

July 10, 1962

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3,043,776

FERROMAGNETIC OXIDIC MATERIAL

Filed April 16, 1958

3 Sheets-Sheet 1

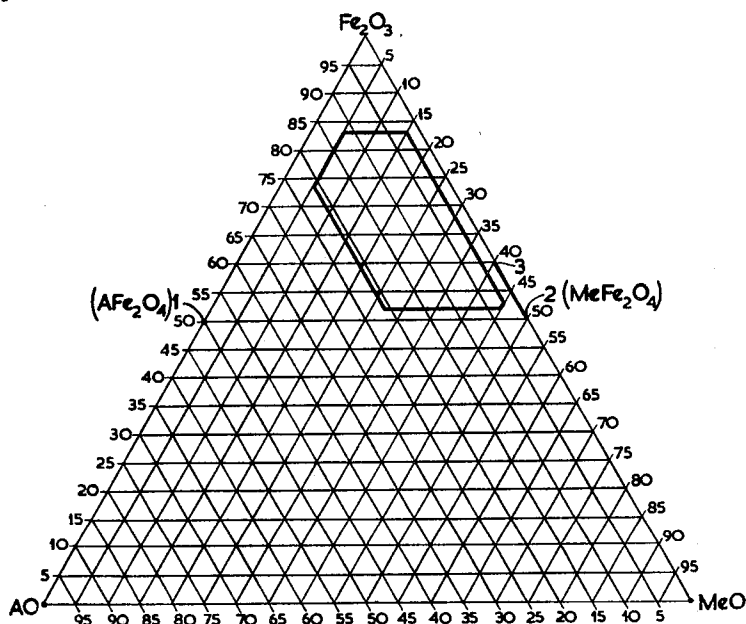


FIG. 1

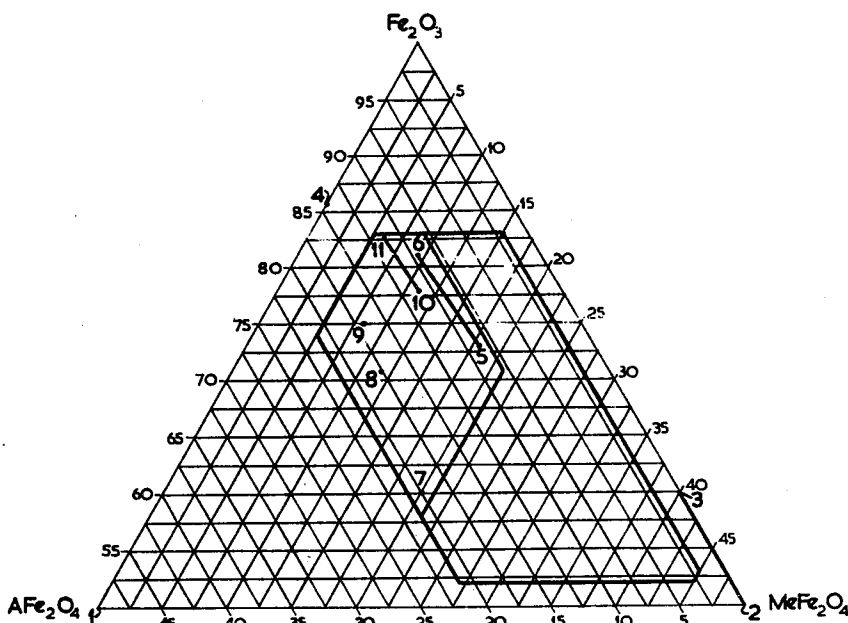


FIG. 2

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3 Sheets-Sheet 2

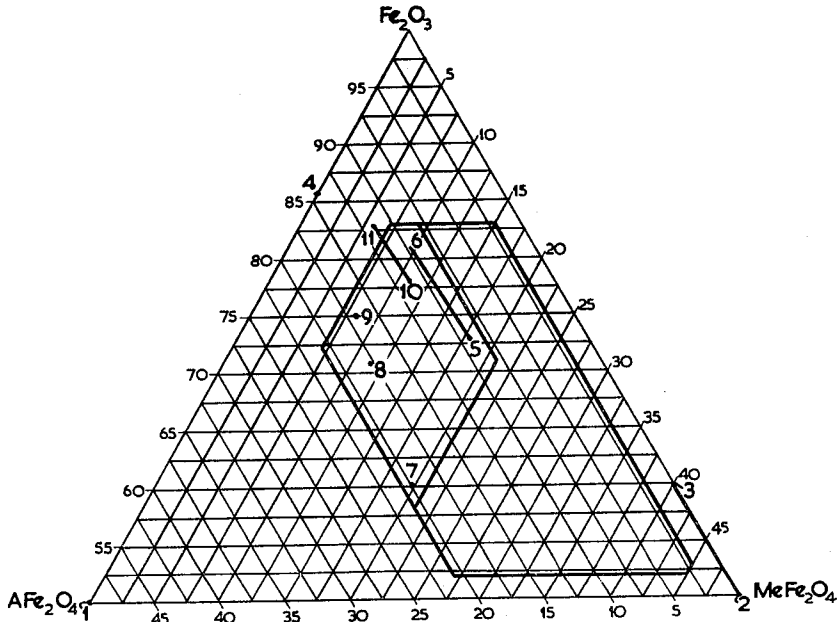


FIG.3

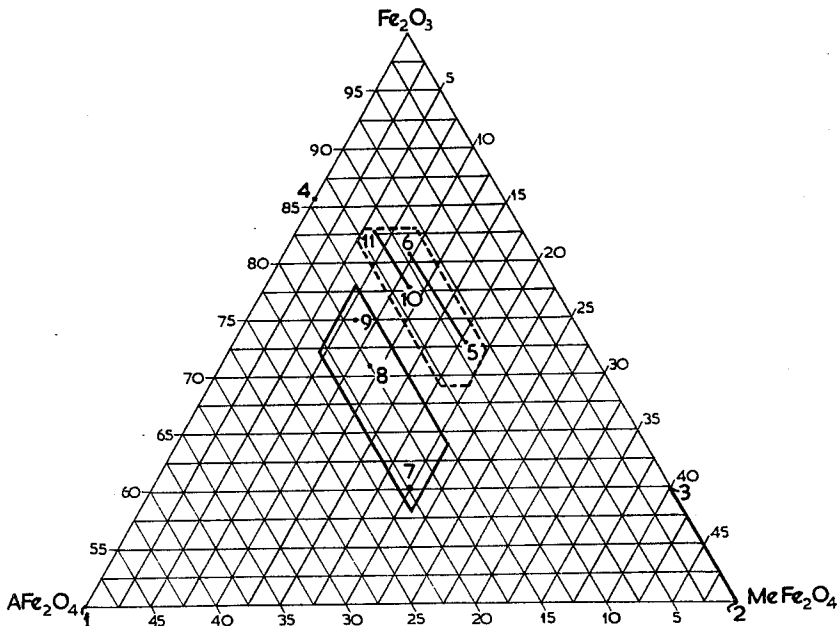


FIG.4

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3 Sheets-Sheet 3

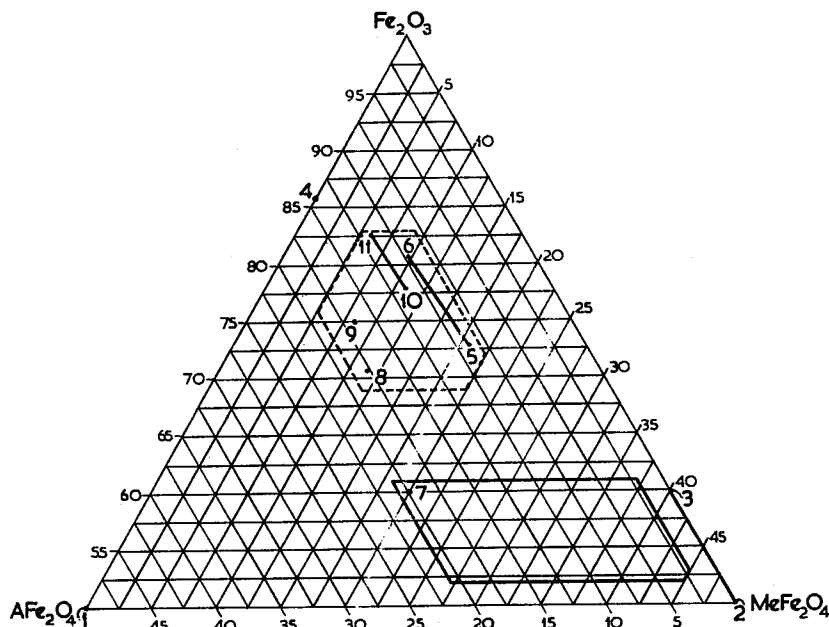


FIG.5

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3,043,776

**FERROMAGNETIC OXIDIC MATERIAL**

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Filed Apr. 16, 1953, Ser. No. 728,849

Claims priority, application Netherlands Apr. 18, 1957  
11 Claims. (Cl. 252-62.5)

My invention relates to ferromagnetic oxidic materials, which have valuable electromagnetic properties and methods of making the same.

More particularly, the materials according to the invention have a saturation magnetization of the same order of magnitude as that of ferromagnetic ferrites having the crystal structure of the mineral spinel, the so-called "spinel structure," and like the ferrites, most materials according to the invention have a high specific resistance. Many of them can be formed as ferromagnetic bodies for use at high frequencies, frequently up to 200 mc./s. and upwards.

Ferromagnetic ferrites having spinel structure, exhibit an initial permeability which is not independent of frequency, but there is a frequency range in which the initial permeability decreases with increasing frequency. This decrease in initial permeability usually begins at a lower frequency when the material has a higher initial permeability at low frequency (see H. G. Beljers and J. L. Snoek, "Philips' Technical Review," 11, pages 313-322, 1949-1950). However, with part of the materials according to the invention, the initial permeability is constant up to a much higher frequency than with ferromagnetic ferrites having spinel structure which have the same value for the initial permeability at low frequency. Since the use of ferromagnetic cores in a frequency range in which the initial permeability is not constant, usually involves the occurrence of high electromagnetic losses, the new materials found can be used as ferromagnetic bodies up to the much higher frequencies previously mentioned, in all those cases in which low electromagnetic losses are desired.

