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METHOD OF AND APPARATUS FOR
DETWINNING QUARTZ CRYSTALS

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2 Sheets-Sheet 1

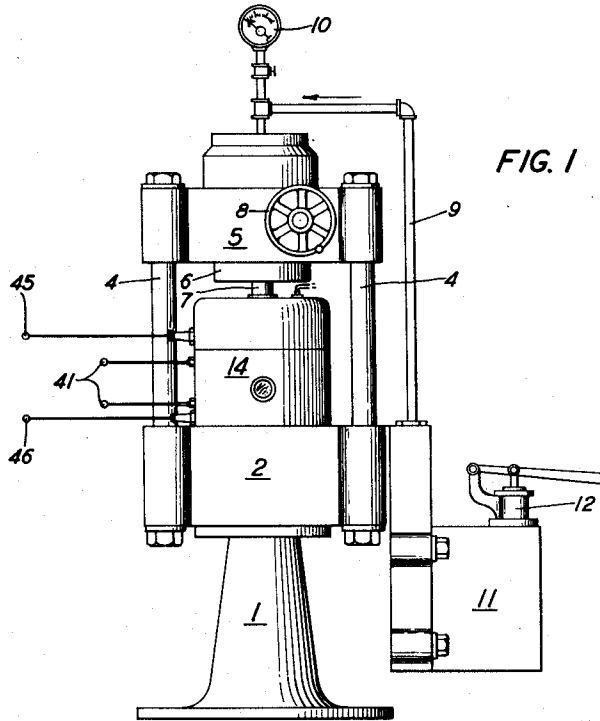


FIG. 1

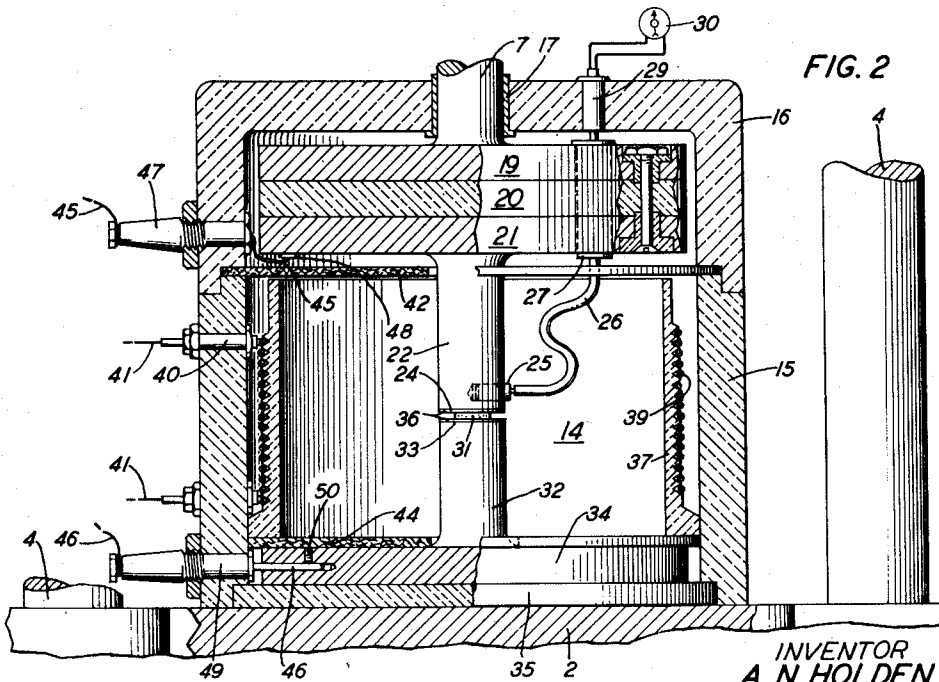


FIG. 2

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FIG. 3

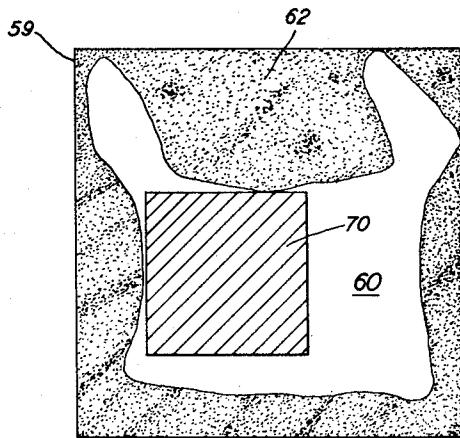
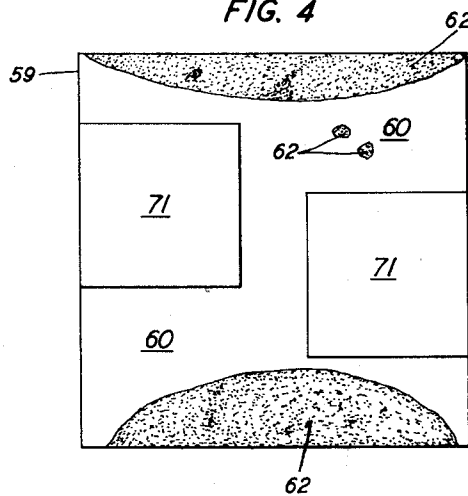


