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NONLINEAR MICROWAVE DIELECTRIC MATERIALS

RAYTHEON

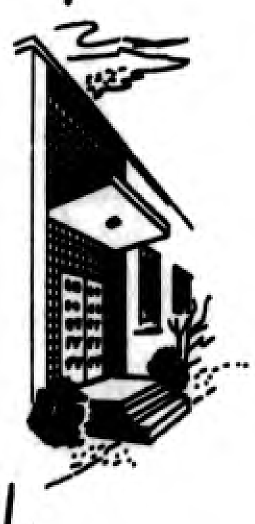
Report No. 9
Contract No. DA 36-039-sc-89126
Order No. 40750 - PM-61-93-93
Continuation of Contract No. DA 36-039-sc-87369

Fifth Quarterly Progress Report

16 September 1962 - 15 December 1962

U.S. Army Electronics Research and Development Laboratory

Fort Monmouth, New Jersey



RESEARCH DIVISION
RAYTHEON COMPANY
WALTHAM 54, MASSACHUSETTS

S-502

NONLINEAR MICROWAVE DIELECTRIC MATERIALS

Report No. 9

Contract No. DA 36-039-sc-89126

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Fifth Quarterly Progress Report

15 September 1962 - 15 December 1962

Object

To conduct research and development investigations to develop nonlinear dielectric materials.

Prepared by

R. O. Bell, B. di Benedetto, P. B. Nutter, J. S. Waugh

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1. PURPOSE

It is the purpose of this work to develop and investigate those materials which exhibit the properties of low loss, low dielectric constant, and high nonlinearity that are required for applications at microwave frequencies.

2. ABSTRACT

The nonlinearity of single crystal $KTaO_3$ has been measured at 108°K and transpires to be comparable with that of $SrTiO_3$. Microwave measurements of dielectric constant and loss tangent for mixed ceramics of the type $K_{1-x}Na_xTaO_3$ have been obtained and show the mixtures to have higher losses than comparable $Ba_{1-x}Sr_xTiO_3$ materials. A fairly marked effect of $SrSnO_3$ substitution in increasing the nonlinearity of $Ba_{0.5}Sr_{0.5}TiO_3$ has been observed with no accompanying increase of loss tangent. Losses in other mixed and doped materials have been measured.

3. PUBLICATIONS AND CONFERENCES

3.1 Publications

P. B. Nutter, "The Status of Ferroelectric and Nonlinear Dielectric Material Investigations," presented to the A.G.E.D. Committee on Conventional Devices in New York, December 11, 1962.

3.2 Conferences

On December 12, 1962 there was a conference at U.S.A.S.R.D.L. Fort Monmouth, New Jersey between Mr. J. Charlton, Mr. C. Neudorfer et alia of the Signal Corps and Dr. P. B. Nutter, Dr. R. Pucel and Mr. M. Harris of Raytheon Company. The work of the contract was discussed together with possible applications of nonlinear dielectrics in specific areas.

4. FACTUAL DATA

4.1 The Nonlinearity of Single Crystal $KTaO_3$

The nonlinearity of single crystal $KTaO_3$ has been measured at S-band frequencies and at a temperature close to 108°K. The measurement technique was the customary one in which a cavity resonance was observed in a suitably electroded slab of the material contained within a coaxial line fed at a convenient fixed S-band frequency. Application of a known field E to the sample lowers the dielectric constant of the sample and so destroys the resonance. The sample temperature may be decreased by an amount ΔT to increase the dielectric constant again and establish the resonance at the original frequency.

The field dependence of the dielectric constant is usually of the form

$$\epsilon(T,E) = \frac{\epsilon(T,O)}{1 + \frac{A}{C}\epsilon^3(T,O)E^2} \quad . \tag{1}$$

If this is so, and if E(T, O) follows the Curie law the experimental data is most conveniently presented as a graph of $(\Delta T)^{\frac{1}{2}}$ vs E. The graph should be a straight line with slope given by

$$\text{Slope} = \epsilon\,(T,O)\ \sqrt{A} \quad . \tag{2}$$

Figure 1 shows the experimental data plotted in this way. The measured slope of the graph is $0.76 \times 10^{-6}\,°C^{\frac{1}{2}}$ V/m. Using dielectric constant data previously reported[1] the nonlinearity coefficient A is found to be $1.53 \times 10^{-18}\,°K m^2/V^2$.

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[1]Section 4.2 in Report No. 8 of this series.

4.2 The Dielectric Constants and Loss Tangents of Mixed $KTaO_3$ and $NaTaO_3$ Ceramics

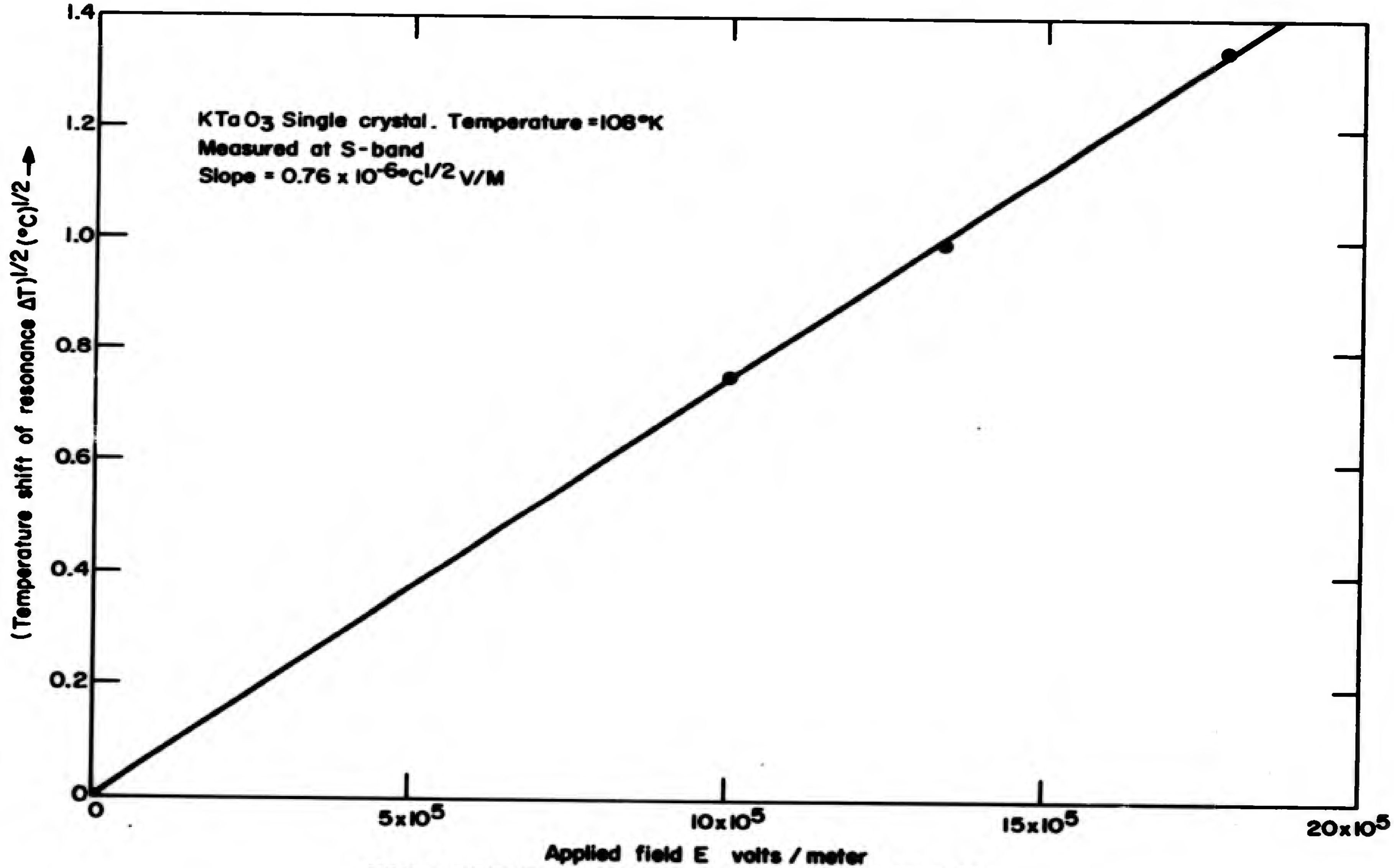
Figure 2 illustrates the temperature dependence of dielectric constant for mixed ceramics of the type $K_{1-x}Na_xTaO_3$. The constitutional parameter x ranges from 0-0.4 and the temperature range 80-180°K is covered. These measurements were obtained by fabricating a parallel plate capacitor from the ceramic and measuring its capacity as a function of temperature with a 10 Kc/s bridge. In order to minimize the effects of defective surface layers, sample thicknesses in excess of 0.010 inch were used for all measurements. Figures 3, 4, and 5 give the results of some microwave measurement of dielectric constant at K-band for the ceramics with x=0, 0.1, and 0.2 respectively. The Curie plots presented in these Figures may be analyzed to give the results shown in Table I.

TABLE I

Material	C	T_c (°K)
$KTaO_3$	4.53×10^4	-16
$K_{0.9}Na_{0.1}TaO_3$	4.83×10^4	-3
$K_{0.8}Na_{0.2}TaO_3$	5.25×10^4	+17

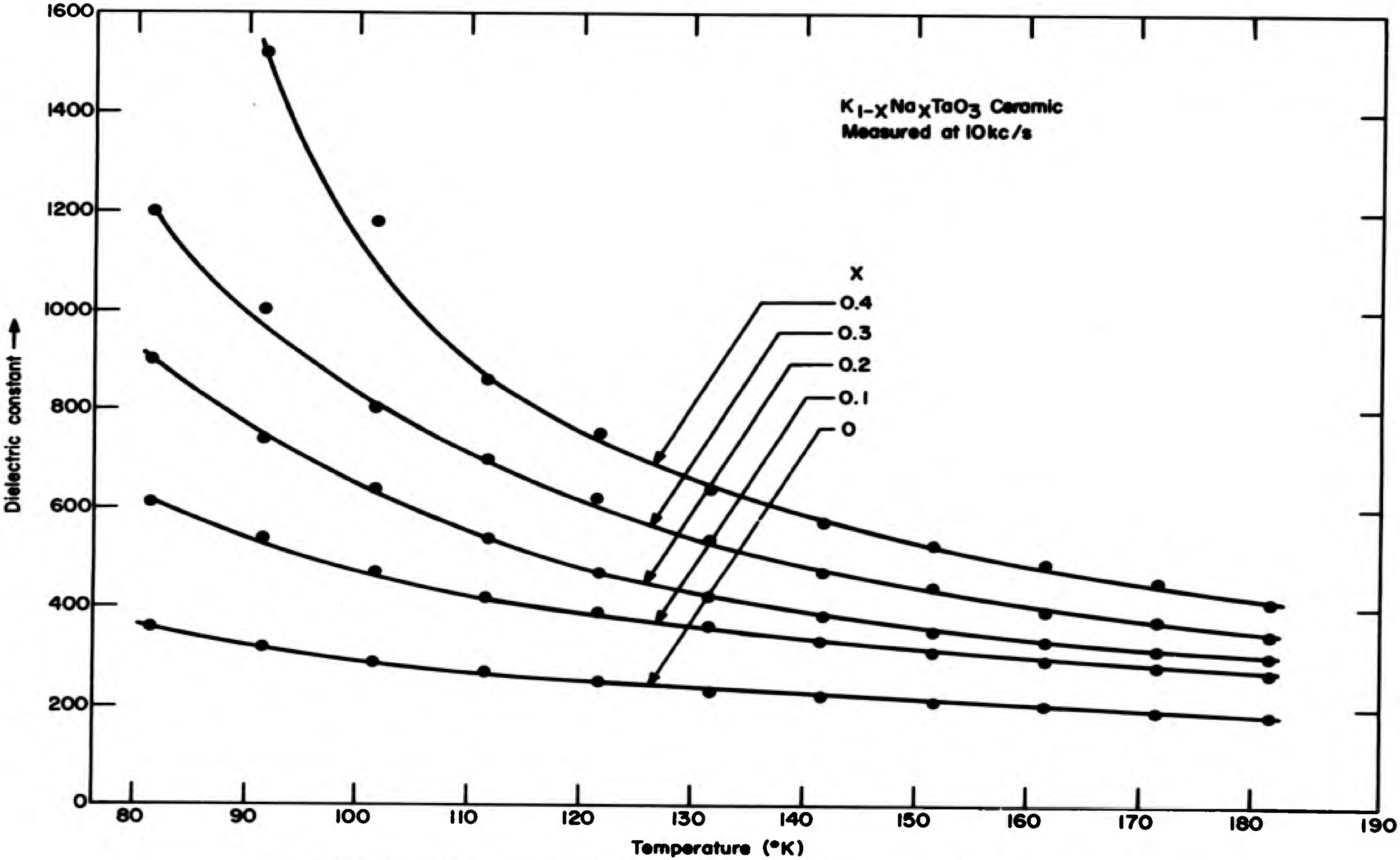
In each case, departures from the Curie law below about 120°K are observed as a curvature of the graphs in Fig. 3, 4, and 5.

