

Sept. 16, 1958

J. P. REMEIKA

2,852,400

BARIUM TITANATE AS A FERROELECTRIC MATERIAL

Filed March 24, 1953

3 Sheets-Sheet 1

FIG. 1

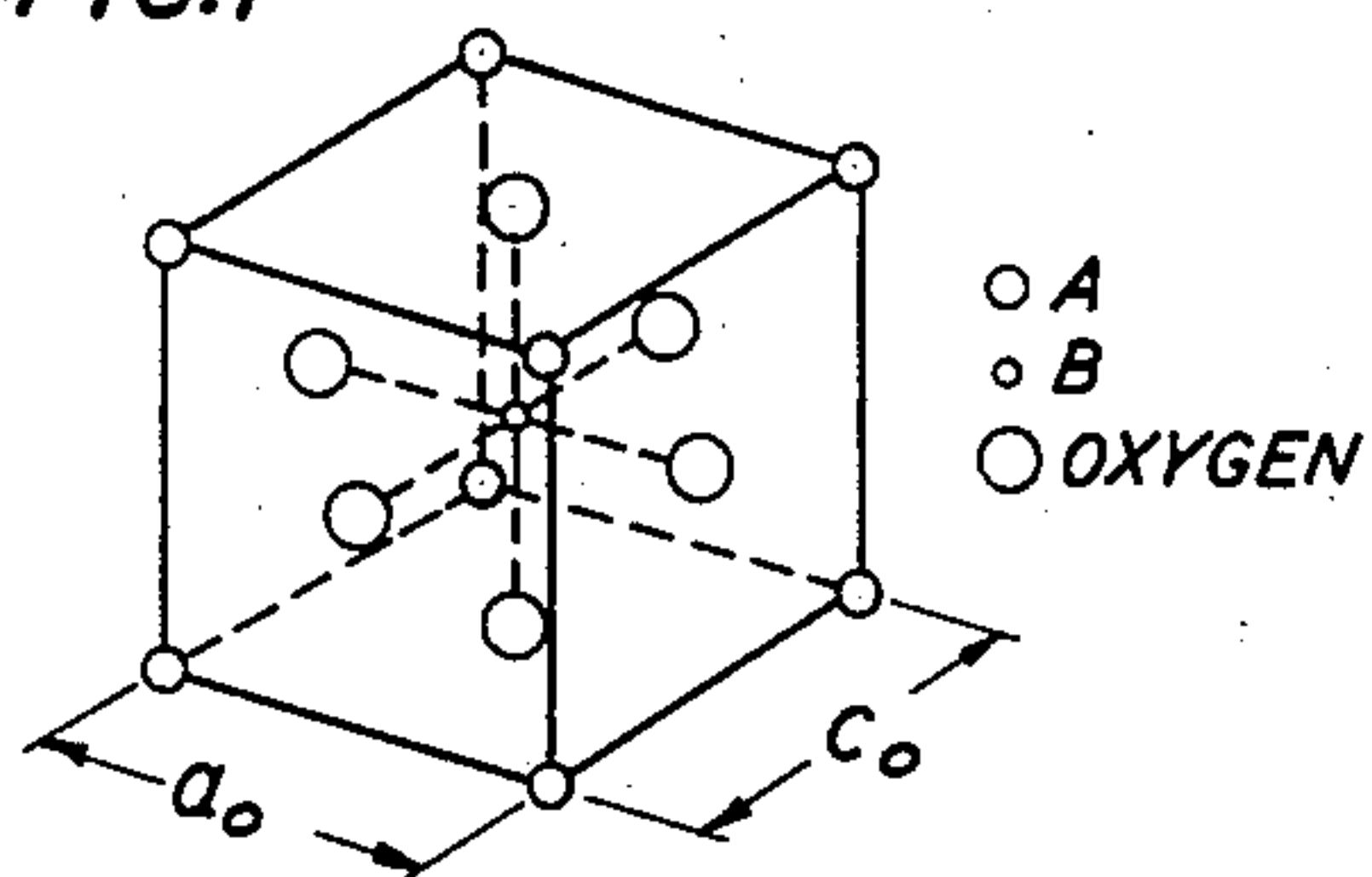
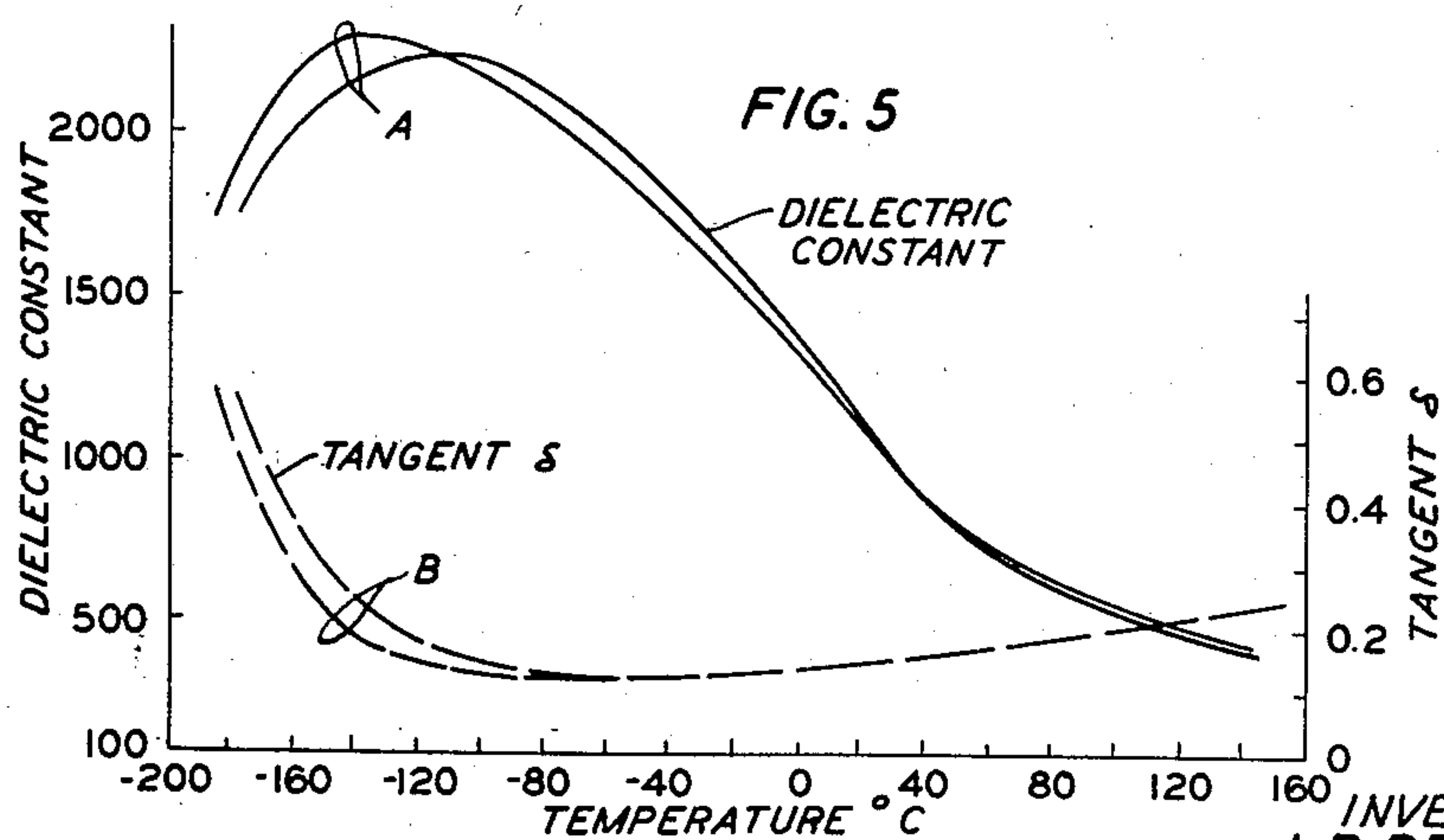
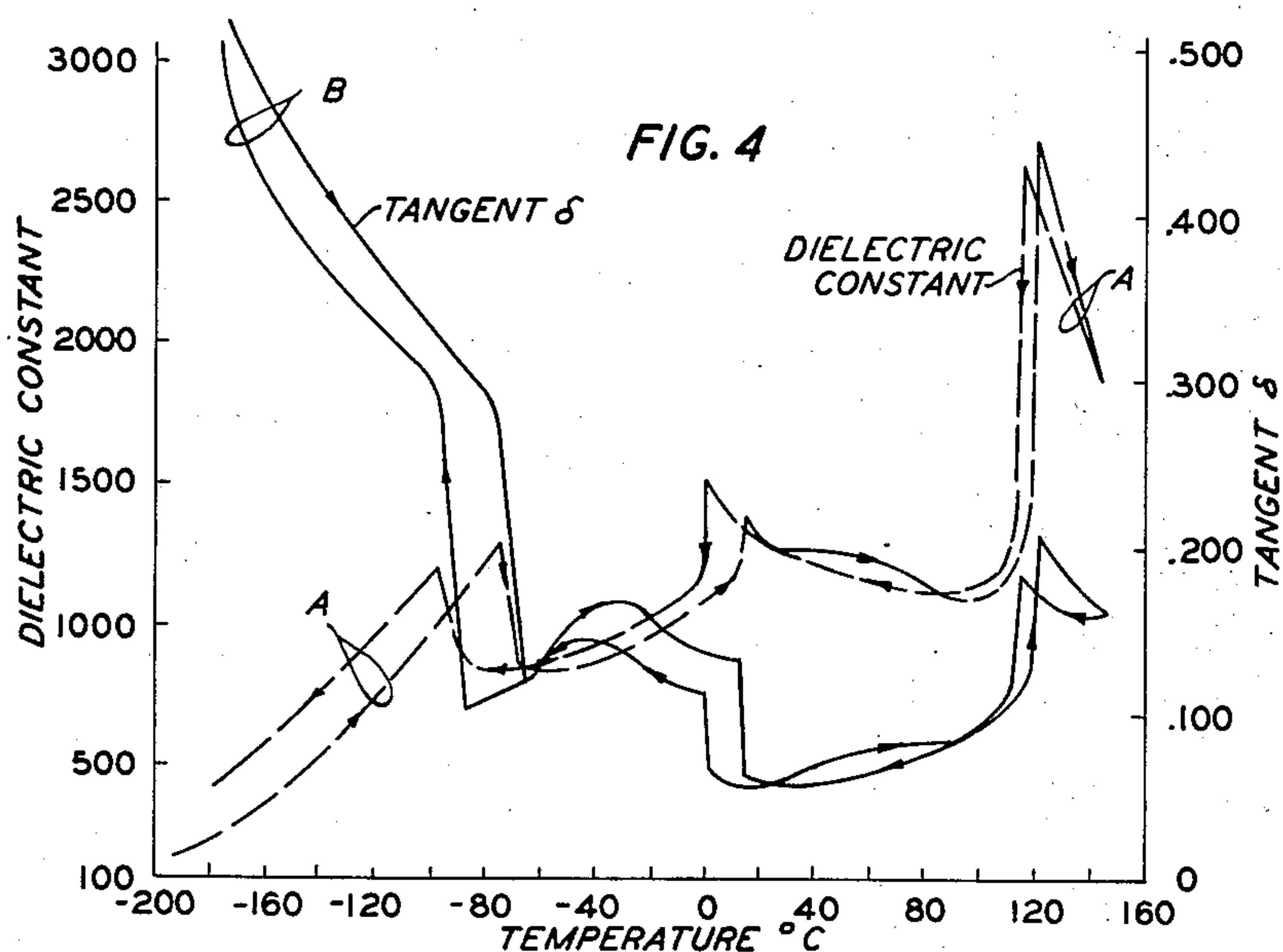
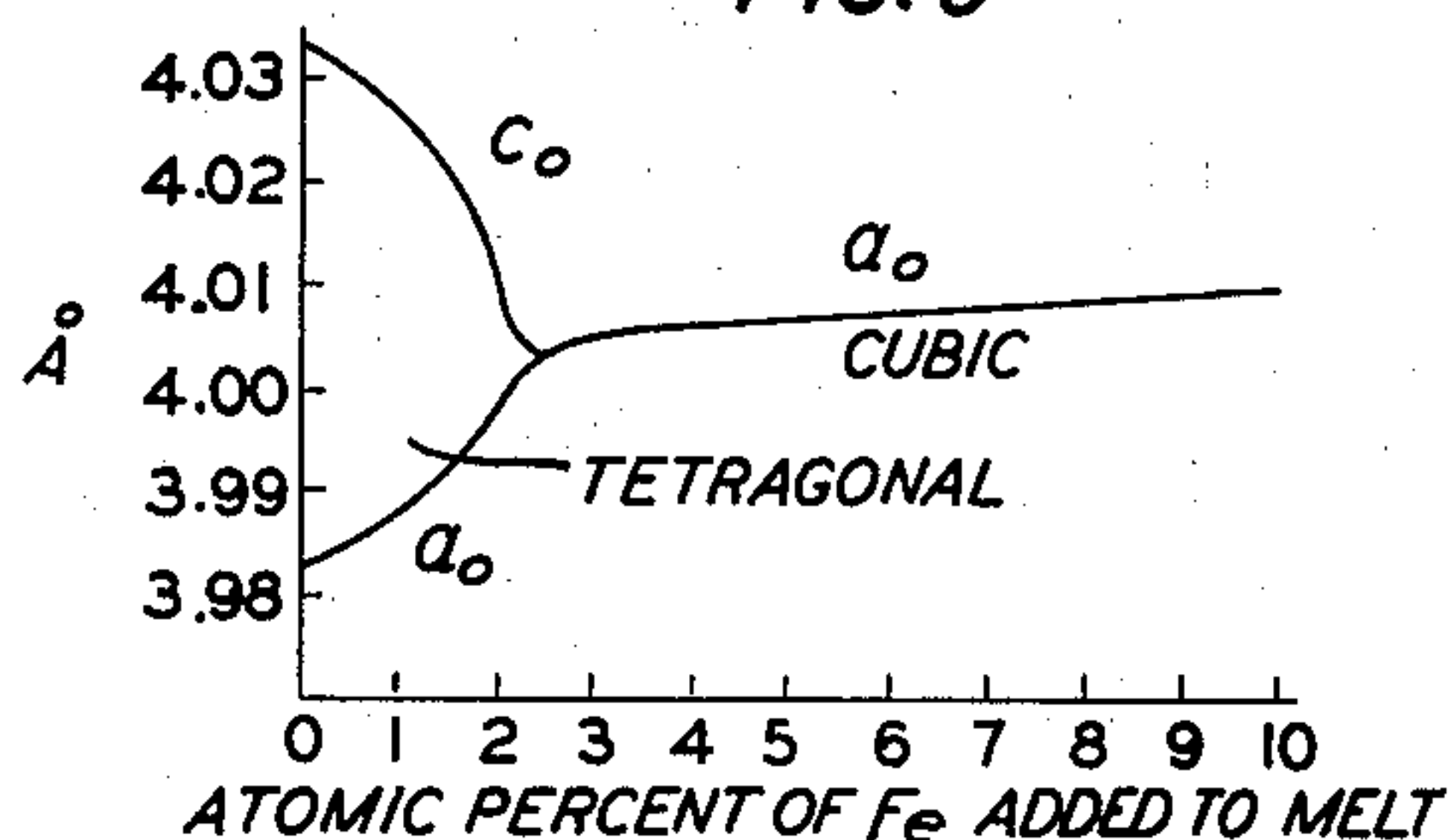