With ferromagnetic materials having hexagonal crystal structure, the crystal anisotropy is given to a first approximation by the expression:

$$F_K = K'_1 \sin^2 \vartheta$$

(see R. Becker and W. Doring, "Ferromagnetismus," 1939, page 114). If for a crystal  $K'_1$  is positive (so-called "positive" crystal anisotropy), the hexagonal axis in this crystal is the preferential direction of magnetization. If, however,  $K'_1$  is negative (in which event reference will be made in this specification to "negative" crystal anisotropy), this means that the spontaneous magnetization is directed at right angles to the hexagonal axis and hence is parallel to the basal plane of the crystal. In the latter case, the crystal has a so-called "preferred plane" of magnetization. However, the possibility of the presence of a comparatively weak preference of the magnetization for given directions in the basal plane remains.

The invention will be described with reference to the accompanying drawing, in which:

FIG. 1 is a ternary phase diagram showing the compositions according to the invention;

FIG. 2 is a portion of the ternary phase diagram of FIG. 1 which shows the compositions according to the invention;

FIG. 3 is a portion of the ternary phase diagram which shows one class of compositions according to the invention;

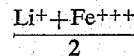
FIG. 4 is a portion of the ternary phase diagram which

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shows another class of compositions according to the invention; and

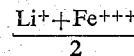
FIG. 5 is a portion of the ternary phase diagram which shows still another class of compositions according to the invention.

As shown in FIG. 1, the angular points of this diagram represent the oxides of which these materials may be regarded to be built up and from which these materials can be manufactured, viz. AO (in which A represents at least one of the bivalent metals Ba, Sr, Pb and Ca),  $Fe_2O_3$  and MeO (in which Me represents at least one of the bivalent metals Fe, Mn, Co, Ni, Zn, Mg, Cu or the bivalent complex



Point 1 in FIG. 1 corresponds to the compound  $AFe_2O_4$ , in which A represents at least one of the bivalent metals Ba, Sr, Pb and Ca. These compounds are not ferromagnetic.