There is good agreement between the microwave and low-frequency measurements except in the case of the pure $KTaO_3$ material. The results of microwave measurements of loss tangents in these materials are presented in Fig. 6 and 7. The data of Fig. 6 comes directly from an experimental measurement of the "temperature half-width" of a dielectric resonance in the sample. (It may be recalled that it is convenient to "tune" these dielectric resonators by altering their temperature thereby varying their



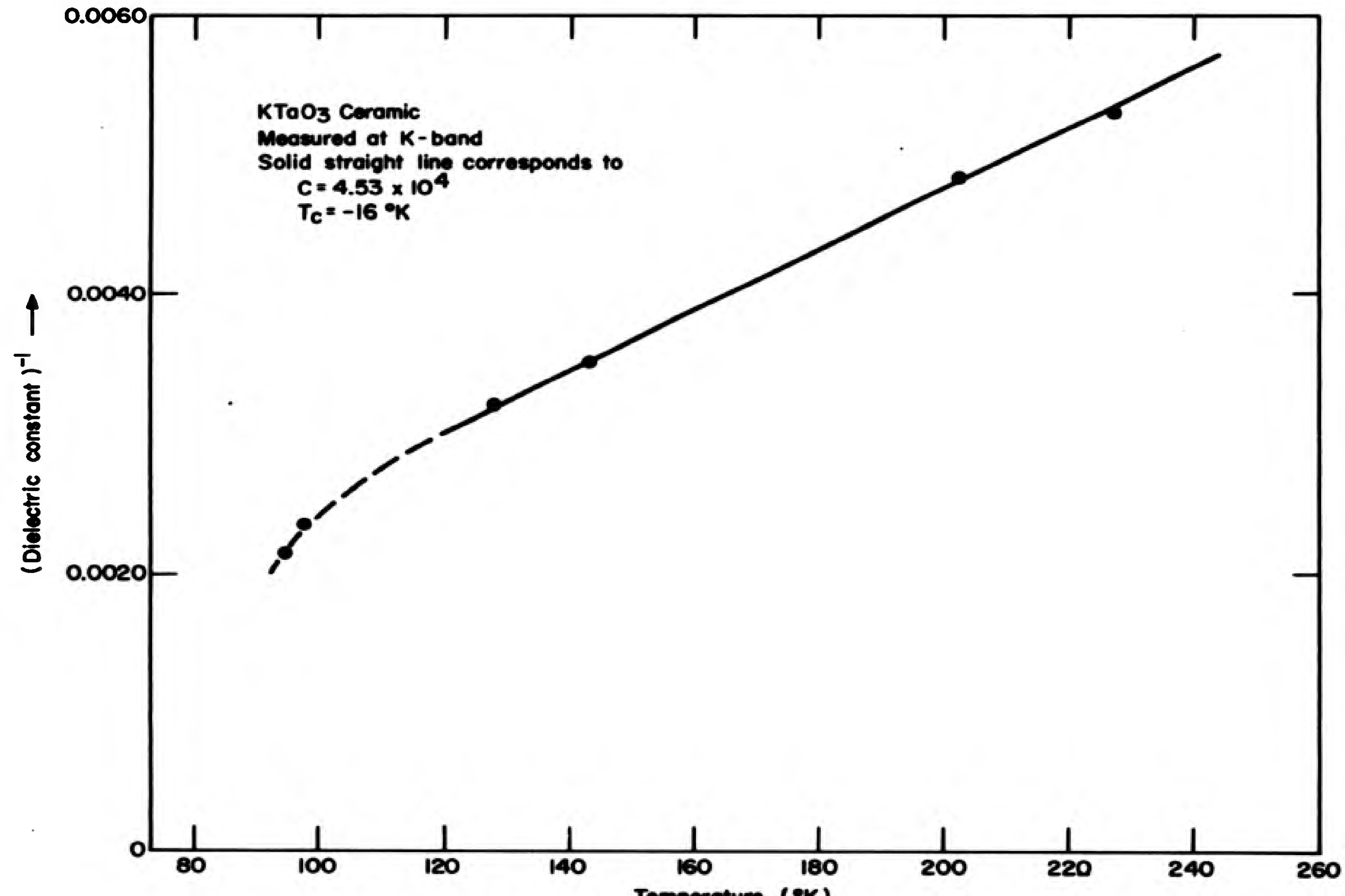
NON-LINEARITY PLOT FOR $KTaO_3$ SINGLE CRYSTAL

FIGURE I



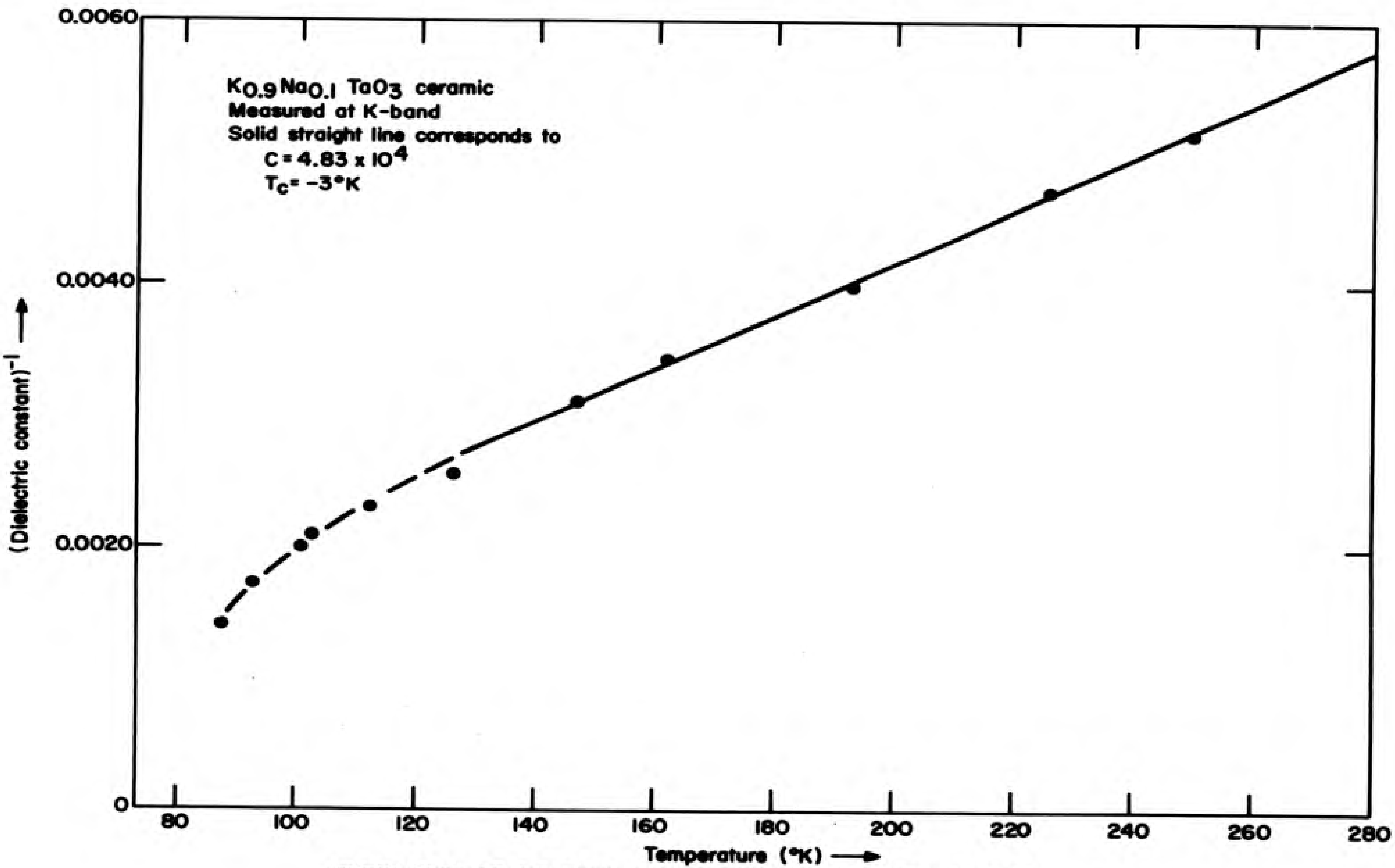
DIELECTRIC CONSTANT VS TEMPERATURE FOR MIXED $KTaO_3$ AND $NaTaO_3$ CERAMIC AT 10kc/s