FIG. 4



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METHOD OF AND APPARATUS FOR DETTWINNING QUARTZ CRYSTALS

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This invention relates to the production of piezoelectric crystals, and particularly to means for converting electrically twinned quartz crystals to a uniform structure.

The employment of piezoelectric crystals for frequency control in oscillators, as elements of band-pass filters, and for a variety of related purposes has become of increasing importance. Those made from quartz are most satisfactory and have been the most widely used, although a few other materials and certain synthetic crystals have been found to give good results. The usable varieties of quartz are available in nature only in very limited quantities. Over half the quartz from which crystals have been cut has had to be discarded because of the presence of twinning, since uniform orientation of the crystalline material is necessary to produce a satisfactory plate. Hence it is of considerable importance to be able to change twinned portions to a uniform crystalline structure.

Twinning is the simultaneous existence, within a single piece of the quartz, of regions of different orientation which might be regarded as derivable each from the other by a single step, such as rotation through 180° about a line through the crystal, or reflection through a plane in the crystal. A number of different types of twinning exist, but only two are of major importance and considered here.

Where the twinning is of the Dauphiné type, which will be defined below, it may be corrected by the apparatus and method constituting the present invention.

This conversion can be accomplished by applying heavy homogeneous unidirectional stress and a strong constant potential in proper directions to the crystal blank after it has been heated to a temperature in excess of the inversion point between high and low quartz, and then allowing it to cool below that point, as will be described more fully hereafter.

A brief consideration of the crystalline structure of quartz will assist in understanding the invention. Quartz is made up of interlocking helices of silica tetrahedra. The helix axes are parallel to the optic axis of the quartz (C or Z). In high quartz, a form which occurs only about 573.3°C ., a two-fold axis of symmetry of each tetrahedron extends parallel to the optic axis. In low quartz, which exists only below 573.3°C ., the two-fold symmetry axes of the tetrahedra make an angle of $18^\circ 26'$ with the optic axis.

The divergences of the axes of symmetry from

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a position parallel to the optic axis may be such that successive tetrahedra are twisted like a right-handed screw, or like a left-handed screw. The direction of twisting is referred to as the "sense" of the helix. Parts of opposite sense are thus related as by mirror reflection. When parts of opposite sense are found in the same piece of quartz, twinning of the "Brazil" type is said to be present. This arrangement is also known as "optical twinning," since it is readily detachable by optical means.

The other type occurring commonly in quartz, known as "Dauphiné" twinning, occurs when the tetrahedra are oppositely tilted from the helix axis in the two twinned portions in such a direction that the helices are related as by rotation about the optic axis through 180° ; expressed in another way, the tetrahedra may be tilted by the characteristic $18^\circ 26'$ to the helix axis in either of two ways. Hence conversion of one type to the other could be effected if it were possible to shift the tetrahedra in one by the difference in tilt, or twice $18^\circ 26'$, and the present invention provides the method and apparatus for so doing.

In high quartz, as in low quartz, the sense of the helices may be either right or left. When right-handed low quartz is heated above 573.3°C ., it becomes right-handed high quartz, in which the tetrahedra are no longer tilted, but the helices are still of the same sense. Therefore, Brazil twinning could not be cured by heat treatment together with the other steps here set forth. In the present state of the art no method is known for detwinning this type of quartz.

In contrast, Dauphiné twinning is not present in high quartz. When such quartz is cooled below 573.3°C ., it may assume either of the low quartz structures, and if means were available to prevent the assumption of more than one form, the formation of this type of twinning could be overcome.

However, in the absence of some procedure such as that of which the subject-matter of the present invention forms an example, the high quartz, in one-quarter to one-half the cases, reverts on cooling to the identical low quartz structure it possessed prior to heating. In the remaining cases, the twinning reoccurs but in different arrangements than before.

