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ELASTIC WAVE DEVICES UTILIZING MIXED CRYSTALS OF POTASSIUM TANTALATE-POTASSIUM NIOBATE

Original Filed March 19, 1964

FIG. 1

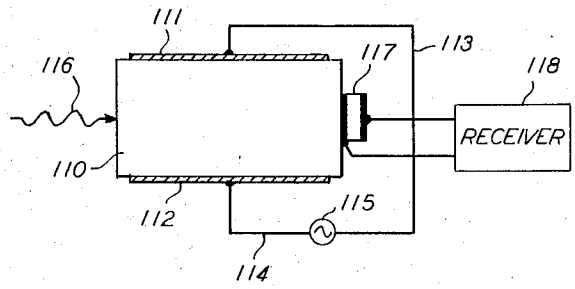


FIG. 2

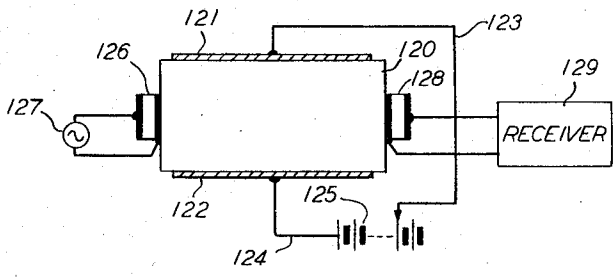
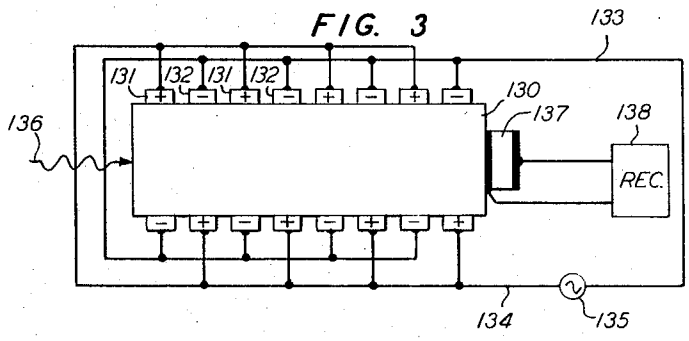


FIG. 3



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ELASTIC WAVE DEVICES UTILIZING MIXED CRYSTALS OF POTASSIUM TANTALATE-POTASSIUM NIOBATE

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11 Claims. (Cl. 330—4.6)

This is a division of my copending application, Serial No. 353,049, filed March 19, 1964, and relates to device elements utilizing compositions within the potassium tantalate-niobate system (hereinafter referred to as "KTN") as the active material and to device utilizing such elements. All included devices depend for their operation on the dependence of elastic wave transmission properties on applied electrical field.

The devices of the invention desirably utilizing bodies of KTN as active elements depend for their operation on the variation in elastic constant with applied electric field. It is significant that in the materials of this invention this effect may be enhanced (while maintaining relatively high values of acoustic Q), so permitting this characteristic, until now considered a scientific curiosity, to find expedient use. An obvious application of this property is in a variable delay line. Another significant use is in a parametric amplifier. The devices of this class can be of the standing wave or traveling wave type, with the generally associated attendant advantages and disadvantages. Such devices will be described in detail.

While the characteristics responsible for the device characteristics set forth are seen in a broad range of KTN compositions containing as little as about 20 percent of either of the end members, $KTaO_3$ and $KNbO_3$, a preferred range exists for the device uses here described. This is conveniently set forth by defining the KTN system as $KTa_xNb_{1-x}O_3$ over the range of from x equals 0.56 to 0.68, inclusive. It is generally true for every included member of the broader range that the dependence of the acoustic transmission characteristic on the magnitude of the applied electrical field is enhanced, with little attendant degradation in Q. This is of particular importance in the preferred range set forth, where this high dependence and low loss quality apply over usual device operating conditions.

It is significant that these materials may be grown easily by, for example, the Czochralski technique. Suitable growth conditions, as well as appropriate measures that may still further improve the optical perfection of the growing crystals, are described herein. Certain of these improvisations take the form of deliberate compositional inclusions. Accordingly, the formula set forth above is intended to define only the ratio of the end members, $KTaO_3$ and $KNbO_3$ in the final composition.

