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METHOD OF GROWING SINGLE CRYSTALS

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The invention described herein may be manufactured and used by or for the Government for governmental purposes, without the payment of any royalty thereon.

This invention relates to a method of growing single crystals of the formula $BaZn_2Fe_{16}O_{27}$.

An object of this invention is to grow single crystals of the formula $BaZn_2Fe_{16}O_{27}$ that are mechanically sound, have well developed crystalline faces and are relatively free of macroscopic pits and foreign inclusions. Another object is to grow single crystals of the formula $BaZn_2Fe_{16}O_{27}$ for use in microwave and millimeter device applications as in isolators, rotators, filters, power limiters, and harmonic generators. A further object is to grow single crystals of the formula $BaZn_2Fe_{16}O_{27}$ that can be recovered by a simple chemical treatment. A still further object is to grow such single crystals at a melting temperature sufficiently low to eliminate the problem of the reduction of Fe^{+3}, thus improving the electronic properties of the product. A further object is to grow the single crystals at a temperature that greatly reduces the loss of volatile components. Another object is to grow the single crystals in such a manner that contamination from the vessels carrying the reactants, as for example crucibles, is negligible. A still further object is to grow single crystals of the formula $BaZn_2Fe_{16}O_{27}$ at least 0.1 inch in length on an edge.

The single crystal prepared by this invention is a magnetic oxide of barium, iron, and zinc having properties which makes it potentially useful as a magnetic component for applications at microwave frequencies. Single crystals are sought because: (1) The resonance line width of polycrystalline materials is so large as to limit the sensitivity and efficiency of the device in which it is incorporated; single crystals intrinsically have narrower line widths; (2) several useful properties are observed only in single crystals; (3) single crystals are important as standards by which to evaluate the performance of polycrystalline materials of the same composition.

In U.S. patent application Serial No. 104,483, filed April 20, 1961, there is disclosed a method of growing single crystals of formula $BaZn_2Fe_{16}O_{27}$ involving dissolving a mixture of the oxides (BaO, ZnO, and Fe_2O_3) in sodium carbonate at a temperature of about 1300° C., crystallizing the compounds by reducing the temperature 1°–5° C. per hour to between 1000° C. and 1050° C., and recovering the crystals by treating the solidified melt with hot, dilute nitric acid solution. The single crystals obtained though reducing the ferrimagnetic line width have a number of disadvantages. One disadvantage is that they do not reduce the ferrimagnetic line width sufficiently for certain applications. Secondly, the single crystals have a number of mechanical imperfections as for example pits, incompletely developed crystalline faces, etc.

We have now found a method of growing single crystals of formula $BaZn_2Fe_{16}O_{27}$ that overcomes the aforementioned disadvantages. The method involves the use

of bismuth oxide (Bi_2O_3) as a fluxing agent. According to the method, the proper proportions of Fe_2O_3, $BaCO_3$, ZnO, and Bi_2O_3 are first weighed out and then ground and mixed together dry or wet with a dispersing agent (water or ethyl acetate, etc.). The mix is then packed into a platinum crucible and heated to between 1250° C. and 1300° C. in an electric resistance furnace. The mix is then cooled at 2.5° C. per hour or slower to 1050° C.; then cooled more rapidly in a furnace to room temperature. The crystals are then removed from the crucible and freed from the flux by leaching with 10 to 20% by volume dilute nitric acid for about 8 to 25 hours. Single crystals of the formula $BaZn_2Fe_{16}O_{27}$ are obtained which are substantially free of mechanical imperfections. The single crystals measure at least 0.1 inch on an edge. Compared to single crystals of the same formula grown by the Serial No. 104,483 method, the single crystals grown by the method of this invention exhibit less mechanical or growth defects and show more numerous and better formed crystalline faces. Moreover, the resonance line width of the single crystals grown by the method of this invention is about 100 oersteds less than the resonance line width of the single crystals grown by the Serial No. 104,483 method. That is, single crystals of formula $BaZn_2Fe_{16}O_{27}$ grown by the Serial No. 104,483 method have a resonance line width of about 350 oersteds, whereas single crystals of formula $BaZn_2Fe_{16}O_{27}$ grown by the method of this invention have a resonance line width of 250 oersteds.

In the method, the initial mixture may contain from 52.1 to 68.5 percent by weight of the mix of Bi_2O_3, 6.8 to 10.3 percent by weight of the mix of BaO, 3.6 to 5.5 percent by weight of the mix of ZnO, and 21.1 to 32.1 percent by weight of the mix of Fe_2O_3.

The foregoing description is to be considered only as illustrative of the invention and not in limitation thereof.

What is claimed is:

The method of growing single crystals of the formula $BaZn_2Fe_{16}O_{27}$ including the steps of

(1) forming a ground mix from 52.1 to 68.5 percent by weight of the mix of Bi_2O_3, 6.8 to 10.3 percent by weight of the mix of BaO, 3.6 to 5.5 percent by weight of the mix of ZnO, and 21.1 to 32.1 percent by weight of the mix of Fe_2O_3,

(2) heating the mix in a platinum crucible in an electric resistance furnace at between 1250° C. and 1300° C.,

(3) cooling the mix at 2.5° C. per hour to 1050° C., and

(4) removing the crystals from the crucible by leaching with 10 to 20 percent by volume dilute nitric acid for about 8 to 25 hours.

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