

THE UNIVERSITY OF MICHIGAN
COLLEGE OF ENGINEERING
Department of Electrical Engineering

Final Report

DIELECTRIC AND OPTICAL PROPERTIES OF
TITANATE AND COLEMANITE FERROELECTRICS

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I. INTRODUCTION

The following report covers the period of from June, 1960, to June, 1961, for research on ferroelectric materials done at The University of Michigan under contract with The Caswell Electronics Corporation of San Jose, California.

The purpose of this program has been to work toward improved ferroelectric materials for ultimate application particularly in the microwave frequency range. One property of the ferroelectric of interest to the applications engineer is the change in dielectric constant of the material under the influence of electric field. The approach of The University of Michigan group toward optimizing this property for applications has been two-fold:

- (1) To identify and understand the physical mechanisms responsible for the change in permittivity with electric field.
- (2) With this knowledge, to specify the theoretical limits of the change in dielectric behavior with electric field and temperature; and also to investigate ferroelectric systems which would have the best chance for successful application.

In connection with the first point above, the writers feel that both an acceptable phenomenological theory for the nonlinear behavior has been worked out, and excellent experimental evidence to corroborate this theory has now been obtained. It must be noted that we have not directly dealt with the problem of dielectric losses, which of course is of extreme importance for applications at high frequencies. However, a suitable theory of dielectric losses (even for linear dielectrics) is not available except for a few isolated special cases. For this reason we feel that a study of this problem would have to be set up on the basis of a separate (and probably fairly extensive) research effort.

In connection with the second purpose stated above, we have noted that it would be pointless to hope to develop a material of the perovskite class (such as barium-strontium titanate) which would exhibit large changes in small-signal permittivity and at the same time not be temperature-sensitive to the extreme. That is, the mechanism for change in permittivity appears to be a thermally determined property, not only for the perovskites but for other ferroelectric systems as well. We find that once this basic mechanism is understood, there is little necessity to base the microwave applications on perovskite-like ferroelectrics, whose uncomfortably high dielectric constant must be dealt with in the microwave range. For this reason we have focused our attention on the mineral colemanite, a low-permittivity ferroelectric.

In the following sections we first consider experimental aspects of non-linear behavior in titanate-like ferroelectrics. This is followed by a description of our research on colemanite.

II. INVESTIGATION OF CHANGE IN SMALL-SIGNAL PERMITTIVITY WITH BIASING FIELDS FOR TITANATE-LIKE FERROELECTRICS

A. INTRODUCTION

In a recent publication,¹ Diamond has demonstrated that the change in permittivity with electric field in polycrystalline, mixed titanate ferroelectrics appears to be due to an induced ferroelectric state in grains which are paraelectric at zero bias rather than due to domain orientation. The reader is referred to the paper for the details (which were worked out prior to the present contract), but the main idea will be indicated here since this theory forms the basis for our calculations on colemanite.

The resultant permittivity $\overline{\epsilon(T,E)}$ of an ensemble of ceramic grains is taken as a statistical average of the permittivities $\epsilon(T,T_c,E)$ of the individual grains:

$$\overline{\epsilon(T,E)} = \frac{\int_0^{\infty} \epsilon(T,T_c,E) e^{-\frac{(T_r-T_c)^2}{\alpha^2}} dT_c}{\int_0^{\infty} e^{-\frac{(T_r-T_c)^2}{\alpha^2}} dT_c} \quad (1)$$

Where T_c is the Curie temperature of the individual grain, T_r is the Curie temperature of a macroscopic single crystal, and α is the variance of the statistical distribution. T and E are temperature and electric field, respectively. The function $\epsilon(T,T_c,E)$ is worked out from the thermodynamic theory of the single-crystal ferroelectric. Hence most of the information and assumptions in the theory are carried by the latter function. The resultant $\overline{\epsilon(T,E)}$ agrees very well with dielectric data obtained about both commercial samples and our laboratory compositions. However, direct observation of the induced ferroelectric state in originally paraelectric grains has, until the present, been lacking.

The object of the present investigation has been to make an optical study of thin sections of titanate materials and to observe directly the mechanism of the permittivity change in the ceramic grains as a function of applied electric fields and temperatures.

A number of investigators² have gathered much illuminating information on the structure of ferroelectric materials by employing the metallographic techniques of polishing and etching. A drawback of this method is its static character. Any changes in the properties of the material due

to environment (mainly those due to temperature and electric field changes in our case) can be readily detected only by renewed polishing and etching of the sample under another set of conditions. To obtain information over a whole range of temperatures and fields would be almost prohibitively time-consuming.

A less laborious method consists of preparing very thin sections of the polycrystalline material which are permeable to transmitted light. A sample of this type can be easily subjected to varying temperatures and electric fields while under microscopic observation. Since the ferroelectric to paraelectric transition goes hand in hand with the anisotropic (tetragonal) to isotropic (cubic) transition, the amount of light transmitted under crossed polars by a grain becomes an indication of the degree of its ferroelectricity, ranging from paraelectric for total extinction to extensively ferroelectric for maximum birefringence and brightness. In addition, domain striations tend to disappear as the samples are heated through their Curie temperatures. Thus this essentially mineralogical technique becomes a sensitive tool for detecting any structural changes in the titanate grains. Results of the investigation conducted along these lines show that, in the main, the method employed is satisfactory.

B. EXPERIMENTAL PROCEDURE

1. Sample Preparation.—Seven compositions of mixed barium-strontium-titanate were chosen for the present investigation (Table I). Except for the commercially obtained sample BKPIA, the ceramics were all prepared in our laboratories. They were chosen with Curie temperatures at or above room temperature so that the tetragonal to cubic transition could be controlled simply by a heating stage. As a sample was heated and cooled, capacitance and light-intensity data were taken. In addition, the changes of the electric and optical properties due to biasing fields were recorded.

Initially, uniformly thin sections, 30 μ in thickness, were ground and polished from ceramic slabs. It was found, however, that the capacitance of such a section as measured across its width was of the order of less than 1 $\mu\mu\text{f}$ and could be measured only with difficulty. This problem was solved by grinding samples in a wedge shape which had a higher over-all capacitance (10 to 30 $\mu\mu\text{f}$), yet were thin enough at one end to allow transmitted light observations (Fig. 1).

The samples are highly polished on both faces and mounted to a microscope slide with Eastman 910 Adhesive, a strong, almost invisible cement because of its similar index of refraction to that of glass. Aluminum foil strips and silver paint leading from opposite sides of the sample provide electrical contact. The slide is then placed on a heating stage and observed through a Leitz Panphot Microscope.

TABLE I

Sample	Composition, mole %	Approximate Peak, ϵ	Curie Temp., $^{\circ}\text{C}$
BKPIA	Aerovox Corp. Formula	5500	22
HS14F2	85% BaTiO ₃ 14% SrTiO ₃ 1% Fe ₂ O ₃	5000	40
HS15	85% BaTiO ₃ 15% SrTiO ₃	4600	82
HS25	75% BaTiO ₃ 25% SrTiO ₃	4400	50
HS25Cd2	73.5% BaTiO ₃ 24.5% SrTiO ₃ 2.0% CdO	5500	50
HS25Nb2	74.25% BaTiO ₃ 24.75% SrTiO ₃ 1.00% Nb ₂ O ₅	6000	20
HS25V	75.0% BaTiO ₃ 24.9% SrTiO ₃ .1% (VO ₂)(NO ₃) ₂	7500	58

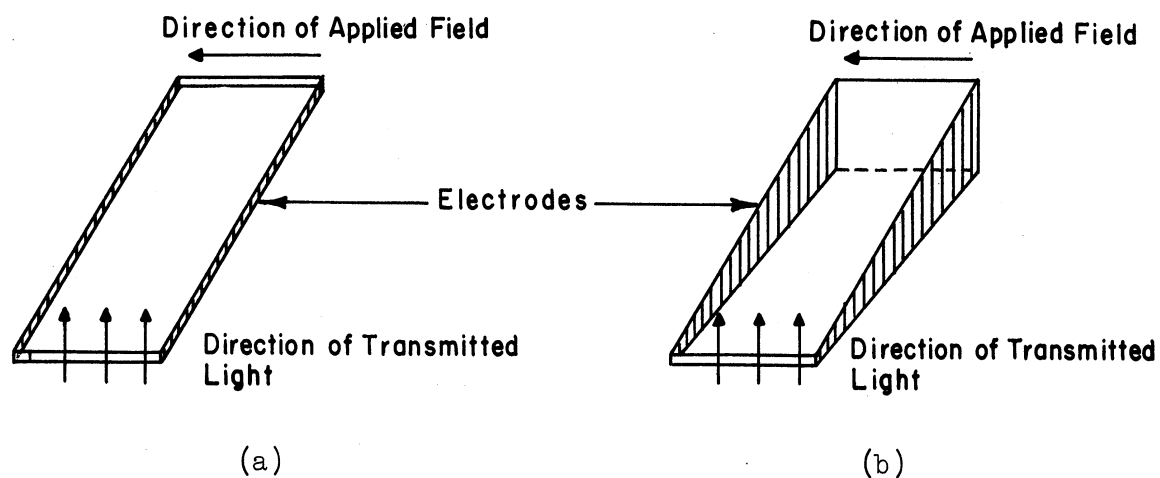


Fig. 1. (a) Uniform thin section; (b) wedge.

