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FERROMAGNETIC MATERIAL AND METHOD OF MAKING THE SAME

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This invention relates to ferromagnetic materials more particularly for piezomagnetic vibrators and to methods of making the same.

Such vibrators are useful for converting electrical energy into mechanical energy, for example, ultrasonic vibrations, and conversely (see for example "Philips Technical Review," 18, 285–298, 1956/57). For this use it is desirable that the material have a maximum electromechanical coupling coefficient and maximum mechanical tensile strength, while the magnetic and mechanical losses must be low and consequently the magnetic and mechanical quality factors must be high.

While certain ferromagnetic materials, e.g. nickel-copper ferrites and nickel-cobalt ferrites, exhibit piezomagnetic properties, their electromechanical coupling coefficients are low, viz. less than about 0.20. Similarly, a nickel-cobalt ferrite in which a portion of the iron has been replaced by chromium, also known to exhibit piezomagnetic properties, has been found to be rather inefficient, particularly when used in a piezomagnetic vibrator.

It is a principal object of our invention to provide a new and novel material having piezomagnetic properties which has a larger electromechanical coupling coefficient and is more efficient in converting mechanical to electrical energy and vice versa.

It is another object of our invention to provide a method of making a piezomagnetic material having a larger electromechanical coupling coefficient.

A still further object of our invention is to provide a new and novel piezomagnetic material which not only exhibits a larger electromechanical coupling coefficient but which also has a maximum mechanical tensile strength.

Another object of our invention is to provide a new and novel material exhibiting not only a larger electromechanical coupling coefficient and maximum mechanical tensile strength but also low magnetic and mechanical losses.

These and further objects of our invention will appear as the specification progresses.

In accordance with our invention, this new and novel ferromagnetic material which exhibits piezomagnetic properties with a large electromechanical coupling coefficient, low losses and high mechanical strength, consists of crystals having spinel structure having a composition corresponding to

29 to 47 mol percent NiO
3 to 20 mol percent CuO
0.5 to 2 mol percent CoO
50 to 52 mol percent Fe_2O_3

In a preferred embodiment of our invention we have found that compositions corresponding to

35 to 43 mol percent NiO
6 to 14 mol percent CuO
0.8 to 1.4 mol percent CoO
50 to 52 mol percent Fe_2O_3

show the highest values of the electromechanical coupling coefficient. Moreover, the nickel oxide and the copper oxide can be replaced in proportional amounts by at most 10 mol percent of ZnO.

Our invention also relates to bodies consisting of the said material and to piezomagnetic vibrators containing vibrator bodies which consist of the said material and must be made to vibrate by magnetic or acoustic alternating fields.

The materials in accordance with the invention have values of the electromechanical coupling coefficient substantially exceeding 0.20, the values of the mechanical quality factor exceeding 2000. Furthermore, the values of the magnetic losses and of the porosity are so low that the materials can be used to advantage in piezomagnetic vibrators. As is known, a low value of the porosity is required for a high mechanical tensile strength and for a high erosion resistance. The term "erosion" as used herein is meant to be understood as the damage to the radiating surface of the vibrator owing to cavitation at high acoustic intensities. The absolute values of the longitudinal saturation magnetostriction of the materials exceed 20×10^{-6}.

The materials in accordance with our invention are produced by sintering, at a temperature between 1000° C. and 1400° C., a finely powdered mixture of nickel oxide, copper oxide, cobalt oxide, iron oxide and the required zinc oxide, which oxides can entirely or partly be replaced by compounds which on heating are converted into these oxides. Preferably sintering is performed at a temperature between 1200° C. and 1300° C. The mixture is preferably heated in air or oxygen but other atmospheres such as nitrogen, carbon dioxide, etc. may be employed. The latter temperatures are lower than the temperatures at which in the known materials, optimum piezomagnetic properties are obtained.

It is essential that the materials in accordance with our invention contain at least 50 mol percent of Fe_2O_3, although larger amounts are permissible since materials which contain less than 50 mol percent of Fe_2O_3 exhibit large mechanical and magnetic losses which would be a serious disadvantage to their application in piezomagnetic vibrators. Amounts of Fe_2O_3 in excess of 50 mol percent may result in a lowering of the resistivity of the material which is not detrimental to the desired piezomagnetic properties.

