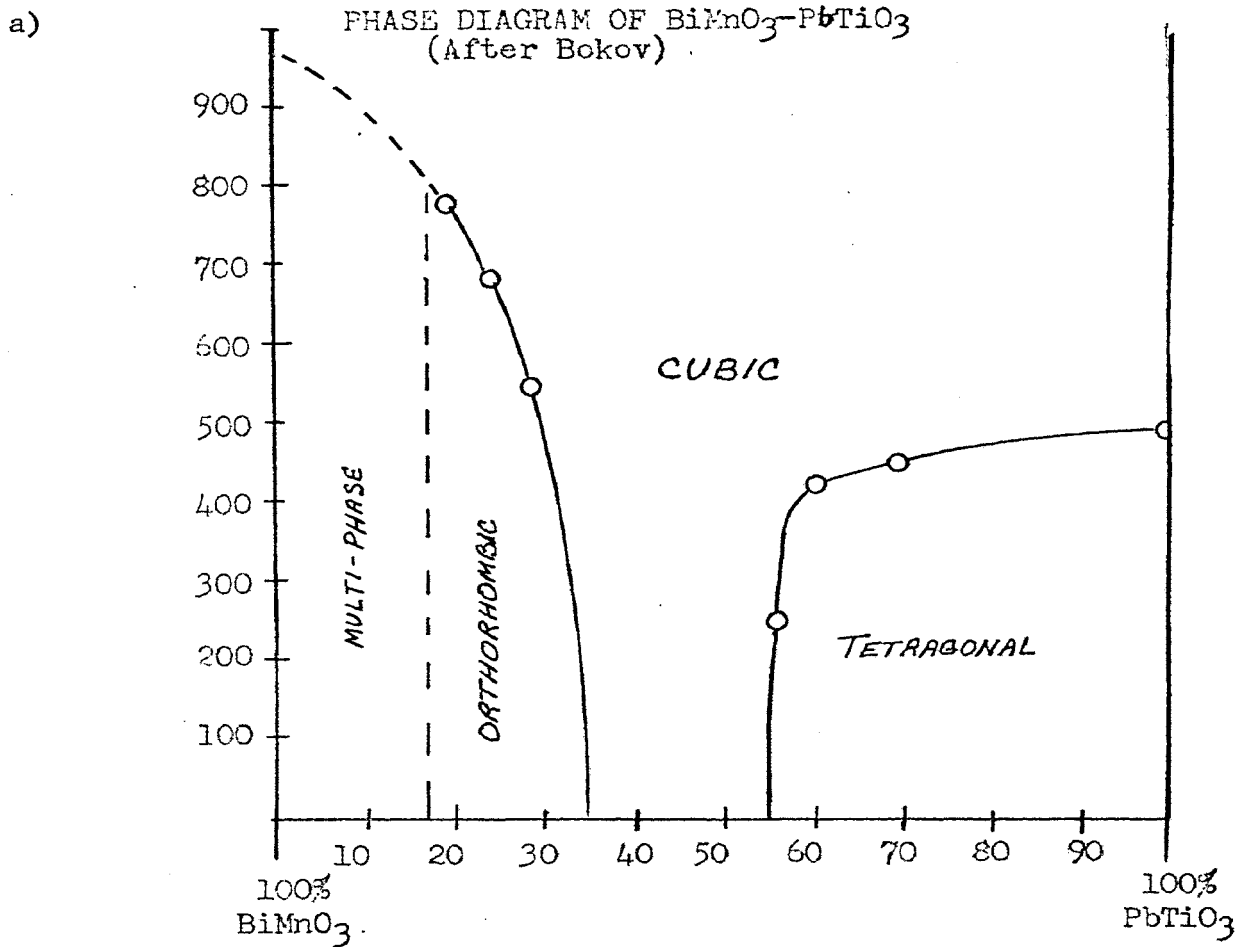
b)   Pure $BiMnO_3$ lattice parameters

Sugawara et al. (triclinic)	Bokov et al. (triclinic)	Bokov et al, (monoclinic*)
$a = c = 3.93Å$	$a = c = 7.86Å$	$A = 10.93Å$
$b = 3.98Å$	$b = 7.98Å$	$B = 11.31Å$
$\alpha = \gamma = 91°25'$	$\alpha = \delta = 91°40'$	$C = 7.98Å$
$\beta = 90°55'$	$\beta = 90°58'$	$\beta' = 92°24'$

* Not necessarily in agreement with triclinic data.

ions is 3.93Å in the $\hat{a}$ direction and 3.98Å 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_2O_3 form and not single phase. Bokov 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_2^3, C_2^3, C_5^3. Two of these are non-centrosymmetric and one is centrosymmetric.