2. The Heating Stage.—The heating stage (Fig. 2) consists of a strip of nichrome wound mica attached to a disk of asbestos. A slit in the center of the disk over which the sample is placed allows free passage of light through the specimen while it is under observation. An iron-constantan thermocouple directly below the thick end of the wedge provides accurate temperature measurement. The heating rate is manually adjusted during the course of an experiment by a variac which is connected to a 110-volt to 6-volt step-down transformer which drives the nichrome resistance wire. The temperature is obtained from potentiometer readings of the thermocouple.

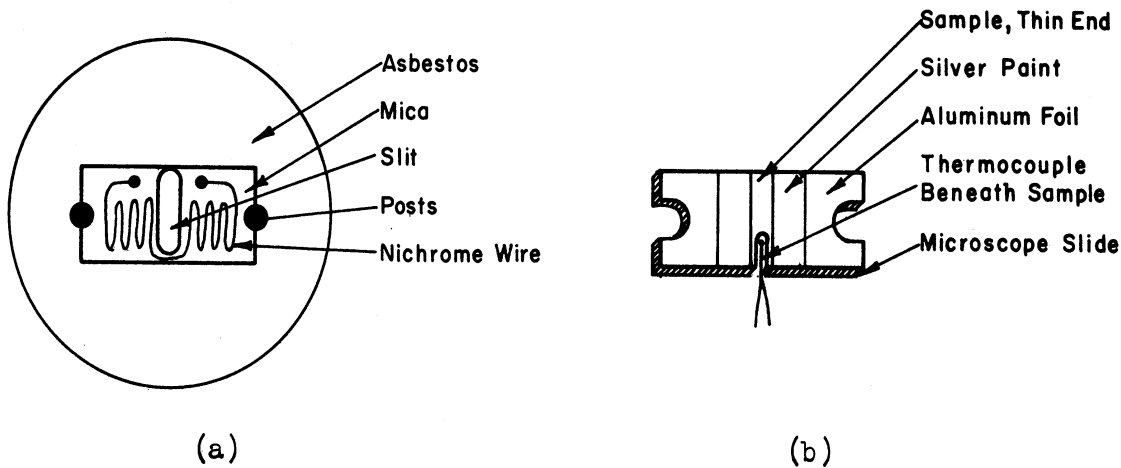


Fig. 2. (a) Heating stage; (b) sample on microscope slide.

3. Capacitance Measurements.—Capacitance measurements were taken at 1600 on a Bontoon Radio Corporation Q-meter. A 1500-volt battery box supplied the bias applied to the ferroelectric wedge. Figure 3 is schematic of the circuit. The large standard resistor and the capacitor are introduced as protective measures: the resistor to isolate the battery box from the sample, and the capacitor to isolate the Q-meter from the battery box. If one knows the effective capacitance as measured across the Q-meter terminals and the capacitance of the sample holder (microscope

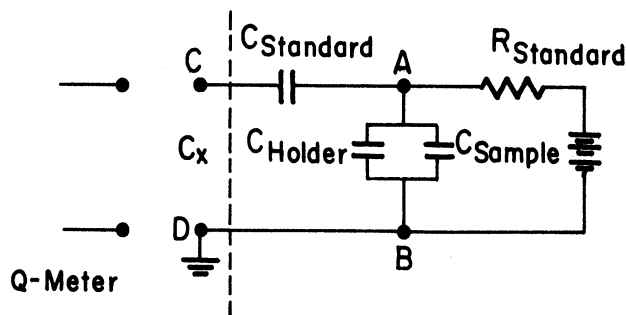


Fig. 3. Circuit for capacitance measurements.

slide with foil leads, heating stage posts and coax cable leading to Q-meter), the actual sample capacitance can be easily calculated (see Fig. 3).

$$Z_{CD} = \frac{-j}{\omega C_X} = Z_{AB} \frac{-j}{\omega C_{ST}}$$

Let

$$C_{HOLDER} = C_2$$

$$C_{SAMPLE} = C_3$$

$$Z_{AB} = \frac{-j}{\omega(C_2+C_3)}$$

$$\frac{-j}{\omega C_X} = \frac{-j}{\omega(C_2+C_3)} \frac{-j}{\omega C_{ST}}$$

$$\frac{1}{C_X} = \frac{1}{C_2+C_3} + \frac{1}{C_{ST}}$$

$$\frac{1}{C_X} = \frac{C_{ST}+C_2+C_3}{C_{ST}(C_2+C_3)}$$

$$C_{SAMPLE}: \quad C_3 = \frac{C_X(C_{ST}+C_2) - C_{ST}C_2}{C_{ST} - C_X}$$

The sample is heated and cooled through its Curie peak and measurements are taken at zero bias and at three different voltages. The results of these measurements shown in Fig. 4 appear to be similar to those obtained for "thick" (or large) samples of ceramic titanate ferroelectrics. The intensity of light traversing through the sample between crossed polars is simultaneously measured as a function of temperature and field.

4. Intensity Measurements.—The light-detecting device consists of a cadmium-sulfide photocell, a battery to drive the photocell, a microammeter,