FIG. 3



INVENTOR
J. P. REMEIKA
BY
Hugh S. Wentz
ATTORNEY

Sept. 16, 1958

J. P. REMEIKA

2,852,400

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FIG. 2

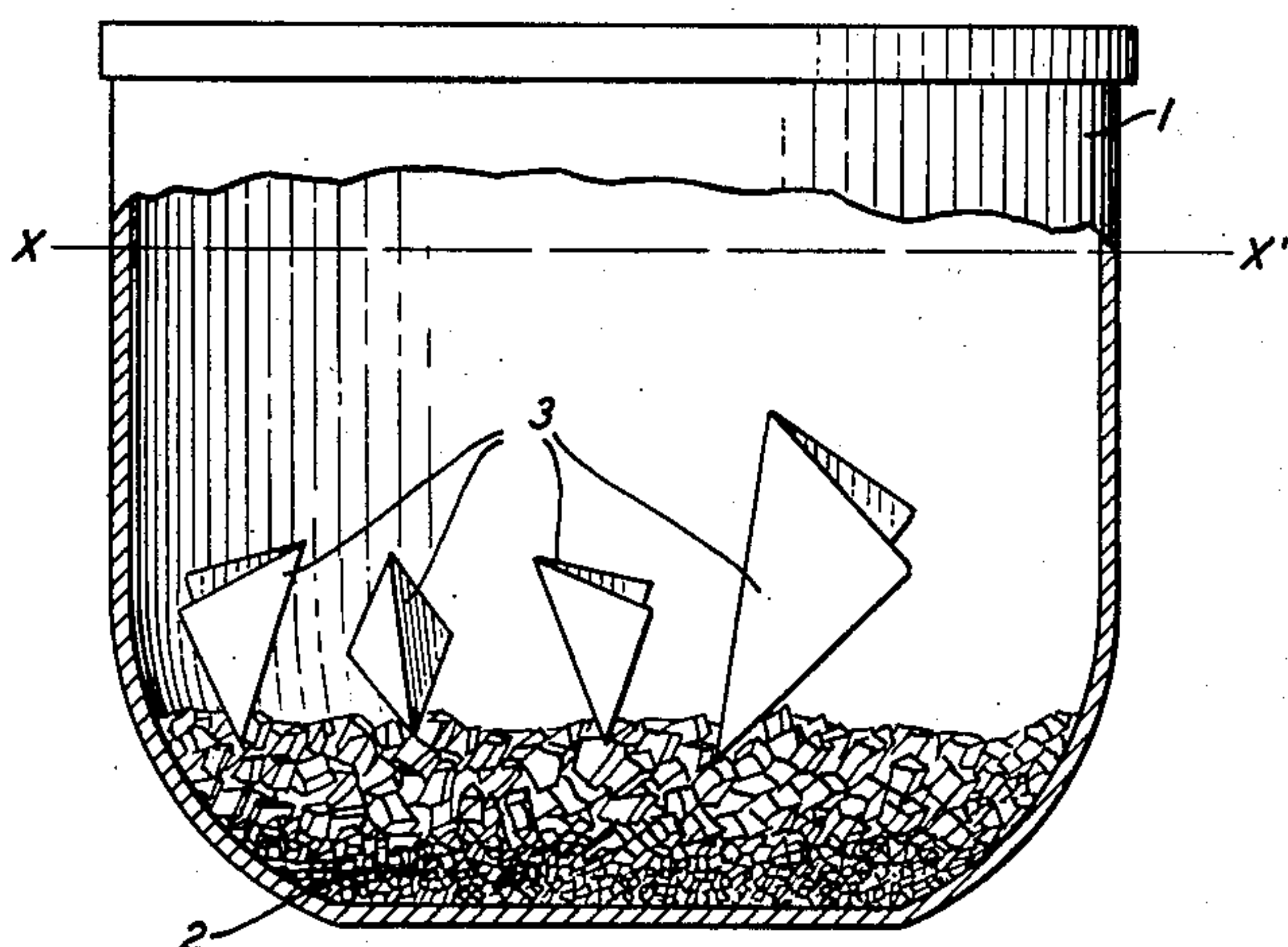


