

1

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METHOD OF PREPARING BARIUM TITANATE CRYSTALS

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1 Claim. (Cl. 23—51)

The present invention relates to dielectric materials and particularly to a method for preparing single crystals of barium titanate which have more stable electrical properties.

Barium titanate is one of several known dielectric materials which exhibit a characteristic of polarization versus applied electric field intensity, somewhat similar to the hysteresis characteristic obtained for magnetic materials, and which adapts these ferroelectric materials for use as memory elements in data storage and transfer systems where the remanent polarization in one sense may be used to represent one binary condition and in the opposite sense to represent the other binary condition with the two conditions controlled by the polarity of an electric field applied to opposite faces of a crystal.

Under certain conditions of pulsing it has been found that the remanent polarization decays, with the rate of decay dependent upon such factors as the magnitude and duration of the pulses as well as upon the pulse frequency. This feature has been a prime deterrent in adapting barium titanate crystals to general memory usage and, in accordance with the present invention, a procedure for preparing crystals is provided wherein a considerable decrease in the amount of remanent polarization decay is achieved.

As described in my copending patent application, Serial Number 497,471, filed March 28, 1955, barium titanate crystals have been grown from a direct melt or liquified with solvents, with crystal formation induced upon cooling the liquid melt at various rates to minimize nucleation and yet preserve the habit of those crystals being formed. Crystals of varied habit including hexagonal or cubic structures, twins and flat plates of non-uniform character and frequently containing included matter are formed by the usual procedures. Single, thin, physically uniform crystals of simple domain structure are desirable as square loop materials and this general character for formation is found in twins or V's comprising a formation of two right triangle plates joined at the hypotenuse at an angle of approximately 39°. Such type of crystal growth has been found to be preponderant with potassium fluoride used as the solvent agent. The process comprises mixing predetermined percentages of BaTiO₃ and the KF flux, heating until the mixture is in a liquid state and then cooling to a temperature just above the melting point of the flux whereupon the flux is normally poured off. It has been determined that if the flux is allowed to solidify about the BaTiO₃ crystals and dissolved away after cooling to room temperature, the crystals obtained have a significantly lesser rate of pulse decay.

One general object of the invention therefore is to provide a method for growing barium titanate crystals having electrical characteristics more suitable for use in memory devices.

A more specific object is to provide a process whereby

2

barium titanate crystals of more desirable pulse decay characteristics are grown employing a solvent comprising potassium fluoride.

Other objects of the invention will be pointed out in the following description and claim, which discloses, by way of example, the principle of the invention and the best mode, which has been contemplated, of applying that principle.

An example of the process by which improved barium titanate crystals are grown comprises the preparation of a mixture of approximately 41.2 grams of BaTiO₃, and 103.8 grams of KF, or a weight ratio of approximately 28% of BaTiO₃ to 72% of the solvent agent. The mixture is placed in a covered 110 cc. platinum crucible and heated to a temperature of 1150° C. at any suitable rate, which for practical purposes requires a period of from one to two hours. The crucible charge is held at this temperature or soaked for a period of ten hours and the temperature thereafter reduced uniformly to about 860° C. during a cooling interval of about six hours and thereafter cooled to room temperature at a rapid rate during an interval of about one hour. After the crucible has been cooled to room temperature with the flux allowed to solidify about the barium titanate crystals, the KF flux is dissolved away with water.

The length of the soaking period controls the degree of solution of BaTiO₃ in KF and a long period yields more crystalline BaTiO₃ than a short period with the number of V habit crystals formed remaining about the same in both cases. To obtain the desired V habit of crystal growth it is important that at least some of the BaTiO₃ charge remain undissolved.

The soak period may vary from six to twelve hours, with melts of about 7 to 20 mol percent of BaTiO₃ soaked at 1120° C. to melt of about 10 to 20 mol percent BaTiO₃ soaked at 1200° C., considered within a useable range of proportions for satisfactory crystal growth.

The V shaped crystals or twins formed by the process described are of increased size as compared with those heretofore known and are of better quality. The long edge dimension of crystals grown by the process in 110 cc. platinum crucibles have ranged up to 3.5 centimeters with the thickness of a single V plate of the order of 0.010 to 0.015 inches.

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 claim.

What is claimed is:

A process for the preparation of ferroelectric crystals having an improved rate of remanent polarization decay comprising the steps of mixing barium titanate with a fluxing agent consisting of potassium fluoride with the latter approximately 75 percent of the total weight of the mixture, heating said mixture to about 1150° C., maintaining this temperature for a period of six to twelve hours, gradually cooling said mixture to about 860° C. over a period of about six hours at which temperature the fluxing agent solidifies, thereafter cooling rapidly to room temperature and subsequently dissolving away the solidified potassium fluoride with water.

References Cited in the file of this patent**UNITED STATES PATENTS**

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