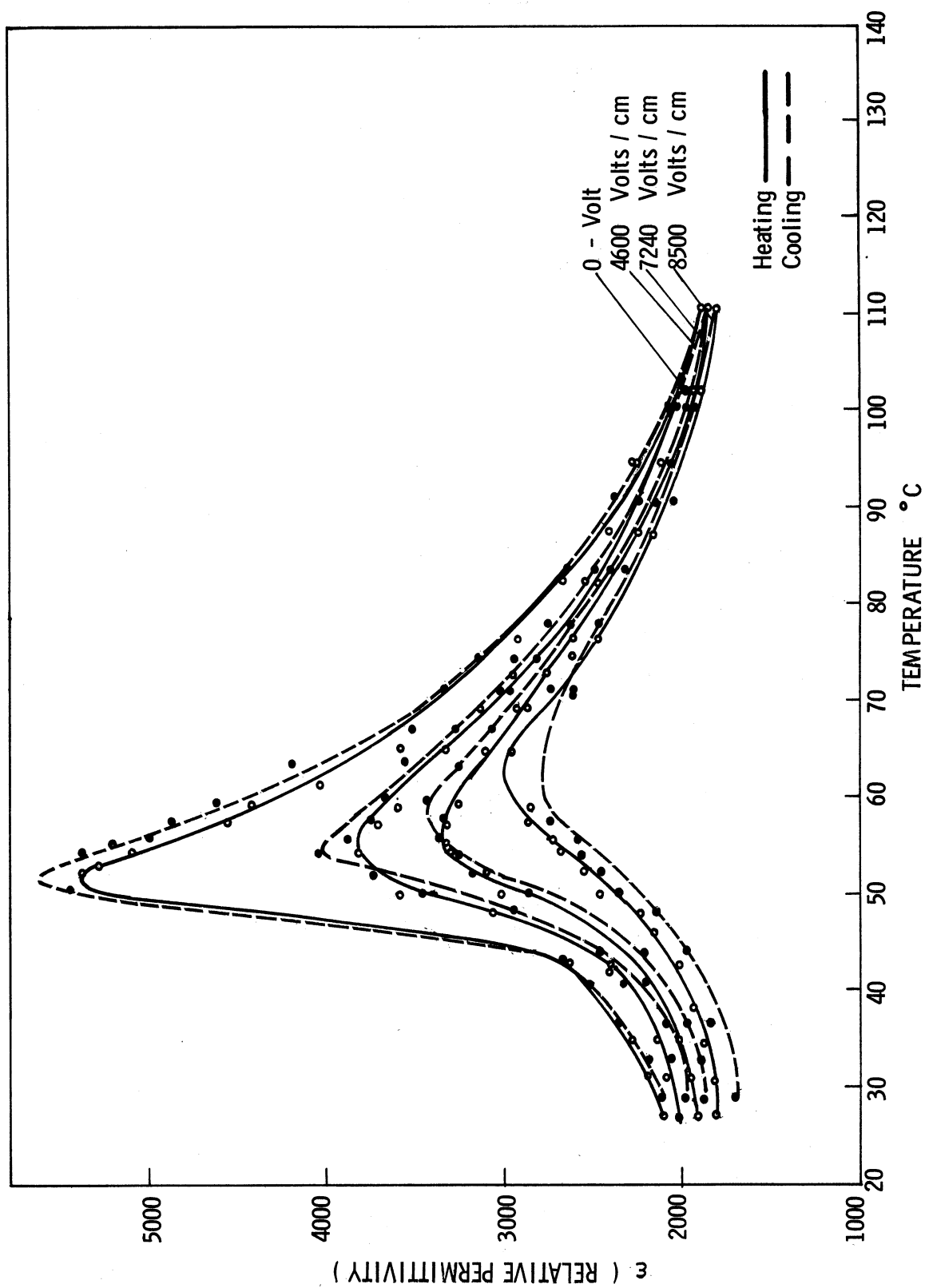


Fig. 4. ϵ vs. temperature of a wedge of ceramic ferroelectric HS25Cd2.

and a variable resistance to provide some degree of control (Fig. 5).

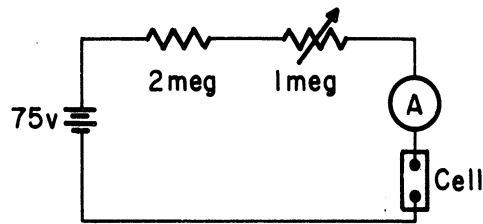


Fig. 5. Circuit for intensity measurements.

The photocell is placed directly over the microscope eyepiece. Before and after every run, it is calibrated against a Kodak density film strip to correlate the microammeter reading with diffuse density values (see Fig. 6). These provide an absolute measure of the amount of light transmitted by the ferroelectric through crossed polars.

Included are the results of the capacitance and light-intensity measurements of a representative sample of a polycrystalline ferroelectric, HS25Cd2 (see Table I). From the diffuse-density-versus temperature curves (Fig. 6), it can be seen that there is a sharp increase in

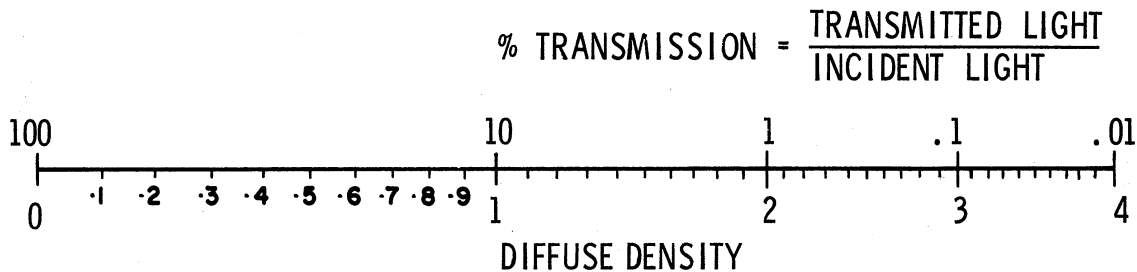


Fig. 6. Scale of diffuse density against scale of percent transmission.

the density as the ceramic is heated above its Curie point, and also that the slope is steepest in the vicinity of the Curie temperature. The effect of a d-c bias on the specimen is to shift the entire curve toward higher temperatures. At any one temperature the thin section is considerably brighter when subjected to a field than when no field is applied. Hence, it is more birefringent and more ferroelectric under the former conditions. Similarly, when a bias is applied to the sample beyond its Curie temperature when it is normally paraelectric and appears dark under crossed polars, some of the grains definitely become bright, indicating that a ferroelectric state has been induced.

5. Concluding Remarks.—The optical behavior of the ferroelectric ceramic thin sections, as observed by light-intensity measurements, follows their electrical behavior very closely. As the incremental permittivity goes through a peak value at the Curie temperature, the ceramic grains pass through a transition from ferroelectric to paraelectric and a simultaneous phase transition from tetragonal to isotropic. This is optically seen in transmitted polarized light as a gradual darkening and subsequent extinguishing of the grains.

It has been observed that the Curie peak shifts to higher temperatures in mixed ferroelectric ceramics when a biasing field is applied. The amount of polarized light passing through such a ceramic shows a maximum intensity change around the Curie temperature and, when the section is subjected to an electric field, this change similarly occurs at a higher temperature.

The voltage sensitivity of the ferroelectric ceramics is a direct result of this phenomenon. When subjected to strong d-c fields, the incremental permittivity of the sample is lowered, especially around the Curie temperature where the voltage sensitivity is greatest. Some workers who have extended their knowledge of the behavior of single crystals to that of ferroelectric ceramics have concluded that the lowering of the incremental permittivity in ceramics is due to the alignment of domains along the field direction. Since the permittivity as measured perpendicular to the polar direction is considerably lower than that measured along the polar direction, the net result of domain alignments throughout the grains of a ceramic would lead to a drop in the total permittivity when measured perpendicular to the field.

It has been demonstrated in a recent publication, however, that the change in permittivity with electric field in polycrystalline, mixed titanate ferroelectrics appears to be due to an induced ferroelectric state in grains which are paraelectric at zero bias rather than due to domain orientation.¹ In support of this point of view are the following optical observations:

(a) No definite signs of domain rotation or motion, as evidenced by a shifting of domain striations, could be observed which would explain the instantaneous drop in capacitance when a d-c field is applied to the ceramic.

(b) The greatest change in the intensity of transmitted light upon field application actually occurs when the ceramic is heated somewhat beyond the Curie temperature where most of the grains are paraelectric.* A strong d-c field applied to the almost extinguished sample results in a brightening equivalent to temperature conditions which existed 15-20°C below the measured one at zero bias, where the sample had been clearly ferroelectric. Thus we think of a field-induced ferroelectric state in the paraelectric grains as the main cause of the voltage sensitivity. Domain alignment in the field direction would

*See diffuse-density-vs.-temperature chart; also photographs of a ferroelectric ceramic submitted in a previous report.