FIG. 6

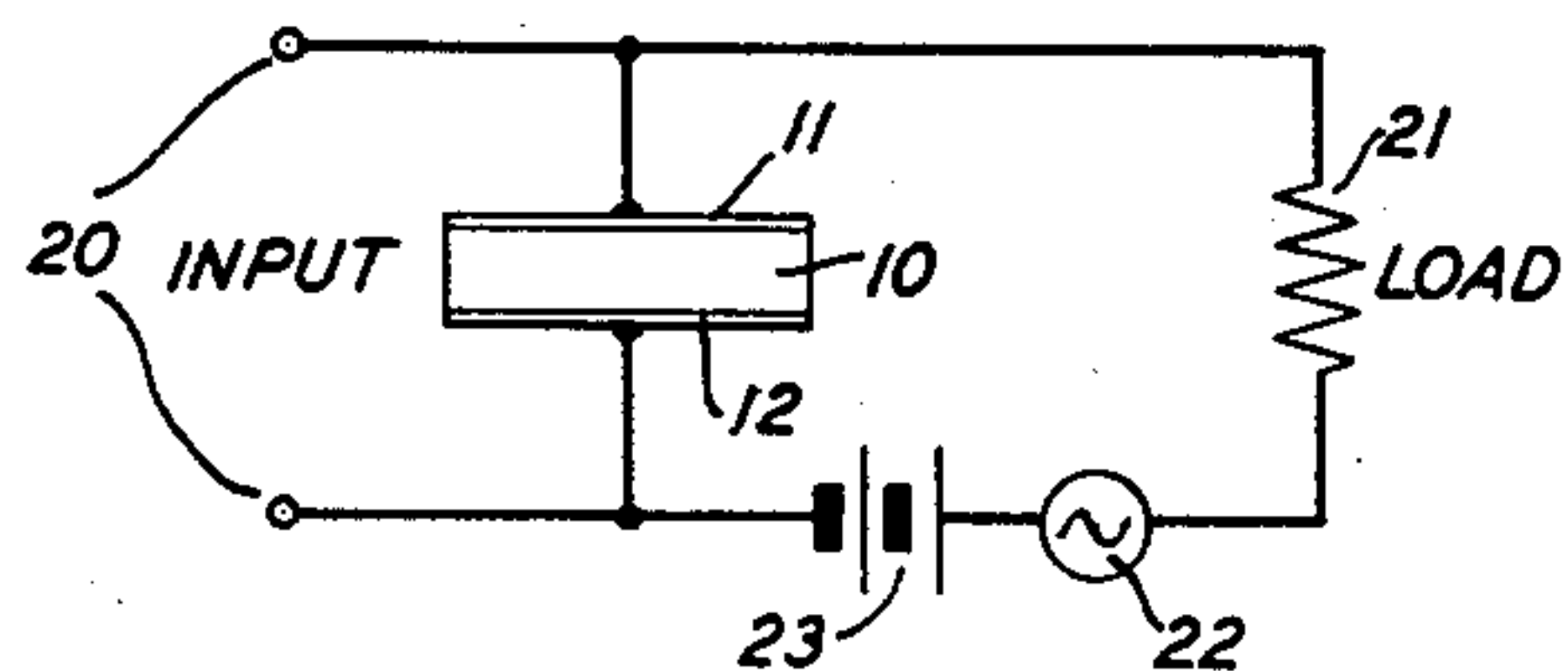


FIG. 8

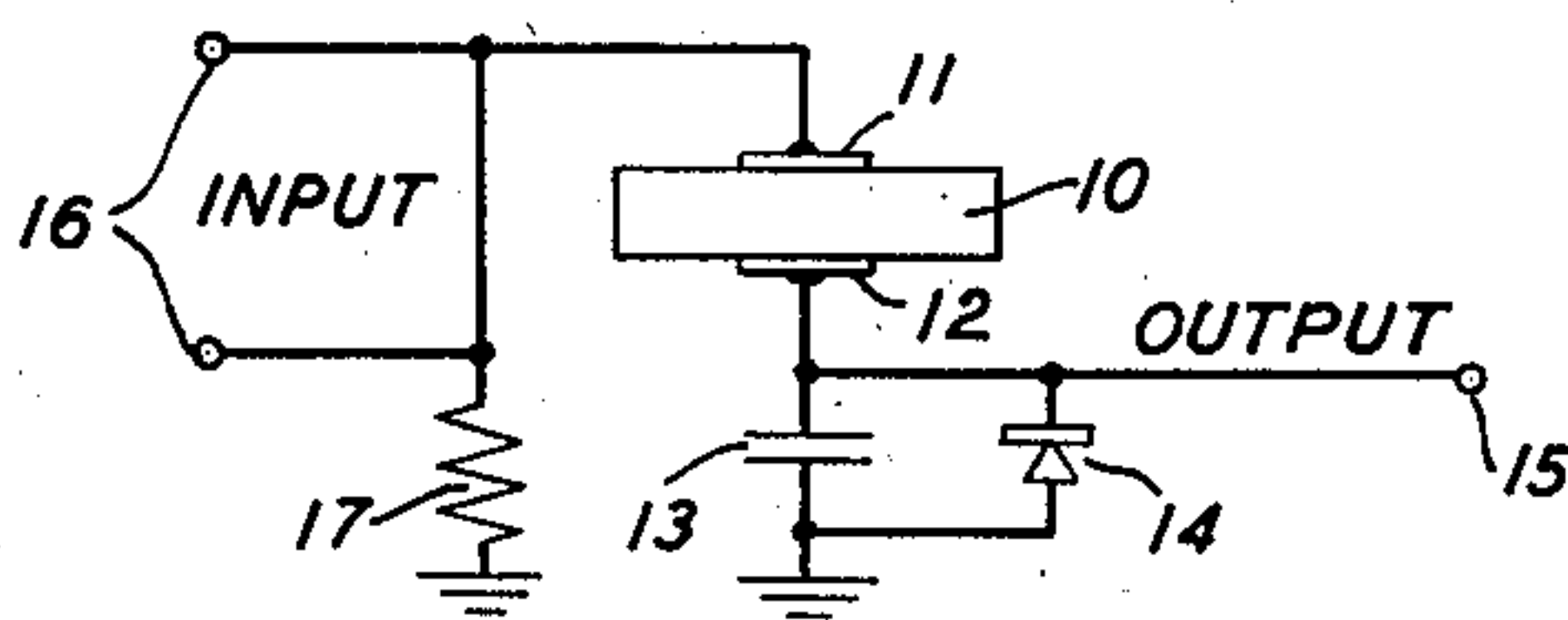


FIG. 7

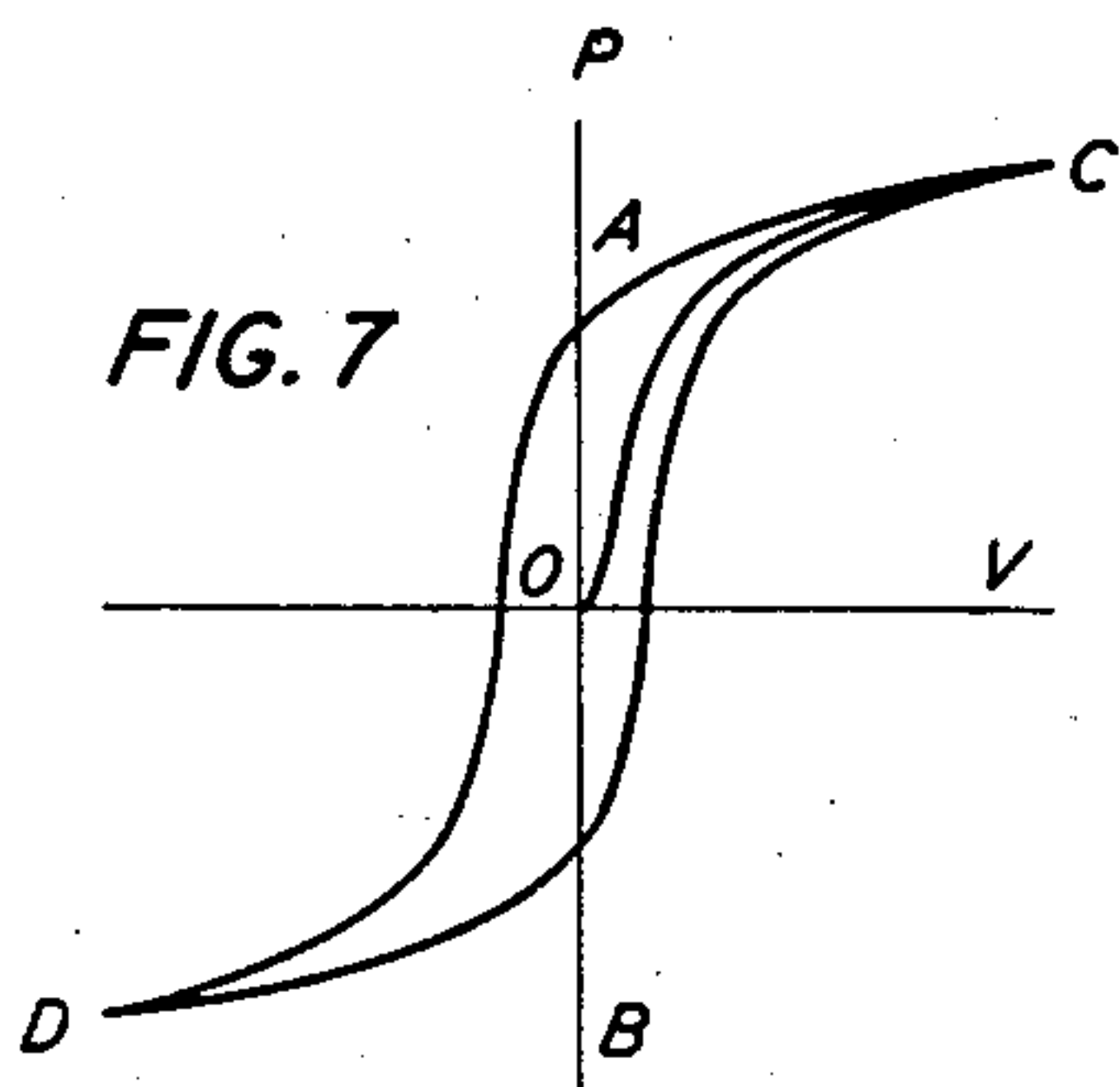
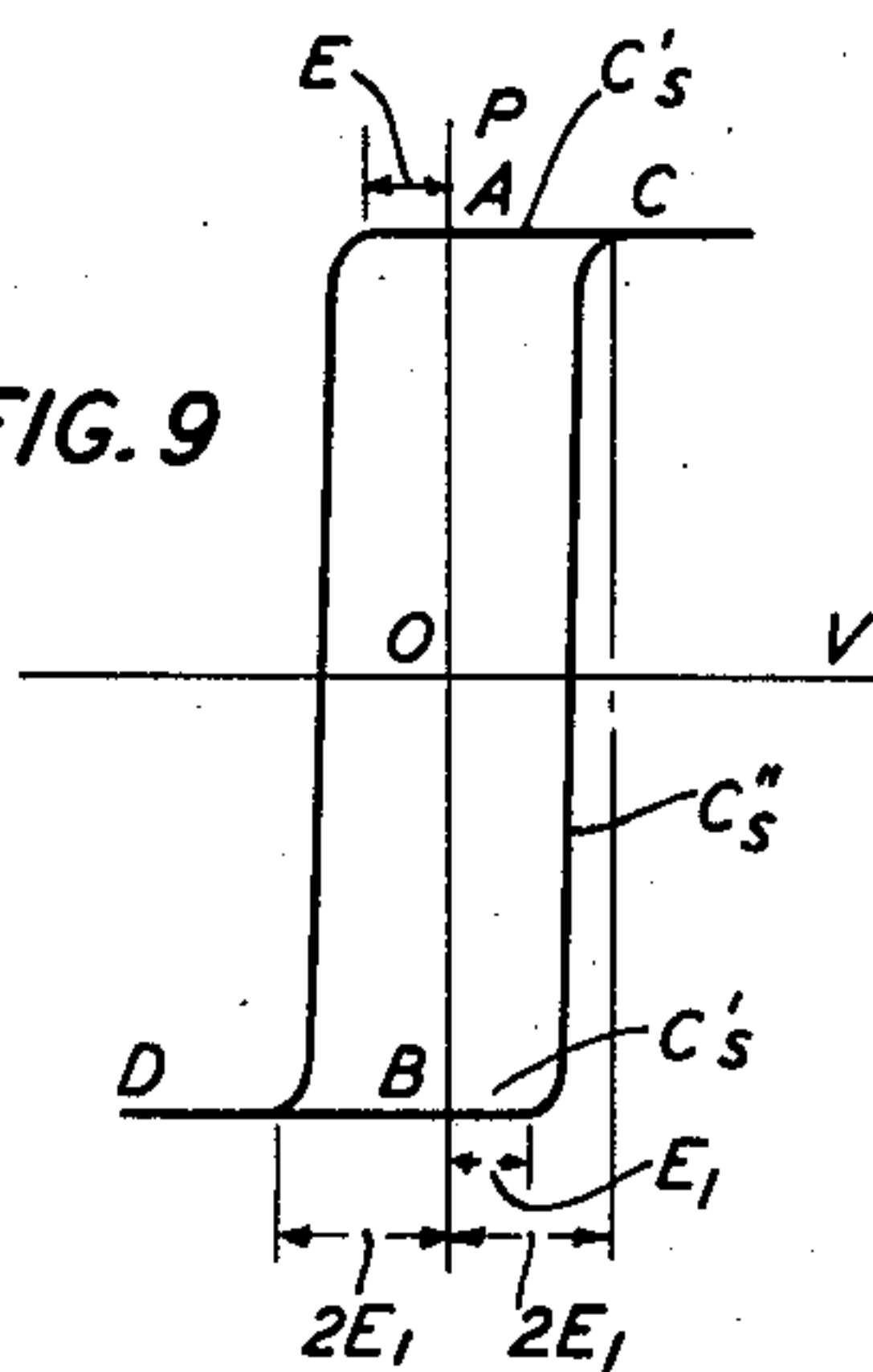