FIGURE 2



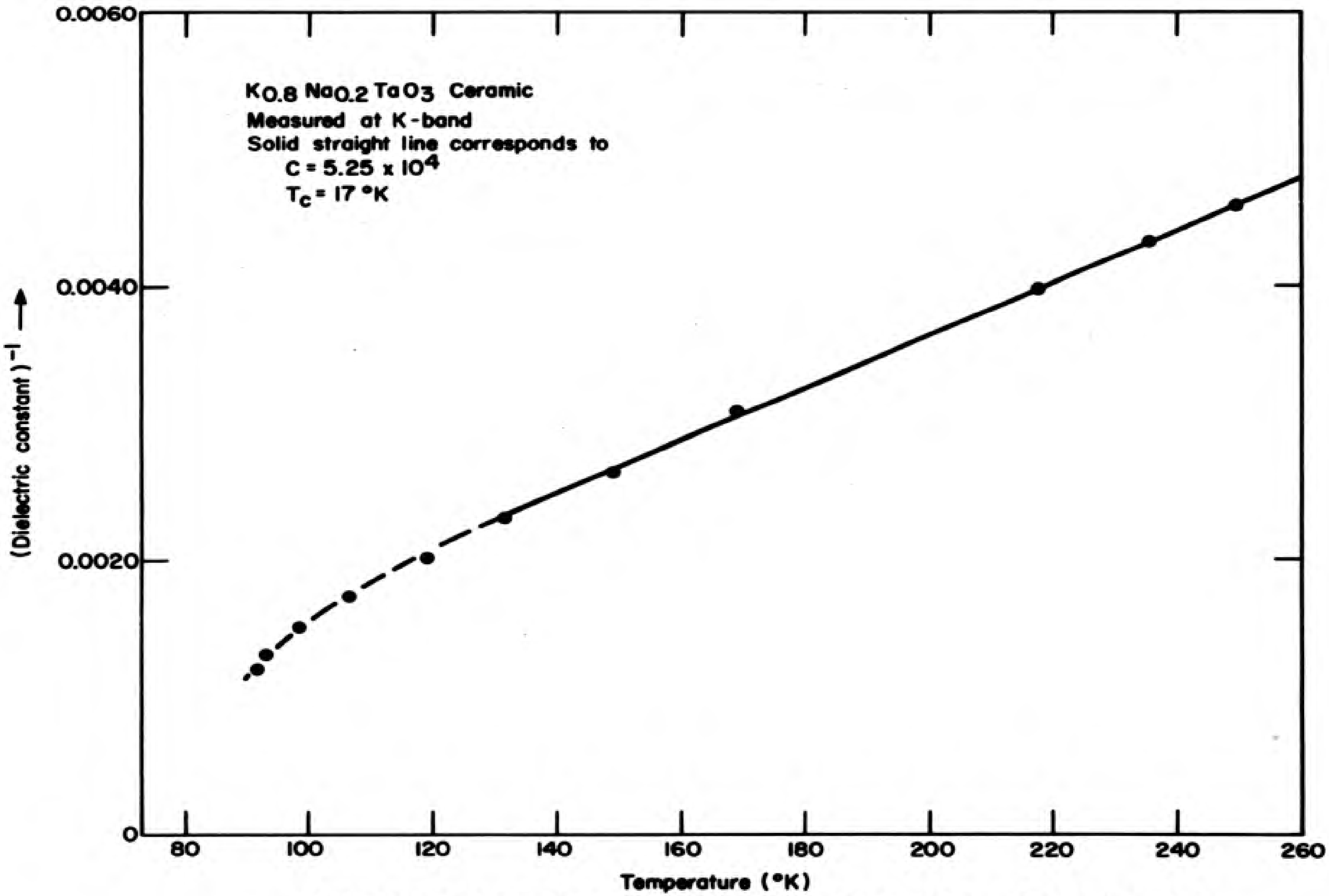
CURIE PLOT OF DIELECTRIC CONSTANT VS TEMPERATURE FOR $KTaO_3$ CERAMIC

FIGURE 3



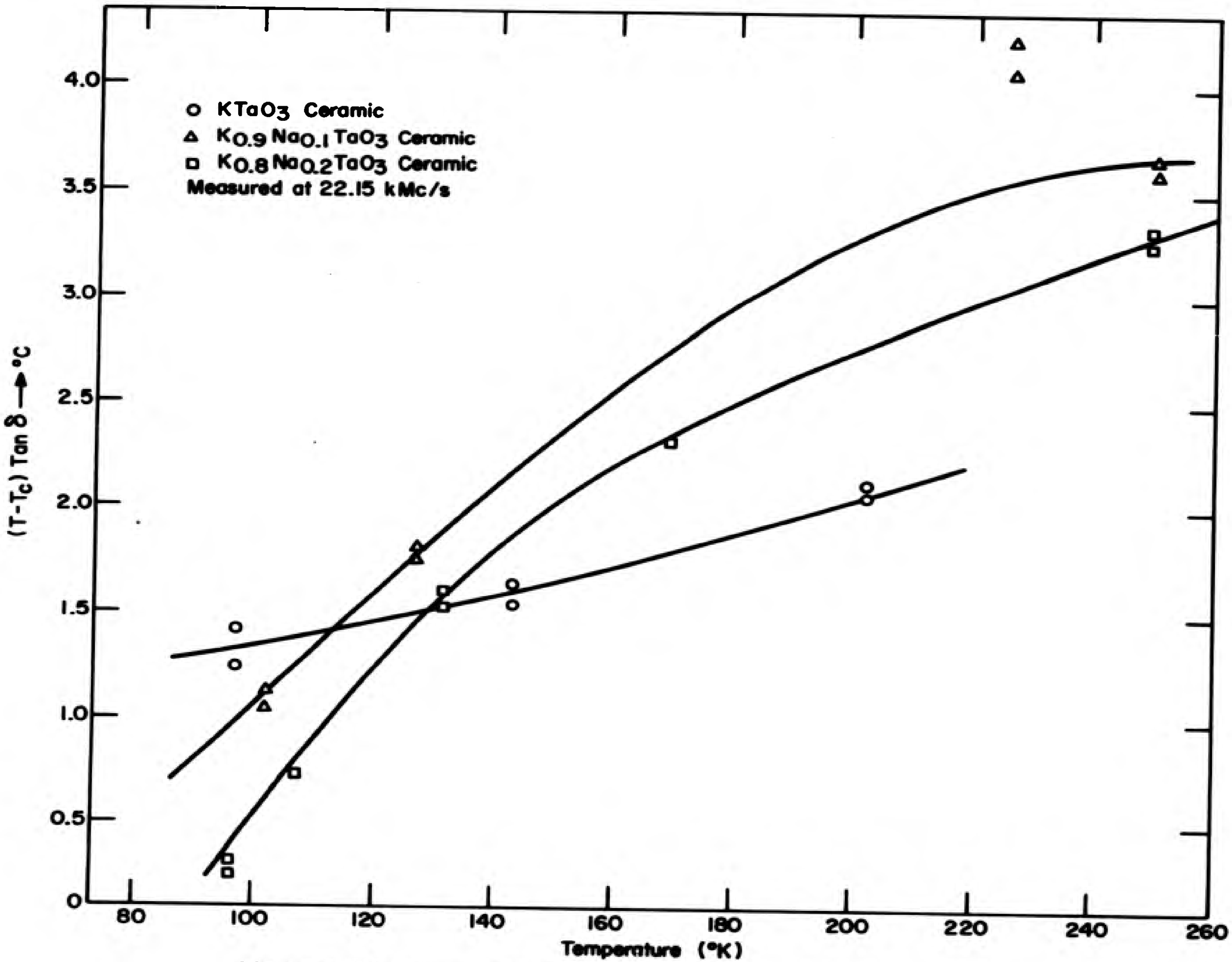
CURIE PLOT OF DIELECTRIC CONSTANT VS TEMPERATURE FOR $K_{0.9}Na_{0.1}TaO_3$ CERAMIC

FIGURE 4



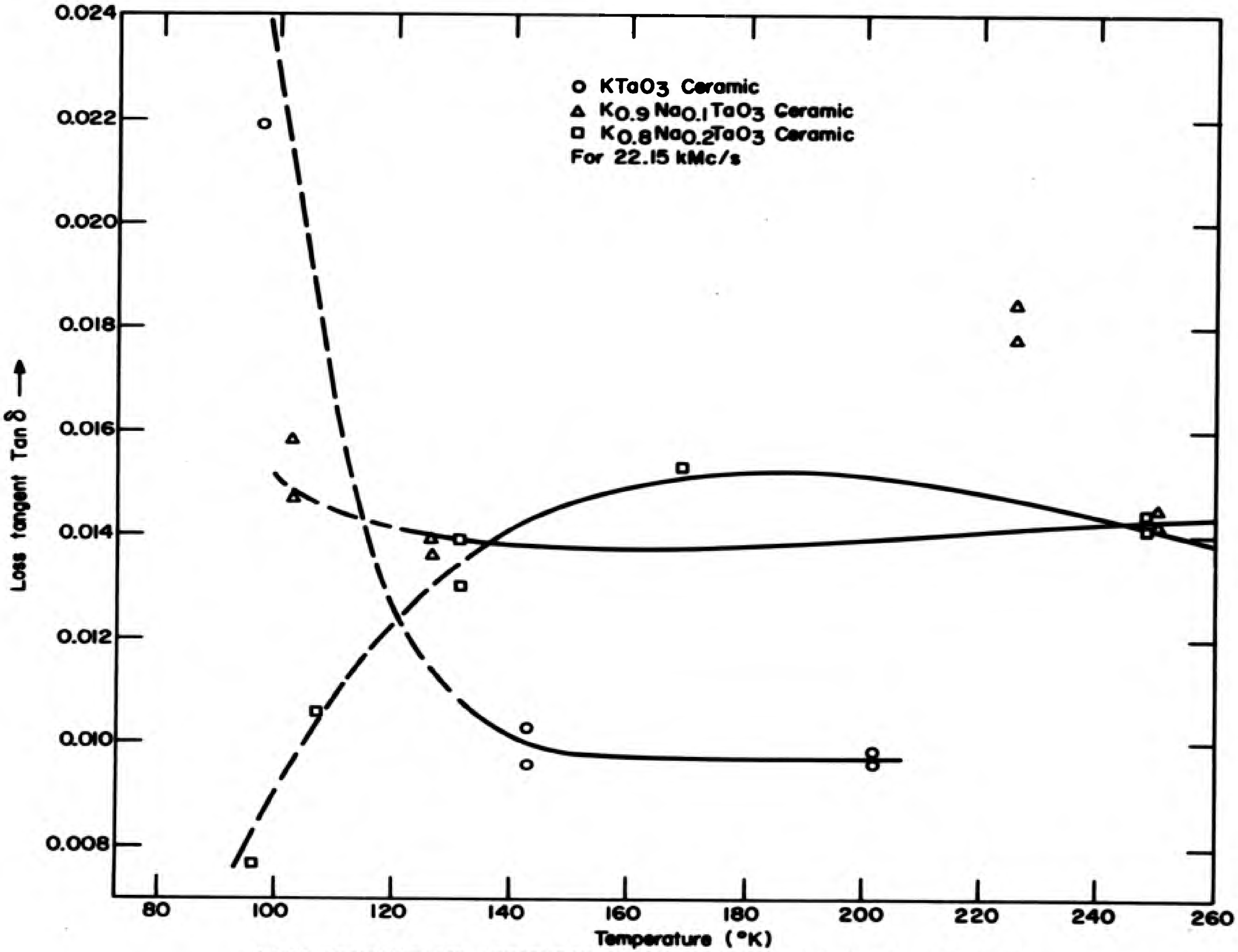
CURIE PLOT OF DIELECTRIC CONSTANT VS TEMPERATURE FOR $K_{0.8}Na_{0.2}TaO_3$ CERAMIC

FIGURE 5



LOSS DATA FOR $KTaO_3$ AND $NaTaO_3$ CERAMIC MIXTURES AT K - BAND

FIGURE 6



LOSS TANGENT VS TEMPERATURE FOR $KTaO_3$ AND $NaTaO_3$ CERAMIC MIXTURES AT K-BAND

FIGURE 7

dielectric constant.) The loss tangents plotted in Fig. 7 are obtained from the data of Fig. 6 merely by dividing by $(T-T_c)$. It is important to point out that this step is justified only if the dielectric is in a temperature range where the Curie law is obeyed. For this reason the loss tangent data below 120°K is questionable since the materials show marked departures from the Curie law in this region. The points actually plotted for this temperature region in Fig. 7 have been obtained by using a suitably chosen local Curie temperature to give the $\partial\epsilon/\partial T$ observed in the vicinity of the experimental resonances.

The data presented is based on K-band measurements at 22.15 kMc/s and covers the temperature range 100-250°K. Rather high loss tangents of the order 0.015 were observed.

4.3 The Dielectric Constant, Loss Tangent, and Nonlinearity of $Ba_{0.5}Sr_{0.5}TiO_3$ Plus One Percent $SrSnO_3$

A previous report[2] gave some evidence of high nonlinearities of $Ba_{0.5}Sr_{0.5}TiO_3$ ceramic doped with $SrSnO_3$. The losses of this material were reported to be very high.

A new sample of material of this type was prepared to confirm these original findings. The preparation procedure followed conventional ceramic techniques of mixing, firing, grinding, pressing, and sintering. The results of various microwave measurements on this new material are given in Fig. 8-11.

Figure 8 gives a Curie plot of the dielectric constant obtained by measuring the frequencies of dielectric resonances observed at K-band and in the temperature range 40-220°C. The data can be analyzed to indicate a Curie constant $C=7.85\times10^4$ and a Curie temperature $T_c=-46$°C.