The following example is illustrative of the method employed in preparing the compositions specified in the table in which lists the properties of a number of examples of material according to our invention.

Example

A mixture of nickel oxide, copper carbonate, cobalt carbonate and ferric oxide was ground with water in a ball mill for 18 hours and subsequently prefired at 950° C. in air for 4 hours. The reaction product was ground in a ball mill with water for 18 hours and after drying a small amount of an organic binder, was added to the product which subsequently was pressed to form rings and rods which were sintered in oxygen at the temperatures given in the following table for 2 hours.

The following table indicates the composition of the initial mixture, the sintering temperature and properties of the sintered rings. In the heading of the table

p is the porosity which is equal to

$$\frac{d_0-d}{d}$$

where d_0 is the X-ray density and d the density,

ρ is the resistivity in ohms cm.,

μ is the initial permeability at 30 kc./s.,

tan δ is the associated loss factor which is equal to

$$\frac{\mu''}{\mu'}$$

where μ'' is the imaginary part and μ' the real part of μ,

k is the electromechanical coupling coefficient with the optimum bias polarization, that is to say, with a bias polarization such that k is a maximum,

Q_E is the associated mechanical quality factor which is equal to

$$\frac{\left(\frac{1}{E_H}\right)'}{\left(\frac{1}{E_H}\right)''}$$

where

$$\left(\frac{1}{E_H}\right)'$$

is the real part and

$$\left(\frac{1}{E_H}\right)''$$

is the imaginary part of

$$\left(\frac{1}{E_H}\right)$$

E_H is the modulus of elasticity at constant magnetic field strength. With the exception of $Q_{E\,(ring)}$ all these quantities are material quantities: in the values given for $Q_{E\,(ring)}$ the bearing losses of the ring are allowed for. Since the value of Q_E measured on a rod substantially is a material quantity, the value of $Q_{E\,(rod)}$ is given also. Since magnetic vibrators can be used in baths having temperatures materially exceeding room temperature, for some preparations the values of k and of $Q_{E\,(ring)}$ at 50° C. are given. The longitudinal saturation magnetostriction at room temperature of all these preparations lies between -25×10^{-6} and -30×10^{-6}.

Composition, mol percent				Sintering temp., ° C.	p	Room temp.						50° C.	
NiO	CuO	CoO	Fe_2O_3			ρ, Ω cm.	μ	Tan δ	k	$Q_{E\,(ring)}$	$Q_{E\,(rod)}$	k	$Q_{E\,(ring)}$
42.5	7.5	---	50.0	1,220	0.052	-----	26.0	0.006	0.170	-----	5,200	-----	-----
38.8	11.2	---	50.0	1,220	0.037	-----	43.5	0.012	0.170	-----	8,200	-----	-----
45.5	3.7	0.8	50.0	1,220	0.044	-----	32.5	0.004	0.221	2,400	5,100	-----	-----
41.8	7.4	0.8	50.0	1,220	0,019	-----	48.5	0.017	0.248	1,730	5,400	-----	-----
38.1	11.1	0.8	50.0	1,220	0.031	-----	42.5	0.013	0.247	1,080	6,500	-----	-----
34.5	14.7	0.8	50.0	1,220	0.038	-----	40.5	0.007	0.228	2,160	5,800	-----	-----
29.5	19.7	0.8	50.0	1,220	0.029	-----	31.5	0.004	0.202	960	6,900	-----	-----
39.1	9.8	1.1	50.0	1,235	0.032	670	34.0	0.005	0.302	1,380	2,600	0.272	2,980
36.7	12.2	1.1	50.0	1,235	0.022	930	34.0	0.006	0.303	1,500	2,300	0.269	3,100
39.0	9.7	1.3	50.0	1,235	0,032	650	38.0	0.006	0.272	1,000	-----	0.276	2,320
37.5	11.0	1.5	50.0	1,220	0.030	-----	31.0	0.008	0.206	-----	2,200	-----	-----
40.4	7.1	2.5	50.0	1,220	0.025	-----	16.0	0.009	0.132	-----	1,500	-----	-----
36.8	10.7	2.5	50.0	1,220	0.030	-----	12.5	0.014	0.145	-----	1,100	-----	-----
39.1	11.4	0.8	48.7	1,200	-----	-----	40.0	0.110	0.272	450	270	-----	-----
35.4	15.1	0.8	48.7	1,200	-----	-----	43.0	0.235	0.250	200	220	-----	-----

