June 8, 1954 H. JAFFE 2,680,720

PIEZOELECTRIC CRYSTAL BODY COMPRISED OF RUBIDIUM COMPOUND

Original Filed June 8, 1944

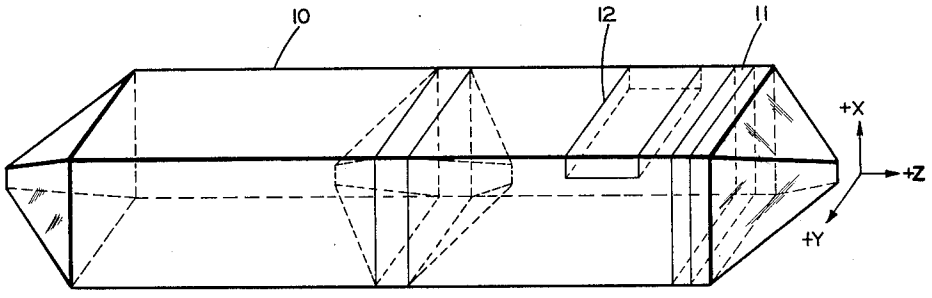


FIG. 1

CRYSTALS FORMED OF PRIMARY RUBIDIUM ARSENATE, OR MIX-CRYSTAL, PRIMARY RUBIDIUM PHOSPHATE AND PRIMARY AMMONIUM PHOSPHATE

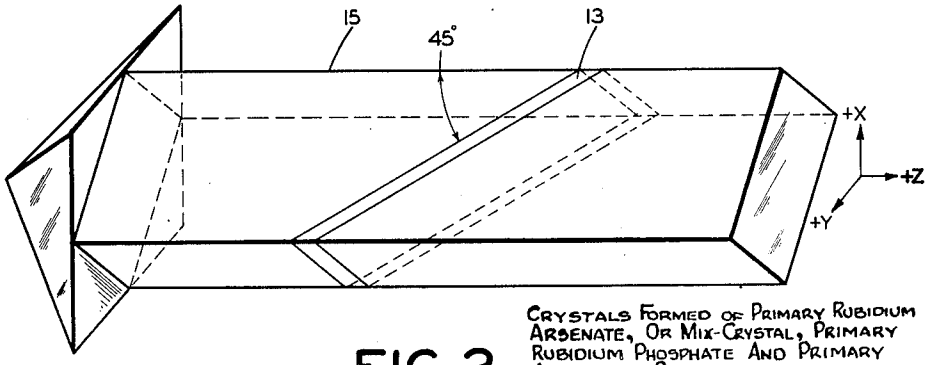


FIG. 2

CRYSTALS FORMED OF PRIMARY RUBIDIUM ARSENATE, OR MIX-CRYSTAL, PRIMARY RUBIDIUM PHOSPHATE AND PRIMARY AMMONIUM PHOSPHATE

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PIEZOELECTRIC CRYSTAL BODY COMPRISED OF RUBIDIUM COMPOUND

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Original application June 8, 1944, Serial No. 539,312. Divided and this application May 18, 1948, Serial No. 27,663

2 Claims. (Cl. 252—62.9)

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This invention pertains to a piezoelectric crystal element cut with particular orientation from any one of a number of representatives of a family of crystals.

This application is a division of copending application filed June 8, 1944, in the name of Hans Jaffe, Serial Number 539,312, for Piezoelectric Crystal Means, now Patent No. 2,463,109.

The present application pertains to a piezoelectric crystal body cut with particular orientation from a P-type mother crystal of tetragonal symmetry comprised at least in part of material selected from the group primary rubidium, cesium or thallium phosphate, and primary rubidium, cesium or thallium arsenate.