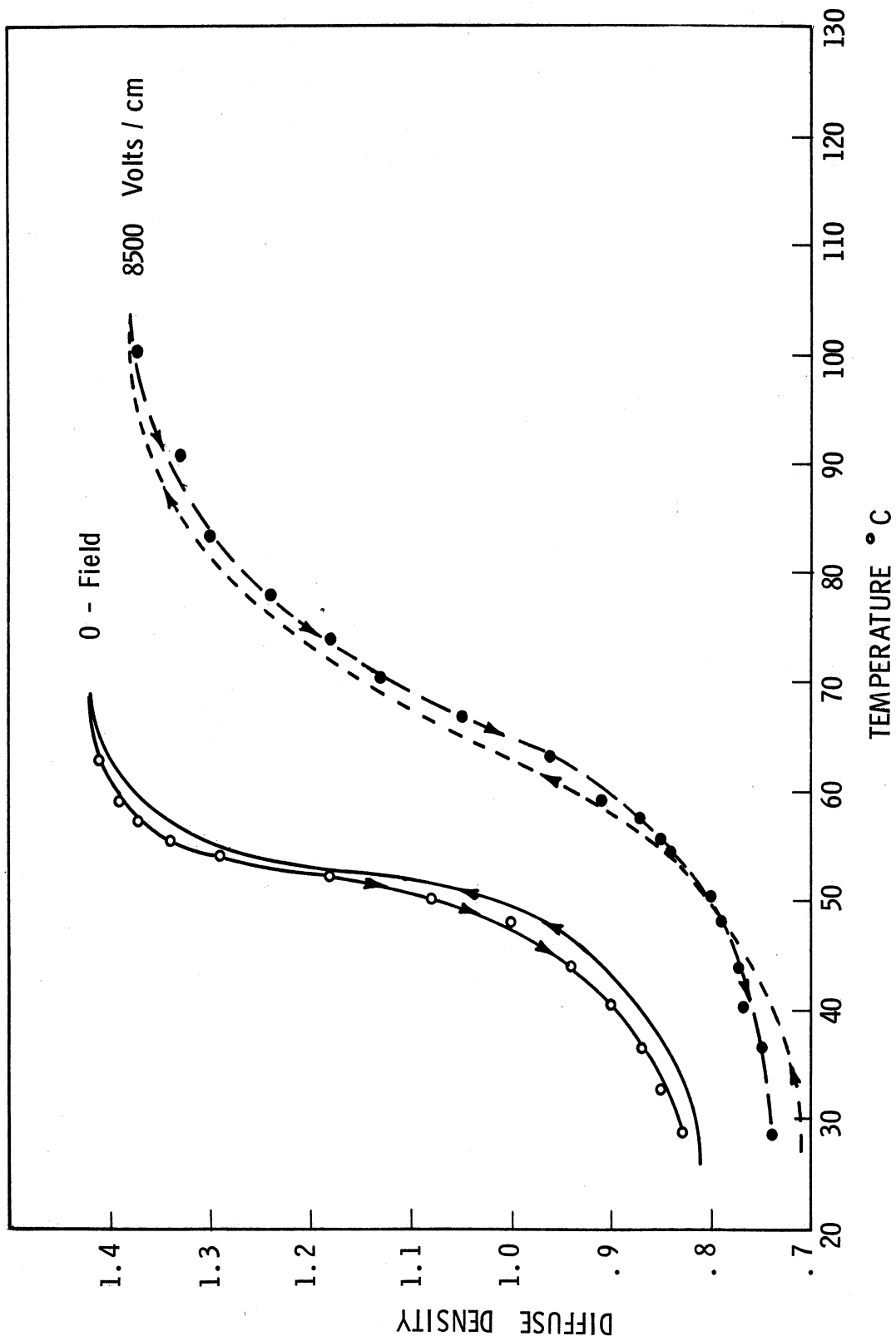


Fig. 7. Diffuse density vs. temperature of a thin wedge of ferroelectric ceramic HS₂₅Cd₂ measured under crossed nicols.

have little influence on the permittivity at this point since most of the grains are isotropic and have no domains.

It should also be pointed out that when domain alignment could occur, i.e., when the ceramic grains are all totally ferroelectric, the applied field changes the light intensity (and the permittivity) by only a very small amount and therefore it seems justified to assume that the domains in the ceramic are "frozen in." A small change in intensity with applied fields has also been observed when the sample is heated to far beyond its Curie temperature. The changes here may perhaps be intuitively explained as strain effects.

III. INVESTIGATION OF COLEMANITE FERROELECTRICS

A. REVIEW

After we had studied the literature of about 100 ferroelectric materials, the mineral colemanite was selected for further study. The main criteria used in selecting a material were;

1. The average permittivity should be as low as possible to mitigate matching problems.
2. The ratio of the value of permittivity at the peak of the ϵ vs. T curve to the minimum permittivity ($\epsilon_{\max}/\epsilon_{\min}$) should be large, (see Fig. 8). Based on the theoretical considerations mentioned earlier, our group feels this ratio is directly related to the change of the small-signal permittivity with electric field.

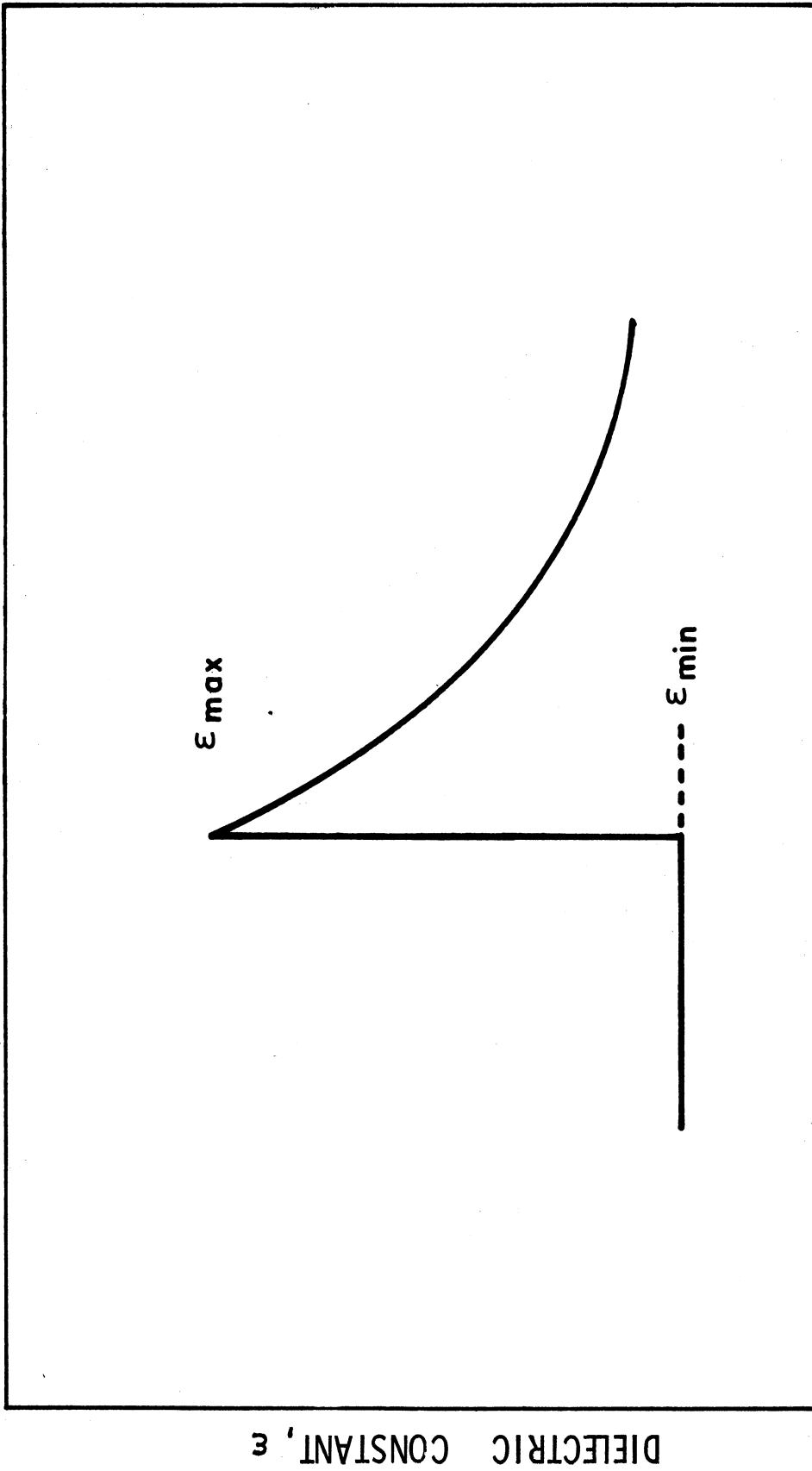
Colemanite met these criteria better than any of the materials on the basis of published data.

Experimental work was first directed toward reproducing Wieder's data³ on colemanite single crystals to check the accuracy of the published data and to get some experience in handling the material. Our results compared favorably with the published data. Two of our original curves are shown in Figs. 9 and 10.

To distribute the Curie temperatures and spread the very sharp peak of the ϵ vs. T curve over a wider temperature range, we wished to devise a colemanite sample in polycrystalline form. Our samples of polycrystalline colemanite have been made by mixing a small amount (5%) of a thermosetting resin binder with colemanite powder (obtained by grinding the single crystal). This mixture was then pressed at 20,000 psi to produce a mechanically rigid sample. Results of initial experiments on these samples are shown in Fig. 11.

In addition to this work, efforts were made to synthesize colemanite single crystals in our laboratory. Our attempts proved to be unsuccessful and this phase was discontinued. Had this work been successful, it might have been possible to initiate controlled experiments on modifying dielectric properties by atomic substitutions in the original colemanite structure.

To use a ferroelectric material in a nonlinear application, it is desirable to optimize the change in magnitude of ϵ as a function of applied field with a minimum of dielectric loss and thermal sensitivity. An attempt to do



TEMPERATURE

Fig. 8. Schematic diagram explaining ϵ_{max} and ϵ_{min} .