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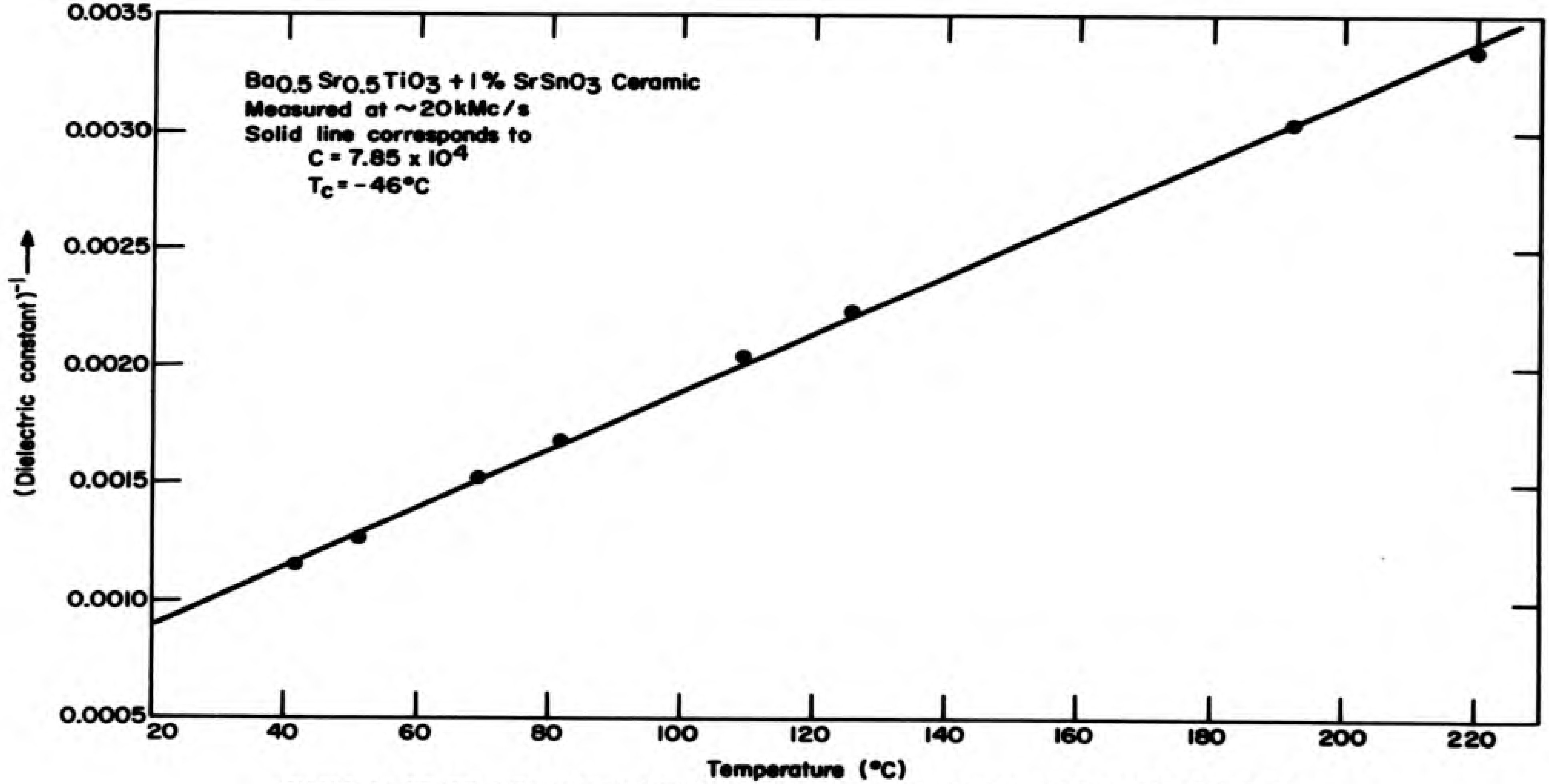
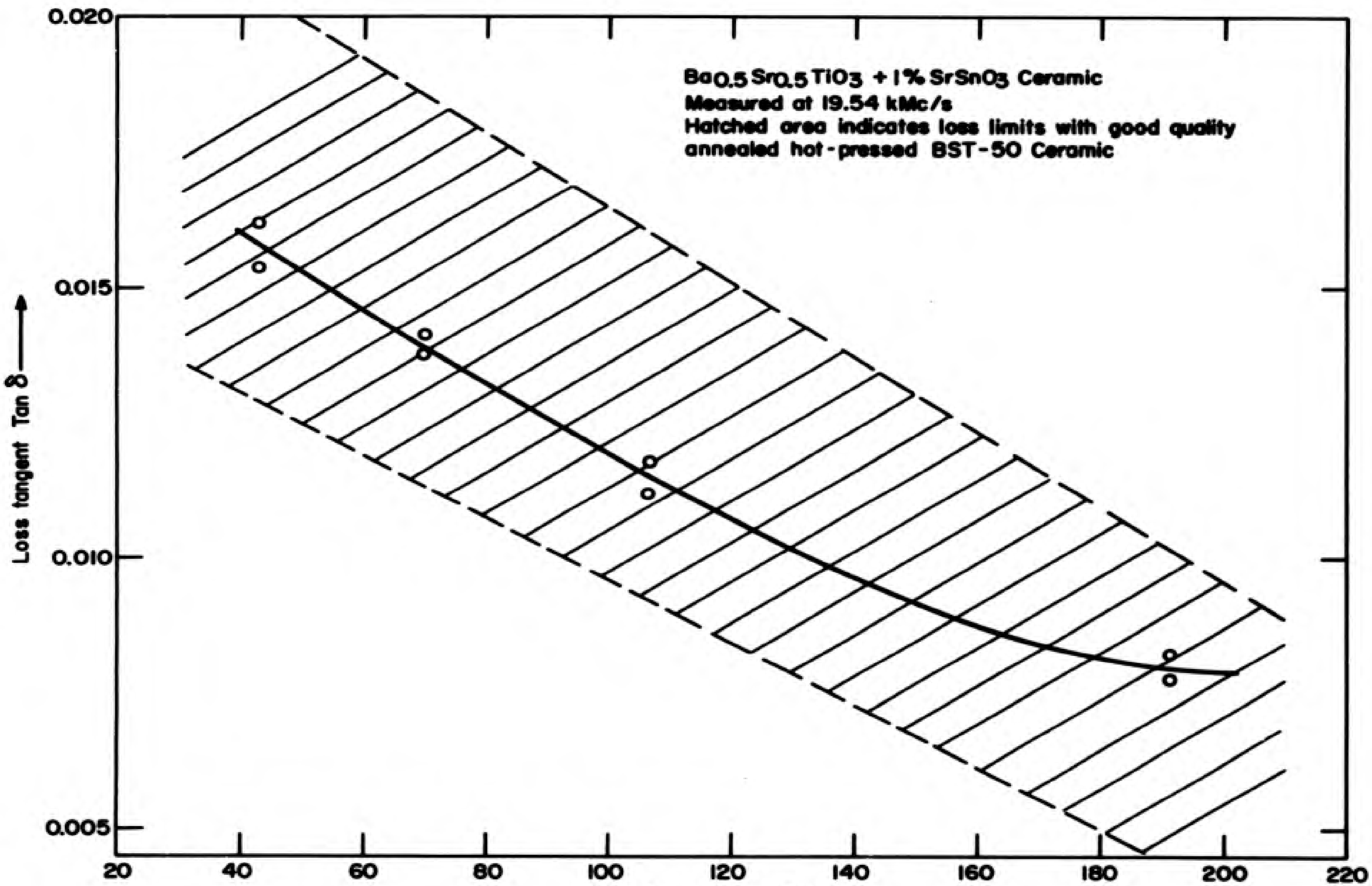
[2] Section 4.4 in Report No. 7 of this series.



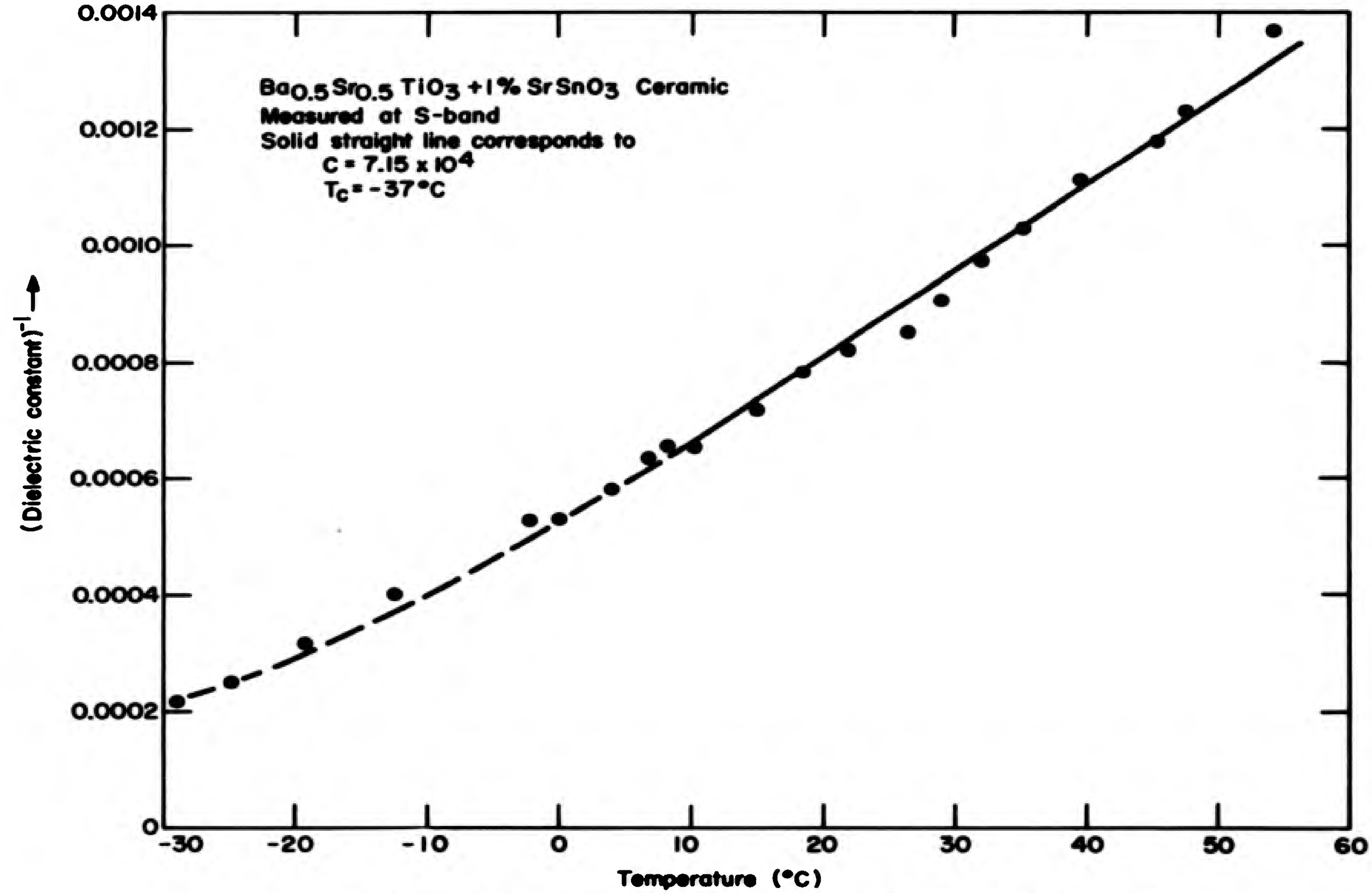
CURIE PLOT OF DIELECTRIC CONSTANT VS TEMPERATURE FOR BST-50 + 1% $SrSnO_3$

FIGURE 8



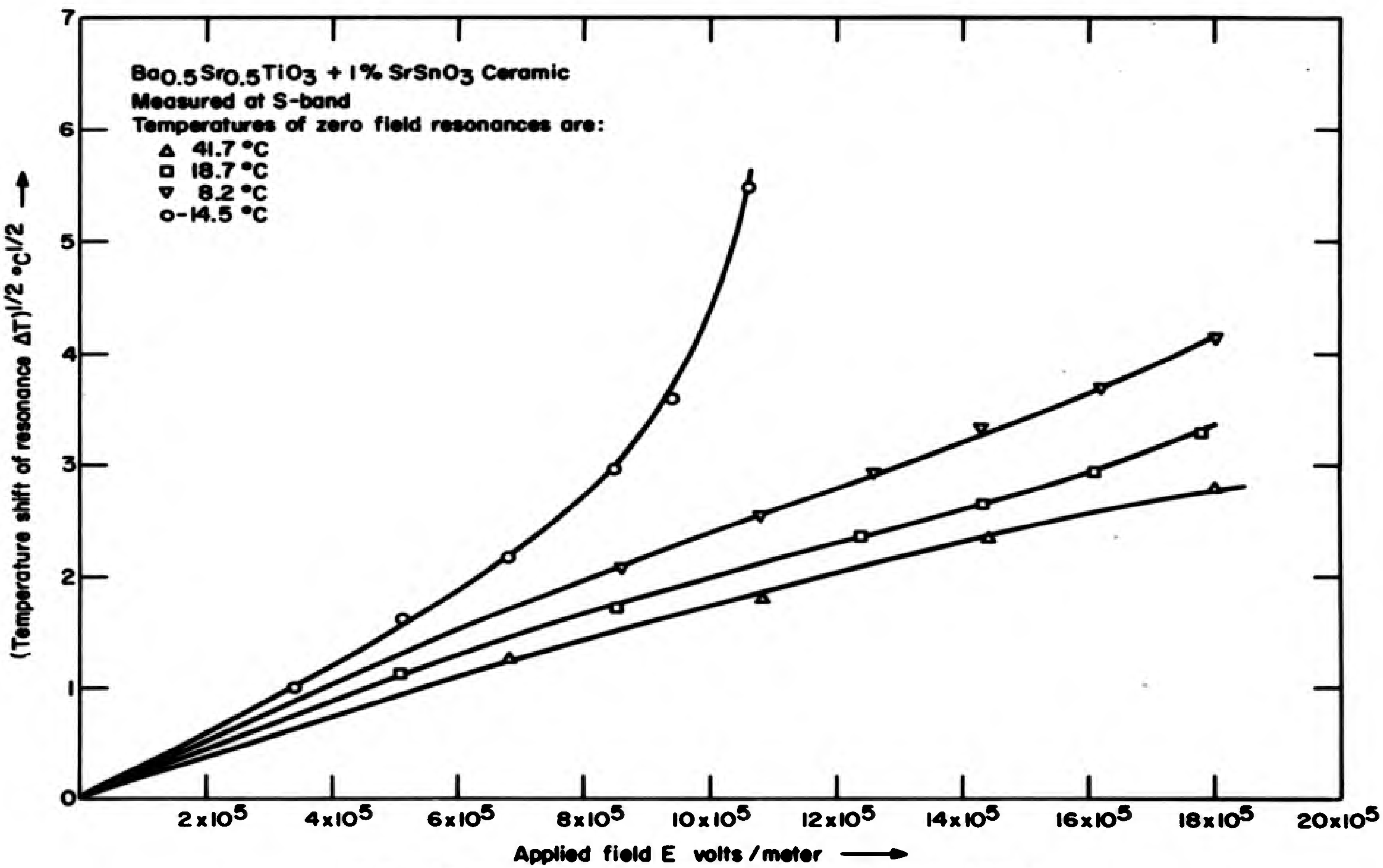
LOSS TANGENT VS TEMPERATURE FOR BST-50 + 1% $SrSnO_3$ AT K-BAND

FIGURE 9



CURIE PLOT OF DIELECTRIC CONSTANT VS TEMPERATURE FOR BST-50 + 1% $SrSnO_3$ AT S-BAND

FIGURE 10



NON-LINEARITY PLOT FOR BST-50 + 1% $SrSnO_3$ CERAMIC

FIGURE 11

The results of loss measurements at 19.54 kMc/s are shown in Fig. 9 and indicate losses rather lower than are considered typical of undoped $Ba_{0.5}Sr_{0.5}TiO_3$.