While the reasons for the occurrence of twinning are not well understood, it is believed that the reoccurrence of exactly similar crystal structure on cooling from high quartz to low quartz is due to the presence of very small amounts of impurities incorporated in the crystals during

their original growth as low quartz. These defects would be present in such a way as to predispose the crystal to assume one or the other of the possible crystal structures, and would hence be similarly effective each time the crystal was cooled through the conversion point from high to low quartz.

When such predisposing factors are not present, it may be that the transitional structure at the composition plane, though at higher energy than the ideal lattice, may be of lower free energy under some transient condition of growth, and this structure would then be "frozen in" because of the high activation energy required for any later reversion to the ideal lattice.

Whatever the exact reason for the observed behavior, it has been found that quartz can be detwinned by allowing it to cool from the high temperature form under the combined application of a mechanical stress and an electric field, provided that the stress and field be in such directions that the scalar product of field and piezoelectric polarization have different values in the twin portions of opposite senses; and that the electrostatic stored energy difference, represented by the difference in scalar products, be larger than any countervailing energy difference, either in elastically stored energy or electrostatic energy allocable to polarization components induced by the field itself.

These conditions are clearly met in X-cut plates for a homogeneous unilateral compressive stress and an electric field applied through the thickness of the plate.

The details of the method and apparatus which form the subject-matter of the invention may be better understood by reference to the drawings in which:

Fig. 1 is in elevational view of apparatus arranged for practicing the method;

Fig. 2 is a schematic sectional view of the chamber for treating the quartz;

Fig. 3 is an enlarged view of a slab of crystalline quartz in which twinning is present; and

Fig. 4 shows comparatively the numbers of crystal plates that may be cut from the quartz shown in Fig. 3 before and after detwinning.

It is to be understood that the exact form of the apparatus shown is exemplary only of the principles of the invention, and that it is susceptible of modification and to the use of equivalent structures and methods within the scope of the appended claims.

In Fig. 1 is shown the equipment for practicing the invention, incorporating a conventional hydraulic press to apply the desired pressure. Mounting pedestal 1 carries the press table 2, from which rise columns 4 holding the top block 5. Within the top block 5 is disposed the working cylinder 6, which actuates the plunger 7. A handwheel 8 is provided to retract plunger 7 when desired. Hydraulic pressure is applied to the working cylinder 6 through a line 9, the pressure being indicated by a gauge 10. The system for producing the pressure is shown conventionally as a tank 11 with a hand pump 12, but it will be obvious that any system for supplying liquid to the working cylinder 6 under adequate pressure would be the full equivalent of the means shown.

The plunger 7 applies the pressure from cylinder 6 to the crystal, which is disposed within the temperature-controlled chamber 14. The chamber 14 may be formed by a cylindrical section 15 of heat insulating material, closed at the top by

an overlappingly seated cover 16. Plunger 7 passes slidably through a collar 17 in cover 16. It then is joined to a pressure plate 19 by conventional means. Pressure plate 19 is many times greater in cross-sectional area perpendicular to the axis of plunger 7 than the plunger itself. The unit pressure is thus reduced to a value consistent with the successful interposition of a sheet 20 of insulating material of high mechanical strength. Such a sheet may be made of "transite," a product formed of closely bonded asbestos fibers and a good insulator of both heat and electricity.

Beneath sheet 20 is fastened a second pressure plate 21 to which is fixed an auxiliary plunger 22 of heat-resisting metal, the lower end 24 of which is carefully finished to provide a flat pressure surface exactly normal to the direction of travel of the plunger 22. The plunger 22 is bored near its lower end 24 to receive a thermocouple 25. Leads 26 passing through a suitable bushing 27 in the pressure plate 21, sheet 20, and pressure plate 19, and through a bushing 29 in cover 16, provide connection to a meter 30 which may be calibrated to indicate the temperature adjacent the crystal slab or wafer 31.

Crystal slab 31 is supported by a lower standard 32, having an anvil 33, exactly planar and normal to the direction in which force is to be applied, mounted on a large pressure plate 34 resting on an insulating plate 35 similar to "transite" plate 20, which in turn is held by the press table 2. This slab must be carefully made so that its major faces are planar and parallel to each other. Thus uniform pressure per unit of area may be applied through the lower end 24 of plunger 22, and anvil 33 on lower standard 32.

This arrangement permits uniform heating and cooling of the crystal 31 and at the same time permits application of adequate pressures. As an aid in securing uniformity of pressure over the entire surface of crystal 31, thin shims 36 may be placed above and below it. These shims may be of a malleable metal such as soft platinum, which will flow sufficiently to equalize the applied pressure over the entire crystal face, if inequalities still exist in spite of the care used in manufacture.

