

March 1, 1949.

H. JAFFE

2,463,109

PIEZOELECTRIC ELEMENT OF P-TYPE CRYSTAL

Filed June 8, 1944

3 Sheets-Sheet 1

PIEZOELECTRIC COEFFICIENTS ROOM TEMPERATURE RANGE							
	CUT	SUB SCRIPT	PIEZO- ELECTRIC COMPLIANCE (d) 10^{-12} COULOMB NEWTON	RELATIVE DIELECTRIC CONSTANT	ELASTO ELECTRIC COEFF (g)	ELASTIC STIFFNESS (c) 10^9 NEWTONS METER ²	PIEZO- ELECTRIC STIFFNESS (h) 10^9 VOLT METER
ROCHELLE SALT	X SHEAR	14	300-10000	150-20000	.186	125	23
	X EXPANDER	^12	150-5000		.093	53	23
	Y SHEAR	25	55	10.5	.60	30	1.8
	Y EXPANDER	^21	28		.30	48	1.8
AMMONIUM ROCHELLE SALT ($\text{Na NH}_4 \text{C}_4 \text{H}_4 \text{O}_6 \cdot 4 \text{H}_2 \text{O}$)	X SHEAR	14	19	10	.21	115	24
	Y SHEAR	25	50	10	.56	28	1.6
QUARTZ	X EXPANDER	12	23	4.5	.058	85	4.2
TARTARIC ACID	Y SHEAR	25	12	5.5	.25		
TOURMALINE	Z THICKNESS EXPANDER	33	19	6.6	.032	270	9.2
PRIMARY AMMONIUM PHOSPHATE	Z SHEAR	36	50	153	.37	63	23
	Z EXPANDER	^31	25		.18	45	23
	X SHEAR	14	1.5	56	.003	8.6	.025
	X EXPANDER	^13	.7		.0015		.025
PRIMARY AMMONIUM ARSENATE	Z SHEAR	36	28	12	.26	66	1.7
	X SHEAR	14	27.5	125	.025	73	.18
PRIMARY POTASSIUM ARSENATE	Z SHEAR	36	22	22			
	X SHEAR	14	21	62			
PRIMARY RUBIDIUM PHOSPHATE	Z SHEAR	36	37	22	.19		
	X SHEAR	14	4.5	35	.015		
PRIMARY POTASSIUM PHOSPHATE	Z SHEAR	36	20	26	.087	60	.52
	X SHEAR	14	1.1	48	.0025		

FIG. 1

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3 Sheets-Sheet 2

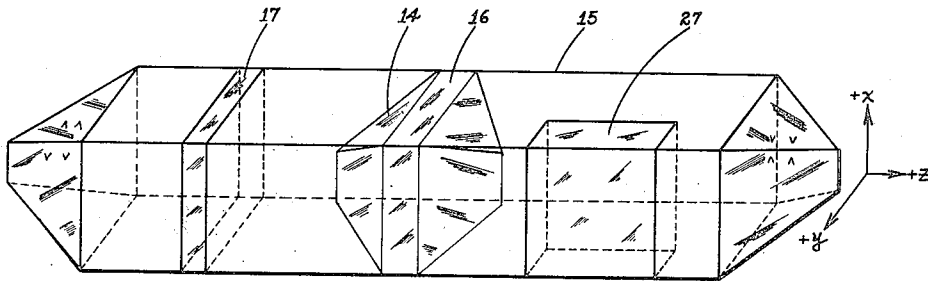


FIG. 2

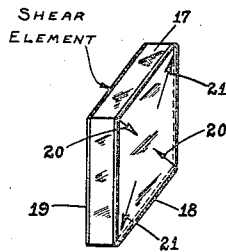


FIG. 3

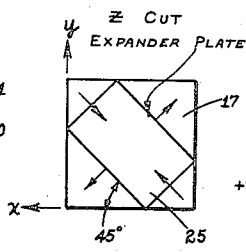


FIG. 4

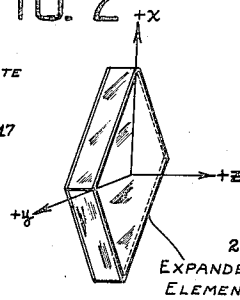


FIG. 5

Y CUT PLATE ELECTRODED
TO FORM A Z CUT
ELEMENT

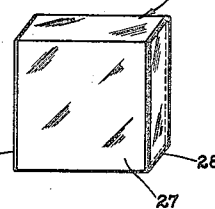


FIG. 6

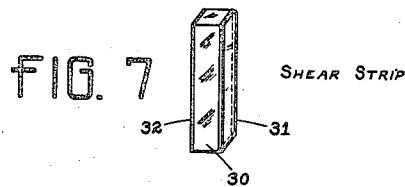


FIG. 7

SHEAR STRIP

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PIEZOELECTRIC ELEMENT OF P-TYPE CRYSTAL