While we have thus described our invention in connection with specific embodiments and specific applications thereof, we do not wish to be limited thereto since other modifications and applications thereof will be readily apparent to those skilled in the art.

What we claim is:

1. A ferromagnetic material having piezomagnetic properties and consisting essentially of crystals having a spinel structure and a composition corresponding to about 29 to 47 mol percent of NiO, about 3 to 20 mol percent of CuO, about 0.5 to 2 mol percent CoO, and at least 50 to about 52 mol percent of Fe_2O_3, said material having an electromechanical coupling coefficient substantially exceeding 0.20.

2. A ferromagnetic material having piezomagnetic properties and consisting essentially of crystals having a spinel structure and a composition corresponding to about 35 to 43 mol percent of NiO, about 6 to 14 mol percent CuO, about 0.8 to 1.4 mol percent of CoO, and at least 50 to about 52 mol percent of Fe_2O_3, said material having an electromechanical coupling coefficient substantially exceeding 0.20.

3. A ferromagnetic material having piezomagnetic properties and consisting essentially of crystals having a spinel structure and a composition corresponding to about 29 to 47 mol percent of NiO, about 3 to 20 mol percent CuO, up to about 10 mol percent ZnO, about 0.5 to 2 mol percent CoO, and at least 50 to about 52 mol percent Fe_2O_3, said material having an electromechanical coupling coefficient substantially exceeding 0.20.

4. A ferromagnetic material having piezomagnetic properties and consisting essentially of crystals having a spinel structure and a composition corresponding to about 35 to 43 mol percent NiO, about 6 to 14 mol percent CuO, up to about 10 mol percent ZnO, about 0.8 to 1.4 mol percent CoO, and at least 50 to about 52 mol percent Fe_2O_3, said material having an electromechanical coupling coefficient substantially exceeding 0.20.

5. A method of making a ferromagnetic material having piezomagnetic properties comprising the steps, forming a finely-divided mixture of about 29 to 47 mol percent of NiO, about 2 to 20 mol percent of CuO, about 0.5 to 2 mol percent of CoO, and at least 50 to about 52 mol percent of Fe_2O_3, and heating said mixture in a non-reducing atmosphere at a temperature of about 1000° to 1400° C.

6. A method of making a ferromagnetic material having piezomagnetic properties comprising the steps, forming a finely-divided mixture of about 29 to 47 mol percent of NiO, about 3 to 20 mol percent of CuO, up to about 10 mol percent of ZnO, about 0.5 to 2 mol percent of CoO, and at least 50 to about 52 mol percent of Fe_2O_3, and heating said mixture in a non-reducing atmosphere to a temperature of about 1000° to 1400° C.

7. A method of making a ferromagnetic material having piezomagnetic properties comprising the steps, forming a finely-divided mixture of about 29 to 47 mol percent of NiO, about 3 to 20 mol percent of CuO, about 0.5 to 2 mol percent CoO, and at least 50 to about 52 mol percent Fe_2O_3, and heating said mixture in a non-reducing atmosphere to a temperature of about 1200° to 1300° C.

8. A method of making a ferromagnetic material having piezomagnetic properties comprising the steps, forming a mixture of about 29 to 47 mol percent of NiO, about 3 to 20 mol percent of CuO, up to about 10 mol percent of ZnO, about 0.5 to 2 mol percent CoO, and at least 50 mol percent to about 52 mol percent Fe_2O_3, and heating said mixture in a non-reducing atmosphere to a temperature of about 1200° to 1300° C.