It is also desirable to introduce a fine layer of graphite as a lubricant. This layer, not visible in the drawings, may cover the crystal faces in contact with the shims 36. In some cases the shims may be omitted and only the lubricant used. The effect of the lubricant is to assist in minimizing the development, at the surfaces of the quartz plates, of large tangential stresses as the press and the crystals cool. Such stresses develop because of the difference between the rates of thermal expansion and contraction in the quartz and in the plunger material, and may cause fracture of the blank in some cases. In some applications it may be desirable to face the plunger 22 and lower standard 32 with a material having a thermal coefficient of expansion equal as nearly as possible to that of quartz in order to minimize these stresses.

Heating the crystal to the desired temperature in excess of 573.3° C., the point of inversion from low to high quartz, is conveniently accomplished by introducing into the chamber 14 a ceramic tube 37 wound with resistance wire 39 such as a chrome-nickel alloy of high melting point. The temperature should be substantially in excess of the inversion point in order that all of the crys-

tals will be completely inverted to high quartz. Suitable means familiar to those skilled in the art may be employed to maintain the temperature at the desired value by controlling the flow of current through the heating wire 39, to which external connection is provided, through wall bushings 40, by means of leads 41. Additional insulation is provided by means of annular asbestos sheets 42 and 44 above and below the ceramic tube 37 and concentric about plunger 22 and lower standard 32. This arrangement of the heating chamber permits uniform heating for all parts of the crystal and facilitates gradual cooling without cracking the material. Gradual cooling may be obtained by progressively reducing the heating current until the chamber temperature reaches about 200° C., which may require a period of about two hours. The current may then be cut off, and cooling to room temperature permitted by radiation, which may require an additional period of the same order. The pressure and potential may be removed at the same time the heating current is cut off.

The steady potential to be applied to the crystal may be of the order of 10,000 volts per centimeter of thickness. It is introduced through plunger 22 and lower standard 32 by means of leads 45 and 46 entering through insulating wall bushings 47 and 49, respectively, and energized by a suitable direct current source, not shown in the figures. Lead 45 may be connected to plate 21 by set screw 48, while lead 46 may be connected to plate 34 by means such as set screw 50. The potential is insulated from the body of the press by the non-conducting plates 20 and 35.

Thus the three factors necessary to accomplish the detwinning action are provided; the crystal heated well above the low-to-high quartz inversion point, high homogeneous unidirectional pressure applied normal to the major faces of the crystal, and high steady potential applied between the faces while the crystal is cooled gradually through the inversion point.

A brief consideration of the results actually obtained by the method may be had by reference to Figs. 3 and 4. A crystal blank 59, about $\frac{3}{8}$ " x $\frac{3}{8}$ " x $\frac{1}{64}$ " in size, is illustrated in Fig. 3. Before treatment it carries the twinned areas irregularly throughout, as indicated by the unshaded area 60 denoting a Dauphiné twinned portion of one sense, and the stippled portion 62 indicating a twinned area of the opposite sense.

The same quartz blank 59 is shown after the detwinning process in Fig. 4. It will be observed that the unstippled area 60 of one sense now covers substantially all of the crystal face. Minor areas of the opposite sense 62 were still observable along the periphery of the crystal. It is thought that this is probably due to inequalities in the pressures actually applied.

The gain in the useful quantity of the quartz is clearly seen by comparing the typical plates which may be cut from the blank 59 before and after treatment. Plates of 35° AT cut, about $\frac{1}{8}$ " square, were to be obtained. The plates are shown in outline, with the cross-hatched plate 70 representing that which could be cut from the original twinned quartz plate, and the unshaded outlined areas 71 denoting those plates which would be available for cutting after the detwinning operation. It will be seen that in the particular specimen of Figs. 3 and 4, two plates could be cut after treatment, whereas only one could be obtained before.

It is believed that about 50 per cent of the

quartz which must now be thrown away because of twinning can be made usable by this process. Thus the invention provides simple means for utilizing more efficiently the limited supplies of natural quartz crystals available for piezoelectric purposes.

What is claimed is:

1. The method of treating a quartz crystal wafer having parallel major faces and containing Dauphiné twinning to produce a uniform crystalline structure therein, comprising the steps of gradually heating said crystal to a point in excess of the low-high inversion temperature, applying a homogeneous compressive stress normal to said faces, applying a steady potential difference to said faces, and simultaneously therewith cooling said wafer through the low-high quartz inversion temperature.

