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GROWTH OF PIEZOELECTRIC BISMUTH OXIDE

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U.S. Cl. 252—62.9 1 Claim

ABSTRACT OF THE DISCLOSURE

Single crystal, optically active, photoconductive, piezoelectric bismuth oxide is obtained by growth from a melt comprising high purity bismuth oxide is obtained by growth from a melt comprising high purity bismuth oxide and small quantities of an oxide selected from among the oxides of germanium, silicon, gallium, aluminum, and titanium.

This invention relates to a technique for the growth of single crystal bismuth trioxide (Bi_2O_3). More particularly, the present invention relates to a technique for the growth of optically active bismuth trioxide manifesting high piezoelectric activity.

Thus far, it has been concluded that bismuth trioxide exists in four crystallographic modifications, namely, (a) a stable low temperature monoclinic form designated α-Bi_2O_3, (b) a metastable body-centered cubic form designated γ-Bi_2O_3, (c) a tetragonal form designated β-Bi_2O_3 and (d) a single cubic form. Although some interest has been generated in these compositions, the literature has heretofore been totally silent with regard to the electrical properties thereof, so negating its potential in the electronics industry.

In accordance with the present invention, a technique is described for the preparation of single crystal Bi_2O_3 manifesting optical activity photoconductivity and high piezoelectric activity, so suggesting its use in electrical optic devices, electromechanical transducers or in acoustic amplifiers. The inventive technique involves growing from a high purity melt comprising Bi_2O_3 and small quantities of at least one oxide selected from among the dioxides of germanium and silicon or the oxides of gallium, titanium and aluminum. The resultant single crystal composition is of good quality, evidences electromechanical coupling coefficients in excess of 25 percent and is found to belong to the rare point group 23.

An important aspect of the present invention lies in the use of specific melt compositions, for example, those containing critical proportions of Bi_2O_3 and additive oxide, hereinafter designated MeO for convenience. In the growth of single crystal Bi_2O_3 as described, it is essential that the mol ratio of Bi_2O_3 to MeO be within the range of 3:1 to 12:1. The preferred range is from 5:1 to 7:1, an optimum being found to correspond with the approximate mol ratio of Bi_2O_3/MeO of 6:1.

It has been determined that the use of mol ratios of Bi_2O_3/MeO less than the noted 3:1 minimum results in an increased incidence of bismuth compounds other than the desired Bi_2O_3. Similarly, studies on the growth of Bi_2O_3 have revealed that the use of mol ratios in excess of the 12:1 maximum result in the formation of the α form of Bi_2O_3.

In accordance with the inventive technique, it has been determined that the desirable physical and electrical properties discussed hereinabove can successfully be generated in Bi_2O_3 obtained by any prior art procedure. However,

it has been found essential to utilize high purity starting materials. Thus, it has been found that the Bi_2O_3 source material must evidence a minimum purity of 99.9 percent. Similarly, the oxide materials employed in the practice of the present invention must necessarily evidence a purity of at least 99.9 percent. Studies have revealed that slight deviations from these minimum impurity levels result in failure to generate either piezoelectric or optical activity in the resultant Bi_2O_3.

With regard to the oxidic materials found suitable in the practice of the present invention, it has been found that at least one compound from among germanium dioxide (GeO_2), silicon dioxide (SiO_2), gallium oxide (Ga_2O_3), titanium oxide (TiO_2) and aluminum oxide (Al_2O_3) is required to obtain the desired properties in Bi_2O_3.

Examples of the application of the present invention are set forth below. They are intended merely as illustration and it is to be appreciated that the processes described may be varied by one skilled in the art without departing from the spirit and scope of the invention.

The examples are in tabular form for convenience and brevity. Each set of data in the table is to be considered as a separate example since each set of data was obtained in a separate process. The procedure followed in the examples is as follows:

A mixture of the starting materials, obtained from commercial sources, was weighed into a platinum crucible and heated to a temperature of the order of 935° C., the melting point of the mixture. Heating was effected by coupling the crucible with an RF induction heater. The crucible, together with its contents was then permitted to attain a temperature of 935° C. at which point the charge was entirely liquid. Next, a 30 ml. platinum wire was inserted into the melt. The Czochralski technique of pulling crystals from the melt was then employed to grow Bi_2O_3 to one-half inch diameter at a growth rate of one-half inch per hour. In order to obtain preferred orientation single crystal Bi_2O_3 obtained in this manner was subsequently employed in seed crystal form and Bi_2O_3 grown upon the seed. The data set forth below is based upon Bi_2O_3 grown upon seed crystals.

After cooling, the crystals were tested qualitatively for piezoelectric activity by means of the well known Giebe-Scheibe test. Thereafter, optical activity was determined by passing light of a fixed frequency (white light) through a given thickness (1 mm.) of Bi_2O_3 and bringing it to extinction. Following, rotation was effected to extinction again and the rotation for a given thickness measured.

Photoconductivity was determined by connecting the output from the piezoelectric detector (employed in the Giebe-Scheibe test) to an oscilloscope, resonant frequency of the Bi_2O_3 crystal being evidenced by multiple peaks. Following, the crystal was exposed to a white light source, so resulting in the loss of the peaks and indicating a change in conductivity of photoconductivity.

Finally, the electromechanical coupling coefficient of the Bi_2O_3 was measured, that is, the degree of efficiency of the piezoelectric body in transforming electrical energy to mechanical energy was determined. In order to determine the coupling coefficient a slice in disk form was taken off a Bi_2O_3 crystal normal to the growth direction and electroded by applying silver paste to the major faces of the disk and firing by conventional techniques. Following, the electroded crystal was studied by scanning the frequency spectrum in search of a strong resonance point. The coupling coefficient was determined by observing the frequency shift from resonance to anti-resonance and computing it by means of well known formulae.

TABLE I

Example	Bi_2O_3 (grams)	Purity, Percent	MeO (grams)	Purity, Percent	Product	Giebe-Scheibe	Coupling Coefficient, Percent	Optical Activity	Photo-conductivity
1	2,795.66	99.9	GeO_2-104.59	99.9	Bi_2O_3	+	25	22°/mm.	+
2	2,795.66	99.9	Ga_2O_3-187.44	99.9	Bi_2O_3	+	25	22°/mm.	+
3	2,795.66	99.9	SiO_2-60.09	99.9	Bi_2O_3	+	25	22°/mm.	+

+=positive.

What is claimed is:

1. Single crystal, optical active piezoelectric composition of matter consisting essentially of Bi_2O_3 having a purity of at least 99.9 percent and at least one compound selected from the group consisting of GeO_2, TiO_2, Ga_2O_3, SiO_2' and Al_2O_3, said compound having a purity of at least 99.9 percent, the mol ratio of Bi_2O_3 to said compound being within the range of 3:1 to 12:1.

References Cited

Kroger: Some Aspects of the Luminescence of Solids, 1948, page 264.

Pen'kov et al.: Effect of Impurities on the Nuclear Quadrupole Resonance Spectra of the α- and γ-Modification of Bi_2O_3, Soviet physics, solid state, vol. 7, No. 1, July 1965, pages 145–147.

Gattow et al.: Ceramic Abstracts, page 238i, 1965.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,470,100 Dated September 30, 1969

Inventor(s) Albert A. Ballman

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Claim 1, column 3, line 10, change "optical" to --optically--.

SIGNED AND
SEALED
DEC 23 1969

(SEAL)
Attest:

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