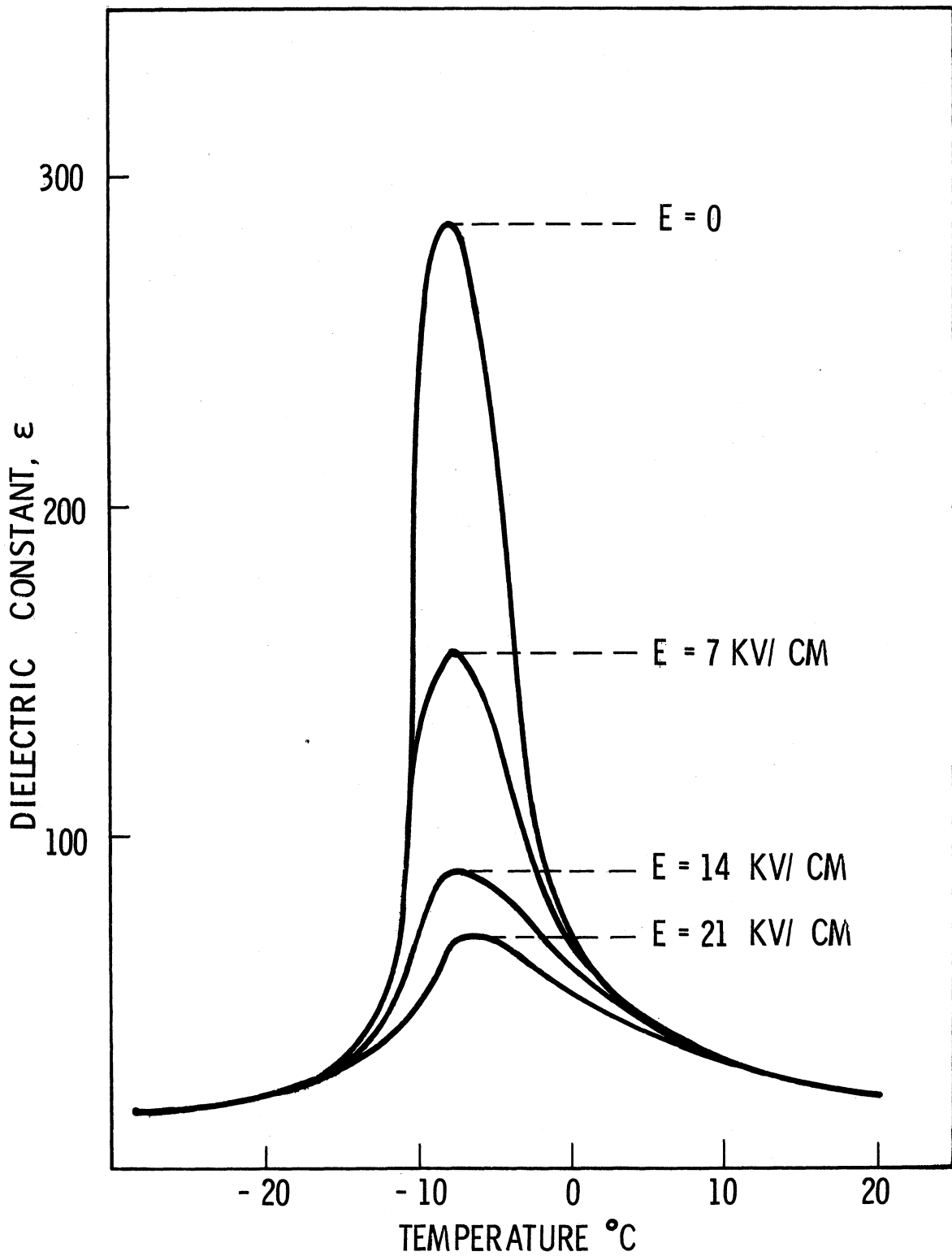


Fig. 9. ϵ vs. temp. for various values of electric field for single crystal colemanite. (Field parallel with the ferroelectric axis.)

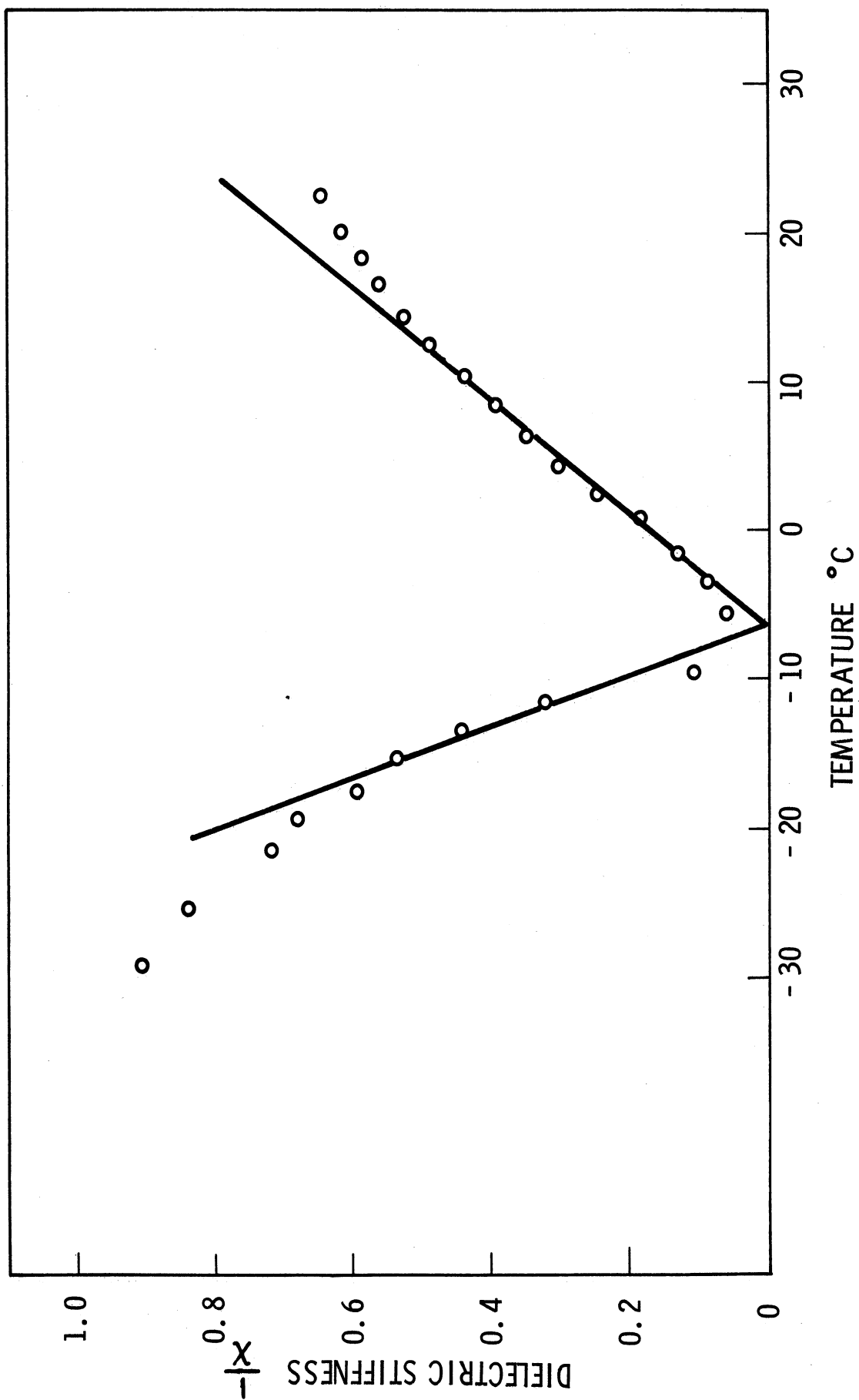
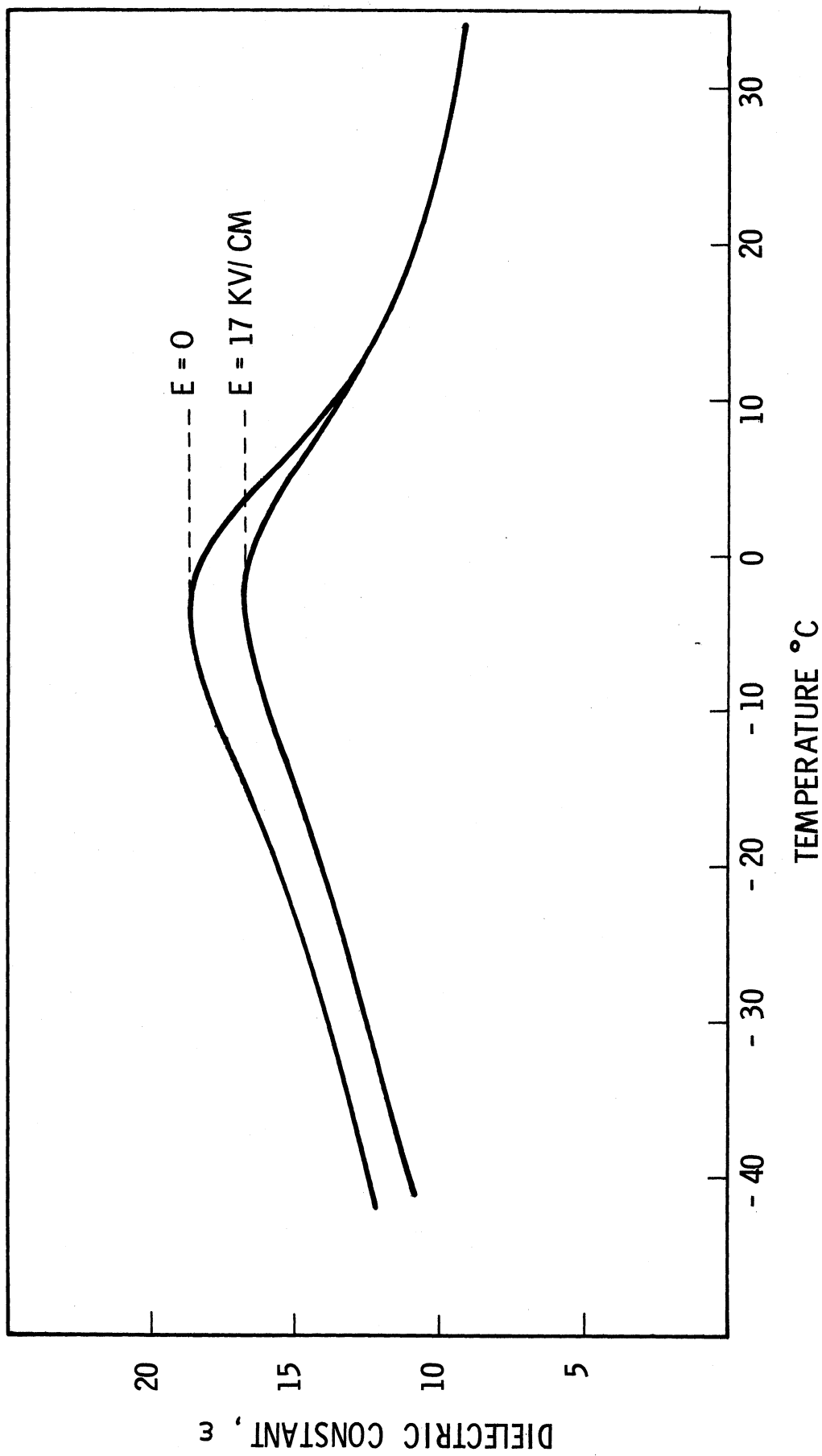