Figure 10 extends the Curie plot of the dielectric constant into the temperature range -30–+50°C on the basis of S-band measurements. This data matches fairly well with the K-band results shown in Fig. 8. However, analysis of the S-band data alone suggests a T_c = -37°C and C = 7.15×10^4. The discrepancy with the K-band results is probably due to experimental error since the points of both Fig. 8 and 10 are somewhat scattered. There is a noticeable departure from the Curie law below 0°C.

Figure 11 displays the experimental data on nonlinearity for this material in the usual way (as discussed in Section 4.1). Four curves are illustrated each being for a different zero-field resonance at temperatures in the range -14.5°C – +41.7°C. It may be observed that none of the lines are straight as should be the case if Eq. 1 and 2 are applicable to these materials. Using the slopes of straight portions of these curves near the origin enables us to calculate the nonlinearity coefficient A as given in Table II.

TABLE II

T (°C)	A (°C m^2/V^2)
41.7	4.4×10^{-18}
18.7	2.71×10^{-18}
8.2	2.19×10^{-18}
-14.5	1.36×10^{-18}

The observed nonlinearity is markedly different from that of undoped $Ba_{0.5}Sr_{0.5}TiO_3$ and is also greater than was found in earlier measurements on $SrSnO_3$ doped material.

4.4 Dielectric Constant and Nonlinearity of $Ba_{0.5}Sr_{0.5}TiO_3$ Ceramic

The dielectric constant and nonlinearity of undoped $Ba_{0.5}Sr_{0.5}TiO_3$ have been measured at S-band in the temperature range -20°C – +30°C. The purpose of the measurements is primarily to provide a valid comparison between this material and the $SrSnO_3$ doped equivalent reported in Section 4.3.

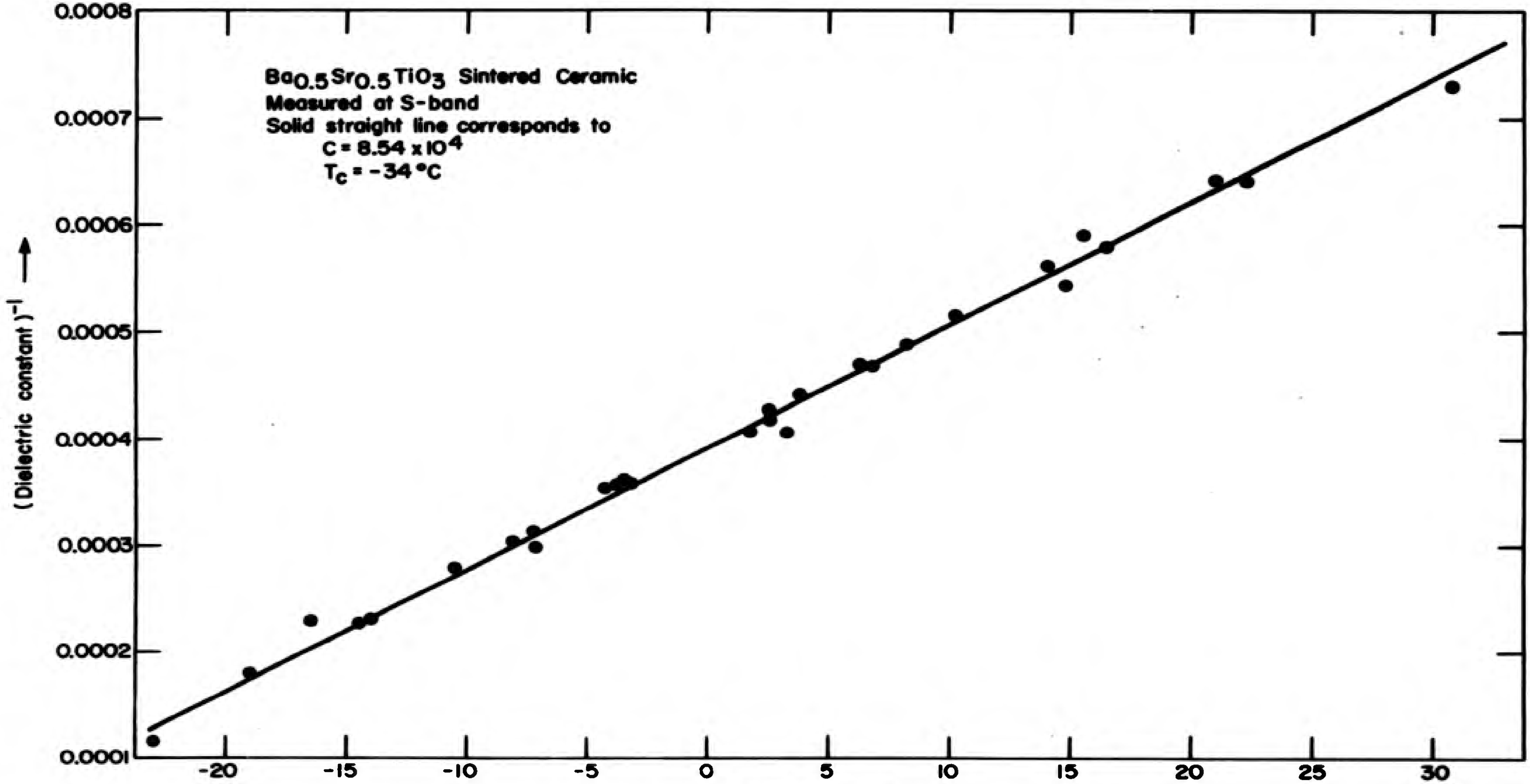
Figure 12 gives a Curie plot of the dielectric constant and may be analyzed to indicate $C = 8.54 \times 10^4$ and $T_c = -34$°C.

The nonlinearity results are plotted in the usual way in Fig. 13 and show curvatures somewhat similar to those of Fig. 11. Taking the initial straight portions of the curve to calculate a nonlinearity coefficient A leads to the results of Table III.

TABLE III

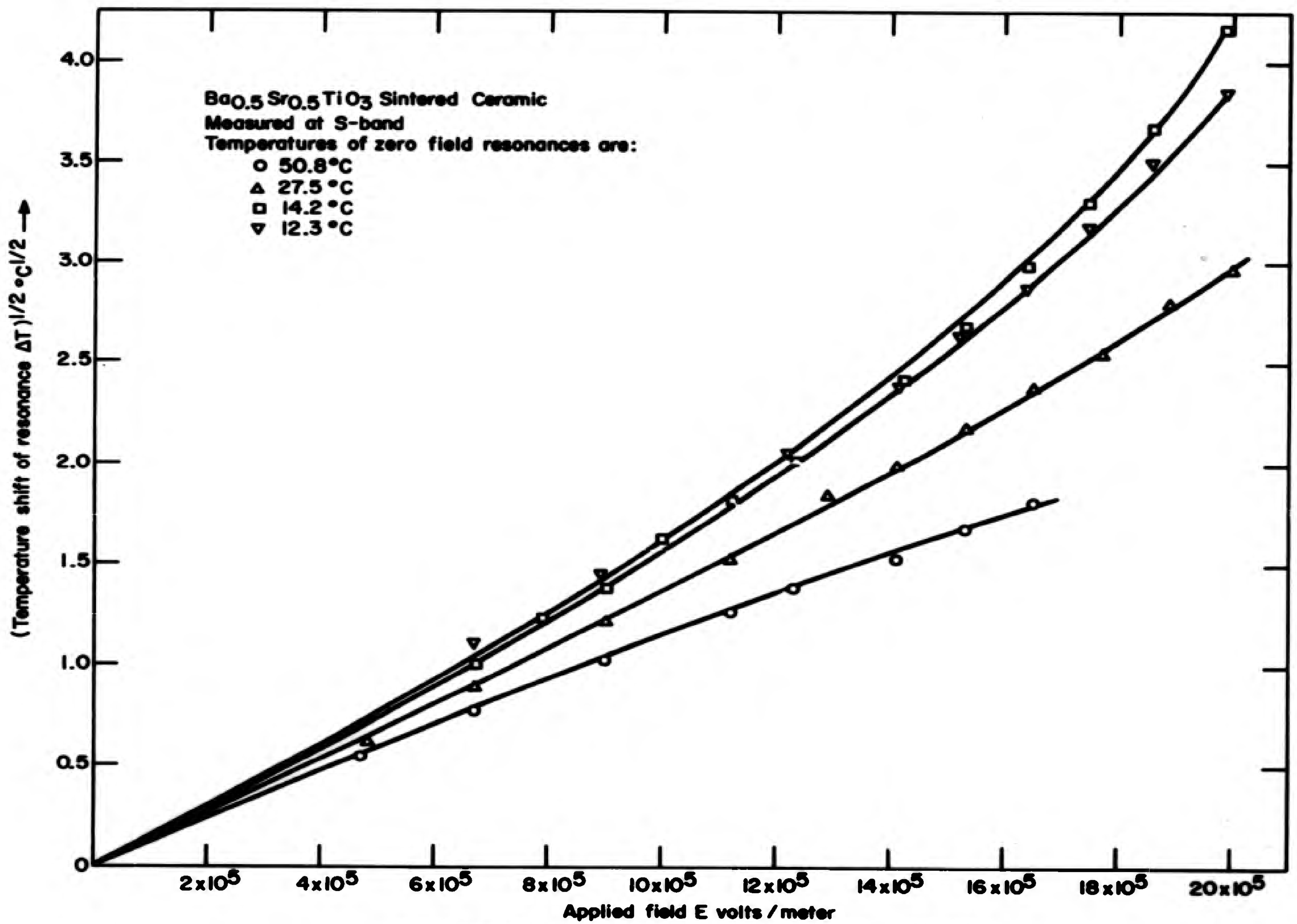
T (°C)	A (°C m^2/V^2)
50.8	1.30×10^{-18}
27.5	0.75×10^{-18}
14.2	0.50×10^{-18}
12.3	0.49×10^{-18}

The value of A obtained at 50.8°C may be compared with a value 1.1×10^{-18} °C m^2/V^2 measured in similar material at temperatures above 50°C on previous occasions.



CURIE PLOT OF DIELECTRIC CONSTANT VS TEMPERATURE FOR BST-50 CERAMIC AT S-BAND

FIGURE 12



NON-LINEARITY PLOT FOR BST-50 SINTERED CERAMIC

FIGURE 13

4.5 The Dielectric Constant and Loss Tangent of $Ba_{0.5}Sr_{0.5}TiO_3$ Hot Pressed in Alumina Die

A new technique for hot-pressing ceramics with less chemical contamination has been developed (see Section 4.9).

Samples of material prepared by this process have been examined to determine their dielectric properties to facilitate comparison with previous materials.

Figure 14 gives a Curie plot of the dielectric constant as measured at K-band in the temperature range 60° - 160°C. The data may be analyzed to indicate a $C = 8.45 \times 10^4$ and $T_c = -32.5°C$.

Data on the microwave loss tangent is presented in Fig. 15. The measurements were taken at 20.9 kMc/s in the temperature range 70 - 190°C and are slightly lower than is typical for previous samples of the same material.

4.6 The Loss Tangent of $SrTi_{0.7}Sn_{0.3}O_3$ Ceramic

A range of materials $SrTi_{1-x}Sn_xO_3$ were prepared and low-frequency data was previously reported.[3]

Measurements of the loss tangent have been made at K-band and X-band for the material of this type with $x = 0.3$ and the results in the temperature range 100 - 270°K are given in Fig. 16. All losses are reduced to their 23.7 kMc/s equivalent. In order to interpret the experimental data and obtain the loss tangents it was necessary to assume the Curie law was obeyed and that T_c was known. The low-frequency data[3] was relied upon to give evidence on these points and a $T_c = -127°K$ was assumed on the basis of this data.

