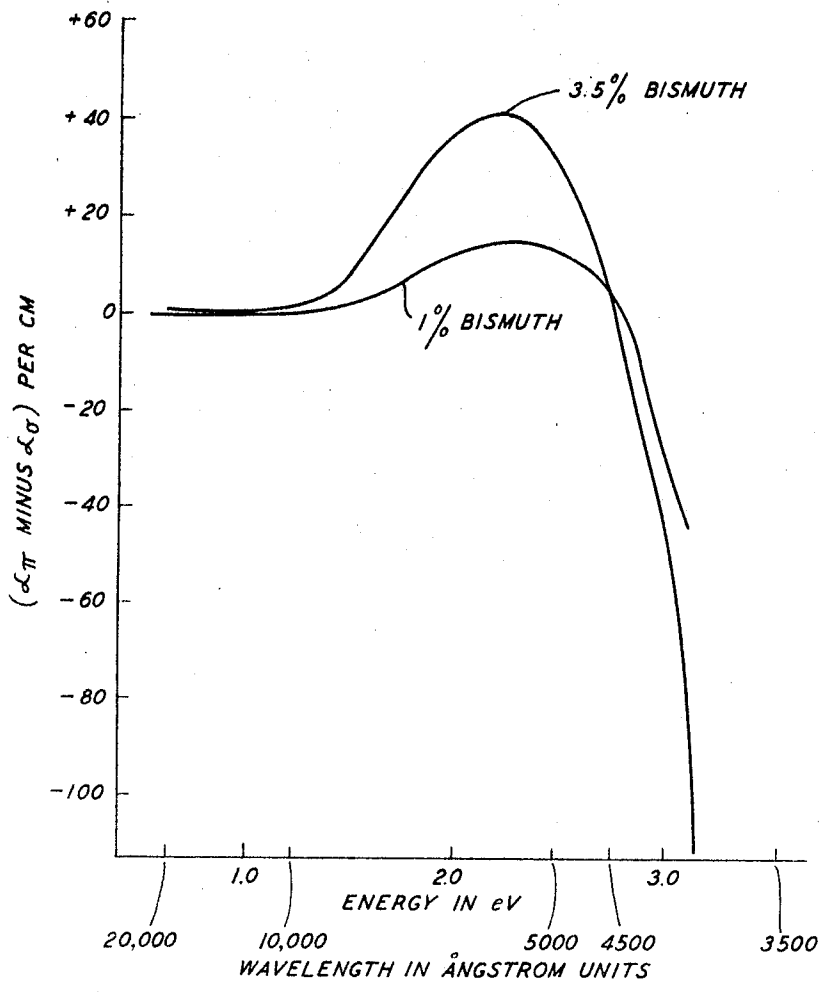
Aug. 19, 1969 J. P. REMEIKA 3,462,378

GROWTH OF a-DOMAIN BARIUM TITANATE

Filed April 19, 1966



INVENTOR
J. P. REMEIKA
BY George S. Indig
ATTORNEY

United States Patent Office 3,462,378
Patented Aug. 19, 1969

3,462,378

GROWTH OF a-DOMAIN BARIUM TITANATE

Joseph P. Remeika, Warren Township, Somerset County, N.J., assignor to Bell Telephone Laboratories, Incorporated, New York, N.Y., a corporation of New York

Filed Apr. 19, 1966, Ser. No. 543,603
Int. Cl. C04b *35/46*; H01v *7/02*; B01j *17/06*
U.S. Cl. 252—62.9 5 Claims

ABSTRACT OF THE DISCLOSURE

Single crystal barium titanate containing small amounts of bismuth show the usual platelike formation which is part of the "butterfly-twin" growth. These plates are *a*-domain rather than the usual *c*-domain and are, therefore, preferred for use in certain devices such as second harmonic generators operating in the visible spectrum.

This invention relates to novel procedures for the growth of barium titanate and to the crystalline material so produced.

Barium titanate, perhaps the best known inorganic ferroelectric material, has received considerable attention over a period of many years. Bodies of this and related compositions have found use in piezoelectric transducers and in various types of ferroelectric devices. Many growth techniques have been used. These include the use of modified melts and flux growth, both by seeding and by spontaneous nucleation.