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3 Sheets-Sheet 3

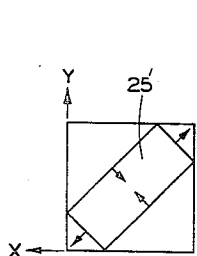


FIG. 8

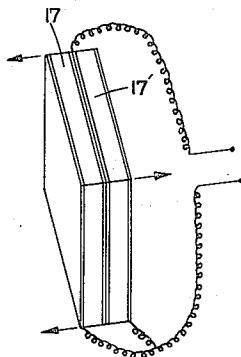


FIG. 9

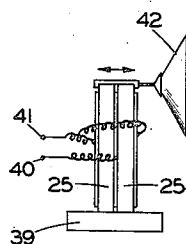


FIG. 10

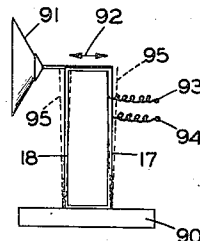


FIG. 11

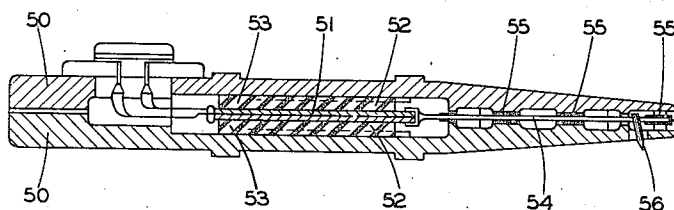


FIG. 12

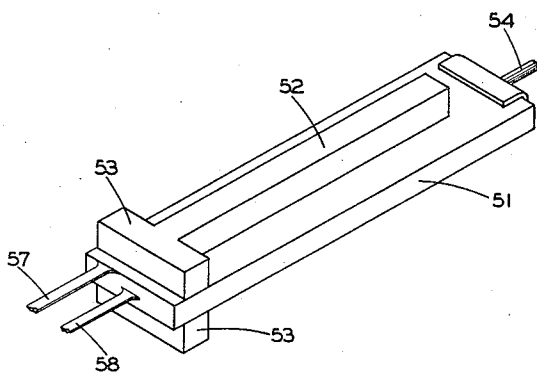


FIG. 13

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UNITED STATES PATENT OFFICE

2,463,109

PIEZOELECTRIC ELEMENT OF P-TYPE
CRYSTAL

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Application June 8, 1944, Serial No. 539,312

3 Claims. (Cl. 171-327)

1 The present invention pertains to piezoelectric substances and devices in general and particularly to certain "cuts" and elements of piezoelectric crystalline substances of the P-type and to devices utilizing such "cuts" and elements.

The term P-type crystal, as herein used, is to be understood as embracing primary ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), primary potassium phosphate, primary rubidium phosphate, the primary arsenates of ammonium, potassium and rubidium, isomorphous mixtures of any of these named compounds, and all other piezoelectrically active crystalline materials isomorphous therewith. In Wyckoff: Structure of Crystal (2nd ed., N. Y., 1931) this crystal type is introduced as KH_2PO_4 -type. In the Strukturbericht (supplement to Zeitschrift fuer Kristallography) this type here introduced as P-type is designated as type H-2-2.

Of the stated P-type crystals primary ammonium phosphate is of the highest value for piezoelectric purposes and to it the present invention more particularly relates.

This application is a continuation-in-part of the joint application of Hans Jaffe, Charles K. Gravley, Edward M. Brazis and Bengt Kjellgren, Serial No. 491,252, filed June 17, 1943, since abandoned, the said Hans Jaffe, the present applicant, being the sole inventor of the Z-cut transducer elements of primary ammonium phosphate disclosed in the said joint application.

In the past plates cut from piezoelectric crystalline material have been extensively used as electro-mechanical transducer elements in such devices as microphones, loud speakers, phonograph pickups, vibration pickups, surface-roughness measuring devices, etc. Such plates are cut from crystals in relation to the crystallographic or the orthogonal axes and are commonly designated with respect to the axes, as (for example) X-cut or Y-cut or Z-cut, accordingly as they have their major faces perpendicular to one or another of the orthogonal axes of the crystal.