Point 2 in FIG. 1 corresponds to the compounds with the formula  $MeO \cdot Fe_2O_3$  or  $MeFe_2O_4$ , in which Me represents at least one of the bivalent metals Fe, Mn, Co, Ni, Zn, Mg, Cu or the bivalent complex

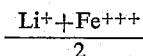


These compounds have a cubic crystal structure corresponding to that of the mineral spinel, the so-called "spinel structure." With the exception of  $ZnFe_2O_4$ , all of them are ferromagnetic. Many of these materials have a high value for the initial permeability, which, however, as previously mentioned, is not independent of frequency. It is possible, for each material, to indicate a frequency range in which the initial permeability decreases with increasing frequency and this decrease begins at a lower frequency as the material has a higher value for the initial permeability at low frequency. It is also possible that  $Fe_2O_3$  in a given form in the spinel lattice dissolves in an amount which is dependent upon the temperature used in the manufacture. Therefore, not only the formula

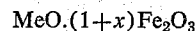


but also the formula  $MeO \cdot (1+x)Fe_2O_3$  wherein, for example,  $x < 0.5$  indicates the composition of these ferrites having spinel structure, which for this example corresponds to the line 2-3 in FIG. 1.

FIG. 2 shows part of the diagram of FIG. 1 and the compositions of the materials according to the invention may also be represented therein. The angular points of this diagram are constituted by  $AFe_2O_4$  (in which A represents at least one of the bivalent metals Ba, Sr, Pb and Ca),  $Fe_2O_3$  and  $MeFe_2O_4$  (in which Me represents at least one of the bivalent metals Fe, Mn, Co, Ni, Zn, Mg, Cu or the bivalent complex



As the line 2-3 in FIG. 1, the line 2-3 in FIG. 2 corresponds to ferrites having spinel structure and having a composition corresponding to the formula

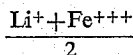


wherein  $x < 0.5$ .

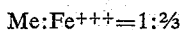
Point 4 in FIG. 2 corresponds to the compounds  $AO \cdot 6Fe_2O_3$  or  $AFe_{12}O_{19}$ , in which A represents at least one of the bivalent metals Ba, Sr, Pb and for at most  $\frac{2}{3}$  part Ca. These materials have permanent magnetic properties. The crystals have a hexagonal structure having a c-axis of about 23.3 A. and an a-axis of about 5.9 A.

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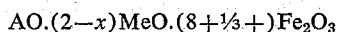
Point 5 in FIG. 2 corresponds to the compounds  $AO.2MeO.8Fe_2O_3$  or  $AMe_2Fe_{16}O_{27}$ , in which A represents at least one of the bivalent metals Ba, Sr, Pb and for at most  $\frac{2}{5}$  part Ca, while Me represents at least one of the bivalent metals Fe, Mn, Co, Ni, Zn, Mg or the bivalent complex



These ferromagnetic materials have a crystal structure, the elementary cell of which can be described in the hexagonal crystal system by a *c*-axis of about 32.8 A. and an *a*-axis of about 5.9 A. Part of these materials is built up of crystals having a preferred plane of magnetization at right angles to the hexagonal *c*-axis and these materials have comparatively high values for the initial permeability also at frequencies up to 200 mc./s. and higher. Such is the case at room temperature if Me represents Co for at least  $\frac{3}{8}$  part, which is, however, still slightly dependent upon the other bivalent metals represented by Me. The crystals of the other part of the materials have a preferred direction of magnetization parallel to the hexagonal *c*-axis. Furthermore, there are compounds having the same crystal structure and corresponding ferromagnetic properties. The compositions of these compounds may be regarded as derived from said compounds by substituting therein  $Fe^{+++}$  for at most one-half of Me in a ratio corresponding to



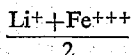
This corresponds to the formula



in which  $x \leq 1$ . These materials are represented by the line 5—6 in FIG. 2.

Point 7 in FIG. 2 corresponds to the compounds  $2AO.2MeO.6Fe_2O_3$  or  $A_2M_2Fe_{12}O_{22}$ , wherein A represents Ba, for at most one-half Sr, for at most one-quarter Pb and/or for at most one-quarter Ca, while Me represents at least one of the bivalent metals Fe, Mn, Co, Ni, Zn, Mg and Cu. These ferromagnetic materials have a rhombohedral crystal structure, the elementary cell of which can be described in the hexagonal crystal system by a *c*-axis of about 43.5 A. and an *a*-axis of about 5.9 A. All these materials are built up of crystals having a preferred plane of magnetization at right angles to the hexagonal *c*-axis, and these materials have comparatively high values for the initial permeability also at frequencies up to 200 mc./s. and higher.

Point 8 in FIG. 2 corresponds to the compounds  $3AO.2MeO.12Fe_2O_3$  or  $A_3Me_2Fe_{24}O_{41}$ , wherein A represents Ba, for at most  $\frac{1}{3}$  part Sr, for at most  $\frac{1}{5}$  part Pb and/or for at most  $\frac{1}{10}$  part Ca, while Me represents at least one of the bivalent metals Fe, Mn, Co, Ni, Zn, Mg, Cu or the bivalent complex



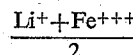
These ferromagnetic materials have a crystal structure, the elementary cell of which can be described in the hexagonal crystal system by a *c*-axis of about 52.3 A. and an *a*-axis of about 5.9 A. Part of these materials is built up of crystals having a preferred plane of magnetization at right angles to the hexagonal *c*-axis and these materials have comparatively high values for the initial permeability also at frequencies up to 200 mc./s. and higher. Such is the case at room temperature if Me represents Co for at least  $\frac{1}{4}$  part which is, however, still slightly dependent upon the other bivalent metals, represented by Me. The crystals of the remaining part of the materials have a preferred direction of magnetization parallel to the hexagonal *c*-axis.

Point 9 in FIG. 2 corresponds to the compounds  $4AO.2MeO.18Fe_2O_3$  or  $A_4Me_2Fe_{36}O_{60}$ , in which A represents Ba, for at most  $\frac{1}{3}$  part Sr, for at most  $\frac{1}{5}$  part Pb

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and/or for at most  $\frac{1}{10}$  part Ca, while Me represents at least one of the bivalent metals Fe, Co, Ni, Zn, Mg and for at most  $\frac{3}{10}$  part Mn or Cu. These ferromagnetic materials have a rhombohedral crystal structure, the elementary cell of which can be described in the hexagonal crystal system by a *c*-axis of about 113.1 A. and an *a*-axis of about 5.9 A. Part of these materials is built up of crystals having a preferred plane of magnetization at right angles to the hexagonal *c*-axis and these materials have comparatively high values for the initial permeability also at frequencies up to 200 mc./s. and upwards. Such is the case at room temperature if Me represents Co, for at least  $\frac{3}{10}$  part, which is, however, still slightly dependent upon the other bivalent metals represented by Me. The crystals of the other part of the materials have a preferred direction of magnetization parallel to the hexagonal *c*-axis.