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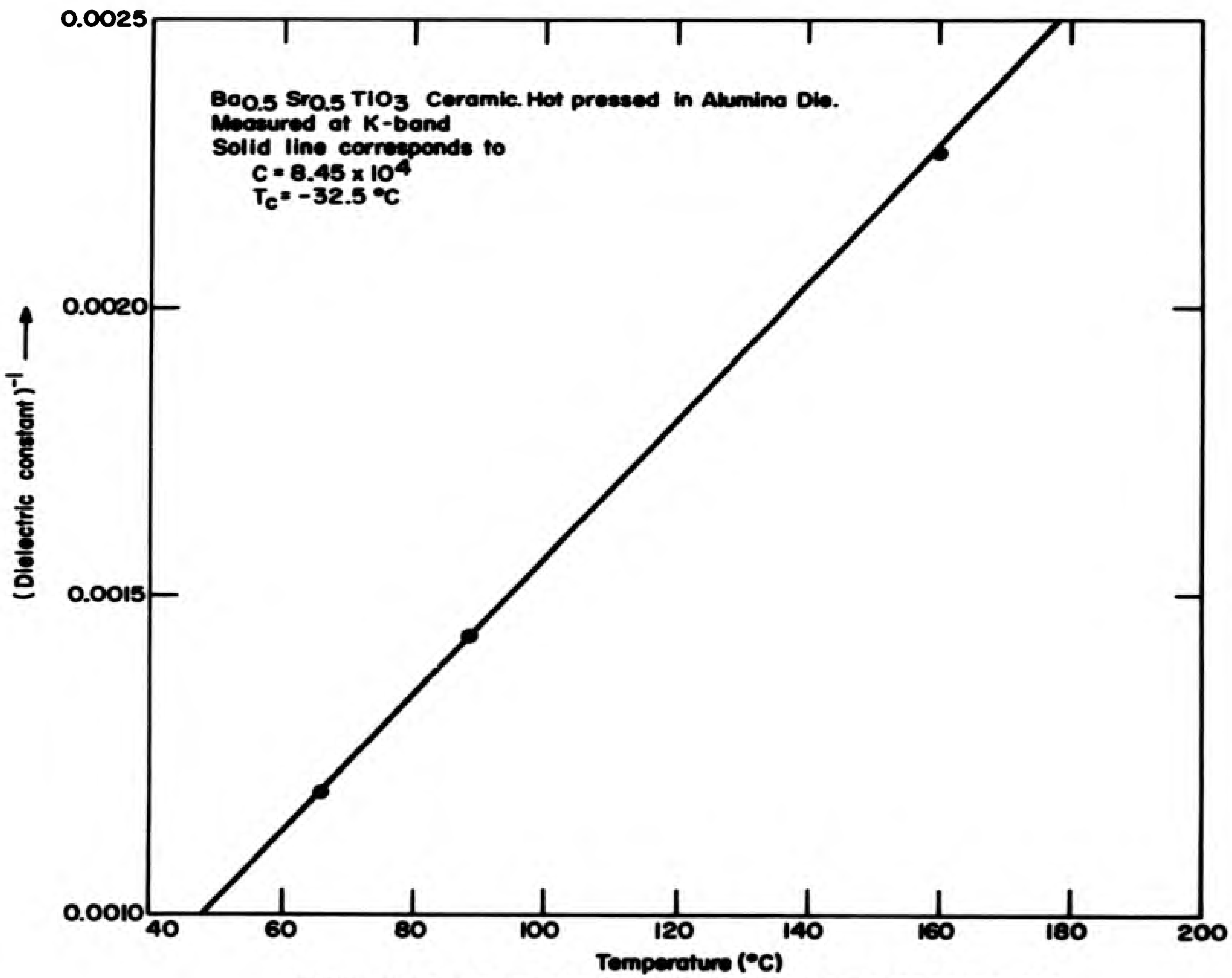
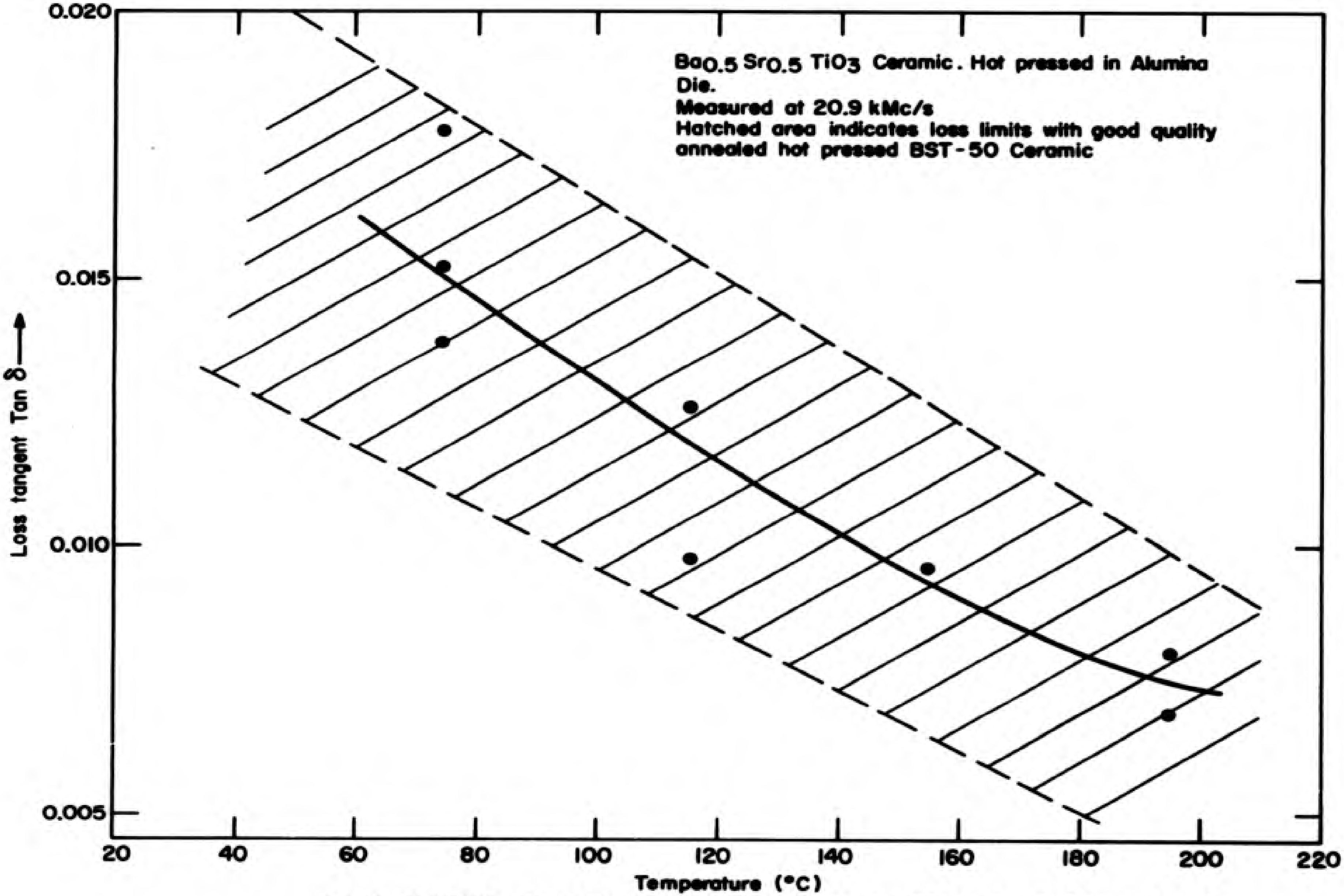
[3] Section 4.8 in Report No. 7 in this series.



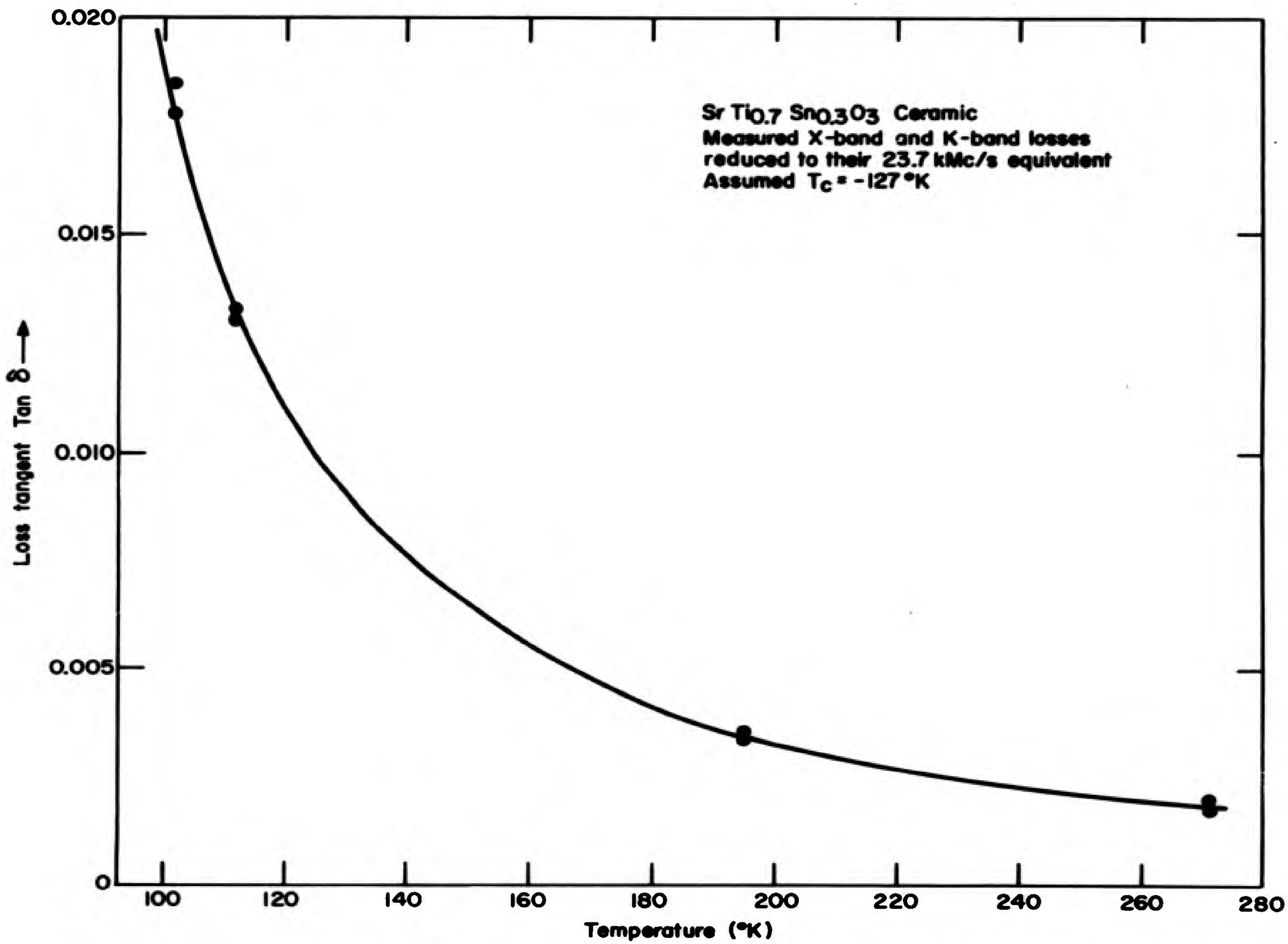
CURIE PLOT OF DIELECTRIC CONSTANT VS TEMPERATURE FOR HOT-PRESSED BST-50 (Alumina Die.)

FIGURE 14



LOSS TANGENT VS TEMPERATURE FOR HOT PRESSED BST-50 (Alumina Die.)

FIGURE 15



LOSS TANGENT VS TEMPERATURE FOR $SrTi_{0.7}Sr_{0.3}O_3$ AT K-BAND

FIGURE 16

The losses in this material rise more steeply at low temperatures than do $BaTiO_3$ and $SrTiO_3$ mixtures. The 30 percent Sn doping seems to produce a larger loss than would a 30 percent Ba doping, provided the comparison is made at temperatures which are equidistant above the Curie temperature.

4.7 The Loss Tangent for $BaTi_{0.9}Hf_{0.1}O_3$ Ceramic

A range of materials $BaTi_{1-x}Hf_xO_3$ were prepared and their low-frequency dielectric constants have been previously reported.[4]

Loss measurements have been made at X-band and are presented in Fig. 17 for the temperature range 150 - 230°C. The losses were calculated assuming a $T_c = 70°C$ as indicated by the low-frequency data.[4]

The losses are high and the scatter of the experimental data reflects the difficulty of observing the low Q dielectric resonances.

4.8 The Dielectric Constants of $Ba_{1-x}Sr_xTi_yHf_{1-y}O_3$ Mixtures

Fresh samples of materials from the Ba-Sr-Hf-Ti quarternary system have been prepared (see Section 4.9). Figures 18 and 19 give low-frequency measurements of dielectric constants for two of these materials ($x = 0.5$ $y = 0.9$ and $x = 0.3$ $y = 0.82$).

Comparison with similar data for earlier materials of this general type[5] shows that the new materials are considerably improved in the sense that the dielectric peak is both higher and narrower.