Plates of Rochelle salt crystals, in particular, have been used in the manner stated. However, the Rochelle salt material has certain inherent properties which are disadvantageous for some applications. If a Rochelle salt crystal element is maintained at a temperature of about 55°C . or above, it will in time lose its piezoelectric properties. This is because Rochelle salt



contains water of crystallization, and at 55°C . the salt decomposes into the components sodium tartrate and potassium tartrate and their saturated

2 solution in water. Also, the water of crystallization is rapidly lost when unprotected Rochelle salt is subjected to a vacuum or to a dry atmosphere. Thus an unprotected Rochelle salt crystal plate cannot be used at elevated temperatures, nor can it be used in a high vacuum. The predominant position of synthetic Rochelle salt crystals in the electroacoustic field is due to the extremely high piezoelectric activity of the X-cut of Rochelle salt. The Y-cut of Rochelle salt, though less active than the X-cut, has found considerable application because its output is less dependent on temperature. The Z-cut of Rochelle salt is also piezoelectric, though to a much lesser extent than the two others, but has not found practical application.

In addition to Rochelle salt the natural piezoelectric crystals quartz and tourmaline have heretofore proven to be extremely valuable for some purposes, namely, frequency control and many measurement purposes. However, their piezoelectric activity is too low for most electroacoustic applications, excepting applications wherein very high ultrasonic frequencies are used.

It must be borne in mind that the assignment of axes to certain natural directions in the crystal is in part controlled by conventions among crystallographers but is to some extent left to the individual investigator. Thus it is now common practice to choose the Z axis as parallel to the optic axis in all optically uniaxial crystals, including the P-type crystals. There are several possibilities in locating the X and Y axes none of which would violate established practice. In the optically biaxial crystal systems, including that of Rochelle salt, the X, Y and Z axes are usually chosen in a fixed relationship to the a , b and c axes which are differentiated by geometric rather than physical criteria. There is thus no intrinsic relationship between piezoelectric effects relating to the Z-cut, for example, of a P-type crystal and the Z-cut of Rochelle salt.

It is an object of the present invention to provide elements of synthetic piezoelectric crystalline material which has no water of crystallization and which has sufficiently high piezoelectric activity to be highly useful in piezoelectric transducer devices.

A further object of the invention is to provide an element of piezoelectric crystalline material suitable for transducer applications which is not as limited in its uses by temperature conditions as is Rochelle salt material.

A further object of the invention is to provide an element of piezoelectric crystalline material

suitable for the conversion of relatively large amounts of electrical energy into mechanical energy without injury from the attendant heating of the element.

Another object of the invention is to provide a piezoelectric transducer element having a satisfactory coupling coefficient.

A further object of the invention is to provide novel piezoelectric crystalline elements practically useful for piezoelectric devices.

Another object of the invention is to produce piezoelectric transducer devices having improved operating characteristics under widely varying working conditions with resultant high utility.

Still another object of the invention is to provide crystalline piezoelectric bodies that can be fabricated from easily grown crystals.

The methods and means of attaining the foregoing objects, and other objects incidental or ancillary to them, have grown out of extended study of the P-type crystalline materials with respect to piezoelectric and other properties of particular cuts of the materials and discoveries incident to that study, and the invention consists primarily in the provision of a piezoelectric crystal body composed, aside from impurities, of primary ammonium phosphate and having a pair of substantially parallel electrodeable surfaces substantially perpendicular to the Z axis of the crystal material. The crystal body, in an important embodiment of the invention, takes the form of a Z-cut plate having electrodeable major faces.

In the further description and explanation of the invention reference is had to the accompanying drawings which present basic or background data of the invention and structures exemplifying it.

In the drawings:

Fig. 1 is a table or chart presenting some piezoelectric constants and other data applicable to piezoelectric materials utilized in carrying out the present invention and additional similar data for other piezoelectric materials, the data now published for the first time being enclosed in heavy line boxes.

Fig. 2 is an isometric view of a mother crystal of P-type material such as primary ammonium phosphate, showing the seed from which it was grown, and indicating two plates which may be cut from the crystal for use in the practice of the present invention.

Fig. 3 is an isometric view of a shear element made by adding electrodes to one of the plates shown in Fig. 2.

Fig. 4 is a face view of a shear plate showing how an expander plate may be cut therefrom.

Fig. 5 is an isometric view of an expander element made by applying electrodes to the expander plate of Fig. 4.