9. A ferromagnetic body adapted for use in a piezomagnetic vibrator and having an electromechanical cou-

pling coefficient substantially exceeding 0.20, said body consisting essentially of a sintered coherent body composed of crystals having a spinel structure and a composition corresponding to about 29 to 47 mol percent of NiO, about 3 to 20 mol percent of CuO, about 0.5 to 2 mol percent of CoO, and at least 50 to about 52 mol percent of Fe_2O_3.

10. A ferromagnetic body adapted for use in a piezomagnetic vibrator and having an electromechanical coupling coefficient substantially exceeding 0.20, said body consisting essentially of a sintered coherent body composed of crystals having a spinel structure and a composition corresponding to about 29 to 47 mol percent of NiO, about 3 to 20 mol percent of CuO, up to about 10 mol percent of ZnO, about 0.5 to 2 mol percent of CoO, and at least 50 to about 52 mol percent of Fe_2O_3.

11. A ferromagnetic body adapted for use in a piezomagnetic vibrator and having an electromechanical coupling coefficient substantially exceeding 0.20, said body consisting essentially of a sintered coherent body composed of crystals having a spinel structure and a composition corresponding to about 35 to 43 mol percent of NiO, about 6 to 14 mol percent CuO, about 0.8 to 1.4 mol percent CoO, and at least 50 to about 52 mol percent Fe_2O_3.

12. A ferromagnetic body adapted for use in a piezomagnetic vibrator and having an electromechanical coupling coefficient substantially exceeding 0.20, said body consisting essentially of a sintered coherent body composed of crystals having a spinel structure and a composition corresponding to about 35 to 43 mol percent of NiO, about 6 to 14 mol percent of CuO, up to about 10 mol percent of ZnO, about 0.8 to 1.4 mol percent of CoO, and at least 50 to about 52 mol percent Fe_2O_3.

13. A method of making a ferromagnetic body adapted for use in a piezomagnetic vibrator and having an electromechanical coupling coefficient substantially exceeding 0.20, comprising the steps, forming a finely-divided mixture of about 29 to 47 mol percent of NiO, about 3 to 20 mol percent of CuO, about 0.5 to 2 mol percent of CoO, and at least 50 to about 52 mol percent of Fe_2O_3, compacting said mixture into a coherent body, and heating said body in a non-reducing atmosphere to a temperature of about 1000° to 1400° C.

14. A method of making a ferromagnetic body adapted for use in a piezomagnetic vibrator and having an electromechanical coupling coefficient substantially exceeding 0.20 comprising the steps, forming a finely-divided mixture of about 29 to 47 mol percent of NiO, about 3 to 20 mol percent of CuO, about 0.5 to 2 mol percent of CoO, and at least 50 to about 52 mol percent of Fe_2O_3, compacting said mixture into a coherent body, and heating said body in a non-reducing atmosphere to a temperature of about 1200° to 1300° C.

15. A method of making a ferromagnetic body adapted for use in a piezomagnetic vibrator and having an electromechanical coupling coefficient substantially exceeding 0.20 comprising the steps, forming a finely-divided mixture of about 29 to 47 mol percent of NiO, about 3 to 20 mol percent of CuO, up to about 10 mol percent of ZnO, about 0.5 to 2 mol percent of CoO, and at least 50 to about 52 mol percent of Fe_2O_3, compacting said mixture into a coherent body, and heating said body in a non-reducing atmosphere to a temperature of about 1000° to 1400° C.

16. A method of making a ferromagnetic body adapted for use in a piezomagnetic vibrator and having an electromechanical coupling coefficient substantially exceeding 0.20 comprising the steps, forming a finely-divided mixture of about 29 to 47 mol percent of NiO, about 3 to 20 mol percent of CuO, up to 10 mol percent of ZnO, about 0.5 to 2 mol percent of CoO, and at least 50 to about 52 mol percent of Fe_2O_3, compacting said mixture into a coherent body, and heating said body in a non-reducing atmosphere to a temperature of about 1200° to 1300° C.

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