

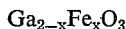
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3,110,674 PIEZOELECTRIC-FERROMAGNETIC MATERIAL

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This invention relates to a ferromagnetic material, more particularly to a ferromagnetic material which concurrently exhibits piezoelectric properties, and to its method of preparation.

The novel material has the chemical formula



where x has a value between .7 and 1.4 and can be described as a gallium-iron oxide. It is believed that this is the only material presently known exhibiting measurable amounts of piezoelectricity and ferromagnetism concurrently.

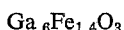
Material of this kind is especially useful in various electrical devices, particularly in forms of transducers, electromechanical resonators and nonreciprocal devices.

The material has been prepared both in ceramic and single crystal form and has exhibited the described properties in each form, although the properties are more pronounced in the single crystal form.

Single crystals of the material can be grown by preparing a melt of gallium sesquioxide (Ga_2O_3), ferric oxide (Fe_2O_3), boron oxide (B_2O_3) and bismuth trioxide (Bi_2O_3), the latter two components being found advantageous for serving as fluxes, and allowing the melt to cool at a controlled rate. The resulting gallium-iron oxide crystals can be extracted from the cooled solid mass by immersing the mass in a hot dilute aqueous solution of nitric acid. The ratio of gallium ions to iron ions in the grown crystal can be controlled by proportioning accordingly the relative amounts of Ga_2O_3 and Fe_2O_3 in the melt.

The ceramic form can be prepared by milling together appropriate amounts of Ga_2O_3 and Fe_2O_3 with water for forming a slurry, pressing the resulting slurry into discs, firing the discs, and then allowing the discs to cool slowly.

In each form, X-ray powder diffraction photographs have shown that a single phase of the orthorhombic crystal structure persists between $\text{Ga}_{1.3}\text{Fe}_{0.7}\text{O}_3$ and



with a regular change in lattice constant. Beyond these limits, free ferric oxide is found in the iron-rich specimen and free gallium sesquioxide in the gallium-rich end.

One specific example of the fabrication of the single crystal form is as follows. There were placed in a 100 cubic centimeter platinum crucible 6.5 grams each of gallium sesquioxide and ferric oxide, 4.0 grams of boron oxide, and 35 grams of bismuth trioxide. The crucible was covered and placed in an electric furnace, heated to 1125 degrees C. and kept at that temperature for five hours. The melt was thereafter cooled at the controlled rate of between four and seven degrees C. per hour until a temperature of about 500 degrees C. was reached, after which power to the furnace was turned off and

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the furnace allowed to cool rapidly at an uncontrolled rate since below this temperature the rate of cooling was found not to be important.

The resulting crystals were extracted from the solidified mass by immersion for several hours, typically four hours, in 15 percent aqueous solution of nitric acid heated to 80 degrees C.

The crystals recovered were found to exhibit magnetic Curie points varying from slightly above room temperature to considerably below room temperature. However, all the crystals were piezoelectric from room temperature to the temperature of liquid nitrogen, 77 degrees K., exhibiting piezoelectricity to about the same extent as quartz. The crystals found by chemical analysis to have substantially equimolar proportions of gallium and iron had magnetic Curie points of about 260 degrees K. The magnetic Curie point was found to be dependent on the iron content, increasing with increasing iron content. The magnetic Curie point was found to be above room temperature for crystals in which the iron concentration by number of atoms was at least about 60 percent of the total iron-gallium content, corresponding to a value of x in the formula set forth above in the range between 1.2 and 1.4.

The stoichiometric form GaFeO_3 at room temperature had a conductivity of 2×10^{-6} ohm-centimeters indicating that the material is an insulator.

As another example, single crystals were grown from a melt formed by adding together in a suitable crucible 12.5 grams of Ga_2O_3 , 10.6 grams of Fe_2O_3 , 14.0 grams of B_2O_3 and 60 grams of Bi_2O_3 . This melt was held at 1100 degrees C. for two hours and then cooled at the rate of about 7.0 degrees C. per hour to 600 degrees C. and the crucible was thereafter air-quenched for cooling.

In such processes the amounts used of the B_2O_3 and Bi_2O_3 fluxes should be adequate to insure complete dissolution of the gallium and iron oxides. The use of extra gallium and iron oxides will simply result in a residue of the excess oxide in the solidified mass. The melting conditions are not critical. The temperature obviously must be sufficiently high to achieve adequate melting and mixing. However, it is found advantageous to avoid temperatures much in excess of 1200 degrees C. so as to remain in the equilibrium range for the desired compound. Under the conditions described, the crystals grown typically are about a centimeter long and several millimeters on a side in cross section.

Ceramic compositions were prepared by adding appropriate amounts of gallium sesquioxide and ferric oxide into a polyethylene jar, adding one-half inch diameter porcelain balls and distilled water, and milling the mixture for sixteen hours. The relative amounts of the two oxides used were chosen to provide a desired ratio in the gallium and iron content of the ceramic. The slurry was then filtered, dried and sieved. Discs of about one centimeter diameter and one millimeter thick were pressed together under five tons of pressure on a three and one-half inch ram. The discs were then placed on a platinum sheet and into an electric furnace which was then heated to 1400 degrees C. and held at that temperature for seven hours. The discs were then allowed to cool at a gradual uncontrolled rate. Of course, the various parameters of this process can be varied over wide limits without too significant a change in the end product.

What is claimed is:

1. Crystalline material having an orthorhombic structure and exhibiting both ferromagnetic and piezoelectric properties having the chemical formula $Ga_{2-x}Fe_xO_3$ where x has a value between .7 and 1.4.

2. Crystalline material having an orthorhombic structure and exhibiting both ferromagnetic and piezoelectric properties having the chemical formula $Ga_{2-x}Fe_xO_3$ where x has a value between 1.2 and 1.4.

3. The process of preparing single crystals of gallium-iron oxide comprising the steps of melting together gallium sesquioxide, ferric oxide, boron oxide and bismuth trioxide, cooling the melt slowly, and recovering gallium iron oxide crystals from the solidified mass.

References Cited in the file of this patent

UNITED STATES PATENTS

2,442,982	Harvey	June 8, 1948
2,509,654	Smith	May 30, 1950

2,657,122	
2,657,458	
2,691,738	
2,715,109	
2,721,182	5
2,848,310	
2,849,404	
2,852,420	
2,872,299	
2,892,739	10
2,957,827	
3,053,770	

Chaudoye et al.	Oct. 27, 1953
Pessel	Nov. 3, 1953
Matthias	Oct. 12, 1954
Albers-Schoenberg	Aug. 9, 1955
Clement	Oct. 18, 1955
Remeika	Aug. 19, 1958
Jaffe et al.	Aug. 26, 1958
Pohl	Sept. 16, 1958
Celmer et al.	Feb. 3, 1959
Rusler	June 30, 1959
Nielsen	Oct. 25, 1960
Counts	Sept. 11, 1962

OTHER REFERENCES

15	Lensen et al.: Comptes Rendus, vol. 236, pp. 1997-8, March 31, 1958.
	Pauthenet: J. Applied Physics, April 1959, pp. 290S-292S.
	Anderson: J. Applied Physics, April 1959, p. 299S, Div. 64.