Fig. 6 is an isometric view showing the Y-cut plate of Fig. 2 electrodeable as a Z-cut element.

Fig. 7 is an isometric view showing a Y-cut crystalline body electrodeable as a Z-cut element but having different dimensional relationships than the element of Fig. 6.

Fig. 8 is a face view of a sheer plate similar to that of Fig. 4 but indicating an expander plate that may be cut therefrom with an orientation different from that of the expander plate indicated in Fig. 4.

Fig. 9 is an isometric view of a parallel-connected multiple flexing crystal unit in accordance with the present invention.

Fig. 10 is a side elevation showing a parallel-

connected multiple flexing unit connected to a diaphragm.

Fig. 11 is a view diagrammatically illustrating an electro-mechanical transducer utilizing a shear plate piezoelectric crystal element in accordance with the present invention.

Fig. 12 is an axial sectional view showing a phonograph pickup utilizing a pair of interconnected plates of primary ammonium phosphate crystalline material as the transducer element.

Fig. 13 is an isometric view of the crystal element of Fig. 12 together with the mounting pads therefor.

As is well known to those familiar with piezoelectric phenomena, qualitative piezoelectric data relative to a crystal substance afford no basis for determining the practical utility or possible useful piezoelectric applications of the substance, and it is only from a knowledge of the quantitative piezoelectric constants or coefficients of the substance that its utility can be determined. Furthermore, complexity arises in such determinations from the fact that for a given piezoelectric substance many different cuts are possible and the constants of the piezoelectric material will vary considerably from cut to cut. There has been a serious lack of quantitative data of the character here referred to. Thus, while some 200 substances have heretofore been shown, by the Giebe and Scheibe qualitative test, to be piezoelectric, the total number of piezoelectric crystal substances on which quantitative data have been published prior to the present invention, is limited to about 20.

The table constituting Fig. 1 of the drawings presents novel quantitative data for P-type crystalline materials including the piezoelectric plates or elements utilized in carrying out the present invention, together with previously known data relative to certain other piezoelectric materials, and serves to indicate, by comparison of the new and old data, the superior adaptability of the new piezoelectric plates or elements of the present invention for use in the piezoelectric art.

In the table are introduced certain piezoelectric coefficients symbolized by the letters d , g and h ; these coefficients are quantitative measures of piezoelectric activity. The d coefficients have been long applied in the art; they give the charge density or ratio of electric charge output per unit pressure input under short circuit conditions, and conversely the deformation obtained per unit applied voltage gradient under no-load conditions or deformation per unit length. The d coefficients may therefore be termed piezoelectric compliance coefficients. The d coefficients thus characterize the usefulness of a crystal cut for acoustic motor devices in air, such as loudspeakers. By dividing the d coefficients by the corresponding dielectric constants, we obtain another set of coefficients g which measure the electromotive force gradient realized per unit pressure applied, and thus characterize the functioning of generator devices such as microphones, phonograph pickups and the like. This coefficient may be termed the elasto-electric coefficient as it gives ratios of elastic stress to electric stress.

If the g coefficients are multiplied by the appropriate elastic stiffness coefficients c , there result yet another set of piezoelectric coefficients here termed h , and properly called piezoelectric stiffness coefficients, which measure electromotive force gradient realized per unit applied mechanical deformation. The product of the d and h coefficients is substantially equal to the square of the coupling coefficient (except where

the latter approaches unity). This squared coupling coefficient is a measure of the relative band width accommodated or transmitted by piezoelectric transducers, filters, and the like.

For any particular cut, two subscripts are affixed to the d , g and h coefficients, the first indicating the electric field component and the second the stress or strain component excited. In Fig. 1, the signs and subscripts have been put in a separate column; they apply equally to the d , g and h coefficients. For the expander plates of Rochelle salt and the P-type salts discussed, the appropriate coordinate systems are used which are rotated by 45° around the electric field direction from the orientation used for the shear plates. This rotation is indicated by the circumflex signs in the subscript column. In these cases, the d and g coefficients for expander plates are for geometric reasons equal to half the corresponding coefficients for the shear plates. The h coefficients are the same for shear plates and the corresponding expanders. For the shear plates the equation $h=cg$ holds, while a more complicated relation involving cross-contraction stresses connects those magnitudes in case of expanders.