Fig. 10. Dielectric stiffness (1/χ) vs. T.



this was the next step in our study of colemanite and was attacked in two ways: first, by reducing the amount of binder in the polycrystalline sample and second, by adding a high dielectric material to fill up the voids between grains. The results of this work are described below.

Reducing the amount of low ϵ material in a mixture of two dielectrics will increase the effective field across the high ϵ material. Because the permittivity of colemanite is of the order of 30 and that of the resin about 5, it is evidently desirable to reduce the amount of resin in our polycrystalline material to a minimum. Several samples were manufactured with varying percentages of resin binder to determine the smallest amount of binder required to produce a mechanically stable product. Experimental tests showed a surprising result. Changing the percentage of resin over a small range has very little effect on the shape and magnitude of the ϵ vs. T curve. Therefore, the ratio of $\epsilon_{\max}/\epsilon_{\min}$ can apparently not be increased appreciably by reducing the percentage of resin.

A second approach to the problem of increasing the electric field in the colemanite was to fill the air voids in the polycrystalline colemanite with a very high ϵ material. Ba-Sr-TiO₃ with a maximum permittivity at 0°C was chosen. Ten to twelve percent of a very fine (300 mesh) powder of Ba-Sr-TiO₃ was added to a mixture of thermosetting resin and colemanite powder before pressing. Measurements on the pressed samples showed that the permittivity is increased, but there is no noticeable effect on the non-linearity (change in permittivity with field). It is difficult to explain this result. Since the permittivity of the sample apparently increased as a result of the addition of the titanate filler, one would naturally expect that the material would also be more field-sensitive—especially since the titanate filler is in itself field-sensitive.

The effect of the electric field on dielectric constant in the polycrystalline samples is disappointingly small compared to that of the single-crystal (see Fig. 9 and compare with Fig. 11). Neither of the two approaches described above seemed to improve the situation. What is even more frustrating is that several other questions are raised by comparing a typical ϵ vs. T curve for a colemanite crystal with that of polycrystalline colemanite. (Compare Fig. 12 with Fig. 9). For example: Why does ϵ_{\max} occur at a higher temperature in the polycrystalline colemanite than in the crystal? The crystal sections and powder were obtained from the same parent crystal. Why does the peak of the heating curve occur at -5°C, while the peak of the cooling curve is 0°C? This is just the opposite of the result that is usually observed in ordinary thermal hysteresis. Why does the minimum dielectric constant of the crystal occur below the Curie temperature, whereas the reverse is true for the polycrystalline material?

The answers to these questions are not known at this time and may appear

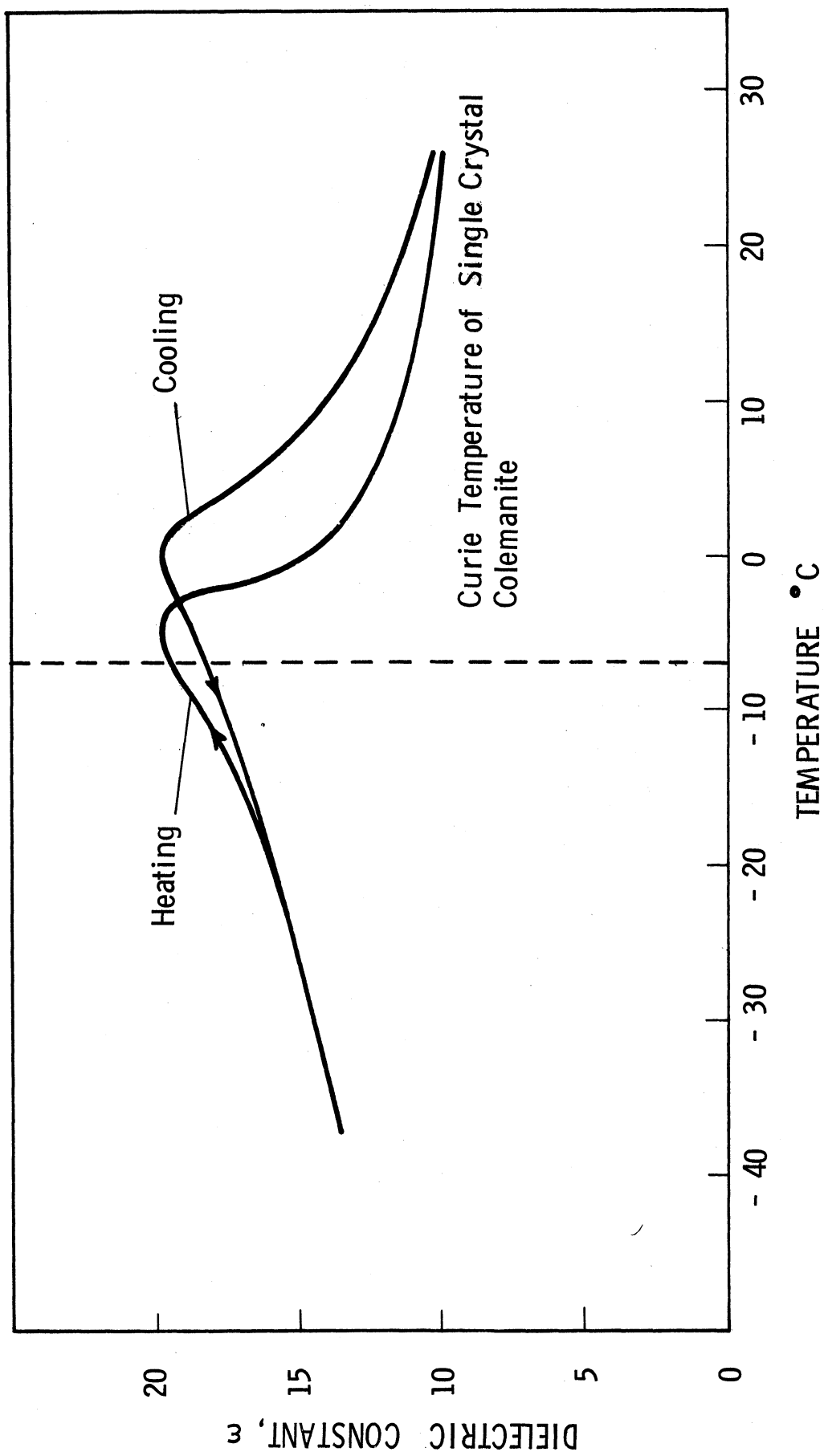


Fig. 12. Heating and cooling curves of polycrystalline colemanite.