FIG. 9



INVENTOR
J. P. REMEIKA
BY
Hugh S. Wertz
ATTORNEY

Sept. 16, 1958

J. P. REMEIKA

2,852,400

BARIUM TITANATE AS A FERROELECTRIC MATERIAL

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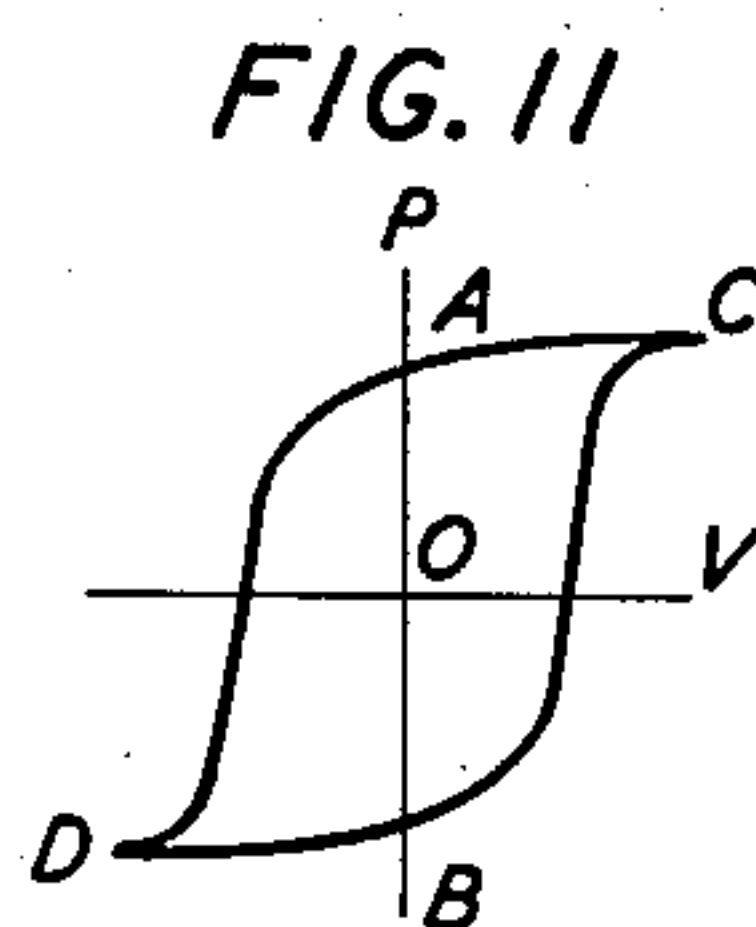
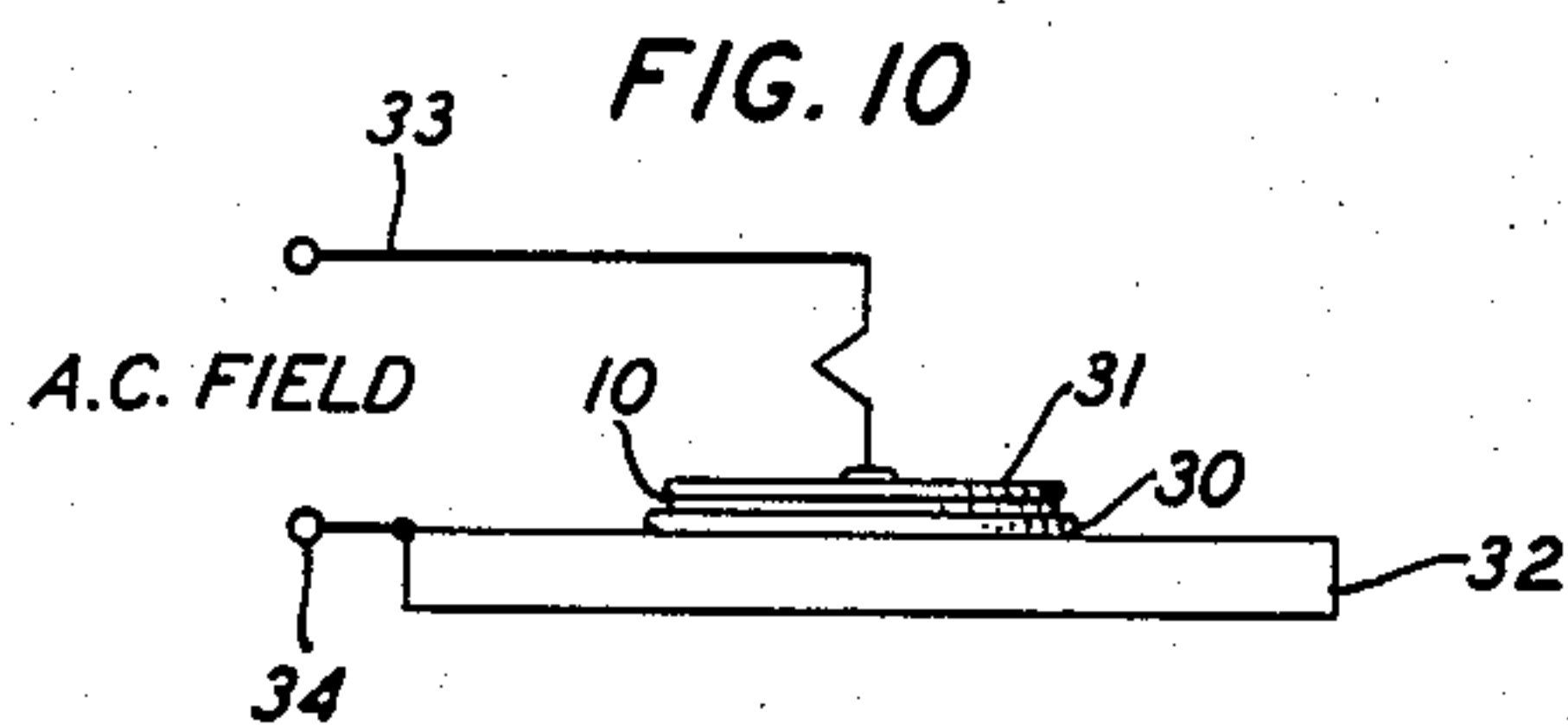