All the crystals enumerated above as members of the P-type group belong to the crystallographic symmetry class designated commonly by the symbol V_d . This class is also known as the ditetragonal alternating crystal class or as the tetragonal phenoidal class, the latter name being the one used in Dana-Ford, Textbook of Mineralogy, 4th ed., N. Y., 1932. This crystal class is characterized by the presence of three two-fold axes of symmetry perpendicular to each other and two planes of symmetry at right angles to each other and intersecting in one of the two-fold axes. The planes cut the other two two-fold axes under angles of 45° . This combination of symmetry elements makes that axis which is parallel to the two planes of symmetry a four-fold alternating symmetry axis which is also the optic axis of the crystal.

For the symmetry class of the P-type crystals there exist according to general principles of piezoelectricity, two separate and independent piezoelectric actions. One of these actions is that due to an electric field or field component parallel to the optic axis. If an orthogonal system with axes X , Y , Z is used which has its Z axis parallel to the optic axis of the crystal and the X and Y axes parallel to the two-fold axes of symmetry, respectively, then this piezoelectric action appears as an interaction between an electric field parallel to the Z axis and a shearing deformation about the Z axis. With such a choice of coordinates the piezoelectric coefficients describing this interaction are characterized by the subscript 36. It is equally proper, and sometimes preferable, to employ another coordinate system $\hat{X}$, $\hat{Y}$, $\hat{Z}$ which is obtained from the first coordinate system by a rotation of 45° around the Z axis. The circumflex sign ($\wedge$) is herein used wherever a new coordinate system rotated by 45° in relation to a standard system is employed. In terms of this new coordinate system a field parallel to the Z axis will produce an elongation or contraction along the $\hat{X}$ axis, and the opposite, as the case may be, along the $\hat{Y}$ axis. The piezoelectric coefficients expressing this interaction would be circumflexed and have the subscript 31, such as $\hat{d}_{31}$. It can be shown readily that there is the relation $\hat{d}_{31}=\hat{d}_{32}=\frac{1}{2}d_{36}$. It is interesting to note that the symmetry of

crystal class V_d is such that the mechanical deformation brought about by an electric field through the action of coefficient $\hat{d}_{32}$ is not coupled elastically to any shearing stress or strain. In this respect all P-type crystals described herein differ advantageously from crystals of the symmetry of Rochelle salt. The coupling between expansion and undesired shear is more pronounced in Rochelle salt Y-cut expanders than in the X-cut expanders.

The other of the two independent piezoelectric actions in crystals of the symmetry class V_d may be most suitably conceived as a shear around the X axis interacting with an electric field parallel to the X axis. It should be pointed out that for the crystal symmetry of this class the X and Y axes are equivalent except for polarity. Thus, the coefficients with subscripts 25, expressing the effect of a field parallel to the Y axis are equal to the coefficients 14 expressing the effect of a field parallel to the X axis.

In connection with the values given in Fig. 1 for the piezoelectric coefficients of primary ammonium phosphate it is observed that variation with temperature of these values has been found to be small throughout the operating range. It is about $-.25\%$ per degree centigrade for d_{36} , and $-.06\%$ for g_{36} . The resonance frequencies of ammonium phosphate bodies which depend on the elastic stiffness coefficients were found to decrease by about $.03\%$ per degree centigrade temperature increase.

For the table of Fig. 1 the units chosen are those of the meter-kilogram-seconds (m. k. s.) system. This system of units has the great advantage that its unit of power is the watt. Since the watt is the common unit of power in the common electrical system of units, the use of the m.k.s. system permits the expression of the interconversion of mechanical and electrical energy without the introduction of complicated numerical factors. The dielectric constants are given relative to vacuum, the dielectric constant of the vacuum being $8.85 \cdot 10^{-12}$ farad/meter. They refer to the mechanically unconstrained medium. The elastic coefficients c give the ratio of stress to strain for the mode of deformation considered while all other motions, such as cross-contraction, are prevented, and for electric open-circuit.

The necessity of having definite quantitative data for determination of the utility of a particular piezoelectric substance for practical application has been pointed out. The truth of this and the inadequacy of theoretical considerations for such determinations are well illustrated in the case of the P-type crystals with which the present invention is concerned. Thus, all of the previously known g coefficients were substantially of similar magnitude, especially for the synthetic crystalline plates such as Rochelle salt X and Y-cuts and tartaric acid Y-cut. Primary ammonium phosphate was known qualitatively to be piezoelectric and the dielectric constants of the Z and X-cut shear plates were known to be about 15 and 55, respectively. From these dielectric constants, and from previous knowledge of the order of magnitude of the g constants it was reasonable to believe that the X-cut shear plate of the ammonium phosphate would have a d constant of attractive value and several times higher than the d constant of the Z-cut shear plate. However, the g constant of the Z-cut shear plate was found by the inventor to be surprisingly high and the g constant of the X-cut