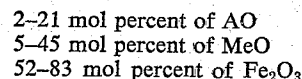
Point 10 in FIG. 2 corresponds to the compounds  $2AO.2MeO.14Fe_2O_3$  or  $A_2Me_2Fe_{28}O_{46}$ , in which A represents at least one of the bivalent metals Ba, Sr, Pb and for at most  $\frac{2}{5}$  part Ca, while Me represents at least one of the bivalent metals Fe, Mn, Co, Ni, Zn, Mg or the bivalent complex



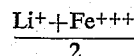
These ferromagnetic materials have a rhombohedral crystal structure, the elementary cell of which can be described in the hexagonal crystal system by a *c*-axis of about 84.1 A. and an *a*-axis of about 5.9 A. Part of these materials is built up of crystals having a preferred plane of magnetization at right angles to the hexagonal *c*-axis and these materials have comparatively high values for the initial permeability also at frequencies up to 200 mc./s. and upwards. Such is the case at room temperature if Me represents Co, for at least one-half, which is, however, still slightly dependent upon the other bivalent metals represented by Me. The crystals of the other part of the materials have a preferred direction of magnetization parallel to the hexagonal *c*-axis. Furthermore, there are compounds having the same crystal structure and corresponding ferromagnetic properties. The composition of these compounds may be regarded to be derived from the said compounds by substituting therein  $Fe^{+++}$  for at most one-half of Me in a ratio corresponding to  $Me+Fe^{+++}=1:\frac{2}{3}$ . This corresponds to the formula  $2AO.(2-x)MeO.(14+\frac{1}{3}x)Fe_2O_3$ , in which  $x \leq 1$ . These materials are represented by the line 10—11 in FIG. 2.

All the compounds above described are monophase compounds, that is to say, compounds built up of crystals or mixed crystals having the same crystal structure.

The present invention relates to ferromagnetic materials having a composition corresponding to:



in which A represents at least one of the bivalent metals Ba, Sr, Pb and Ca and Me represents at least one of the bivalent metals Fe, Mn, Co, Ni, Zn, Mg, Cu or the bivalent complex



and consist principally of at least two ferromagnetic crystal phases belonging to the group formed by the following six members:

- The cubic crystal structure of the mineral spinel,
- The hexagonal crystal structure having a *c*-axis of about 32.8 A. and an *a*-axis of about 5.9 A.,
- The hexagonal crystal structure having a *c*-axis of about 43.5 A. and an *a*-axis of about 5.9 A.,
- The hexagonal crystal structure having a *c*-axis of about 52.3 A. and an *a*-axis of about 5.9 A.,

The hexagonal crystal structure having a *c*-axis of about 113.1 Å., and an *a*-axis of about 5.9 Å., and

The hexagonal crystal structure having a *c*-axis of about 84.1 Å. and an *a*-axis of about 5.9 Å. The range comprising the compositions of the materials according to the invention is shown in FIGS. 1 and 2.

The invention relates more particularly to those of the ferromagnetic materials above-described which do not contain or contain only a small amount of the cubic crystal phase corresponding to that of the mineral spinel. The composition of these materials corresponds to:

8-21 mol percent of AO  
5-21 mol percent of MeO  
58-83 mol percent of Fe<sub>2</sub>O<sub>3</sub>

The range comprising the compositions of these materials is shown in FIG. 2.

The crystals of the above-mentioned hexagonal crystal phases have either a preferred plane of magnetization at right angles to the hexagonal *c*-axis or a preferred direction of magnetization parallel to the hexagonal *c*-axis. In order to determine whether in a given case crystals having a preferred plane of magnetization or crystals having a preferred direction of the magnetization are concerned, the following identification test, for example, may serve:

A small amount, for example, 25 mgs., of the material to be tested, in the form of a finely ground powder, is mixed with a few drops of a solution of an organic binder or adhesive in acetone, which mixture is spread on a glass slide. This slide is arranged between the poles of an electromagnet so that the lines of magnetic force are at right angles to the surface of the slide. By slowly increasing the electric direct current of the electromagnet, the magnetic field strength is increased so that the particles of the powder rotate in the field in a manner such that either the preferred direction or the preferred plane of magnetization becomes approximately parallel to the direction of the lines of magnetic force. By proceeding carefully, it is possible to prevent the powder particles from coagulation. After the acetone has evaporated, the powder particles keep adhering to the glass surface in the magnetically oriented condition. By means of radiographs, it is then possible to determine which orientation of the powder particles has been produced by the action of the magnetic field. This can be effected inter alia with the aid of an X-ray diffractometer (for example, an apparatus as described in "Philips" Technical Review," 16, pages 123-133, 1954-55), wherein in the case of a preferred direction parallel to the hexagonal *c*-axis one observes as intensified occurrence of the reflections at planes at right angles to this *c*-axis (so-called "001-reflections") in comparison with a radiograph of a non-oriented preparation. In the case of a preferred plane at right angles to the hexagonal *c*-axis, one observes an intensified occurrence of reflections at planes parallel to this *c*-axis (so-called "*hk0*-reflections").

It will be evident that the materials according to the invention may contain at the same time hexagonal crystal phases having a preferred plane of magnetization at right angles to the hexagonal *c*-axis and hexagonal crystal phases having a preferred direction of magnetization parallel to the hexagonal *c*-axis. However, since the physical properties of the materials are greatly dependent upon the kind of the preference of the magnetization, those materials according to the invention are preferable which have the same crystal anisotropy with regard to the hexagonal crystal phases. Those materials according to the invention, the hexagonal crystal phases of which have a preferred plane of magnetization at right angles to the hexagonal *c*-axis, have an initial permeability which is constant to a much higher frequency than with ferromagnetic ferrites having spinel structure which have the same value for the initial permeability at low frequency. Those

materials according to the invention, the hexagonal crystal phases of which have a preferred direction of magnetization parallel to the hexagonal *c*-axis, afford new possibilities for the manufacture, for example, of ferromagnetic bodies having permanent magnetic properties and ferromagnetic bodies for use in micro-wave equipment.