FIG. 12

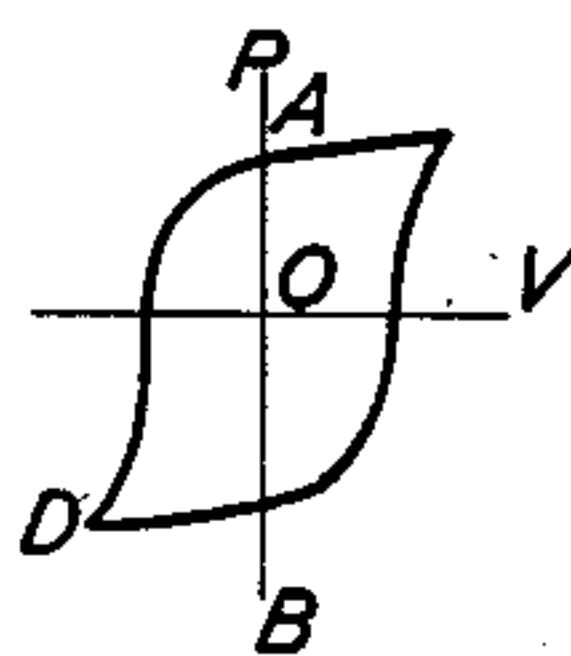
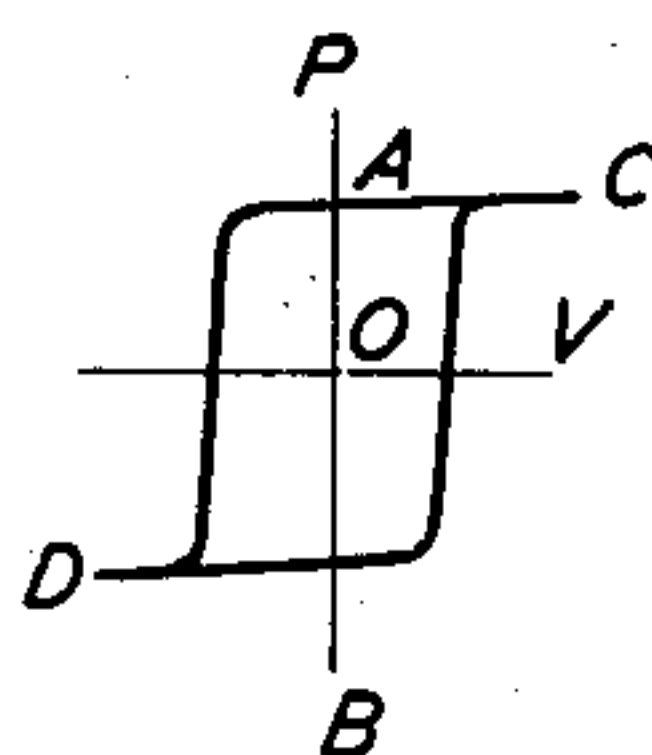


FIG. 13



INVENTOR
J. P. REMEIKA
BY *Hugh S. Wentz*
ATTORNEY

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2,852,400

BARIUM TITANATE AS A FERROELECTRIC MATERIAL

Joseph P. Remeika, Berkeley Heights, N. J., assignor to Bell Telephone Laboratories, Incorporated, New York, N. Y., a corporation of New York

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8 Claims. (Cl. 106—39)

This invention relates to ferroelectric materials, and to their preparation and use. This application is a continuation-in-part of application Serial No. 303,196, filed August 7, 1952, and now abandoned.

Certain crystalline materials when exposed to an alternating polarizing voltage exhibit a relationship between the electric polarizing force and the polarization in the direction of the applied force that is similar to the hysteresis loops exhibited by magnetic materials. Such materials, of which barium titanate is an outstanding example, are called "ferroelectrics," and they are generally characterized further by high dielectric constants and high electromechanical coupling constants. The practical applications of such materials are diverse and they include, for example, electrical condensers, electromechanical transducers of various kinds, dielectric amplifiers and "memory circuits." In some applications, one or more of the following properties also are significant: coercive force, remanent polarization, symmetry of hysteresis loop, dielectric constant and temperature coefficient of dielectric constant.

It is therefore an object of this invention to improve the electrical characteristics of ferroelectric materials, in general, and of barium titanate in particular.

A more specific object of the invention is to improve the form and symmetry of the hysteresis loop of barium titanate and related ferroelectric materials, and more specifically to lower the coercive force, to increase the remanent polarization, and to increase the ratio of maximum to minimum slope on the hysteresis loop.

Another object of the invention is to reduce dielectric loss in ferroelectric materials.

Another object of the invention is to reduce strains within the structure of crystalline dielectric materials.

Other objects of the invention are to increase the dielectric constant and improve the temperature coefficient of dielectric constant in crystalline materials of the character of barium titanate.

The foregoing and other objects are attained in a ferroelectric material in accordance with the present invention in which amounts of iron are incorporated into the crystal structure, and more particularly in a form of barium titanate to be designated hereinafter $\text{Ba}(\text{Ti,Fe})\text{O}_3$ in which trivalent iron ions (or atoms) replace the tetravalent titanium ions (or atoms) in different specified percentages, depending on the amount of iron added to the melt from which the crystals are derived.

It has been found, however, that added iron in significant amounts is not readily absorbed into the structure of barium titanate crystals prepared by a commonly employed prior art method from a mixture containing barium chloride, titanium dioxide, and barium carbonate. Moreover, in preparation of barium titanate crystals as above, amounts of the ingredients considerably in excess of stoichiometric proportions are required to produce a prescribed amount of the product.

