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METHOD OF PREPARATION OF SINGLE CRYSTAL FERROELECTRICS

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FIG. 1

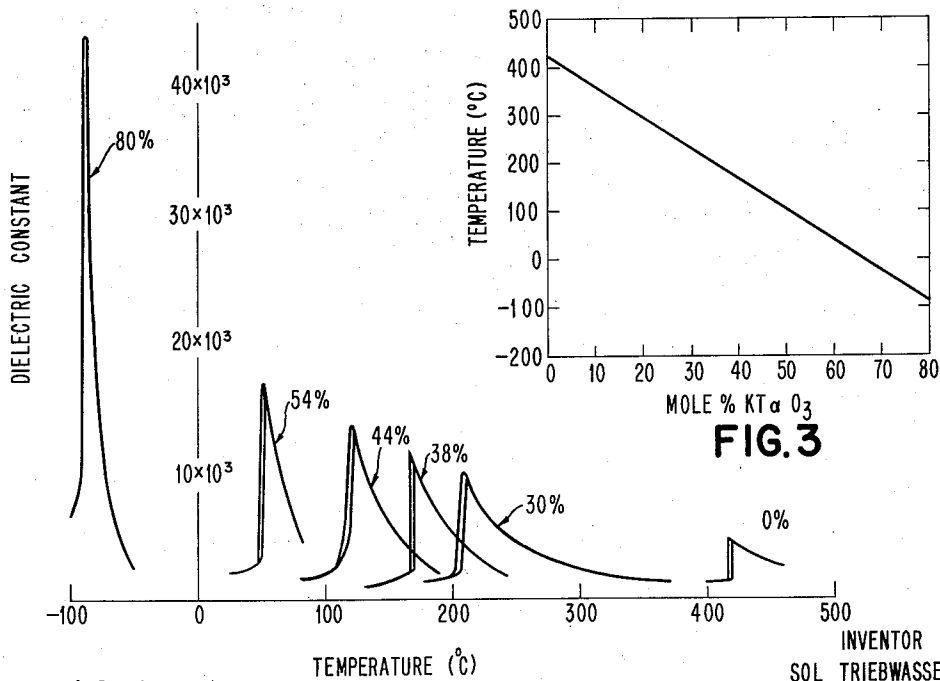
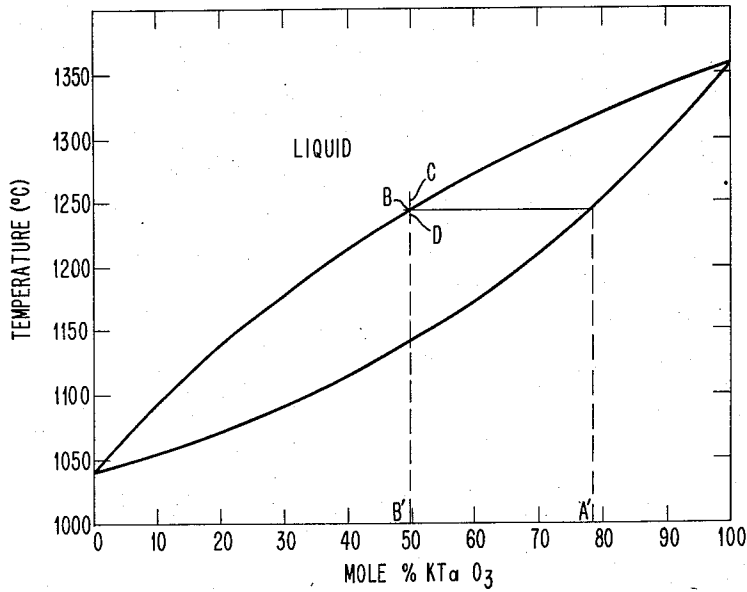


FIG. 2

FIG. 3

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METHOD OF PREPARATION OF SINGLE CRYSTAL FERROELECTRICS

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4 Claims. (Cl. 106—39)

This invention relates to new and improved ferroelectric materials and, more particularly, to a method of preparation of solid solution single crystals of ferroelectric compounds.