The ferromagnetic compounds having a cubic crystal structure corresponding to that of the mineral spinel are substantially all important on account of their value for the initial permeability. Consequently, in a physical sense, they are more similar to the above-mentioned hexagonal crystal phases having a preferred plane of magnetization than to the above-mentioned hexagonal crystal phases having a preferred direction of magnetization. Consequently, of the materials according to the invention, in which the cubic crystal phase having a structure of that of the mineral spinel is present, those are preferable which contain hexagonal crystal phases having a preferred plane of magnetization. Ferromagnetic compounds having the cubic spinel structure, are preferred for which the losses at the frequency at which the material is useable because of the properties of the hexagonal crystal phases, has not increased to a high value. Those compounds are ones which have a comparatively low value for the initial permeability at low frequency.

The hexagonal crystal phases of the materials according to the invention have a preferred plane of the magnetization at room temperature if these materials are of the following composition:

2-21 mol percent of AO  
*x* mol percent of CoO  
0-(45-*x*) mol percent of MeO  
52-83 mol percent of Fe<sub>2</sub>O<sub>3</sub>

wherein  $7 \leq x \leq 45$ . This range of compositions is shown in FIG. 3, which represents the same diagram as FIG. 2.

The materials according to the invention having a composition corresponding to

8-21 mol percent of AO  
*y* mol percent of CoO  
0-(21-*y*) mol percent of MeO  
58-83 mol percent of Fe<sub>2</sub>O<sub>3</sub>

wherein  $7 \leq y \leq 21$ , contain substantially hexagonal crystal phases and these crystal phases have a preferred plane of magnetization at room temperature. This range of composition is shown in FIG. 3.

The hexagonal crystal phases of the materials according to the invention also have a preferred plane of the magnetization at room temperature if these materials are of the following composition:

15 to 21 mol percent of AO  
*z* mol percent of CoO  
4 to (21-*z*) mol percent of MeO  
58 to 78 mol percent of Fe<sub>2</sub>O<sub>3</sub>

wherein  $3 \leq z \leq 17$ . These materials contain substantially hexagonal crystal phases. This range of compositions is represented in FIG. 4, which shows the same diagram as FIG. 2.

Finally, a preferred plane of the magnetization at room temperature occurs in the hexagonal crystal phases of materials according to the invention having a composition corresponding to

18-45 mol percent of AO  
18-45 mol percent of MeO  
52-61 mol percent of Fe<sub>2</sub>O<sub>3</sub>

This range of compositions is represented in FIG. 5, which shows the same diagram as FIG. 2.

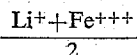
A preferred direction of magnetization at room temperature occurs in the hexagonal crystal phases of ma-

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materials according to the invention having a composition corresponding to

8-19 mol percent of AO  
 a mol percent of CoO  
 (5-a)-(20a) mol percent of DO  
 69-83 mol percent of Fe<sub>2</sub>O<sub>3</sub>

wherein  $a \leq 2.5$ . In this case D represents at least one of the bivalent metals Fe, Mn, Ni, Zn, Mg, Cu or the bivalent complex

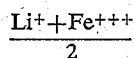


These materials contain substantially hexagonal crystal phases. This range of compositions is represented in FIG. 5.

The hexagonal crystal phases of the materials according to the invention also have a preferred direction of the magnetization at room temperature if these materials are of the following composition:

8-13 mol percent of AO  
 b mol percent of CoO  
 (c-b) mol percent of DO  
 69-83 mol percent of Fe<sub>2</sub>O<sub>3</sub>

wherein  $b \leq 6$ ,  $5 \leq c \leq 20$  and  $(c-b) \geq 0$ . In this case also D represents at least one of the bivalent metals Fe, Mn, Ni, Zn, Mg, Cu or the bivalent complex



These materials contain substantially hexagonal crystal phases. This range of compositions is represented in FIG. 4.

The materials according to the invention are manufactured by heating (sintering) a finely-divided mixture of the component metal oxides of the materials chosen approximately in the correct proportion. It is, of course, possible for one or more of the constituent metal oxides to be replaced wholly or in part by compounds converting into metal oxides upon heating, for example, carbonates, oxalates and acetates. Furthermore, the component metal oxides may be replaced wholly or in part by one or more compounds of at least one of the component metal oxides, for example, BaFe<sub>12</sub>O<sub>19</sub>. The term "correct proportion" is to be understood in this case to mean a ratio of the amounts of metals in the initial mixture equal to that in the materials to be manufactured and hence this ratio must naturally not be equal to that of one of the above-described monophase compounds.

If desired, the finely-divided initial mixture may first be presintered, the reaction product again pulverized and the resultant powder again sintered, which series of treatments may be repeated once or several times, if desired. Such a method of sintering is known per se, for example, in the manufacture of ferromagnetic ferrites with spinel structure (inter alia J. J. Went and E. W. Gorter, "Philips' Technical Review," 13 page 183, 1951-1952). The temperature of the sintering process or the final sintering process is chosen between about 1000° C. and about 1450° C. and preferably between 1200° C. and 1350° C.

In order to facilitate the sintering process, it is possible to add sintering agents, such as silicates and fluorides. Bodies, consisting of the ferromagnetic materials previously described may be obtained by sintering the initial mixture of the metal oxides or the like right from the beginning in the desired form and also by pulverizing the reaction product of the presintering process, giving it the desired shape, if desired after the addition of a binder, which may be followed by a subsequent sintering or hardening treatment.

Sintering at a temperature considerably higher than 1200° C. and/or sintering in a gaseous atmosphere comparatively poor in oxygen results in a material having a comparatively high Fe<sup>++</sup> content, so that the specific re-

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sistance may be decreased to values lower than 10Ω cm. If this is not desired, because the material is intended to be used as an initial material for magnetic cores at high frequencies without being hindered by eddy-current losses, then either undue production of ferrous ions must be avoided or ferrous ions produced in excessive quantity must be oxidized afterwards in known manner to form ferric ions, for example, by subsequent heating in oxygen at a temperature between 1000° C. and 1250° C.

With respect to the above-described monophase compounds, the materials according to the invention have the advantage that their initial mixtures may be sintered to greater density more readily than in the manufacture of the aforementioned monophase compounds. This greater density, which is conducive to the attainment of a higher value for the magnetization per unit volume and also for the initial permeability, may thus be obtained at a lower temperature in the manufacture of the materials according to the invention, which is advantageous since a smaller Fe<sup>++</sup> content is thus produced than with sintering at a higher temperature.

The electromagnetic losses are indicated, as is common practice, by a loss factor

$$\tan \delta = \frac{\mu''}{\mu'}$$

(see J. Smit and H. P. J. Wijn "Advances in Electronics," VI, 1954, page 69, Formula No. 37). The magnitude  $\mu'$  is the so-called "real" part of the initial permeability. The magnitude  $\mu''$  is the so-called induction component of the initial permeability.