Certain of the included devices may utilize polycrystalline bodies of the KTN composition. Since these materials may be easily prepared by ordinary hot pressing techniques, now used, for example, for potassium-sodium niobate ferroelectric bodies, and since these procedures are well known to those skilled in the art, they are not described. Suitable hot pressing techniques are set forth in: "Treatise on Powder Metallurgy" by C. G. Goetzel, Interscience Publishers, Inc., New York (1949).

In accordance with this invention, therefore, it has been discovered that members of the KTN system containing at least 20 percent of either end member $KTaO_3$ or $KNbO_3$, having the preferred composition range as set forth, manifest unusually strong variations in elastic constant under the influence of an applied electrostatic field

coupled with low loss, in turn giving rise to the use of these materials in a large class of devices.

For convenience, the illustrative physical and electrical properties are tabulated below. All of these values have actually been measured on materials grown in accordance with the examples set forth.

Peak dielectric constant: 30,000, as measured at frequencies up to 100 k.mc.

Index of refraction: 2.3 over the visible and near visible band.

Absorptions: From about 1000 k.mc. up to about 6 microns and above .3 micron.

Electrical Q: About 200–500 down to about 5 degrees above the Curie point; about 150 within 5 degrees of the Curie point.

Acoustical Q: 40,000 at 500 mc.

Hardness: Comparable to quartz—about 6 mhos—sufficient to take a good optical polish.

Stability: Good both physically and chemically; not readily soluble in acids or bases.

Growth: Single crystals by Czochralski or other techniques; polycrystals by hot pressing.

Crystal class: Perovskite (body centered cubic therefore not birefringent in the absence of an applied field and having several equivalent directions for application of field or transmission of wave energy).

Device fabrication: May be cut and polished in manner or quartz.

Electrode application is desirably by evaporation of silver or aluminum, for example. Temporary electrodes may be applied by use of indium gallium eutectic, or capacitative mount may be used.

Description of the invention is expedited by reference to the drawings, in which:

FIG. 1 is a front elevational view, partly in section, of a resonant-type elastic wave parametric amplifier;

FIG. 2 is a front elevational view, partly in section, of a variable delay line; and

FIG. 3 is a front elevational view of a traveling elastic wave parametric amplifier.

The devices of FIGS. 1, 2, and 3 are based on the dependence of elastic constant on bias. Since the effect is basically quadratic but acts linearly because of biased polarization, any D.-C. bias is applied only for the purpose of setting the operating portion of the curve. The amplifier of FIG. 1 consists of a sample of KTN 110 which has an elastic resonance at the desired signal frequency. Electrodes 111 and 112 are attached to opposite faces of the body 110, and an R.-F. pump voltage at twice the signal frequency emanating from source 115 is applied across electrodes 111 and 112 by means of leads 113 and 114. An elastic wave 116 is coupled into the KTN crystal and is amplified parametrically as it propagates through the sample. Transistor 117, which may operate on any of the familiar electromechanical principles, may be utilized at the other end of the crystal for detecting the amplified elastic wave which, then converted into an electrical signal, is measured by receiver detector 118. In the absence of transducer 117, the amplified wave may be coupled out to propagate on as an elastic wave.

If no elastic wave input is applied, an elastic wave parametric oscillator may result with the application of appropriate pump energy. Operation of this nature has been obtained by use of a hundred millivolts of pump at 1.4 megacycles, with oscillations being detected at 700 kilocycles. The same structure may be used for parametric up conversion and down conversion.

The variable delay line of FIG. 2 consists of a sample of KTN 120, provided with electrodes 121 and 122, in

turn connected with a variable D.-C. voltage source **125**, by means of leads **123** and **124**. Means such as piezoelectric transducer **126** and A.-C. source **127** are provided for exciting an elastic wave at one end of body **120** and means such as transducer **128** and receiver or detector **129** are furnished at the other end to sense the delayed energy. Since the elastic constant is a function of the applied voltage, the transit time for the elastic wave through the KTN body is varied by varying the applied D.-C. field.