Accordingly, it is a further object of the present inven-

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tion to provide greater facility in compounding barium titanate crystals, BaTiO_3 , and more particularly



In accordance with a specific example of practice of the present invention, iron is added in the form of Fe_2O_3 together with potassium fluoride flux, to barium titanate, or to intimately mixed stoichiometric proportions of barium carbonate and titanium dioxide. The crucible containing the reactants is placed in a temperature controlled furnace at a temperature between 1150°C . and 1225°C ., for a time long enough for the barium titanate to dissolve in the flux. From the peak temperature, the melt is cooled at the rate of 20°C . per hour until a temperature of 855°C . is reached. The still liquid flux is then poured off, and the crystals are then allowed to cool rapidly to room temperature, except when they are extraordinarily thick, in which case they are annealed by slowly cooling to room temperature to prevent fracture. From a melt prepared and cooled in the manner described, a small proportion of the crystals grow in the form of triangular plates in which the dimensions of the surface area are much greater than the thickness dimension. Assuming the crystals are cooled slowly to room temperature, optical analysis shows that they have only a small number of electrical domains. Further analysis shows that substantially all of the added iron has entered into the crystal structure.

Another technique in accordance with the present invention for improving the hysteresis loops of ferroelectric crystals grown as above, involves etching the surfaces thereof with a concentrated solution of phosphoric acid at temperatures above the Curie temperature, to remove surface imperfections, thereby reducing strains in the resultant crystal structures; and more particularly, reducing the crystals to the desired thickness without necessity for grinding and lapping, which operations tend to destroy the domain alignment in the crystals. A further technique for improving the domain alignment within the crystal structure is the application of electrolytic films to serve as electrode contact for 60 cycle alternating-current.

The addition of iron in accordance with the present invention produces crystals having numerous improved characteristics. Barium titanate crystals which contain amounts of iron from 0.1 to somewhat less than 2.4 atomic percent, exhibit coercive forces that are lower than those of commercial barium titanate crystals and hysteresis loops which are symmetric, and more nearly rectangular, having high remanent polarizations and high ratios between the slopes of the steep and flat portions thereof.

The addition of amounts of iron greater than approximately 2.4 atomic percent to melts of barium titanate produces crystals which are non-ferroelectric at room temperature, and hence, do not exhibit hysteresis at room temperature. However, all barium titanate specimens treated in accordance with the present invention to include significant amounts of added iron up to about 10 atomic percent, whether or not they are ferroelectric, exhibit certain other useful characteristics within the room temperature region. These include a lowering of the dielectric losses, the percentage varying with the amount of iron added, reduction of strains within the crystal structure, increased dielectric constant, and improved temperature coefficient of dielectric constant, all of which may be of interest for numerous applications, including, for example, capacitors and dielectric amplifiers.

Another significant result is that the Curie temperature is progressively shifted in the direction of the low tem-

perature end of the scale as more and more iron is added. This is accompanied by a corresponding shift in the maxima and minima of several important characteristics, such as, for example, the dielectric constant. This shift in characteristics toward the low temperature end of the scale should be taken into account in the preparation of crystals of $\text{Ba}(\text{Ti,Fe})\text{O}_3$ from melts containing large amounts of added iron, say, in excess of 10 atomic percent.

Other objects, features, and advantages of the invention will be better understood from a study of the following description and the attached drawings, in which

Fig. 1 is a diagrammatic showing of the structure of BaTiO_3 ;

Fig. 2 shows the appearance of the melt during preparation of crystals of $\text{Ba}(\text{Ti,Fe})\text{O}_3$;

Fig. 3 is a graphical showing of the variation of lattice constants at room temperature with the amount of added iron in $\text{Ba}(\text{Ti,Fe})\text{O}_3$;

Figs. 4 and 5 are graphical showings of the variation of dielectric constant and loss angle with temperature for barium titanate crystals without and with 10 atomic percent of added iron respectively;

Fig. 6 shows a simple circuit schematic for a dielectric amplifier including as its active element crystalline material prepared in accordance with the present invention;

Fig. 7 shows a representative hysteresis loop at 60 cycles per second for BaTiO_3 crystals grown by a prior art method;

Fig. 8 shows a simple circuit schematic for a memory cell including as its active element a crystal of $\text{Ba}(\text{Ti,Fe})\text{O}_3$ prepared in accordance with the present invention;

Fig. 9 shows an idealized ferroelectric hysteresis loop for memory device applications;

Fig. 10 shows liquid electrodes applied to the surfaces of a test crystal of barium titanate prepared in accordance with the present invention; and

Figs. 11, 12, and 13 respectively are oscilloscopic showings of hysteresis loops at 60 cycles per second, observed using liquid electrodes, for a specimen crystal of $\text{Ba}(\text{Ti,Fe})\text{O}_3$ containing 0.2 atomic percent of added iron, respectively, untreated as grown, after etching with phosphoric acid above the Curie temperature, and after both etching as above and treatment for reorientation with a 60 cycle field.

Experiments by the present inventor performed with a number of ferroelectric materials lead to the conclusion that the Fe^{+++} ion enters substitutionally to displace ions of comparable ionic radius in structures of the general formula ABO_3 , with accompanying beneficial results, as will be described in detail hereinafter. In each of the materials found operative for the purposes of the present invention, the diameter of the ion represented by B in the general formula ABO_3 falls between 0.6 and 0.7 angstrom units, which range includes 0.67, the measured diameter of the Fe^{+++} ion. In addition to barium titanate ferroelectric perovskite-type crystals include potassium niobate, KNbO_3 ; sodium niobate, NaNbO_3 ; and tungsten trioxide, WO_3 .

The typical perovskite structure which characterizes barium titanate, is indicated in Fig. 1 of the drawings. The barium atoms take the positions indicated by A at the corners of the pseudo-cube. The titanium atom takes the central position indicated by B, and the oxygen atoms O assume positions at the center of each of the faces of the pseudo-cube. The dimensions of the vertical rectangle, which are represented by a_0 in one direction and c_0 in the other direction, differ from each other slightly below the Curie point, below which the crystal is ferroelectric. At temperatures corresponding to the Curie point and above, the dimension a_0 becomes equal to the dimension c_0 , so that the structure becomes a perfect cube, and ceases to be ferroelectric.

The crystallization of large plates of barium titanate,

in which the substitution of iron for a small amount of titanium results in improved crystals, entails use of potassium fluoride as a solvent for ferric oxide and barium titanate or its components. The barium titanate used is either a pure commercial material or is made by intimately mixing stoichiometric proportions of barium carbonate and titanium dioxide and then calcining the same at a temperature suitable to effect reaction. Iron in the form of ferric oxide is added to the reacted barium titanate, together with anhydrous potassium fluoride. Platinum crucibles with platinum lids are used for the reactions which take place while the melt is heated up to a temperature sufficiently high to effect solution of the reactants in the potassium fluoride. According to one theory, during the reaction, iron enters substitutionally into the structure of the crystals formed.

Solubility data for $\text{Ba}(\text{Ti,Fe})\text{O}_3$ in potassium fluoride, in which not more than 0.5 percent of the titanium atoms are replaced by iron, is as follows. At respective temperatures of 1150, 1175, 1200, and 1225 degrees centigrade, held constant for two hours, it is calculated that the number of grams of $\text{Ba}(\text{Ti,Fe})\text{O}_3$ which dissolve in 100 grams of potassium fluoride flux are respectively 22, 26, 30, and 34.

Typical charge and program for the production of $\text{Ba}(\text{Ti,Fe})\text{O}_3$ triangular plates are given as follows:

BaTiO_3 -----	40.0 grams.
Fe_2O_3 -----	.0275 gram (this is equivalent to 0.2 atomic percent.)
Anhydrous KF-----	100.0 grams.

The materials named are placed in a 100 cubic centimeter platinum crucible, which is covered with a platinum cover and placed in a temperature regulated furnace at a temperature of, for example, 1190° C. For this purpose, a furnace of the type advertised as Model 7610 by the Harper Electric Furnace Co., has been found suitable. The furnace is held at this stated temperature for say, 10 hours. The composite is then cooled at the rate of 20° C. per hour, until the temperature has reached 855° C. A substantial temperature gradient is believed to exist from bottom to top of the crucible while present in the furnace. The flux, while still in a liquid state, is poured off at this point, and the crystals are then allowed to cool to room temperature.