irrelevant to the problem at hand. However, these thermal properties of polycrystalline colemanite must undoubtedly be related to the nonlinear electrical properties as is the case for the single crystal. An interpretation of the electrical behavior, based on a thermodynamic analysis, is given in the next section.

One further point should be mentioned in connection with our experiments with polycrystalline colemanite. It is well known that for a single crystal of this material, the permittivity ϵ depends on the direction in the crystal. Moreover, only one direction in the crystal exhibits ferroelectric properties. In directions perpendicular to this ferroelectric axis, the material shows no Curie temperature, and does not display nonlinear properties with electric field. In other words, in these latter directions the substance is for all practical purposes a well-behaved linear dielectric. Hence in a polycrystalline sample the grains would be expected to be randomly oriented so that the nonferroelectric orientations would tend to "dilute" the ferroelectric properties of those grains which are favorably oriented. This is not really what happens for colemanite, however. This mineral has a very definite cleavage plane normal to the ferroelectric axis, causing it to form small flakes when ground into a powder. These flakes tend to compact under pressure to form a material which has a high percentage of grains with a ferroelectric axis along the direction of pressing. That this is the case may be seen from the results of experiments depicted in Fig. 13. Here we compare dielectric constant for a polycrystalline colemanite both parallel and transverse to the direction of pressing. A definite difference is seen and is attributed to the way in which the flakes compact under pressure.

B. COMPUTATION OF ϵ VS. T AND E FOR POLYCRYSTALLINE COLEMANITE

To obtain a theoretical estimate of what may be expected for the field-sensitivity and thermal behavior for polycrystalline colemanite, the following analysis was made, with these assumptions:

1. Polycrystalline colemanite consists of a collection of grains, each one of which has the dielectric properties of a miniature single crystal.

2. The ferroelectric axis of each grain is presumed to lie along the direction of the applied field. This is only an approximation but may not be too unrealistic because of the way the colemanite grains must compact under pressure with the flake-like grains oriented normal to the direction of pressing. Because of this assumption the computed permittivity vs. field will be the maximum expected value.

3. The Curie points of the crystallites are taken in a statistical distribution about some convenient temperature, say the Curie temperature of a macroscopic single crystal (-7°C). We call this temperature T_r .

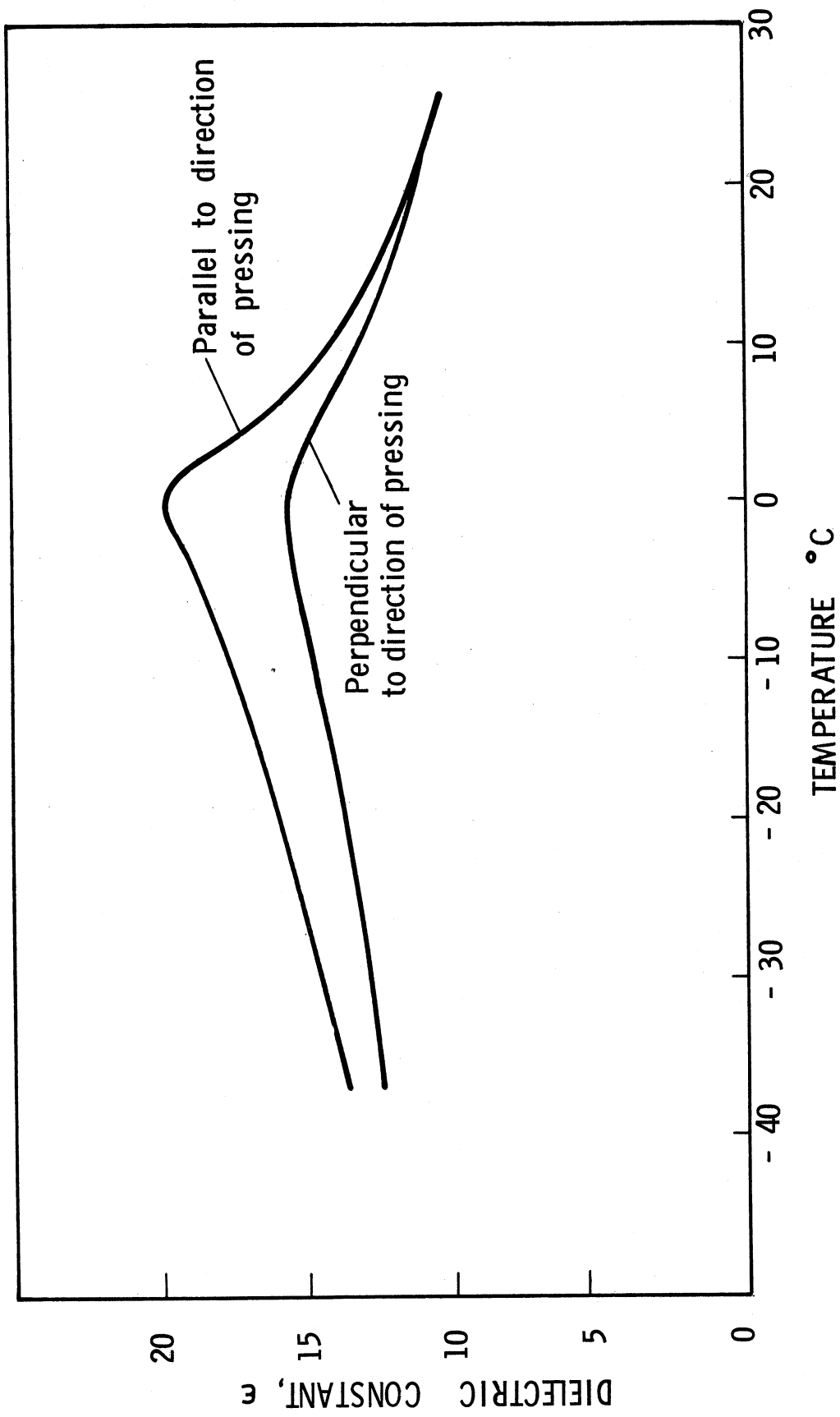


Fig. 13. ϵ vs. T for polycrystalline colemanite measured parallel and perpendicular to direction of pressing.

This distribution is thought to be produced by chemical inhomogeneities and strains on the individual grains.

4. The thermodynamic free-energy function of the crystallites is of the same form as that for the single crystal.

Under these assumptions, the average permittivity $\overline{\epsilon(T,E)}$, of such a collection of grains has the following form, using a Gaussian distribution:

$$\overline{\epsilon(T,E)} = \frac{\int_0^{\infty} \epsilon(T, T_c, E) e^{-\frac{(T_r - T_c)^2}{\alpha^2}} dT_c}{\int_0^{\infty} e^{-\frac{(T_r - T_c)^2}{\alpha^2}} dT_c} \quad (1)$$

where

T_c is the Curie temperature of each individual grain,
 T_r is the Curie temperature of a macroscopic single crystal,
 E is the electric field,
 T is the temperature, and
 α is the variance of the distribution.

The function $\epsilon(T, T_c, E)$ is obtained from the Helmholtz free-energy function in the following way.