The device of FIG. 1 is, as indicated, a resonant structure. While such a structure affords maximum interaction with the signal and KTN body, traveling wave structures are, as is well known, desired for certain uses.

Such a structure is shown in FIG. 3. This device consists of KTN crystal **130** having affixed thereto two sets of spaced, parallel-connected electrodes **131** and **132**, attached to pump source **135** by means of leads **134** and **133**. An elastic wave **136** is coupled into the crystal **130**, as shown, is amplified parametrically within crystal **130**, and is sensed at the other end by means of piezoelectric transducer **137** and receiver or detector **138**. The particular electrode configuration shown is designed to obtain the necessary phase relationship among pump, signal, and idler frequencies. Spacing between successive, parallel-connected electrodes determines the wavelength of the pump energy, with the spacing between successive, consecutive electrodes being set equal to one-quarter the signal wavelength.

Note has been taken of the fact that many of the devices herein may make use of a polycrystalline body, for example as prepared by hot pressing. While this may be disadvantageous for any device operating at high frequency in the visible or near visible spectrum, little objection exists in microwave devices. Particularly for low frequency devices, polycrystalline bodies are perhaps equally suitable. The elastic wave parametric amplifier of FIGS. 1 and 2 is expected to be particularly useful for underwater sound systems. It is well known that, with loss increasing as the first or higher power of the frequency, such systems advantageously operate at very low frequencies, up to of the order of 1 or 2 kilocycles. Devices of this nature are prime examples of structures which may suitably use ceramic KTN bodies.

Illustrative examples are set forth below to demonstrate the magnitude of change of dielectric constant which may be accomplished for some biasing conditions. A detailed theoretical discussion of the responsible mechanism is not considered appropriate to this description. In terms of voltage gradients, it has been found that typical operating conditions may result in a quarter wave rotation or in a maximum variation with an applied voltage of as little as ten volts or less. Field requirements for a given number n, of π phase shifts follow the equation

$$V_{n\pi}=\sqrt{n}V_{\pi} \tag{1}$$

in which $V_{n\pi}$ is the voltage gradient required for $n\pi$ phase shifts, n equals number of phase shifts, and V_{π} equals voltage required to produce π phase rotation. Accordingly, the sixteenth π phase point results upon application of $\sqrt{16}$, or $4\times V_{\pi}$, which, if V_{π} equals 640 volts, results in a requirement of 2560 volts. The seventeenth π rotation at these levels results upon application of an additional 80 volts. The limitation on the D.-C. bias is the breakdown voltage gradient that can be applied to the crystal, which is of the order of 15,000 volts/cm.

The power required to charge and discharge the capacitance of the modulator at some rate, R, may be determined from:

$$P_c=1/2CV^2_{(n\rightarrow n+1)\pi}R \tag{2}$$

in which P_c is the power required in watts, C is the capacitance of the modulator in farads, and R equals the repetition rate in pulses per second. $V_{(n\rightarrow n+1\pi}$ in Equation (2) equals

$$\sqrt{n+1}-\sqrt{n}V_{\pi}\approx\frac{1}{2\sqrt{n}}V_{\pi}$$

and is the applied R.F. field gradient that must be applied to result in an additional π phase shift.

Power dissipated in the crystal, P_s, is determined from:

$$P_s=\frac{P_c}{Q} \tag{3}$$

where Q is the n factor in dimensionless units.

Discussion has thus far been largely in terms of device applications advantageously resulting from the discovery of the unusually efficient low loss coupling mechanisms which have been discussed. While such uses may be premised on single crystal or polycrystalline materials within the specified compositional ranges, it has been determined that certain of the properties may be optimized by use of particular growth conditions and by control of both included and excluded minor ingredients. The following discussion relates to these considerations. The most significant properties are optimized since they are concerned largely with crystalline perfection and with transmission properties in the optical and near optical frequency range. However, growth of more perfect crystals results generally in reduced loss properties and, consequently, in improved value of Q. For these reasons, adherence to the compositional limits and generalized growth conditions discussed is to be considered preferred in the preparation of crystals for any of the devices described herein, as well as for any other devices based on the relationships here of concern.