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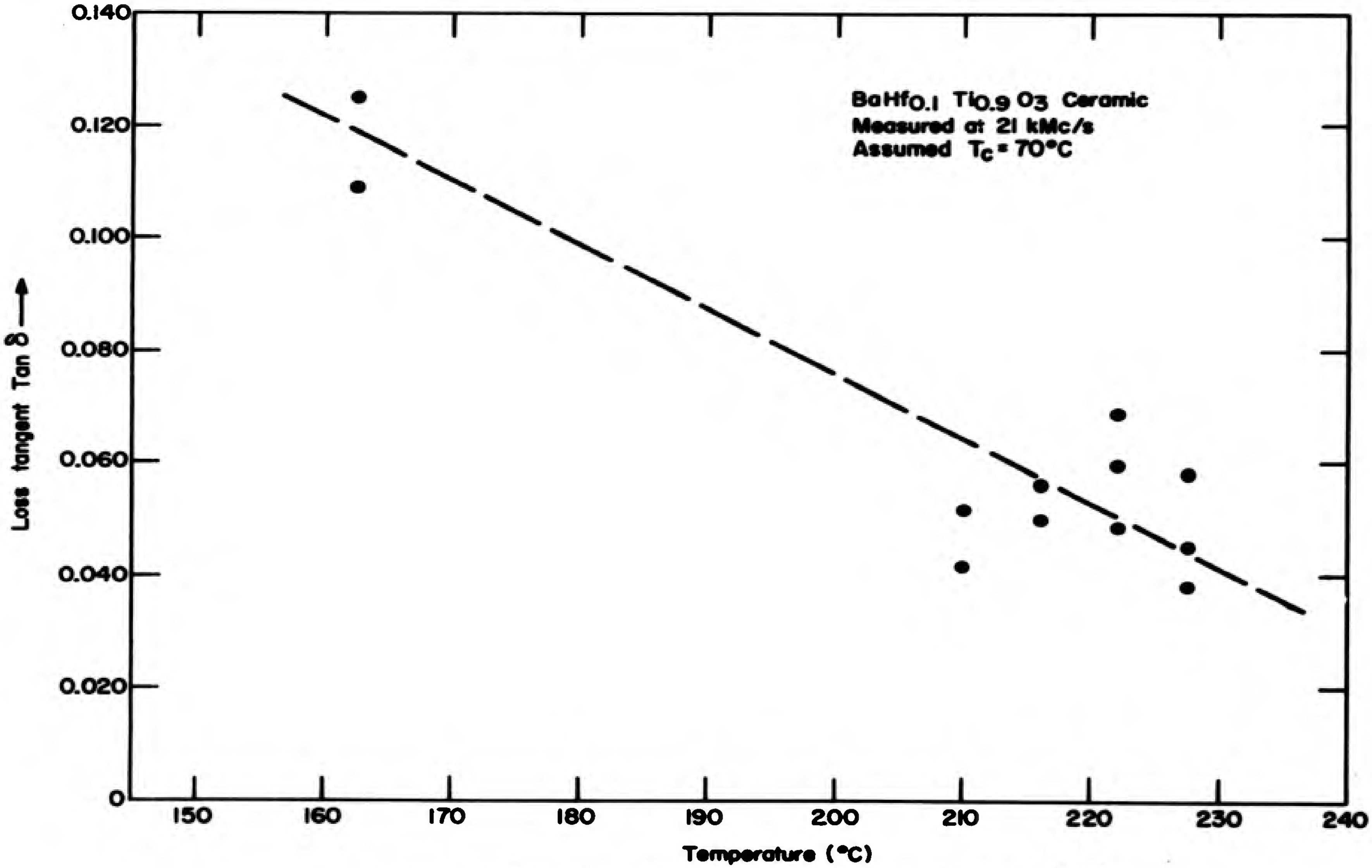
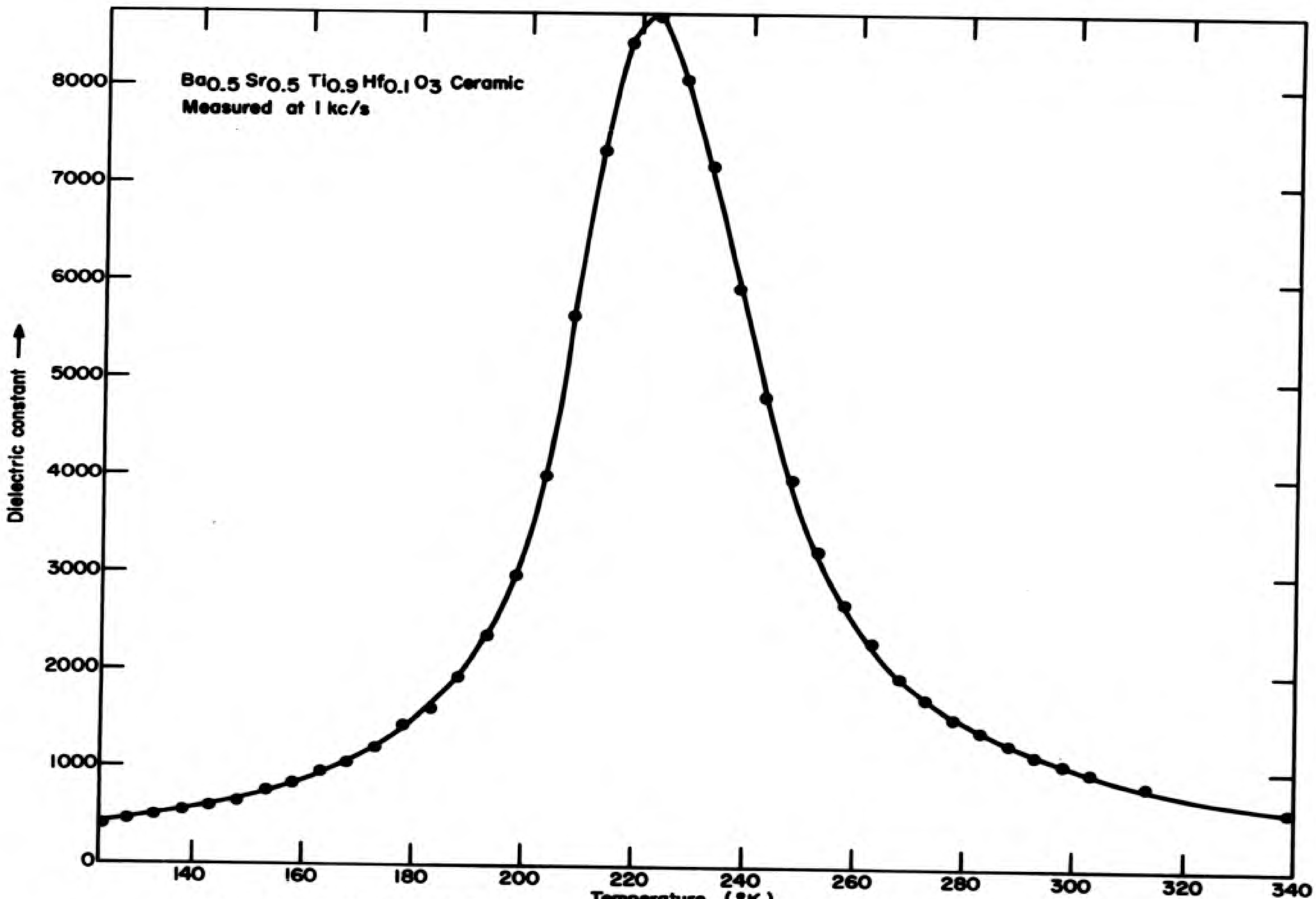
[4]Section 4.9 in Report No. 7 in this series.

[5]Section 4.10 in Report No. 7 in this series.



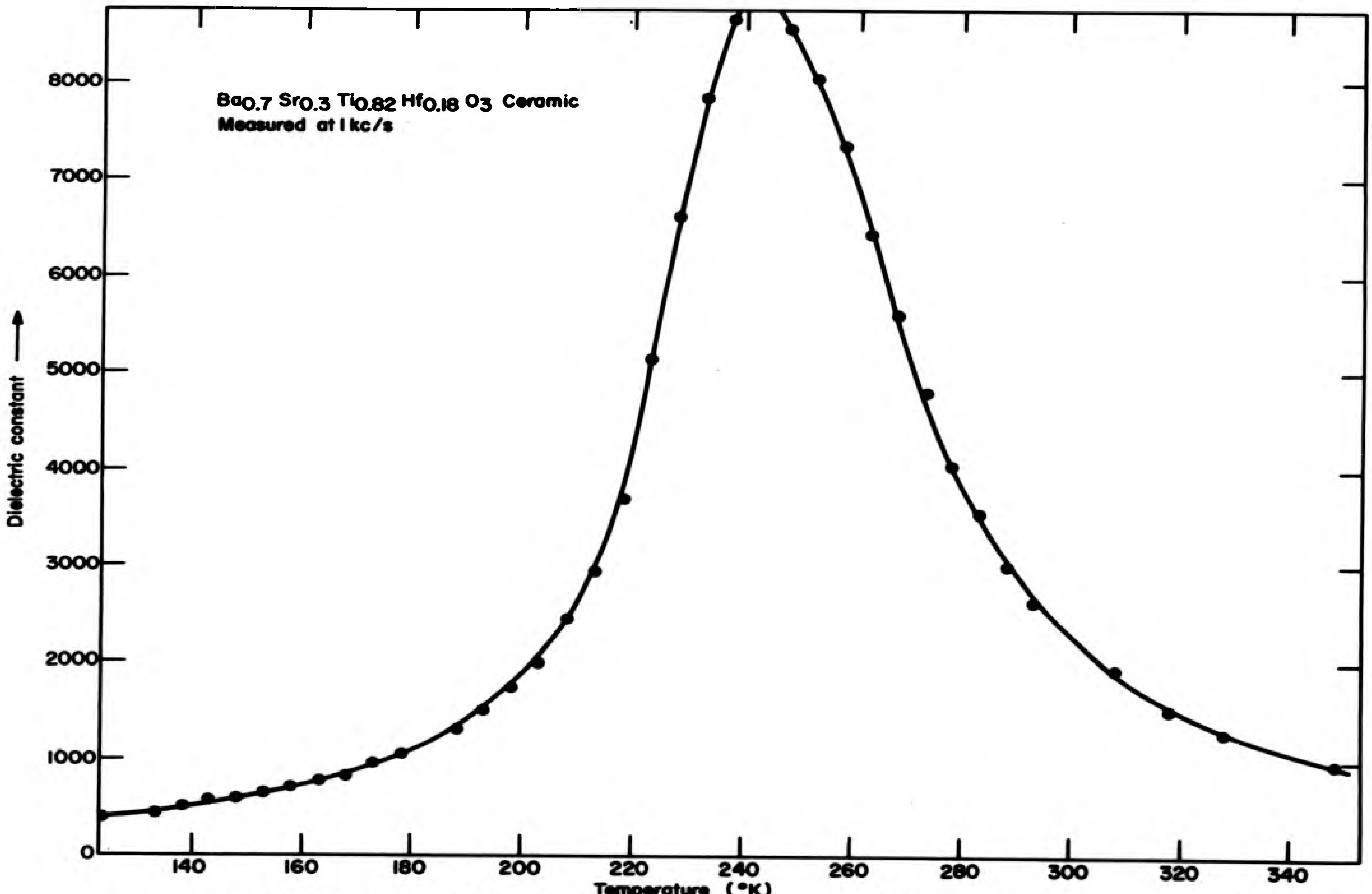
LOSS TANGENT VS TEMPERATURE FOR BTH - 10 AT K-BAND

FIGURE 17



DIELECTRIC CONSTANT VS TEMPERATURE FOR BSTH-50/10 CERAMIC AT LOW FREQUENCY

FIGURE 18



DIELECTRIC CONSTANT VS TEMPERATURE FOR BSTH-30/18 AT LOW FREQUENCY

FIGURE 19

4.9 Preparation of Materials

4.9.1 Single crystal $KTaO_3$

Single crystals of $KTaO_3$ have been grown from the melt using an excess of K_2CO_3 to act as a fluxing agent.

A mixture of 1.22 parts K_2CO_3 to one part of Ta_2O_5 was heated to 1400°C in a platinum crucible. After a six hour soak at this temperature the melt was cooled to 1250°C at a rate of 4.5°C per hour and then brought to room temperature in a few hours. The solidified matrix contained many clear crystals and some bluish ones. Crystal size seems limited by the large number of nucleation centers on the walls of the crucible. Attempts are being made to increase crystal size by using the techniques reported by Miller.[6]

4.9.2 Mixed $KTaO_3$ and $NaTaO_3$ ceramics

Various mixtures of the type $K_{1-x}Na_xTaO_3$ have been prepared in the following way.

Potassium carbonate, sodium carbonate, and tantalum pentoxide are mixed in the desired molecular ratios (1-x):x:1. Mixing is accomplished by milling a methanol suspension for four hours in a polyethylene mill. The slurry is dried overnight, calcined to 700°C, milled, and calcined again at 1000°C.