The term P-type crystal is to be understood as embracing the tetragonal crystal form of primary ammonium phosphate ($NH_4H_2PO_4$), primary potassium phosphate, primary rubidium phosphate, the primary arsenates of ammonium, potassium, and rubidium, isomorphous mixtures of any of these named compounds among each other and with primary thallium phosphate, and all other piezoelectrically active crystalline materials isomorphous therewith. In Wyckoff, Structure of Crystal (2nd edition, N. Y. 1931) this crystal type is introduced as KH_2PO_4-type. In the Strukturbericht (supplement to Zeitschrift fuer Kristallographie) this type here introduced as P-type is designated as type H–2–2.

A further object of my invention is to provide a plate of piezoelectric crystalline material useful in a transducer and which is not as limited in its uses by temperature conditions as plates of Rochelle salt crystalline material.

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

A further object of my invention is to provide new piezoelectric crystalline materials and new elements cut therefrom.

Still another object of my invention is to provide improved synthetic piezoelectric elements for filter circuits.

A further object of my invention is to provide cuts of piezoelectric crystalline material which exhibit an electro-optic effect to a marked degree.

It is also an object of my invention to provide means for and a method of light intensity and color modulations utilizing a piezoelectric crystal element.

For a better understanding of the present invention, together with other and further objects thereof, reference is had to the following description taken in connection with the accompanying

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drawings, and its scope will be pointed out in the appended claims.

Fig. 1 is an isometric view of a mother crystal with crystal bodies cut therefrom in accordance with the invention, and Fig. 2 is an isometric view of a mother crystal after it has been partially processed in order to obtain another crystal body.

In an embodiment of the invention, there is provided, as an article of manufacture, a piezoelectric crystal body cut from a crystal of tetragonal symmetry comprised at least in part of material selected from the group primary rubidium phosphate, primary cesium phosphate, primary thallium phosphate, primary rubidium arsenate, primary cesium arsenate and primary thallium arsenate; and the body has a pair of substantially parallel electrodable surfaces substantially perpendicular to the Z axis of the crystal material.

In the parent application Serial Number 539,312 (now Patent No. 2,463,109) there is described and claimed a crystal body comprised, aside from any impurities, of primary ammonium phosphate. I have further found that useful piezoelectric elements are obtained from crystals grown from a solution which contains, in addition to primary ammonium phosphate, such other chemicals as the primary phosphates of potassium, rubidium, cesium, or thallium, and the primary arsenates of these same metals. Crystals grown from a solution containing primary ammonium phosphate and one or more of the quoted chemicals are found to be "mix-crystals," or solid solutions, containing considerable amounts of the added phosphates or arsenates.

About the crystal substance primary rubidium phosphate there are contained in the literature only few and contradictory statements on the crystal system to which it belonged; one author, Berg (Berichte Deutsche Chemische Gesellschaft, vol. 34, p. 4182, 1901), stating that it crystallized in "quadratic" prisms; another author, West (Zeitschrift f. Kristallographie, vol. 74, p. 306, 1930), stating that it was optically biaxial and hence of a different symmetry from primary ammonium phosphate. I have discovered that actually primary rubidium phosphate may crystallize in one of two entirely different crystal types, one of which is piezoelectric. The non-piezoelectric type crystallizes upon rapid cooling of a concentrated solution; it is optically biaxial and belongs to the monoclinic system. No trace of piezoelectricity could be found with this crystal by the "click" test. The piezoelectric type of crystal which I usually obtained upon slow cooling or by evaporation of solutions near room tem-

perature is of tetragonal symmetry and in habit closely resembles primary ammonium phosphate. The crystal is optically strictly uniaxial and its birefringence is about half that of primary ammonium phosphate. The crystal is stable over long periods of time; upon heating, it is found to be subject to a transition somewhat above 70° C., which will result in destruction of the crystal. The type of piezoelectric effects which I obtained on this substance show definitely that the symmetry of the substance is the same as that of primary ammonium phosphate.