#### EXAMPLE I

A mixture consisting of barium carbonate, zinc oxide and ferric oxide in a ratio at 17.6 mol percent of BaO, 11.8 mol percent of ZnO and 70.6 mol percent of Fe<sub>2</sub>O<sub>3</sub>, which corresponds to the compound Ba<sub>3</sub>Zn<sub>2</sub>Fe<sub>24</sub>O<sub>41</sub>, was mixed with ethyl alcohol in a ball mill for 1 hour and subsequently presintered at 1000° C. in air for 15 hours. The reaction product was ground with ethyl alcohol in a ball mill for 1 hour. Subsequently, after drying, part of the product, to which a small amount of an organic binder had been added, was pressed to form rings. These rings were sintered in oxygen at 1200° C. for 2 hours. The density of these rings was 3.57 g./cm.<sup>3</sup>. The remaining part of the product was presintered at 1000° C. and ground, was again presintered in air at 1200° C. for 2 hours. This reaction product was ground with ethyl alcohol in a ball mill for 1½ hours and subsequently, after drying, the product, to which a small amount of an organic binder had been added, was pressed to form rings which were sintered in oxygen at 1260° C. for 2 hours. The density of these rings was 3.73 g./cm.<sup>3</sup>. An X-ray examination revealed that all rings consisted of crystals, the elementary cell of which can be described in the hexagonal crystal system by a c-axis of about 52.3 Å. and an a-axis of about 5.9 Å.

In a similar manner, rings were manufactured from an initial mixture corresponding to 18.1 mol percent of BaO, 13.8 mol percent of ZnO and 68.1 mol percent of Fe<sub>2</sub>O<sub>3</sub>. The rings were sintered at 1200° C. and had a density of 3.92 g./cm.<sup>3</sup>. The density of the rings sintered at 1260° C. at 4.06 g./cm.<sup>3</sup>. An X-ray examination reveals that all these rings contain two hexagonal crystal phases, one, the principal, having a c-axis of about 52.3 Å. and an a-axis of about 5.9 Å., and a second, present in small quantity, having a c-axis of about 43.5 Å. and an a-axis of about 5.9 Å.

#### EXAMPLE II

A mixture consisting of barium carbonate, cobalt carbonate and ferric oxide in a ratio of 17.6 mol percent of BaO, 11.8 mol percent of CoO and 70.6 mol percent of Fe<sub>2</sub>O<sub>3</sub> which corresponds to the compound Ba<sub>3</sub>Co<sub>2</sub>Fe<sub>24</sub>O<sub>41</sub> was presintered twice in the manner indicated in Example

I and pressed into rings. These rings were sintered in oxygen at 1220° C. for 2 hours. The density of these rings was 4.14 g./cm.<sup>3</sup>. An X-ray examination revealed that the rings consisted of crystals, the elementary cell of which can be described in the hexagonal crystal system by a *c*-axis of about 52.3 Å. and an *a*-axis of about 5.9 Å. In a similar manner, rings were manufactured from an initial mixture corresponding to 18.1 mol percent of BaO, 13.8 mol percent of ZnO and 68.1 mol percent of Fe<sub>2</sub>O<sub>3</sub>. The density of these rings was 5.25 g./cm.<sup>3</sup> and, according to an X-ray examination, the rings were found to contain two hexagonal crystal phases, one, the principal, having a *c*-axis of about 52.3 Å. and an *a*-axis of about 5.9 Å. and another, present in small quantity, having a *c*-axis of about 43.5 Å. and an *a*-axis of about 5.9 Å.

### EXAMPLE III

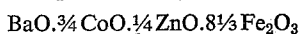
A mixture consisting of 33 gms. of BaFe<sub>12</sub>O<sub>19</sub>, 2.67 gms. of BaCO<sub>3</sub> and 3.19 gms. of CoCO<sub>3</sub>, which mixture contains the metals in quantities corresponding to 17.2 mol percent of BaO, 12.2 mol percent of CoO and 70.6 mol percent of Fe<sub>2</sub>O<sub>3</sub> (or about the compound Ba<sub>3</sub>Co<sub>2</sub>Fe<sub>24</sub>O<sub>41</sub>) was ground with ethyl alcohol in a ball mill for 1 hour and subsequently, after drying, the product, to which a small amount of an organic binder had been added, was pressed to form rings. These rings were sintered in oxygen at 1250° C. for 2 hours. The density of these rings was 4.09 g./cm.<sup>3</sup>. An X-ray examination revealed that the rings consisted of crystals, the elementary cell of which can be described in the hexagonal crystal system by a *c*-axis of about 52.3 Å. and an *a*-axis of about 5.9 Å.

In a similar manner, rings were manufactured from an initial mixture consisting of 33 gms. of BaFe<sub>12</sub>O<sub>19</sub>, 2.96 gms. of BaCO<sub>3</sub> and 3.50 gms. of CoCO<sub>3</sub> (17.4 mol percent of BaO, 13.1 mol percent of CoO and 69.5 mol percent of Fe<sub>2</sub>O<sub>3</sub>). The density of these rings was 4.45 g./cm.<sup>3</sup>. The density was 4.59 g./cm.<sup>3</sup> for rings manufactured from a mixture of 33 gm. of BaFe<sub>12</sub>O<sub>19</sub>, 3.56 gms. of BaCO<sub>3</sub> and 4.12 gms. of CoCO<sub>3</sub> (17.9 mol percent of BaO, 14.9 mol percent of CoO and 67.2 mol percent of Fe<sub>2</sub>O<sub>3</sub>). An X-ray examination revealed that all the rings of the last two groups contained two hexagonal crystal phases, one, the principal, having a *c*-axis of about 52.3 Å. and an *a*-axis of about 5.9 Å. and another, present in small quantity, having a *c*-axis of about 43.5 Å. and an *a*-axis of about 5.9 Å.

### EXAMPLE IV

Rings were manufactured, in the manner indicated in Example I, from a mixture consisting of barium carbonate, cobalt carbonate, zinc oxide and ferric oxide, in

a ratio of 9.7 mol percent of BaO, 7.3 mol percent of CoO, 2.4 mol percent of ZnO and 80.6 mol percent of Fe<sub>2</sub>O<sub>3</sub>, which corresponds to the compound



The rings were sintered in oxygen at 1320° C. for 2 hours. The density of the rings was 3.3 g./cm.<sup>3</sup>. An X-ray examination revealed that the rings consisted of crystals, the elementary cell of which can be described

in the hexagonal crystal system by a *c*-axis of about 32.8 Å. and an *a*-axis of about 5.9 Å.