Probably the most prevalent growth technique for barium titanate is that reported by J. P. Remeika in Journal of the American Chemical Society, volume 76, pages 940,941, for February 1954. In accordance with this technique, growth proceeds by spontaneous nucleation from a potassium fluoride flux. The product is a high yield of a crystal of tetragonal structure and of butterfly twin morphology. This designation of obvious derivation has two thin triangular plate "wings." These plates are *c*-domain, that is, the *c* axis or ferroelectric axis is normal to the plane of the major surface. Plates cut from such butterfly twins have been extensively used for the many devices which have been reported. The orientation in the plates so produced is particularly appropriate for most ferroelectric applications, including many light modulating devices in which it is desired that transmission be along a ferroelectric axis.

Recently some attention has been given the possibility of using barium titanate as the functional element in a second harmonic generator. Work of this nature has been reported by Robert C. Miller in Phys. Rev., vol. 134, page A–1313, June 1964. For this use it is desired that transmission be normal to the ferroelectric axis. While Dr. Miller reports the use of such *a*-domain plates, that is, plates with the *c* axis in the plane of a major surface of such a crystalline section, the prior art offered only one technique for producing such materials. This technique involves poling above the Curie point of 120° C. and at substantial fields (10^3–10^4 volts per centimeter). The technique does not result in reproducibly useful *a*-domain crystals and is generally considered less than satisfactory for this purpose.

It has now been discovered that the use of critical amounts of a specific dopant material, bismuth, may have an effect on the orientation and on certain other characteristics of barium titanate. For example, when incorporated in the spontaneous nucleation growth technique, conditions generally resulting in butterfly twin morphology yield *a*-domain rather than *c*-domain plates.

Bismuth-doped barium titanate, produced in accordance with this invention, evidences a strong dichronism never before reported in this material, whether of the ordinary *c*-domain plate form, of the poled *a*-domain form, or of the commonly occurring prismatic form. This dichroism, which has been observed over a wavelength range of from 0.4 micron to about 2 microns, is electric field dependent and is apparently somehow related to the ferroelectric spontaneous polarization. From a device standpoint, it is significant that the dichroism may be rotated by use of electric fields of the magnitude ordinarily found useful in poling while at temperatures substantially below the poling temperature. By analogy to the recreation of ferroelectricity at temperatures slightly above the usual ferroelectric Curie point by application of fields a bit in excess of the usual poling fields, it is found that the dichroism, too, may be re-introduced, and, by removal of the field, extinguished at will.

In accordance with this invention, it has been discovered that certain modifications in orientation and characteristic may be produced in barium titanate by bismuth doping. Introduction of bismuth into the crystalline product over the range of 0.1 to 6.0 weight percent based on the entire composition results in the growth of striation free *a*-domain plates when incorporated in a growth technique otherwise suitable for the growth of plates. Use of the same bismuth level in crystalline material however produced results in a dichroism which is field-dependent, as descrbied. A preferred embodiment of this invention takes the form of spontaneous nucleation from a potassium fluoride-containing flux, in accordance with the method described in JACS, supra. This embodiment makes use of a bismuth content of from 0.05 to 5.0 weight percent based on the total weight of barium titanate present.

Discussion of the characteristics of the bismuth doped barium titanate of this invention is expedited by reference to the figure. This shows, for two samples of different nominal weight percent bismuth content, the variation of $(\alpha_\pi - \alpha_\sigma)$ per cm. with energy in electron volts (ev.). When optical measurements are made in polarized radiation and the electric vector, E, is parallel to the optic axis of the crystal, then the absorbance can be denoted A_π and equals

$$\log_{10}\frac{I_{o\pi}}{I_\pi}$$

where Io_π is the intensity of radiation entering the sample and I_π is the intensity of radiation leaving the sample. If E is perpendicular to the optic avis, corresponding quantities are written with σ subscripts. Furthermore, α_π is defined as $A\pi/d$ where d, expressed in cm., is the light path length in the sample; similarly, $A\sigma/d$ is designated α_σ. From the drawing, it is seen that, at ~2.2 ev. or 5700 Angstrom units $(\alpha_\pi - \alpha_\sigma)$ reaches a peak value which is directly dependent upon the bismuth content. It is also evident that above ~2.8 ev. (below ~4500 Angstrom units), α_σ is greater than α_π and so $(\alpha_\pi - \alpha_\sigma)$ is negative.

The following examples illustrate the inventive processes of the invention.

EXAMPLE 4

37 grams barium titanate ($BaTiO_3$) powder, 90 grams potassium fluoride (KF) and 0.037 gram bismuth oxide (Bi_2O_3) were placed in a platinum crucible. The crucible containing this charge was covered with a platinum lid and placed directly into a furnace which was at a temperature of 1100° C. The furnace was held at this temperature for eight hours and then cooled at a slow constant rate until a temperature of 900° C. was reached. The still liquid flux was poured off at this point and the

crystals were annealed by slowly cooling down to room temperature.