Suppose the free-energy function $A(P, T)$ can be expressed as a power series expansion in the polarization³ P as follows:

$$A(P, T) = A_0 + a(T)P^2 + bP^4 + cP^6 \dots \quad (2)$$

From elementary thermodynamics we know that

$$\left(\frac{\partial A}{\partial P}\right)_T = E \quad \text{and} \quad \left(\frac{\partial^2 A}{\partial P^2}\right)_T = \left(\frac{\partial E}{\partial P}\right)_T = \frac{1}{\chi} \quad (3)$$

$$\text{also, } E(P, T) = 2a(T) + 4bP^3 + 6cP^5 + \dots \quad (4)$$

The factor χ is called the dielectric stiffness and is related to the permittivity ϵ via

$$\chi = \frac{\epsilon - 1}{4\pi} \quad \text{in cgs units} \quad (5)$$

From the above and from (2) we have

$$\frac{4\pi}{\epsilon-1} = \frac{1}{\chi} = 2a(T) + 12bP^2 + 30cP^4 + \dots \quad (6)$$

Since via relation (4) P depends on E, one can solve (6) for $\epsilon(T, T_c E)$ and this in turn is substituted into the integral in (1). In general the evaluation of these integrals must be done numerically on an electronic computer. The constants a, b, and c in (2) have been determined experimentally for colemanite by Wieder.³

Actual computations based on Wieder's constants and for a variance α of 10°C are shown in Fig. 14. The permittivity vs. temperature is given for zero field and for a field of 15 kv/cm. Over the temperature range considered for the latter curves (-12°C to +3°C), the relative change in permittivity with electric field is comparable to that obtained experimentally (compare Fig. 14 with Fig. 11). The most striking feature about the theoretical curves is that the permittivity is fairly high (about twice that of the experimental data). Both the theoretical and experimental change in ϵ with field is disappointingly small for most applications.

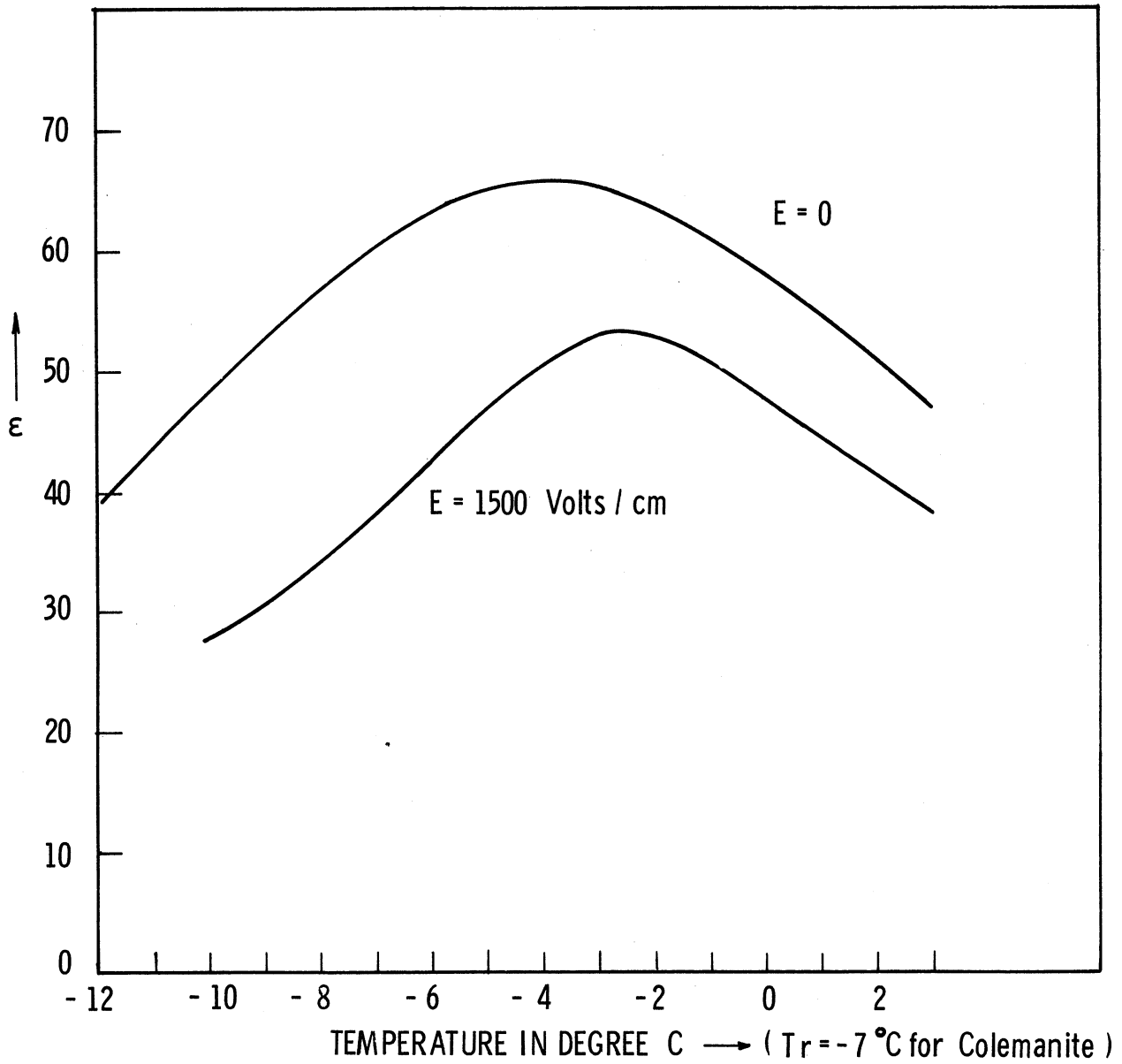


Fig. 14. Theoretical ϵ vs. T for polycrystalline colemanite for zero field and for a field of 15 kv/cm.

IV. CONCLUSIONS

The following conclusions may be drawn from the work described in this report.

A. On the basis of the optical study of titanate ferroelectric thin sections, we have direct experimental verification of the fact that the change in dielectric constant with electric field does not depend on domain rotation and alignment. The change of dielectric constant is observed to be correlated with a field-induced change of phase (cubic to tetragonal) in the individual crystallites making up the ceramic. The implication of this result is that it is theoretically necessary that the change in permittivity with field is maximum where the thermal instability is maximum. That is, in order that the ferroelectric be field-sensitive, it must also be proportionately temperature-sensitive.

In light of this positive identification of the mechanism for the non-linear behavior in the titanates, we extended the investigation to other classes of ferroelectrics which potentially would behave in a manner similar to the mixed titanates. The latter materials are somewhat difficult to apply at microwave frequencies due to the problem of matching into their very high value of permittivity. Thus we focused attention on the comparatively low-permittivity but field-sensitive material colemanite.

B. Experimental data on single-crystal colemanite show that very large changes in dielectric constant with field are obtainable but at the price of extreme thermal sensitivity (see Fig. 9). This was expected, however, on the basis of the discussion above. The general levels of the dielectric constants are about an order of magnitude less than those for the titanates, however. In an attempt to smooth the temperature variation, a colemanite "ceramic" (polycrystalline aggregate) was made. We were successful in reducing the thermal sensitivity, but the change in permittivity with electric field was severely limited (Fig. 11). It is interesting to note that the dielectric constants run only between 15 to 20 for this composition. Other experiments made on the polycrystalline colemanite (such as thermal hysteresis, etc.) appeared too erratic and inconsistent to afford an explanation at this time.

C. Computations based on the considerations of Section III show that the results of experimental measurements of ϵ vs. T and E for polycrystalline colemanite are roughly what is expected theoretically. One notes, however, that the experimental voltage-sensitivity is not as great as that predicted theoretically. This is probably because of several idealizations and simplifying

assumptions made in the latter case. An example of this is that the calculations were based on the supposition that the colemanite grains will be oriented during the pressing procedure (due to the flake-like character of the grain) in such a way that the ferroelectric axis of all the grains would be aligned. Any deviation from this assumption would effectively produce a "diluted" ferroelectric and a lower voltage-sensitivity would result.

We conclude this report with the following remarks. Our approach to the study and ultimate improvement of nonlinear dielectrics has been contrary to the cookbook or recipe variation prevalent in the materials field today. With the positive identification of the nonlinear mechanism and with our experience in applying the principles of the theory to a substance such as colemanite, several other substances naturally suggest themselves at this time as being potentially superior to either colemanite or the titanates. Among the more interesting substances are the polar solids and low-permittivity ferroelectrics of the double Curie point type.

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