shear plate extremely low. In fact, the g constant of the Z-cut shear plate is the highest known for any inorganic crystalline material, and the g constant of the X-cut shear plate is believed to be the lowest ever reported for any inorganic crystalline material with the possible exception of X-cut shear plates of potassium phosphate. The g constant (voltage output constant) of the ammonium phosphate Z-cut shear plate is almost twice that of the commonly used Rochelle salt X-cut. The h constant

$$\left(g \times \text{mechanical stiffness or } \frac{\text{Volts out}}{\text{Applied motion in}} \right)$$

of the Z-cut expander plate of primary ammonium phosphate is 2.3, comparing favorably with X-cut and Y-cut Rochelle salt expanders, while for the X-cut expander it is .023 which is too low to permit practical application of the plate as a transducer.

Fig. 2 illustrates a crystal 15 of primary ammonium phosphate, and shows one choice of the directions of the X, Y and Z axes. The habit of this P-type crystal is a combination of tetragonal prism and tetragonal bi-pyramid of the second order. It is characteristic for the P-type crystals that they are elongated parallel to the axis of the prism, which is the optic axis of these crystals and designated as Z axis herein.

As indicated in Fig. 2, a seed plate 16 has been caused to grow into the seed crystal 14, and the latter, in turn, into the mother crystal 15. Suitable processes of obtaining seed material and growing mother crystals of P-type are described in detail in the continuation applications of Jaffe, Brazis and Kjellgren, Serial No. 728,310 and Gravley, Serial No. 728,293, both filed February 13, 1947.

After the mother crystal 15 has grown, plates 17 are cut from the clear unflawed material with a pair of major faces perpendicular to the Z axis and lying in the plane of the X, Y axes. The plate 17 is a Z-cut shear plate suitable for sale as an article of manufacture. Such a plate may have a pair of electrodes 18, 19 applied to its major faces, as is shown in Fig. 3, for use as a piezoelectric element, or it may be connected to another plate, suitable orientation being maintained, to form a multiplate flexing unit which will later be described in detail. When the electrodes 18 and 19 are connected into an alternating electric circuit, a field is applied to the element 17 which causes expansion and contraction in directions in the X-Y plane and at 45° to the direction of the X and Y axes as is shown by the arrows 20, 21. It is to be understood that for an electric signal of one polarity the plate tends to contract in accordance with the direction of arrows 20 and to expand in accordance with the direction of arrows 21, and that for an electric field of the opposite polarity the plate will tend to expand in a direction opposite to the direction of the arrows 20 and will tend to contract in a direction opposite to the direction of the arrows 21 in accordance with the well-known piezoelectric action.

The natural tendency of a crystal of primary ammonium phosphate is to grow more readily along the Z axis than along the X and Y axes and to grow substantially equally well in the X and Y directions. This results in a crystal which is substantially square in cross-section if a square seed-plate 16 is used, and by cutting the crystal perpendicular to the Z axis plates or piezoids are obtained which have their major electrode

faces in a plane perpendicular to the direction of the Z axis and which have one pair of minor or edge faces perpendicular to the X axis, and the other pair of minor or edge faces perpendicular to the Y axis.

If from the shear plate 17 there is cut a plate 25 (Fig. 4) having each of its edge faces lying at an angle 45° to both of the X and Y axes, there is obtained a Z-cut expander plate. The directions of its expansion and contraction for a given electrostatic field are illustrated by the arrows in Fig. 4. For an electrostatic field of the opposite polarity the direction of the arrows will reverse as has been explained in connection with Fig. 3.

Fig. 5 shows an expander element made from the expander plate 25 by connecting electrodes to the major faces thereof. Such an expander element is useful in transducers such as that shown in Fig. 7 of Frank Massa's Patent Number 2,427,062, filed on June 2, 1944. In an apparatus of this character it may be desirable to convert a large amount of electrical energy into mechanical energy in order to obtain the desired acoustical power output. The primary ammonium phosphate crystal element has proven to be especially well adapted for such service because of its ability to withstand temperatures up to about 120° C. without melting or loss of its piezoelectric effect.

The piezoelectric transducer elements of the present invention may be advantageously used for the production of multiplate flexing type units which may be made to function as "benders" or "twisters," such multiple plate units being disclosed and explained in U. S. Patents Reissue Nos. 20,213 and 20,680.