Since the discovery of ferroelectricity in such materials as barium titanate, strontium titanate, potassium tantalate and potassium niobate, it has been the object of considerable research to provide ferroelectric materials of high purity exhibiting useful physical properties. Such materials find ready application in numerous devices well known in the art. For example, temperature regulators are known wherein the variation of the dielectric constant versus temperature of a temperature sensitive ferroelectric material is utilized in conjunction with appropriate circuitry to achieve a temperature controlling element. The useful range of such an element is limited to the temperature at which there is a sharp break in the dielectric constant versus temperature curve or at the Curie temperature of the material. For single crystals of barium titanate, for example, this temperature is 120° C. For such a device it is extremely useful to provide other single crystal ferroelectric materials having Curie points extending over a wide temperature range.

Accordingly, an object of this invention is to provide a method by which a number of single crystal ferroelectric materials exhibiting Curie points extending over a wide temperature range may be conveniently prepared.

Other objects of the invention will be pointed out in the following description and claims and illustrated in the accompanying drawings, which disclose, by way of example, the principle of the invention and the best mode, which has been contemplated of applying that principle.

In the drawings:

Fig. 1 is a phase diagram for the system KNbO_3 — KTaO_3 .

Fig. 2 shows a plot of dielectric constant versus temperature for various solid solutions in the system KNbO_3 — KTaO_3 .

Fig. 3 is a plot of Curie temperature vs. mol percent KTaO_3 for the system KNbO_3 — KTaO_3 .

This invention is based upon a discovery that homogeneous solid solution single crystals of ferroelectric materials of any desired concentration may be prepared directly from a melt containing the individual constituents. The embodiment of the process described herein utilizes to advantage KTaO_3 and KNbO_3 as the individual ferroelectric materials. As shown in Fig. 1, these materials form solid solutions over the entire composition range, which have Curie points varying between 13° K. and 700° K.

According to the process of the present invention, a single crystal of a solid solution of desired composition A' may be grown by first providing a melt at temperature C of KTaO_3 and KNbO_3 in proportions given by composition B'. The melt is then cooled slowly to point D just below the liquidous temperature B at a rate of about 0.1° C. per hour and maintained at this temperature for some time. During this latter time interval a solid solu-

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tion single crystal of desired composition A' will crystallize from the melt. A crystal whose mass is small in relation to the mass of the charge, preferably about 5%, should be crystallized during this step. Thereafter the crystal is separated from the melt and cooled to room temperature over a 3–4 day period to permit the solid solution single crystal to assume a more homogeneous state.

The solid solution constituents may be conveniently formed in situ by mixing Nb_2O_5 , Ta_2O_5 and K_2CO_3 in predetermined amounts required to form a charge comprising $\text{K}(\text{Ta}_{1-x}\text{Nb}_x)\text{O}_3$, where x ranges from $0 < x < 1$. Upon reacting these materials at elevated temperatures CO_2 is evolved and a KTaO_3 — KNbO_3 solid solution melt is formed. An excess of K_2CO_3 may be used with similar results. In such a ternary system, crystallization will occur at a slightly lower temperature than from the binary system. During the crystal growth, a small seed crystal suspended on a platinum wire in touching contact with the melt may be used to insure good homogeneity in the resultant crystal.

Example.—A charge of 49.80 grams comprising 22.17 grams Nb_2O_5 (0.0834 mole), 12.26 grams Ta_2O_5 (0.0278 mole) and 15.37 grams K_2CO_3 (0.1112 mole) and having the formula $\text{KTa}_{0.25}\text{Nb}_{0.75}\text{O}_3$ was prepared in a 60 cc. platinum crucible. The crucible and contents were heated in air at 1165° C., cooled to 1158° C. during 24 hours and maintained at that temperature for an additional 24 hours. A solid solution single crystal formed which was then separated from the melt and cooled to room temperature during a 3 to 4 day period. The resultant crystal weighed 2.95 grams and had a specific gravity of 5.84, indicating a concentration of 54 mol percent KTaO_3 or a solid solution having the formula $\text{KTa}_{0.54}\text{Nb}_{0.46}\text{O}_3$. This composition exhibited a dielectric anomaly at 50° C. and peak dielectric constant was 17×10^3 .