This technique is subject to variation with the use of different types of equipment. The principal considerations are: (1) to dissolve a considerable quantity of barium titanate; (2) to allow crystallization to take place slowly enough for large crystals to grow at the lowest possible temperature; and (3) to permit the crystals to cool in an unstrained condition.

Two different habits of crystal growth have been observed to result from the process described, as shown in Fig. 2 of the drawings. On the bottom of the crucible 1 is usually found a mass of chunky cubical crystals, larger in the upper layers, growing out of which are a number of thin plates, always in pairs, which extend upwards into the melt. For want of a better term, these are known as "butterfly wings." Dotted line $x-x'$ represents the level of the flux before pouring off. The crystal plates are separated from the remaining flux by soaking the crucibles in hot water which dissolves the fluoride rapidly. The thin, large-area crystals, so obtained comprise primarily so-called "c" domains when cooled at 20° C. per hour to room temperature, in which the polar direction (c-axis) is perpendicular to the major crystal faces, an important factor in obtaining the desired rectangular hysteresis loops and low coercive force.

Triangular plates having dimensions as large as 3.4 by 2.4 by 2.4 by .04 centimeters have been obtained by this process.

Certain improvements result from the addition of iron in the manner described to barium titanate and the

other materials mentioned. These include improvements in the form of the hysteresis loop, such as reduction in the coercive force; greater symmetry and rectangularity; reduction in the dielectric losses; reduction of strains within the crystal, and a substantial increase in the dielectric constant.

In accordance with one theory, these improvements are attributed to two major factors, the first of which is the progressive change, with the addition of iron, of the conductivity of the material from N-type to P-type through a balance condition in which the material becomes an intrinsic semiconductor, with equal numbers of current carriers of each sign, whereby conductance is at a minimum.

Experiments in which the sign of the thermoelectric effect was measured to determine the semiconductor type, showed that barium titanate grown in potassium fluoride without added iron has N-type conductivity. Crystals of barium titanate to which significant amounts of iron had been added were found to be P-type. One theory to account for this is that barium titanate loses oxygen when held at high temperatures in the potassium fluoride flux, this reduction producing donor centers, defined as ions bound into the crystal lattice structure, which contribute extra unbound electrons. The addition of Fe^{+++} acceptor centers, defined as ions bound into the crystal lattice structure which provide a net positive charge or "hole," in numbers sufficient to compensate for loss of oxygen, restores balance in the crystal, resulting in a change from N to P-type under growth conditions stated hereinbefore. At the balance condition, which is observed at about 0.25 atomic percent of added iron, the conductivity of the crystals appears to reach a minimum at which the crystals become intrinsic semiconductors. This, of course, greatly reduces the dielectric losses in the material. The correct proportion of iron to bring about this condition of minimum conductivity and minimum loss varies with holding time and crystallizing temperature.

Crystals in which the balance has been restored by the addition of iron in accordance with the present invention are more readily polarized by the applied electric field, thus improving the character of the hysteresis loop.

The second of the major factors believed to account for some of the improvement resulting from the addition of iron to barium titanate and related materials is the shifting of the Curie temperature in the direction of the low temperature end of the scale (by an amount which is a function of the amount of iron added).

Fig. 3 of the drawings shows the variation of lattice constants at room temperature with the amount of iron added to the melt for $\text{Ba}(\text{Ti},\text{Fe})\text{O}_3$. At about 2.4 atomic percent of added iron, the Curie point occurs at room temperature, and the structure becomes a true cube, and hence is no longer ferroelectric at room temperature or above. Hence in the preparation of $\text{Ba}(\text{Ti},\text{Fe})\text{O}_3$ suitable for memory cells at room temperature, the amount of added iron should be considerably less than this critical amount, preferably less than one percent.

Figs. 4 and 5 are comparative showings of the variations in dielectric constant and dielectric loss with temperature over the range -200 to $+160$ degrees centigrade, inclusive, for barium titanate prepared with potassium fluoride flux and containing no added iron in Fig. 4 and ten atomic percent of iron in Fig. 5.

The curves A in the two figures represent variations in the dielectric constants in each case, as the temperature is raised up to the maximum and lowered again to the starting point; and the curves B represent variations in tangent δ of the loss angle

$$\frac{g}{\omega c}$$

where g is the conductance in mhos, ω is 2π times the

frequency, and c is the capacitance of the crystal in farads.

The addition of iron has the effect of causing shifts in the Curie temperature in the direction of the low temperature end of the scale, by an amount which is in each case a function of the amount of iron added. Hence, since the dielectric constant varies with the position of the Curie temperature, the values of this parameter at any selected temperature may be regulated by the amount of added iron. For a particular application in which the value of the dielectric constant is of primary interest, sufficient iron is added to the melt from which the crystals are derived to place the Curie point at such a temperature with respect to room temperature that the desired value of the dielectric constant is obtained. Curves A of Figs. 4 and 5 show the two extremes.

$\text{Ba}(\text{Ti},\text{Fe})\text{O}_3$ prepared in accordance with the present invention is suitable for capacitors because of its low-loss characteristic, and because its temperature coefficient of dielectric constant may be shifted by the addition of more or less iron. Crystals for this purpose should preferably be selected from a melt having above approximately 2.4 atomic percent of added iron, so as to be non-ferroelectric at room temperature.

Dielectric amplifiers, for example, may utilize the high dielectric constant and low dielectric loss obtainable at room temperature with crystal elements prepared in accordance with the present invention.

What is claimed is:

1. A single crystal consisting essentially of barium titanate, in the crystal lattice of which are incorporated amounts of iron impurity atoms substitutionally for titanium atoms within the range 0.2 to 10 atomic percent.

2. A single crystal consisting essentially of barium titanate, in the crystal lattice of which are incorporated amounts of iron impurity atoms substitutionally for titanium atoms within the range of 0.2 to 2.4 atomic percent.

3. A single crystal consisting essentially of barium titanate, in the crystal lattice of which about 0.2 percent of iron impurity atoms are incorporated substitutionally for titanium atoms.

4. The method of preparing single crystals consisting essentially of barium titanate, modified by the substitution, in the lattice structure, of iron atoms for a small minority of the titanium atoms, which comprises mixing barium titanate with a potassium fluoride flux in the proportions of about 40 parts of the titanate to 100 parts of the flux by weight, and with ferric oxide in an amount such as to incorporate from 2 to 100 iron atoms per 1,000 titanium atoms, heating the mix to a temperature in the range 1150°C. to 1225°C. , holding said temperature for a period sufficient to melt said flux and to dissolve said titanate and said oxide therein, gradually cooling the melt until crystalline plates are formed at the base of the melt, and decanting the liquid overlying the crystals.

5. A monocrystalline plate, the lateral dimensions of which are many times as great as its thickness dimension, consisting essentially of barium titanate in "c" domains modified in that iron atoms replace from .2 to 10 percent of the titanium atoms in the crystal lattice.

6. A monocrystalline plate whose lateral dimensions are greater than one-half centimeter consisting essentially of barium titanate, modified in that iron atoms replace from .2 to 10 percent of the titanium atoms in the crystal lattice.

7. A monocrystalline plate, the lateral dimensions of which are of the order of one centimeter, and the thickness dimension of which is of the order of one millimeter, consisting essentially of barium titanate, modified in that iron atoms replace from .2 to 10 percent of the titanium atoms in the crystal lattice.

8. A monocrystalline plate whose lateral dimensions are many times as great as its thickness dimension, consisting essentially of barium titanate, modified in that

iron atoms replace from .2 to 10 percent of the titanium atoms in the crystal lattice.

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