A preferred compositional KTN range has been set forth at $KTa_xNb_{1-x}O_3$, in which x equals from 0.56 to 0.68. A still narrower range may be prescribed as that in which x equals from 0.60 to 0.68. This range of atom ratios of tantalum to niobium is not varied by other compositional variations set forth.

In addition to the fundamental ingredients, there are two important compositional considerations. The first has to do with unintentional inclusions. Here, in addition to prescribing overall maximum impurity content of the order of one atom percent based on potassium, there are specific ingredients which should be kept to lower values, particularly for optical uses. To prevent reduction of tantalum or niobium to the 4^+ state, it is necessary to maintain the level of calcium, chlorine, fluorine, strontium or barium at a maximum permissible level of the order of 0.1 atom percent total, based on the potassium present. Sodium or lithium inclusions substitute in potassium sites and have the general effect of reducing the dielectric constant of the material. Sodium should be kept to a 1.0 atom percent maximum and lithium at a 0.5 atom percent maximum, both based on the potassium present.

To maintain high resistivity values, of the order of 10^{10} ohm-cm. and higher, it is desirable to include one of the elements tin, silicon, germanium or titanium, of which tin is preferred. This inclusion, which probably owes its beneficial effect to the prevention of reduction of tantalum or niobium, should be in the range of from 0.0001 to 0.02 in atomic units based on the formula above. A preferred range of addition on this basis is from 0.0003 to 0.01.

It is well known that crystalline materials intended to transmit wave energy, particularly at higher frequencies, are desirably as nearly perfect as possible. It is well known that optimum transmission properties are obtained by the elimination of inclusions, strains and other defects of sizes approaching or exceeding the wavelength of the energy to be transmitted. The KTN crystals of this invention are no exception. To aid the practitioner, a growth procedure found suitable and use of which re-

sulted in certain of the crystals from which the measured properties here included were derived, is described.

The single crystal growth technique utilized was a modification of that of Czochralski. Growth was on an oriented seed lifted at a rate of about one-third of an inch a day, while being rotated at a rate of about 40 r.p.m. to minimize the effect of compositional gradients in the melt. The KTN compositions of concern have a melting point of approximately 1225 degrees C. Initial ingredients were rendered molten in a 300 cc. crucible by use of silicon carbide heating elements controlled by a saturable core reactor so as to maintain the temperature at the bottom of the crucible at about 1250° C. An oxygen-containing atmosphere such as air or oxygen was found desirable. The use of a high concentration of oxygen in the atmosphere tends to prevent reduction of niobium or tantalum, and in this manner may, to some extent, serve the function of the tin addition. In fact, where the reduction tendency is low, the use of tin may be obviated by use of an oxygen atmosphere.

By virtue of a higher tantalum distribution coefficient, growth of a prescribed composition requires an excess of niobium in the melt. To produce a composition within the range specified, in which x is from 0.56 to 0.68, the amount of tantalum in the melt on the same basis ranges from about 0.24 to 0.35. Use of potassium deficiencies of more than 5 percent is observed to result in a structure different from the intended perovskite. Consequently, the amount of potassium in the melt should be at least as great as 5 percent deficient, based on stoichiometry. A permissible range is from 5 percent deficient up to an excess, of the order of 25 atom percent of the potassium present with a preferred range of from stoichiometry to a 15 atom percent excess. A still greater preference exists for a total inclusion in the melt of from stoichiometry to a 2 atom percent excess.

Tin, which may be added in the elemental form or as an oxide, is found to have a distribution coefficient of approximately unity. Accordingly, the amount in the melt is that desired in the final crystal.

It has been observed that quiescent growth conditions, probably due to the tendency of niobium to rise in the melt, result in an increased niobium content in successive portions of the grown crystal, the amount increasing at a rate somewhat in excess of that which would be theoretically expected. This gradation is of little or no consequence for most, if not all, applications, the size of the crystal element generally being so small as to minimize any electrical effect due to this ingredient. For mass production, however, where reproducibility is desirable, the tendency of the niobium concentration to increase at the crystal interface may be minimized by agitation. An oscillating crucible in the apparatus specifically discussed in conjunction with a rotated pulling crystal is suggested. Of course, the gradient is at least in part dependent on the size of the melt, such effects being minimized by the simple expedient of increasing the melt size. Alternative procedures which have found use in related arts include doping the melt at a rate such as to offset tantalum loss during growth. This doping may take any of the usual forms, i.e., pellet, powder, liquid, gas, or by use of continuous introduction of KTN composition at a rate and of a composition such as to exactly compensate.