As in the case of the multiplate flexing units of the prior art, those utilizing P-type crystalline material of the present invention may be made in several ways. For example, a "bender" unit can be produced as illustrated in Fig. 10. Here two similarly cut and oriented expander plates 25, 25 such as are shown in Fig. 4 or Fig. 8 are electroded on both faces and connected face-to-face to form a multiplate unit supported by base 39. With the electrodes connected in parallel with conductors 40, 41 the electrostatic field is impressed upon the two plates in opposite directions to cause one to expand and the other to contract with resultant bending of the unit. A vibratile member, such as microphone or speaker diaphragm 42, is connected to the top of the unit.

By using other orientations and electroding of the Z-cut crystal plates according to known principles alternative forms of flexing units can be provided.

Again, Fig. 9 shows the construction and electrical connections of a "twister" multiplate flexing piezoelectric unit. Two shear plates 17 and 17' having the same orientation with respect to the crystallographic axes have electrodes on their major faces, and are connected together and electrically connected in parallel and to a signal source in such a manner that when a field of a given polarity is applied one plate tends to expand along one of its diagonals and contract along its other diagonal while the second plate tends to contract and expand along its corresponding diagonals. This results in a composite or "saddle-shaped" bending action wherein diagonally opposite corners of the unit tend to move in the same direction but in a direction opposite to the next adjacent corners, as indicated by the arrows in Fig. 9. The crystal plates 17, 17' may

have different orientations with respect to the crystallographic axes and the electric fields may be applied in the same direction to achieve a twisting action.

Figs. 12 and 13 illustrate the use of a twister type of multiplate piezoelectric crystal element of primary ammonium phosphate material in a phonograph pickup. United States Patent No. 2,222,056 describes in detail such a pickup utilizing Rochelle salt type of piezoelectric crystal element. Briefly the pickup (Fig. 12) comprises a two-piece housing 50 within which is clamped a twister crystal element 51. Yieldable mounting pad means 52, 52 extend along the longitudinal axis of the crystal element 51, and yieldable mounting pad means 53, 53 extend along one end edge of the element 51. When the two halves of the housing are connected together with the crystal element and mounting pads 52, 53 in place the one end and the central longitudinal portion of the element are substantially restrained from movement. A drive wire 54 is connected to the other end of the crystal element 51 and extends through several rubber bearing members 55 and is connected to a stylus 56. As the stylus tip is actuated laterally under the influence of a phonograph record a twisting motion is imparted to the crystal element 51 and sufficient voltage is established across the leads 57, 58 to control an amplifier in accordance with the movements of the stylus.

Fig. 6 illustrates a piezoid or plate 27 cut from the mother crystal 15 as shown in Fig. 2. The plate 27 is a "Y-cut," i. e., has its major faces perpendicular to the Y axis, but is electroded to form a Z-cut element. In other words, the electrodes 28 and 29 are applied to the minor faces which are perpendicular to the Z axis so that the field is applied along the Z axis.

The mode of mechanical vibrations excited in plate 27 (Fig. 6) by an electric field between the electrodes 28, 29 is substantially a pure shear. The resonant frequencies of this shear mode are controlled substantially only by the smallest dimension of this plate which is at right angles to the field direction, thus differing from the commonly used high frequency shear plates. As is well known to those skilled in the art, this high frequency shear mode leads to a substantially harmonic series of overtone resonances.

Fig. 7 illustrates a piezoid 30 which may be called a shear strip. The electrodes 31 and 32 are applied to the pair of faces which are perpendicular to the direction of the Z axis; so, technically, the shear strip 30 is a Z-cut plate as is the plate 27 in Fig. 4. In its mechanical behavior the element 30 is similar to the element 27 but as its dimension in the Z direction is on the order of its thickness dimension, its electrical capacity is greater than the capacity of the element 27.

Fig. 11 shows a form of the invention wherein a single shear plate 17 of P-type crystalline material is edge-mounted on a fixed base 90 by means of cement or the like. The major faces are electroded; the front electrode 18 is shown but the back electrode is not as it is believed that the necessary dotted lines might cause confusion. Fig. 3, however, illustrates a shear plate 17 and its two electrodes 18, 19. Leads 93, 94 are connected, respectively, to the front and back electrodes of the crystal plate, and are adapted to be connected to the input or output of an electrical circuit depending upon whether the crystal device is being used as a generator or a motor device. To one of the unconnected or free corners

of the crystal plate 17 there is attached a mechanical device such as a diaphragm 91. Examples of other mechanical devices which may be connected to the crystal plate 17 are a phonograph record cutter and a phonograph pickup stylus. The crystal 17 vibrates in a shear mode in the direction of arrow 92, the dash lines 95 outlining the two positions of maximum amplitude of motion. The diaphragm 91, if the device is of the loudspeaker type, will be vibrated back-and-forth substantially linearly by the crystal 17.