In a similar manner, rings were manufactured from initial mixtures corresponding to

- 5 10.7 mol percent of BaO, 8.0 mol percent of CoO, 2.7 mol percent of ZnO and 78.6 mol percent of Fe<sub>2</sub>O<sub>3</sub>,  
12.0 mol percent of BaO, 9.0 mol percent of CoO, 3.0 mol percent of ZnO and 76.0 mol percent of Fe<sub>2</sub>O<sub>3</sub>,  
10 13.7 mol percent of BaO, 10.2 mol percent of CoO, 3.4 mol percent of ZnO and 72.7 mol percent of Fe<sub>2</sub>O<sub>3</sub>.

The densities of these rings were 3.8 g./cm.<sup>3</sup>, 5.0 g./cm.<sup>3</sup> and 4.6 g./cm.<sup>3</sup>, respectively. An X-ray examination revealed that all of the rings contained two hexagonal crystal phases, one, the principal, having a *c*-axis of about 32.8 Å. and an *a*-axis of about 5.9 Å. and another, present in small quantity, having a *c*-axis of about 43.5 Å. and an *a*-axis of about 5.9 Å.

### EXAMPLE V

Rings were manufactured, in the manner indicated in Example I from barium carbonate, zinc oxide, cobalt carbonate and ferric oxide in ratios of

- 20 18.5 mol percent of BaO, 14.8 mol percent of ZnO and 66.7 mol percent of Fe<sub>2</sub>O<sub>3</sub>,  
18.5 mol percent of BaO, 11.1 mol percent of ZnO, 3.7 mol percent of CoO and 66.7 mol percent of Fe<sub>2</sub>O<sub>3</sub>,  
25 18.5 mol percent of BaO, 7.4 mol percent of ZnO, 7.4 mol percent of CoO and 66.7 mol percent of Fe<sub>2</sub>O<sub>3</sub>,  
30 18.5 mol percent of BaO, 3.7 mol percent of ZnO, 11.1 mol percent of CoO and 66.7 mol percent of Fe<sub>2</sub>O<sub>3</sub>,  
18.5 mol percent of BaO, 14.8 mol percent of CoO and 66.7 mol percent of Fe<sub>2</sub>O<sub>3</sub>.

- 35 The presintering process took place in air at 1000° C. for 15 hours and the rings were sintered in oxygen at 1250° C. for 2 hours.

- Rings were manufactured in an analogous manner from a mixture consisting of 33 gms. of BaFe<sub>12</sub>O<sub>19</sub>, 3.3 gms. of BaCO<sub>3</sub>, 1.5 gms. of ZnO and 1.94 gms. of CoCO<sub>3</sub>, which corresponds to 17.8 mol percent of BaO, 6.8 mol percent of ZnO, 7.2 mol percent of CoCO<sub>3</sub> and 68.2 mol percent of Fe<sub>2</sub>O<sub>3</sub>. An X-ray examination revealed that all rings contained two hexagonal crystal phases, one having a *c*-axis of about 52.3 Å. and an *a*-axis of about 5.9 Å. and another having a *c*-axis of about 43.5 Å. and an *a*-axis of about 5.9 Å. while in the manner above-described, it was also determined that, except in the first preparation, both hexagonal crystal phases have a preferred plane of magnetization at right angles to the hexagonal *c*-axis.

Properties of these rings are specified in Table 1.

Table 1

Composition, mol percent				10 mc./s. μ'	80 mc./s.		160 mc./s.		260 mc./s.		500 mc./s.	
BaO	ZnO	CoO	Fe <sub>2</sub> O <sub>3</sub>		μ'	tan δ	μ'	tan δ	μ'	tan δ	μ'	tan δ
18.5	14.8		66.7	10.0	6.8	0.26	6.0	0.32	5.5	0.41	4.0	0.70
18.5	11.1	3.7	66.7	6.7	5.8	0.09	5.7	0.19	5.7	0.30	4.5	0.51
18.5	7.4	7.4	66.7	18.7	15.8	0.13	16.1	0.25	16.2	0.33	8.8	0.90
18.5	3.7	11.1	66.7	12.2	11.2	0.07	11.0	0.18	11.1	0.29	8.9	0.64
18.5		14.8	66.7	11.4	8.6	0.02	8.5	0.05	9.0	0.16	9.7	0.32
17.8	6.8	7.2	68.2	12.2	11.0	0.03					8.9	0.70

### EXAMPLE VI

Rings were manufactured in the manner indicated in Example I, from mixtures consisting of barium carbonate, cobalt carbonate, zinc oxide and ferric oxide in ratios corresponding to

- 70 15.1 mol percent of BaO, 8.4 mol percent of CoO, 8.4 mol percent of ZnO and 68.1 mol percent of Fe<sub>2</sub>O<sub>3</sub>, respectively,



13.2 mol percent of BaO, 10.8 mol percent of CoO, 10.8 mol percent of ZnO and 65.2 mol percent of Fe<sub>2</sub>O<sub>3</sub>.

The presintering process took place in air at 1000° C. for 15 hours and the rings were sintered in oxygen at 1280° C. for 4 hours. An X-ray examination revealed that the rings contain two hexagonal crystal phases, one having a *c*-axis of about 43.5 Å. and an *a*-axis of about 5.9 Å. and another having a *c*-axis of about 32.8 Å. and an *a*-axis of about 5.9 Å.

In a similar manner, rings were manufactured from mixtures consisting of barium carbonate, cobalt carbonate, zinc oxide and ferric oxide in ratios corresponding to

11.4 mol percent of BaO, 13.0 mol percent of CoO, 13.0 mol percent of ZnO, 62.6 mol percent of Fe<sub>2</sub>O<sub>3</sub>, and 9.6 mol percent of BaO, 15.2 mol percent of CoO, 15.2 mol percent of ZnO and 60.0 mol percent of Fe<sub>2</sub>O<sub>3</sub>.

An X-ray examination revealed that the rings contained two hexagonal crystal phases, one having a *c*-axis of about 43.5 Å. and an *a*-axis of about 5.9 Å. and another having a *c*-axis of about 32.8 Å. and an *a*-axis of about 5.9 Å., while also a small amount of the cubic crystal phase corresponding to that of the mineral spinel was present.