The following typical example indicates starting ingredients and final composition.

	Gms.
K_2CO_3	330
TA_2O_5	304
Nb_2O_5	448
SnO_2	0.7

When the above components are reacted a melt having the approximate composition $KTa_{.29}Nb_{.71}O_3:Sn_{.001}$ is obtained. The grown crystal has the approximate composition $KTa_{.63}Nb_{.37}O_3:Sn_{.001}$.

Initial ingredients have been in the form of oxides or carbonates, and such compounds are considered most expedient. However, other compounds having melting points or reaction temperatures below the melt temperature of 1250° C. and which are otherwise suitable may be utilized. Obvious alternatives include, for example, the use of oxides, tantalates, or niobates of potassium.

While crystals grown in the described manner are possessed of excellent optical properties, it is found that still further improvement may result from highly polishing the seed or by a strain-relieving etch. For example, the use of molten potassium hydroxide over a temperature range slightly above its melting point of 360° C. for a few minutes has been found to reduce the light dispersion of a finely cut and polished crystal to a minimum. Improvements of the order of 50 db have been seen.

The invention has been described in terms of a limited number of device embodiments. An important aspect of the invention is considered to derive from the discovery that the variation of elastic constant by applied electric field can be made high in this material and that this can be achieved with low loss. In fact, such dependence can be maximized with only slight attendant deence in Q value. This discovery is considered to be of value in any device in which transmitted elastic wave energy is in any way modified by changing or adjusting elastic constant under the influence of an applied electric field. Such an effect is considered to be of value in any device design accommodating any wave energy which can be passed through the KTN material, that is, any wave energy of a frequency or frequencies outside of the principal absorptions which have been noted.

The descriptive matter relating to compositional considerations and actual growth conditions, while including some information resulting in real improvement in properties for certain specified applications, is largely included for the assistance of the practitioner. For certain applications, compositional tolerances, particularly for unintentional impurities, may be considerably higher. Alternate single crystal growth techniques are known and may be utilized and, as has been indicated, for certain uses polycrystalline bodies prepared by conventional ceramic-forming techniques are suitable. Claims are to be construed accordingly.

What is claimed is:

1. Device comprising a body consisting essentially of the composition:

$$KTa_xNb_{1-x}O_3$$

in which x equals from 0.2 to 0.8, together with a first means for applying an electric field across at least a portion of the said body and a second means for transmitting elastic wave through a portion of the said body, the said first and second means being such that the presence of an electric field affects a transmission property of the said body for the said elastic wave.

2. The device of claim **1** in which x equals from 0.56 to 0.68.

3. The device of claim **2** in which x equals from 0.60 to 0.68.

4. The device of claim **2** in which the said composition additionally includes an element selected from the group consisting of tin, silicon, germanium, or titanium in the amount of from 0.0001 to 0.02 in atomic units based on the said composition.

5. The device of claim **4** in which the said element is tin, and in which the inclusion is in the amount of from 0.0003 to 0.01 in atomic units based on the said composition.

6. The device of claim **2** in which the said electric field comprises a first D.-C. component of sufficient magnitude to bias the said body to several π phase retardations, together with a second component of a maximum value equal to an additional π phase retardation.

7. The device of claim **6**, together with means for applying an A.-C. electric pump field across at least a por-

tion of the said body, the frequency relationship between said pump field and the said electric wave being such that amplification of the latter results.

8. The device of claim 6 in which the said wave energy is introduced into the said body as plane polarized energy.

9. The device of claim 2 in which at least a component of the said electric field is alternating, and in which the frequency relationship between the said field and the said wave energy is such that amplification of the said wave energy results.

10. The device of claim 2 in which the said electric field is adjusted to produce an elastic constant such as to result in a desired transit time for the said wave energy.

11. The device of claim 9 in which the magnitude of the said electric field is varied at least once during use.

No references cited.

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