While the invention has so far been described in connection with a mother crystal of primary ammonium phosphate, it is to be understood that this mother crystal does not necessarily have to be formed from a solution containing pure primary ammonium phosphate salt.

Several grades of primary ammonium phosphate are obtainable commercially. One grade is known as chemically pure and is guaranteed to contain less than specified amounts of a number of impurities such as sulphate, calcium, chloride, iron, aluminum and fixed alkalis. Other commercial grades have considerably more of these impurities, and impurities other than those noted may be present. It has been discovered that crystals grown from primary ammonium phosphate of commercial grades may have rather low resistivity and that this is primarily due to the presence of sulphate impurity. The purity of the salt as to sulphate content must be kept lower than the limit of commercially pure material if it is desired that the resistance of the crystal plates obtained be extremely high. It has also been discovered that barium, too, lowers the resistance of primary ammonium phosphate plates, but it is not so apt to be found in the commercial primary ammonium phosphate. Calcium, chloride, iron, aluminum, arsenic acid and potassium may be present in quantities such as are found in commercial primary ammonium phosphate without materially reducing the resistivity of the crystal plates produced therefrom.

It is believed that the reason why calcium, chloride, iron, aluminum and potassium do not reduce the resistivity of the plates is that as ions they do not in size and configuration closely resemble constituents of the primary ammonium phosphate lattice. The SO_4^{--} and Ba^{++} ions, on the other hand, are of such size as to fit into the lattice; having different charge from PO_4^{--} and NH_4^+ which they replace, they will disturb the electrostatic balance of the lattice. To restore this balance, there will be established a deficiency of hydrogen ions (protons) in the lattice. The deficiencies thus created in the proton distribution in the lattice are believed to be the reason for the decrease in resistivity found in primary ammonium phosphate grown from solutions containing Ba^{++} or SO_4^{--} . The process of electric conduction created by these impurities might be termed "proton hole conduction," in analogy to the "electron hole conduction" well known to those versed in the physics of electric conductors.

Accordingly, in growing primary ammonium phosphate crystals it is not necessary to use relatively pure primary ammonium phosphate except as stated above, and excess phosphoric acid may be added to the solution without disadvantageously affecting the quality of the crystalline material obtained.

The data contained in the table of Fig. 1 reveal that the crystals primary ammonium arsenate and primary potassium arsenate are similar to

primary ammonium phosphate in some of their piezoelectric properties. In particular they also show the phenomenon that the piezoelectric compliance coefficients d_{33} , referring to the Z-cut, are higher than the constants d_{14} which refer to the X-cut, even though the previously known dielectric constants for the X-cut are much higher than for the Z-cut in both these crystal substances. Thus in the case of the arsenates, as in the case of the corresponding phosphates, the Z-cuts offer particular advantages.

The range of the number of existing salts of P-type is further extended by the replacement of some or all of the hydrogen contained in these salts by heavy hydrogen.

From what has been said, it will be apparent that the described Z-cut plates of the P-type crystalline materials, and particularly of the primary ammonium phosphate, have marked advantages for piezoelectric uses, because of the strength of their piezoelectric response and the fact that the critical temperatures of the materials are outside the limits within which most piezoelectric apparatus functions; because also they contain no water of crystallization and are correspondingly free of structural change incident to the loss of such water, and, finally, because easily operated methods are available for the artificial growth of such crystalline materials, making possible their commercial production in ample quantities and at moderate cost.

It will be understood that the foregoing description of the invention is presented for purposes of illustration and explanation and that the invention intended to be covered is defined in the appended claims.

What is claimed is:

1. As an article of manufacture, a piezoelectric crystal body composed, aside from any impurities, of primary ammonium phosphate and having a pair of substantially parallel electrotable surfaces substantially perpendicular to the Z axis of the crystal material.

2. An article of manufacture as claimed in claim 1 in which the crystal body is in the form of a plate having electrotable major faces substantially perpendicular to the Z axis of the crystal material.

3. As an article of manufacture, a crystal plate as claimed in claim 2 which is quadrilateral in outline with one pair of side surfaces parallel to one of the symmetry planes of the crystal material.

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