2. The method of producing a crystal wafer of uniform crystalline structure from a quartz wafer having twinned areas of the Dauphiné type, comprising heating said wafer about the low-to-high quartz inversion point, applying a potential across said crystal, applying a pressure distributed uniformly per unit of area to the major faces of said crystal, and cooling said wafer evenly to a temperature below said inversion point while continuing to apply pressure and potential thereto.

3. The method of detwinning a quartz crystal wafer having substantially parallel major faces, and in which Dauphiné twinning is present, which comprises heating said wafer gradually and uniformly to a point above the temperature of inversion from low quartz to high quartz, applying a constant potential between said major faces, applying a substantial pressure uniformly distributed over the normal to said major faces, and cooling said wafer below the temperature of inversion from low quartz to high quartz while applying such constant potential and substantial pressure.

4. The method of treating a quartz crystal wafer having substantially parallel major faces to remove Dauphiné twinning, which comprises heating said wafer to a temperature above the point of inversion from low quartz to high quartz, cooling said wafer evenly below the said inversion point, and applying a steady potential and homogeneous unidirectional pressure to said faces during such cooling.

5. The method of detwinning a quartz crystal wafer having substantially parallel major faces in which Dauphiné twinning is present which comprises heating said wafer to a temperature above the low-to-high quartz inversion point, permitting said wafer to cool through said inversion point, maintaining a homogeneous unidirectional pressure on said major faces during such cooling and applying a potential difference between said major faces during such cooling.

6. The method of converting a quartz crystal slab in which Dauphiné twinning is present to a uniform crystalline structure, comprising heating said slab above the inversion point, applying uniform mechanical stress and a fixed electric field, controlling the direction of application of stress and potential so that the scalar products of field and piezoelectric polarization have different values in the twinned portions of opposite sense; and insuring that the electrostatic stored energy difference, represented by the difference in scalar products, be larger than any countervailing energy difference either in elastically stored energy or electrostatic energy

allocable to polarization components induced by the field itself while said crystal is cooled through the inversion temperature from high to low quartz.

7. Apparatus for detwinning a quartz crystal slab in which Dauphiné twinning is present, comprising means for heating said slab above the inversion temperature of quartz, and means for producing a homogeneous unidirectional stress in said slab and for applying a steady potential difference to said slab during cooling after heating.

8. Apparatus for detwinning a quartz piezoelectric plate having substantially parallel major surfaces, comprising means for applying uniformly distributed mechanical pressure to the said major surfaces of the piezoelectric plate, means for applying a constant electric potential to said plate simultaneously with application of the mechanical pressure, and means including a heater and enclosing chamber for heating said plate above the inversion point temperature of quartz and cooling said plate through said inversion point simultaneously with the application of said pressure and the application of electric potential thereto.

9. Apparatus for detwinning a quartz wafer, comprising means including electrodes for applying homogeneous unidirectional stress normal to the major faces of said wafer, means for including said electrodes for applying a unipolar electric field to said quartz wafer simultaneously with the application of stress thereto, and means including a heater and enclosing chamber for heating said quartz wafer above the quartz inversion point temperature of 573.3° C., and for cooling said wafer through said inversion point simultaneously with the application of stress and electric field to said wafer.

10. Apparatus for removing Dauphiné twinning from a piezoelectric quartz crystal blank having substantially parallel planar faces, comprising means for producing a homogeneous unidirectional stress within said blank, means for applying a constant potential to said blank, means for heating said blank beyond the tem-

perature of inversion from low-quartz to high-quartz, and means for permitting cooling through that temperature while maintaining the application of potential and stress.

11. Apparatus for detwinning a quartz crystal slab, comprising means for applying homogeneous unidirectional pressure to the major faces of said crystal slab, means for applying a constant potential difference between the faces of said crystal slab, means for heating said slab above the inversion temperature of quartz, and means for cooling said slab slowly below said temperature while maintaining pressure and potential difference thereon.

12. Apparatus for detwinning a quartz crystal slab, comprising means for setting up a homogeneous unidirectional stress throughout said slab, means for applying a potential difference across said slab which will be the same at all points, and means for heating said slab above the inversion point from low quartz to high quartz and permitting said slab to cool slowly while maintaining compressive stress and potential difference thereacross.

13. Apparatus for detwinning a quartz slab having substantially planar and parallel major faces and in which Dauphiné twinning is present, comprising means for applying homogeneous unidirectional pressure to the major faces of said slab, means for applying a unipolar potential across said major faces, means for heating said slab above the inversion temperature from low quartz to high quartz, and means for cooling said slab through said inversion temperature while applying such pressure and potential thereto.

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