C. THE JAHN-TELLER EFFECT

The Jahn-Taller 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:

$$V(x) = V_0 + Ax^2 + Bx^4 + Cx^6 + \ldots \tag{35}$$

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^{3+} or Mn^{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^{3+} or Mn^{3+} ion would jump between states. At a sufficently high temperature the maximum probability of $\vec{x}$ 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 monotomically decreasing function.

2. The transition temperature should be very high so that $Pr(\vec{x})$ is a maximum at the center of the well.
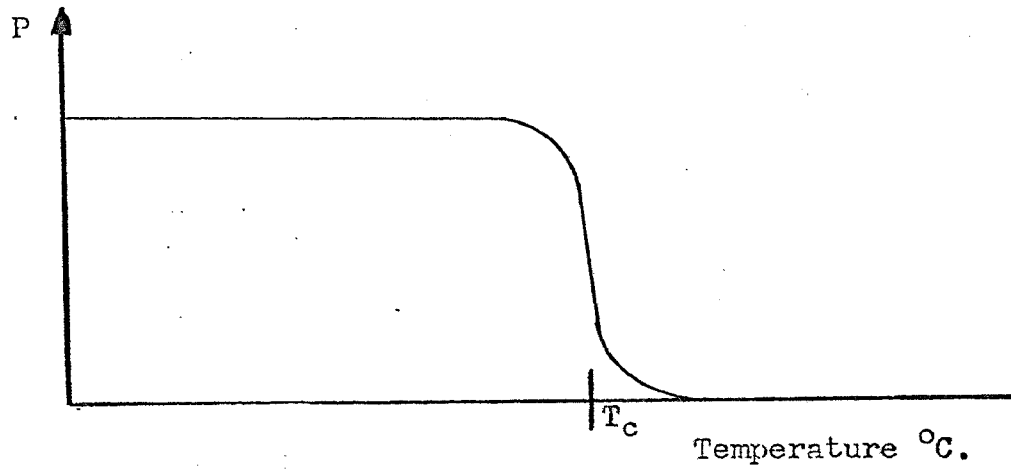
These criteria are fulfilled by solid solutions of $BiFeO_3$. From the data

Figure 11

(a)   The Proposed One-Dimensional Jahn-Teller Potential
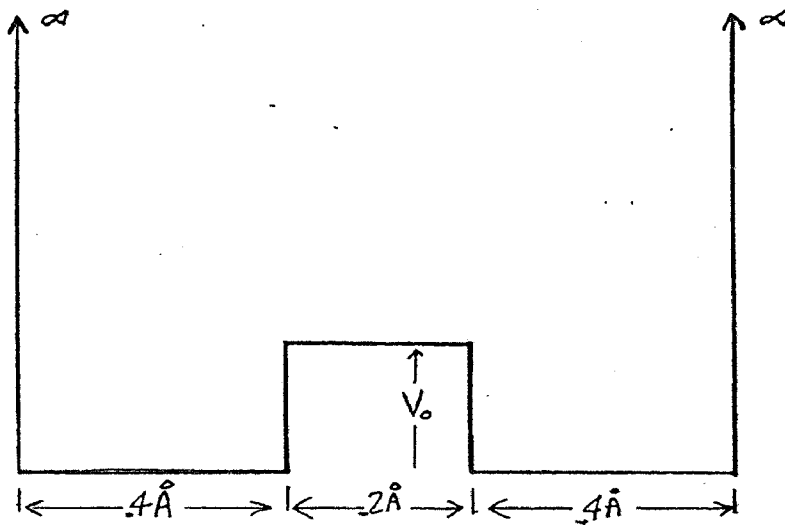
(b)   Polarization From Cochran's Theory