Aproximately half of the crystallized matter was of butterfly wing morphology. Plates of these crystals were generally striation free and *a*-domain, as evidenced by use of a polarizing microscope. Resistivity was of the order of 10^{13} ohm-centimeters.

EXAMPLE 2

The procedure of Example 1 was repeated using, however, 6.50 grams of bismuth oxide. At least half of the resulting crystals were again butterfly twin morphology and were striation free *a*-domain.

EXAMPLE 3

Procedure of Example 1 was repeated, however, utilizing 0.30 gram of bismuth oxide. Fifty percent of the crystalline product was again observed to be butterfly twin and of *a*-domain.

EXAMPLE 4

Procedures of Example 3 was repeated, however, substituting 30 grams of barium titanate. Upon reaching the indicated temperature, it was observed that the entire contents were in solution. Cooling was, however, permitted to proceed at the slower rate of 2° C. per hour.

The crystalline end product was prismatic in morphology.

The examples set forth above describe procedures which have been used to advantage. In general, depending on the desired end product, growth rate may be varied over a fairly broad range from 30° C./hour to <1° C./hour. For example, for flux growth in general, barium titanate to potassium fluoride ratio may vary from 3.0:9.0 to 5.0:9.0, with the upper range of from 3.5:9.0 to 4.0:9.0, defining the best conditions for butterfly twin growth. Bismuth content in terms of final crystal composition may vary over the range of from .05 to 5.0, as has been indicated. For flux growth out of potassium fluoride the corresponding range may vary from .5 to 6.0 expressed in terms of weight percent bismuth over weight percent total final composition. While the minimum indicated is adequate for the purpose of growing *a*-domain butterfly twins, which can only be grown in a flux process, larger bismuth contents result in stronger dichroism in a crystalline product however produced. For such crystals, which may be prepared from the melt, or by spontaneous nucleation or seeded growth from a flux, a minimum bismuth content in the final crystal of 0.5 weight percent is preferred.

From the examples, it is seen that the cooling rate for the production of prismatic crystals from a flux was caused to proceed more slowly than that for the butterfly twins. This is in accordance with usual practice which

acknowledges the fact that slower cooling often results in larger crystalline end product. Such slow cooling rates are not desired for butterfly twins, in general, since the additional growth in such instances is normal to the major surface of the plate, and since for most device uses such thickened plates are not desired.

All crystals containing from 1.0 to 3.5 nominal weight percent bismuth have evidenced dichroism from ~1 ev. to ~3 ev. as shown in the figure. This dichroism vanishes at the Curie point. It is interesting to note that the Curie temperature for largest bismuth doping within the included range is increased from the usual value of about 120° C. to a value of about 135° C. with smaller increase for smaller bismuth content. Below the Curie temperature, the dichroism may be rotated by application of an electric field across the plane with the *c* axis of ferroelectric axis aligned in the direction of the applied field. Effective fields for this purpose are of the order of 10^3 to 10^5 volts per centimeter. It is observed also that immediately above the Curie temperature at which ferroelectricity and dichroism are both extinguished, the two characteristics may be re-induced by application of a field of the same order of magnitude.

What is claimed is:

1. Single crystal product consisting essentially of *a*-domain barium titanate containing from .05 percent to 5.0 percent bismuth by weight.

2. Product of claim 1 in which the bismuth content is from 0.3 percent to 2.0 percent.

3. Method for producing a single crystal product consisting essentially of barium titanate comprising growing said crystal from a nutrient consisting essentially of barium titanate bismuth oxide and a flux containing such amount of bismuth as will yield at least 0.5 percent in the final product.

4. Process of claim 3 in which the said nutrient consists essentially of a mixture of barium titanate bismuth oxide and potassium fluoride.

5. Process of claim 4 in which the said nutrient is produced from powdered barium titanate and in which it is at all times partially solid.

References Cited

UNITED STATES PATENTS

2,803,519	8/1957	Karan	106—39 XR
2,885,521	5/1959	Fotland.	
2,908,579	10/1959	Nelson et al.	106—39
3,103,440	9/1963	Cline et al.	106—39
3,103,441	9/1963	Cline et al.	106—39

TOBIAS E. LEVOW, Primary Examiner

R. D. EDMONDS, Assistant Examiner