Attempts to improve the density were made by firing the mixture close to the melting point for about 10 hours. It appears to be unusually difficult to sinter these materials and to get high density even though temperatures within 5° of the melting point have been used with some materials.

---

[6] C. E. Miller, J. Appl. Phys. 29, 233 (1958).

This difficulty is probably associated with the large size of the monovalent cation and its presumably low diffusion rate. The best densitites attained have been ~ 0.91 of theoretical.

X-ray analysis of the material shows it to be well reacted, of one phase, and with a cubic lattice parameter following Vegards law.

Lattice parameters measured at room temperature for various constitutions are given in Table IV.

TABLE IV

Composition	Lattice Parameter
$KTaO_3$	3.9883±0.0003 A°
$K_{0.9}Na_{0.1}TaO_3$	3.9820±0.0003 A°
$K_{0.8}Na_{0.2}TaO_3$	3.9770±0.0004 A°
$K_{0.7}Na_{0.3}TaO_3$	3.9716±0.0004 A°
$K_{0.6}Na_{0.4}TaO_3$	3.9669±0.0004 A°

4.9.3 Hot-pressed materials using an alumina die

The hot-pressing techniques previously used brought the hot ceramic into contact with hot metal or zirconia sand. The recently used procedure presses the sample between two alumina pistons in a cylindrical alumina die. The dies and pistons (obtained from McDanel Refractory Porcelain Company) are reputedly better than 99.5 percent pure alumina and so provide a relatively clean way of pressing ferroelectric ceramics.

Samples of the composition $Ba_{0.5}Sr_{0.5}TiO_3$ have been pressed with better than 95 percent theoretical density. The material is glass-like and before annealing has grain sizes of about 1 micron. The material does not appear to be oxygen deficient. Annealing at 1400°C for four hours in oxygen improves the dielectric properties.

4.9.4 Materials of the type $Ba_{1-x}Sr_xTi_yHf_{1-y}O_3$

The compositions with $x = 0.5$ $y = 0.9$ and $x = 0.3$ $y = 0.82$ have been remade with considerable emphasis upon properly reacting the materials, preserving purity, and maintaining stoichiometry.

High purity HfO_2 (free of ZrO_2) was used and firing temperatures of 1400° - 1800°C were tried with soaking times from 2 - 100 hours.

High temperatures are required to react materials containing the highly refractory HfO_2, but, if temperatures in the 1700 - 1800°C are used there is a loss of BaO. For this reason it transpires to be better to calcine and fire several times at lower temperatures.

The materials so prepared are dense, homogeneous, and exhibit higher and narrower Curie peaks than we previously observed in materials of the quarternary system.

The second and third phase transitions observed below the Curie temperature in barium titanate are not observed in these materials.

5. CONCLUSIONS

5.1 Nonlinearity of $KTaO_3$

The nonlinearity coefficient A as measured for single crystal $KTaO_3$ at 108°K is 1.53×10^{-18} °C m^2/V^2. This may be compared with the value for $SrTiO_3$ in the [110] direction of $\sim 0.96 \times 10^{-18}$ °C m^2/V^2.

Since the nonlinearity coefficient appears in combination with the dielectric constant (see Eq. 1) in the form $A\epsilon^3/C$ a comparison of the nonlinearities of the two materials is more properly based upon the value of the quantity AC^2. This combination provides a measure of the nonlinearity of any material at a given temperature above its Curie point.

The values of AC^2 for $KTaO_3$ and $SrTiO_3$ respectively are 5.02×10^{-9} °C^3 m^2/V^2 and 4.84×10^{-9} °C^3 m^2/V^2. We therefore conclude that $KTaO_3$ has a nonlinearity effect only slightly superior to that of $SrTiO_3$. It is still thought that the low-temperature losses of $KTaO_3$ will be more favorable than is the case for $SrTiO_3$.

The sample used in the experiment was not oriented in any specifically known crystal direction. This was because the prime requirement in cutting up a rather small and irregularly shaped crystal was to ensure getting a suitably large experimental sample. Anisotropy effects of nonlinearity will be measured when more crystals are available.

5.2 The Mixed $KTaO_3$ and $NaTaO_3$ Ceramics

We should first emphasize the difficulty of preparation of these tantalate ceramics (see Section 4.9.2). X-ray examination of the material seems to indicate that the components are properly reacted and form a homogeneous sample, but it is difficult to make this statement a quantitative one. The densities of these ceramics are not too good but no density corrections have been applied to any of the data quoted here. Before discussing the mixed ceramics we should point out the discrepancy between the dielectric data for single crystal and polycrystal $KTaO_3$. The experimental data is summarized in Table V.

TABLE V

Material	C	T_c	ϵ_1
Single Crystal $KTaO_3$	5.72×10^4	7°K	45.8
Polycrystal $KTaO_3$	4.53×10^4	-16°K	---

Applying the density correction to the polycrystalline results (according to Lewin[7]) only partially explains the discrepancy in the Curie constant and has no bearing on the discrepancy in T_c.

Examination of the Curie plot in Fig. 3 shows departures from linearity at low temperatures in which the curvature is concave down. The same feature is evident in the mixed tantalates for which the dielectric data appears in Fig. 4 and 5. This behavior may be contrasted with the more typical departures from the Curie law which are commonly observed in mixed or inhomogeneous materials. An example of this type may be seen in Fig. 10, where the low temperature part of the graph deviates from a straight line and is concave up.

The dielectric constants evident in Fig. 3, 4, and 5 are of the type which approximate to

$$\epsilon = \epsilon_1 + \frac{C}{T-T_c} \qquad (3)$$

rather than the simpler Curie law. The available data does not extend over a wide enough temperature range for a reliable analysis in the form to be obtained, but, the extent of the curvature and the temperature at which it is evident suggests a larger ϵ_1/C ratio than is found in the single-crystal material. Bearing in mind the discrepancies between the single and polycrystal results for $KTaO_3$ we must be cautious in interpreting the dielectric properties (including losses) of the mixed $K_{1-x}Na_xTaO_3$ as being solely due to the Na content.

The general trends in properties as Na content is increased are easily summarized. Curie constant and Curie temperature increase as x increases (see Fig. 3, 4, and 5). The effect of Na substitution on T_c however, is surprisingly small. Table I lists the results of the analysis of the experimental data.

---

[7] L. Lewin, J. I. E. E., 94, 65 (1947).

In the case of mixtures $Ba_{1-x}Sr_xTiO_3$ the Curie temperature and constant change almost linearly with x as the constitution ranges from $x = 0 \rightarrow 1$.

The fact that this does not appear to occur for the mixed tantalates (since T_c for $NaTaO_3$ is ~ 400°C) suggests that we should anticipate that a small amount of $KTaO_3$ in $NaTaO_3$ should have a large effect in diminishing the Curie temperature. We should, accordingly, investigate materials at the other end of the consitutional range.

The losses illustrated in Fig. 7 do not call for much comment. They are rather high bearing in mind the small amount of mixed Na, and the experimental data is not good. There is little evidence of a strong temperature dependence in the region above 120°K and the data below this temperature is untrustworthy (see Section 4.2).

One noteworthy point is that the material with $x = 0.2$ shows lower losses at all temperatures than for $x = 0.1$ but not as low as are found in the pure $KTaO_3$. The significance of this is uncertain. It may merely be that the losses are more dependent upon the preparation procedures than upon the constitution i.e. the observed losses are not of any fundamental origin.

Further investigation of these materials seems warranted.

5.3 The Properties of $Ba_{0.5}Sr_{0.5}TiO_3$ Plus One Percent $SrSnO_3$

This material is the first doped Ba-Sr titanate mixture to have been extensively studied concerning its dielectric properties. Previous materials of this type had undergone preliminary investigations[2] which were encouraging.

The present measurements indicate that this material has some very desirable properties. The loss tangent is good, in fact for conventional ceramic material it is very good. The data of Fig. 9 compares the loss tangents observed in this material with those found in "good, hot-pressed, annealed BST-50." This comparison may be made more specific here. The lower limit of the hatched area in Fig. 9 corresponds to the lowest loss ever found in a $Ba_{0.5}Sr_{0.5}TiO_3$ mixture.[8] The upper limit of the hatched area corresponds to losses in a material known by the code number BST-50 HP # 7. Losses of this material have been measured many times and it is better than the average hot-pressed material.

The nonlinearity data of Fig. 11 shows marked departures from the form of nonlinearity expressed by Eqs. 1 and 2.

This is to be expected since these equations are developed on the assumption that the polarization is small and that the zero-field dielectric constant follows the Curie law. Both these assumptions become invalidated near the Curie point in materials with high dielectric constant, and both effects can be recognized in the data of Fig. 9.

Ignoring these defects and calculating a nonlinearity coefficient A from the slopes of the curves of Fig. 9 at low fields we get the results assembled in Table II.

These nonlinearity coefficients are substantially greater than we have previously observed in undoped $Ba_{0.5}Sr_{0.5}TiO_3$. By way of emphasizing this fact we have included similar data for an undoped $Ba_{0.5}Sr_{0.5}TiO_3$ material prepared and measured along with the $SrSnO_3$ doped sample. The data for comparison is included in Section 4.4 and Fig. 12 and 13.

Further experimentation with this substitution is clearly necessary both to confirm and to extend these results.

---

[8] Data as reported in Report No. 1 of this series.

[9] BST-50 being a common abbreviation for $Ba_{0.5}Sr_{0.5}TiO_3$

5.4 Hot-Pressed Materials

Loss data for $Ba_{0.5}Sr_{0.5}TiO_3$ hot pressed in the alumina die and annealed as described in Section 4.9.3 is illustrated in Fig. 15. The cross-hatched limits of "good" material are the same as were discussed in Section 5.3 in connection with other loss measurements.

It is evident that this material also represents an improvement over the average hot-pressed ceramic.

No other microwave measurements have been performed on this material.

5.5 Other Mixed Materials

Figures 16 and 17 give loss data for $SrTi_{0.7}Sn_{0.3}O_3$ and $BaHf_{0.1}Ti_{0.9}O_3$. It is fruitful to compare these losses with those of the best known of mixed materials $Ba_{0.5}Sr_{0.5}TiO_3$. For this "standard" material at about 180° above the Curie temperature loss tangents of 0.010 can be obtained.

At comparable temperatures for $SrTi_{0.7}Sn_{0.3}O_3$ the loss tangent is probably in excess of 0.020 and that for $BaHf_{0.1}Ti_{0.9}O_3$ will be ~0.030.

These must be considered as high losses in view of the relatively small admixture in these materials. On the basis of loss measurements alone therefore, extensive substitutions of this type do not appear attractive. A final decision on the merits of such materials must await non-linearity measurements.

As the discussion in Section 4.9.4 indicates, the successful preparation of good mixed materials is not always easy and for this reason also it is not safe to make decisions on the basis of these loss measurements alone.

6. PLANS FOR NEXT QUARTER

The investigation of nonlinearities in mixed and doped perovskites will be continued and the loss tangents of these materials will be measured at microwave frequencies. In the established case, where $SrSnO_3$ doping has been shown to affect the nonlinearity of BST-50 studies will be continued to seek to establish the reproducibility of these results and to seek an optimum doping level.

Other dopants will be investigated.

Field dependent loss measurements will be conducted on some of these mixed and doped materials.

Measurements of loss and nonlinearity will be conducted close to and, if possible, below the Curie temperature.

Other single-crystal ferroelectric perovskites will be grown and investigated.

7. ACKNOWLEDGMENTS

It is a pleasure to express our appreciation of the care and thoroughness of P. Balboni, J. Matsinger, and D. Howe in making many of these measurements and assisting with others.

8. IDENTIFICATION OF PERSONNEL

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R. O. Bell	- Senior Research Scientist	16
J. S. Waugh	- Senior Research Scientist	120
B. di Benedetto	- Associate Research Scientist	80
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Report No. 9 Progress 15 September 1962 - 15 December 1962,
by R. O. Bell, B. di Benedetto and others. 7 January 1963, 40p illus., tables.

Contract DA 26-039-sc-89126 Unclassified

DESCRIPTORS: Material Investigation, Dielectric constant, Loss tangent, Nonlinearity data.

Identifiers: Single crystal $KTaO_3$, Polycrystalline $PbTiO_3$.

The nonlinearity of single crystal $KTaO_3$ has been measured at 108°K and transpires to be comparable with that of $SrTiO_3$. Microwave measurements of dielectric constant and loss tangent for mixed ceramics of the type $K_{1-x}Na_xTaO_3$ have been obtained and show the mixtures to have higher losses than comparable $Ba_{1-x}Sr_xTiO_3$ materials. A fairly marked effect of $SrSnO_3$ substitution in increasing the nonlinearity of $Ba_{0.5}Sr_{0.5}TiO_3$ has been observed with no accompanying increase of loss tangent. Losses in other mixed and doped materials have been measured.

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