In a similar manner many different solid solution compositions in the series were prepared. The dielectric properties of these single crystals are also shown in Figs. 2 and 3. The homogeneity of the crystals thus prepared was demonstrated by the character of the plots of dielectric constant versus temperature as shown in Fig. 2. Ceramic materials of the same composition showed rounded peaks at the peak dielectric constant and decreasing values of dielectric constant with increasing concentration of KTaO_3 , whereas single crystals exhibited sharp transitions and increasing peak dielectric constants with increasing concentration of KTaO_3 .

While there have been shown and described and pointed out the fundamental novel features of the invention as applied to a preferred embodiment, it will be understood that various omissions and substitutions and changes in the form and details of the device illustrated and in its operation may be made by those skilled in the art without departing from the spirit of the invention. It is the intention, therefore, to be limited only as indicated by the scope of the following claims.

What is claimed is:

1. A method of preparation of homogeneous solid solution single crystals of ferroelectric materials having Curie points extending over a wide temperature range, comprising the steps of providing a melt of KTaO_3 — KNbO_3 in predetermined proportions at a temperature just above the liquidous temperature of said material, cooling said melt at a rate of about 0.1° C. per hour to a point just below the liquidous temperature of said melt, maintaining said melt at said lower temperature during a time interval in which a single crystal solid solution is formed the mass of which is small in relation to the mass of the melt, separating the crystal thus formed from the

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bulk of the melt, and thereafter cooling said crystal to room temperature over an extended period of time.

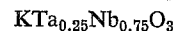
2. A method of preparation of homogeneous solid solution single crystals of ferroelectric materials having Curie points extending over a temperature range of from 13° K. to 700° K., comprising the steps of providing a melt of KTaO_3 — KNbO_3 in predetermined proportions at a temperature just above the liquidous temperature of said material, cooling said melt at a rate of about 0.1° C. per hour to a point just below the liquidous temperature of said melt while maintaining said melt in touching contact with a seed crystal, maintaining said melt at said lower temperature during a time interval in which a single crystal solid solution is formed the mass of which is small in relation to the mass of the melt, separating the crystal thus formed from the bulk of the melt, and thereafter cooling said crystal to room temperature over an extended period of time.

3. A method of preparation of homogeneous solid solution single crystals of ferroelectric materials having Curie points extending over a wide temperature range, comprising the steps of mixing K_2CO_3 , Ta_2O_5 and Nb_2O_5 in predetermined proportions, heating said mixture at a temperature just above the liquidous temperature of said material, cooling said melt at a rate of about 0.1° C. per hour to a point just below the liquidous temperature of said melt, maintaining said melt at said lower temperature during a time interval in which a single crystal solid solution is formed, the mass of which is small in relation to the mass of the melt, separating the crystal thus formed from the bulk of the melt, and thereafter cooling said

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crystal to room temperature over an extended period of time.

4. A method of preparation of homogeneous ferroelectric solid solution single crystals of the formula $\text{KTa}_{0.54}\text{Nb}_{0.46}\text{O}_3$ having a Curie point of 50° C., comprising mixing K_2CO_3 , Ta_2O_5 and Nb_2O_5 in predetermined proportions corresponding to the formula



heating said mixture at 1165° C. to form a solid solution melt of said constituents, cooling said melt to 1158° C. during 24 hours, maintaining said melt at said latter temperature for an additional 24 hours, separating the crystal thus formed from the bulk of the melt, and cooling the crystal to room temperature during the three-day period.

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