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SEMICONDUCTING NIOBATE TANTALATE COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

Single crystalline and polycrystalline sodium/potassium niobate/tantalate of increased electronic conductivity results from the addition of divalent ions of barium, strontium, calcium, or lead as solute during formation.

This invention relates to the preparation of tantalates and niobates of sodium and potassium by techniques in accordance with which electrical conductivity is increased and also to materials so prepared. The techniques of this invention are applicable to mixed crystals of the noted compositions and to polycrystalline as well as single crystalline products.

Currently there is a significant effort directed toward the development of a class of devices depending for their operation upon an interaction between acoustic and electrical energy. One important class of such devices now being given some serious consideration as a replacement for the common carbon microphone is dependent for its operation upon such interaction via a piezoresistive mechanism. Studies to date have indicated the suitability of a class of tantalates and niobates for this purpose. Such materials are inherently possessed of a desirably high piezoresistive coefficient as well as reasonable values of electron mobility and have been obtained at such conductivity levels as to make this use feasible.

The same class of materials is also considered for use in a new class of devices depending for their operation upon a sharp dependence of dielectric constant on applied field or temperature change. For this use, operation is over a temperature range including or adjacent a peak in dielectric constant. One such peak approximately corresponds with the ferroelectric Curie point. The use of mixed crystals containing, for example, both niobate and tantalate anions in such relative amounts as to result in a Curie point within the desired operating range has already been described. This and other reasons may dictate mixed crystals of differing composition, for example, sodium-potassium mixed crystals may avoid abrupt discontinuities in structure in a given temperature range such as have been observed for sodium niobate-tantalate crystals.

Some difficulty has been encountered in devising a technique for the consistent preparation of any of these materials with sufficiently high electrical conductivity.

To date, for seemingly unexplainable reasons, materials grown have at times manifested the blue coloration associated with the free carrier absorption characteristic of n-type conductivity; at other times have been water white in appearance with no significant conductivity; and at times have exhibited striations with alternating clear and blue regions.

These difficulties are, to a large measure, alleviated by use of the present invention.

In accordance with this invention, a modification of any of the usual composition forming techniques for the materials of concern by addition of one or more of the divalent ions of barium, strontium, calcium or lead results in an increase in conductivity. Compositions to which preparation of which the inventive processes are directed

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include potassium niobate, potassium tantalate, sodium niobate, sodium tantalate, and mixed crystalline compositions containing both anions and/or both cations.

Techniques to which the invention is applicable include single crystal growing processes such as flux growth by spontaneous nucleation or seeded nucleation, melt growth by spontaneous nucleation or seeded nucleation (crystal pulling, zone melting, etc.), flame fusion, and polycrystalline formation procedures such as hot pressing and sintering. Regardless of growth technique, it is considered that the minimum effective addition to the final composition is at least three divalent ions per million formula units. This is equivalent to a minimum of from three to thirty ions on the same basis in the starting mixture, of course, depending on the ion and process. For example, calcium alone in a flux or melt requires thirty while three ions of lead suffices for any process. Use of lower divalent ion inclusions does result in an increase in conductivity, but in general results are inadequate for most device uses. For many purposes, as for example, in the semiconductive microphone, still higher conductivities are to be preferred so indicating a preferred minimum divalent ion inclusion in the order of ten atoms per million formula units. A maximum inclusion of the order of 10,000 atoms per million formula units derives from the observation that greater additions result in crystalline imperfections which in turn introduce trapping mechanisms so limiting the improvement in conductivity that can be produced.

In general, the tantalates manifest higher carrier mobilities than do the niobates. In consequence, it is this class of materials upon which interest presently centers for many applications. Application of the inventive processes to this class of materials, in consequence, constitutes a preferred embodiment herein. Experimentally, it is observed that a greater number of carriers may be produced in potassium tantalate than in sodium tantalate. Application of the inventive processes to potassium tantalate, therefore, constitutes a still more preferred embodiment. For those applications in which reliance is had upon a dielectric constant dependency on field or temperature, compositions of the potassium tantalate-potassium niobate series are particularly suitable. The inventive processes are advantageously practiced on such materials.

A description of the invention is expedited by reference to the examples.