By experimenting with mixed aqueous solutions of primary ammonium phosphate and primary rubidium phosphate, for instance, in the ratios 1:1 and 1:2, I have ascertained that there exists an unbroken series of "mix-crystals" of primary ammonium phosphate and primary rubidium phosphate. Crystals grown from the solution containing the components in molar ratio 1:2 contained .85 mols of primary ammonium phosphate per one mol of primary rubidium phosphate. The piezoelectric constant d_{36} for "mix-crystals" of this composition was found to be substantially the same as for pure primary rubidium phosphate. However, such "mix-crystals" have the advantage that the transition point mentioned before for the case of pure primary rubidium phosphate is shifted to higher temperatures. For the "mix-crystals" of the aforementioned composition it is found not to be below 145° C.

I have found that crystals of primary ammonium phosphate grown from an aqueous solution of this salt and varying amounts of primary cesium phosphate do contain certain amounts of cesium. Solutions containing cesium up to the molar ratio Cs to NH_4=1:1 can be employed advantageously. With cesium contents substantially in excess of this ratio, deposition of monoclinic primary cesium phosphate crystals is observed; the latter I found not to be piezoelectric. On the other hand the aforesdescribed ammonium phosphate crystals containing certain amounts of cesium have been found to have a piezoelectric coefficient d_{36} about equal to and possibly higher than the corresponding constant for pure primary ammonium phosphate.

I have also studied primary thallium phosphate and the "mix-crystals" obtained from aqueous solutions containing both primary ammonium phosphate and primary thallium phosphate, and found the monoclinic crystals of primary thallium phosphate not to be piezoelectric. Marked piezoelectric effects are obtained however from the tetragonal crystals obtained from solutions containing primary ammonium phosphate and primary thallium phosphate up to a molar ratio thallium to ammonium about 1.5 to 1. It is known by the work of Rammelsberg published in 1882 (Sitzungsberichte Akad. Wiss. Berlin and quoted in P. Groth, Chemische Kristallogr., vol. 2, p. 794) that tetragonal mix crystals containing up to 33 mol per cent of primary thallium phosphate grow in such solutions. The crystals obtained from aqueous solution containing ammonium and thallium in substantially equal molar amounts show a piezoelectric compliance coefficient $d_{14}=40\times10^{-12}$ meter/volt or some 30 times as high as the corresponding constant for pure ammonium phosphate. The constant d_{36} for this mix-crystal was found to be of similar magnitude as for pure ammonium phosphate. The optic birefringence of this mix-crystal is only about one-

half that of pure ammonium phosphate, which fact is of advantage in electro-optic applications where a beam of considerable angular aperture is to be modulated.

Figure 1 shows a mother crystal **10** comprised of any of the materials heretofore mentioned, and indicates the X, Y and Z crystallographic axes.

The plate **11** which may be cut from the mother crystal **10** is called a Z-cut plate because the major parallel electrodable faces are substantially perpendicular to the Z axis.

The plate **12** which may be cut from the mother crystal **10** is called an X-cut plate because the major parallel electrodable faces are substantially perpendicular to the direction of extension of the X axis. This plate may also be called a Y cut because in crystals of this type the X and Y axes are equivalent to each other.

Figure 2 illustrates a bar **15** having faces cut at 45 degrees to the natural edge faces of a mother crystal in accordance with this invention. A plate or body **13** may be cut from the bar **15** in such a direction that a line normal to the major faces of the plate makes substantially equal angles with the X, Y and Z crystallographic axes. This plate **13** may be called a thickness expander plate because it expands and contracts in its thickness direction when an alternating field is impressed thereon in a direction parallel to the thickness dimension.

The aforementioned plates are of particular value where the plate is cut from a mother crystal containing a substantial amount of thallium.

Each of the aforedescribed plates is adapted to have an electrode applied to its major faces, as is known to the art.

While there have been described what are at present considered to be the preferred embodiments of this invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the invention, and it is, therefore, aimed in the appended claims to cover all such changes and modifications as fall within the true spirit and scope of the invention.

I claim:

1. As an article of manufacture, a tetragonal piezoelectric crystal body comprised of primary rubidium arsenate.

2. As an article of manufacture, a tetragonal piezoelectric mix-crystal body comprised of primary rubidium phosphate and primary ammonium phosphate.

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