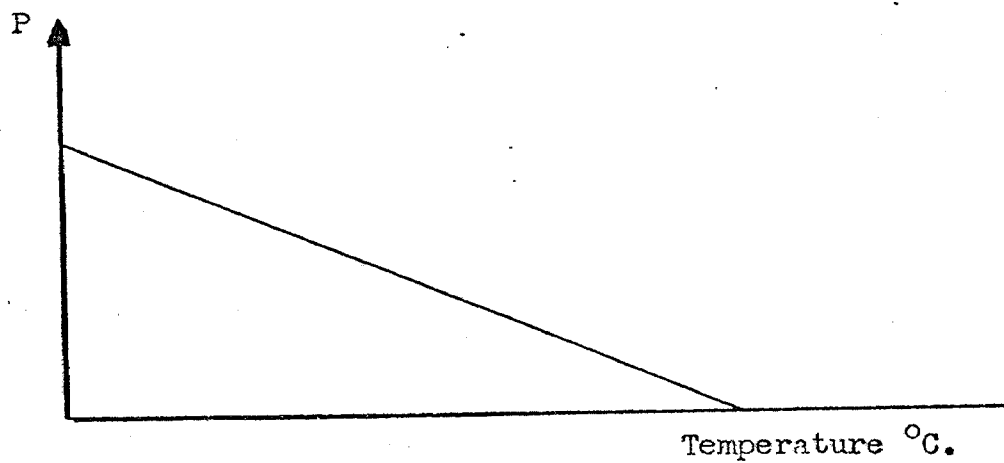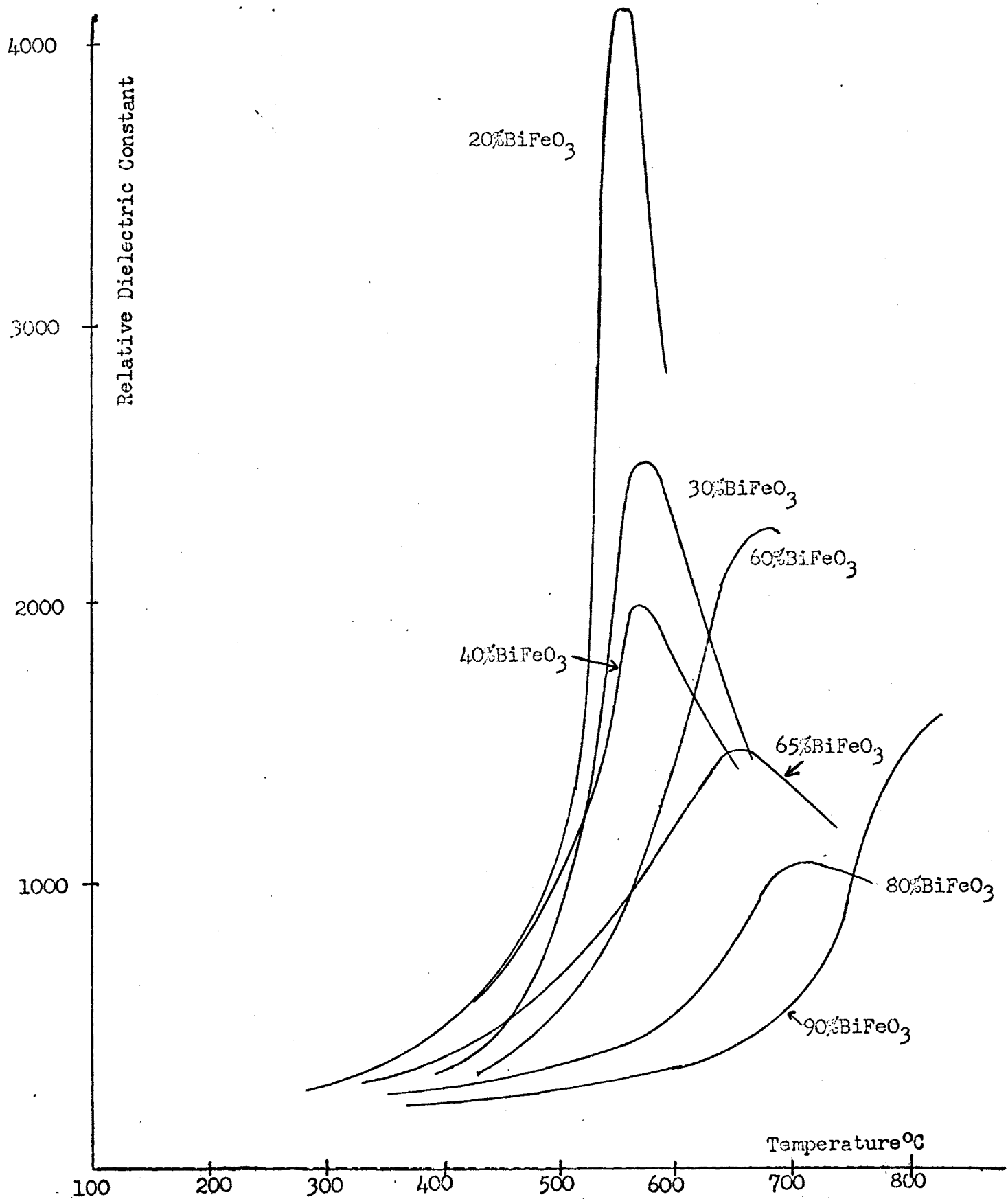(c)   Polarization due to Jahn-Teller effect