Example I.—Growth of lead-containing potassium tantalate

Two separate melts were prepared; the first containing 52 grams of potassium carbonate (K_2CO_3) and 100 grams of tantalum oxide (Ta_2O_5), and the second containing the same amounts of the same ingredients together with $\frac{1}{10}$ gram of lead oxide (PbO). Starting ingredients in both melts are equivalent to 62.5 mol percent potassium, 37.5 mol percent tantalum, these amounts resulting in a 66 percent excess of potassium. An excess of approximately this order or greater is desirable to lower the melt point in accordance with accepted crystal growing procedure. With the melt at a temperature of about $1250^\circ C.$, a seed crystal of potassium tantalate was partially immersed, was permitted to partially melt back, and the melt temperature was slowly decreased so as to initiate growth. The growing crystal was raised at a rate of about one-quarter inch per day until its dimension in the growth direction was in the order of one-half inch, after which it was withdrawn. The crystal grown from the first melt, the non-lead containing melt, was water white in appearance and had a measured resistivity of approximately 10^{12} ohm-cm. The crystal grown from the lead-containing melt was of uniform dark blue coloration and had a resistivity of about .007 ohm-cm. The

lead content of the blue crystal was analyzed at 6500 atoms per million formula units. No lead was detected in the clear crystal.

Example II.—Growth of calcium-containing potassium tantalate niobate (KTN)

Two melts were prepared each containing potassium carbonate (K_2CO_3), tantalum oxide (Ta_2O_5), and niobium oxide (Nb_2O_5) in amounts of 89.0 grams, 80.1 grams, and 118.0 grams, respectively, this representing a .3 weight percent excess of potassium, in this instance to compensate for potassium loss by evaporation during growth. To one of the two melts there was added 0.003 gram of calcium oxide (CaO). Growth was initiated and caused to proceed in the manner described in Example 1. The crystal grown from the melt containing calcium addition was blue and had a resistivity of the order of 1.0 ohm-cm. The crystal grown from the unmodified melt was water white and had a resistivity of approximately 10^{10} ohm-cm.

The examples are merely exemplary and represent a considerable number of runs in which each of the divalent ions noted was added to a variety of compositions produced by different growth processes. While optimum growth conditions varied from composition to composition and from method to method, no deviation from usual practice was required when the process was modified to result in introduction of the divalent ion or ions noted.

Analysis of certain of the crystals containing lead additions showed an increase not just in lead content but also in calcium which was known to be present in one of the starting ingredients. In fact, the highest conductivity values thus far realized were found in such specimens. It is apparent that the distribution coefficient, that is, the ratio of concerned solute in the solid to that in the liquid at the growing interface for calcium is, for some reason, increased when lead is added to the starting ingredient either in a flux or in a melt process. In fact, measurements of this value indicate an increase from about .1 to 1.0 or higher in potassium tantalate.

It has been observed that certain growth conditions may result in a blue coloration and concomitantly in increased conductivity. One condition tending to bring about higher conductivity is a reflecting inner furnace wall. It is postulated that this brings about increased energy absorption at the UV end of the spectrum in the melt, so increasing photo-disassociation and thereby increasing the number of free electron carriers. For certain compositions, increase in the potassium excess also results in an increase in conductivity. It is uniformly observed, however, that regardless of growth conditions and regardless of composition, the number of carriers, and consequently the conductivity of the final product, is measurably increased by the intentional addition of one or more of the noted divalent ions.

Other melt additions while not predictably increasing conductivity may usefully be incorporated together with at least one of those to which the invention is directed. For example, it has been found that bismuth addition tends to set a limit on the maximum number of free carriers that can be induced by addition of any of the noted divalent ions. Incorporation of bismuth may render the conductivity of the final composition less dependent on melt composition.

Lithium and tin inclusion should be kept to a minimum where maximum conductivity is desired, experimentation having shown that these ions increase resistivity. It is postulated that this result derives from the fact that these ions are sufficiently small so that they can at least partially replace tantalum or niobium.

The invention has been described in terms of a limited number of exemplary embodiments. The true scope of the invention has, however, been generally described in terms of an increase in conductivity resulting from incorporation of any of the divalent ions, barium, strontium, calcium, and lead into any of the noted materials. Such result obtains regardless of growth techniques or conditions and regardless of these or other impurities ordinarily present. Claims are to be construed accordingly.

What is claimed is:

1. Composition containing at least one compound selected from the group consisting of sodium tantalate, sodium niobate, potassium tantalate, potassium niobate, prepared by a process which comprises adding to initial ingredients which yield such composition a material which yields at least one solute ion selected from the group consisting of Ba^{2+} , Sr^{2+} , Ca^{2+} , and Pb^{2+} in amount which yields from three to 10,000 of the said ions per million formula units of the said composition.

2. Composition of claim 1 in which the amount of such additive is such as to yield at least ten of the said ions per million formula units of the said composition.

3. Composition of claim 1 which consists essentially of potassium tantalate.

4. Composition of claim 1 which consists essentially of a mixture of potassium tantalate and potassium niobate.

5. Composition of claim 1 in which the said ion is Pb^{2+} .

6. Composition of claim 1 in which the said ion is Ca^{2+} .

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