Figure 12
BiFeO$_3$-PbTiO$_3$ 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 absorbtion 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 $e^{-\frac{\Theta}{\Theta}}$ where Θ is the Debye temperature.

E.E. 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

1. R.T. Smith, G.D. Achenbach, R. Gerson, and W.J. James, J. Appl. Phys. 39, 70 (1968).

2. Helen D. Megaw, Ferroelectricity in Crystals (Methuen, London, 1957), Chap. 1, pp 1-19.

3. J.C. Burfoot, Ferroelectrics: An Introduction to the Physical Principles (Van Nostrand, London, 1967) Chap. 1, pp 1-12.

4. F. Jona and G. Shirane, Ferroelectric Crystals, (Macmillan, New York, 1962), Chap. 1, pp 1-27.

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

6. E. Fatuzzo and W.J. Merz, Ferroelectricity (John Wiley, New York, 1967) p.185.

7. J.C. Slater, Phys. Rev. 78, 748 (1950).

8. H. Frohlich, Theory of Dielectrics (Oxford, London, 1949).

9. W. Cochran, Advances in Phys. 9, p. 387 (1960).

10. Cochran, op. cit., p. 389 (1960).

11. C. Kittel, Introduction to Solid State Physics (John Wiley, New York, 1966) 2nd. Ed. p. 149.

12. Fatuzzo and Merz, op. cit., p. 160 (1967).

13. C. Haas, Phys. Rev. 140, p. A863 (1965).

14. K.P. Bekov, Magnetic Transitions (Consultants Bureau, New York, 1959) Chap. 1.

15. F.E. Goldrick and J.L. Berman, Phys. Rev. 167, p. 528 (1968).

16. A.F. Devonshire, Phil. Mag. 40, p. 1040 (1949).

17. A.F. Devonshire, Phil Mag. 42, p. 1065 (1951).

18. A.F. Devonshire, Advances in Phys. 3, p. 85 (1954).

19. Kittel, op. cit. pp. 409-410 (1960).

20. Fatuzzo and Merz, op. cit., pp 109 and 137 (1967).

21. Jona and Shirane, op. cit., pp 15-22 (1962).

22. G.A. Smolenskii, Soviet Phys. - Solid State $\underline{4}$, p. 807 (1962).

23. M. Abramowitz and I. Stegun, Handbook of Mathematical Functions (Dover, New York, 1964) p. 14.

24. R.T. Smith, Unpublished thesis for Doctor of Philosophy in Physics at University of Missouri at Rolla (1967).

25. Smith, op. cit., pp 153-155 (1967).

26. Smith, op. cit., p. 86 (1967).

27. V.A. Bokov, N.A. Grigoryan, and M.F. Bryzhina, Soviet Phys. Solid State $\underline{9}$, p. 262 (1967).

28. V.A. Bokov, I.E. Myl'nikova, S.A. Kishaw, M.F. Bryzhina, and N.A. Grigoryan, Soviet Phys. - Solid State $\underline{7}$, p. 2993 (1966).

29. F. Sugawara and S. Iida, J. Phys. Soc. Japan $\underline{20}$, p. 1529 (1965).

30. R.S. Roth, J. Nat. Bur. Standards $\underline{58}$, p. 75 (1957).

31. Kittel, op. cit., pp. 105-106 (1966).

32. Smith, op. cit., pp 76-88 (1967).

33. Smith, op. cit., pp 109-110 (1967).

34. Burfoot, op. cit., pp 146-147 (1967).

35. E.E. Havinga, Philips Res. Reports $\underline{21}$, p. 49 (1966).

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..

In September 1966 he enrolled in physics at the Graduate School of the University of Missouri at Rolla. From September 1966 to July 1968 he was appointed a research assistant in the Physics Department with funds provided by the Atomic Energy Commission.