In a similar manner, rings were manufactured from mixtures consisting of barium carbonate, cobalt carbonate, zinc oxide and ferric oxide in ratios corresponding to

7.9 mol percent of BaO, 17.3 mol percent of CoO, 17.3 mol percent of ZnO and 57.5 mol percent of Fe<sub>2</sub>O<sub>3</sub>, and

4.7 mol percent of BaO, 19.5 mol percent of CoO, 19.5 mol percent of ZnO and 56.3 mol percent of Fe<sub>2</sub>O<sub>3</sub>, and

3.1 mol percent of BaO, 21.5 mol percent of CoO, 21.5 mol percent of ZnO and 53.9 mol percent of Fe<sub>2</sub>O<sub>3</sub>.

An X-ray examination revealed that the rings contained three crystal phases, two hexagonal crystal phases, of which one having a *c*-axis of about 43.5 Å. and an *a*-axis of about 5.9 Å. and another having a *c*-axis of about 32.8 Å. and an *a*-axis of about 5.9 Å. and the cubic crystal phase corresponding to that of the mineral spinel.

It is determined in the above-described manner that all hexagonal crystal phases which occur in this example have a preferred plane of magnetization at right angles to the hexagonal *c*-axis.

Properties of these rings are specified in Table 2.

Table 2

Composition Mol Percent				10 mc./s., /μ'	100 mc./s.		260 mc./s.	
BaO	CoO	ZnO	Fe <sub>2</sub> O <sub>3</sub>		/μ'	tan δ	/μ'	tan δ
15.1	8.4	8.4	68.1	7.1	6.8	0.05	6.8	0.21
13.2	10.8	10.8	65.2	7.0	6.6	0.06	6.3	0.22
11.4	13.0	13.0	62.6	6.7	6.0	0.05	5.8	0.17
9.6	15.2	15.2	60.0	7.8	7.2	0.07	7.0	0.23
7.9	17.3	17.3	57.6	5.8	5.7	0.06	5.6	0.19
4.7	19.5	19.5	56.3	6.8	6.4	0.07	6.2	0.22
3.1	21.5	21.5	53.9	7.7	7.4	0.08	7.2	0.27

### EXAMPLE VII

In the manner described in Example I, rings were manufactured from mixtures consisting of barium carbonate, cobalt carbonate, zinc oxide and ferric oxide. The presintering process took place in air at 1000° C. for 15 hours and the rings were sintered in oxygen for 2 hours at the temperature specified in Table 3.

The rings of the composition corresponding to 15.7 mol percent of BaO, 6.9 mol percent of CoO, 3.5 mol percent of ZnO and 73.9 mol percent of Fe<sub>2</sub>O<sub>3</sub> were found, according to an X-ray examination, to contain two hexagonal crystal phases, one having a *c*-axis of

about 113.1 Å. and an *a*-axis of about 5.9 Å., and another having a *c*-axis of about 52.3 Å. and an *a*-axis of about 5.9 Å.

The rings of a composition corresponding to 17.3 mol percent of BaO, 6.9 mol percent of CoO, 3.4 mol percent of ZnO and 72.4 mol percent of Fe<sub>2</sub>O<sub>3</sub> contained according to an X-ray examination, two hexagonal crystal phases, one having a *c*-axis of about 52.3 Å. and an *a*-axis of about 5.9 Å. and another having a *c*-axis of about 84.1 Å. and an *a*-axis of about 5.9 Å.

The rings having a composition of 15.5 mol percent of BaO, 6.9 mol percent of CoO, 5.2 mol percent of ZnO and 72.4 mol percent of Fe<sub>2</sub>O<sub>3</sub> and of 17.1 mol percent of BaO, 6.8 mol percent of CoO, 5.1 mol percent of ZnO and 71.0 mol percent of Fe<sub>2</sub>O<sub>3</sub>, contained, according to an X-ray examination, two hexagonal crystal phases, one having a *c*-axis of about 32.8 Å. and an *a*-axis of about 5.9 Å. and another having a *c*-axis of about 52.3 Å. and an *a*-axis of about 5.9 Å.

The rings of a composition corresponding to 15.4 mol percent of BaO, 8.5 mol percent of CoO, 5.1 mol percent of ZnO and 71.0 mol percent of Fe<sub>2</sub>O<sub>3</sub> were found, according to an X-ray examination, to contain three hexagonal crystal phases, one, the principal, having a *c*-axis of about 32.8 Å. and an *a*-axis of about 5.9 Å., while the phase having a *c*-axis of about 52.3 Å. and an *a*-axis of about 5.9 Å. and that having a *c*-axis of about 43.5 Å. and an *a*-axis of about 5.9 Å. were present in small quantities.

The rings of a composition corresponding to 16.9 mol percent of BaO, 8.5 mol percent of CoO, 5.1 mol percent of ZnO and 69.5 mol percent of Fe<sub>2</sub>O<sub>3</sub> contained, according to an X-ray examination, three hexagonal crystal phases, one having a *c*-axis of about 52.3 Å. and an *a*-axis of about 5.9 Å. and another having a *c*-axis of about 43.5 Å. and an *a*-axis of about 5.9 Å., while also a small quantity of the phase with a *c*-axis of about 32.8 Å. and an *a*-axis of 5.9 Å. were present.

The rings of a composition corresponding to 16.8 mol percent of BaO, 10.1 mol percent of CoO, 5.0 mol percent of ZnO and 68.1 mol percent of Fe<sub>2</sub>O<sub>3</sub> contained, according to an X-ray examination, three hexagonal crystal phases, one having a *c*-axis of about 52.3 Å. and an *a*-axis of about 5.9 Å., one having a *c*-axis of about 32.8 Å. and an *a*-axis of about 5.9 Å. and one having a *c*-axis of about 43.5 Å. and an *a*-axis of about 5.9 Å.

The rings of a composition corresponding to 18.3 mol percent of BaO, 10.0 mol percent of CoO, 5.0 mol percent of ZnO and 66.7 mol percent of Fe<sub>2</sub>O<sub>3</sub> contained, according to an X-ray examination, two hexagonal crystal phases, one having a *c*-axis of about 52.3 Å. and an *a*-axis of about 5.9 Å. and one having a *c*-axis of about 43.5 Å. and an *a*-axis of about 5.9 Å.

The rings of a composition corresponding to 16.7 mol percent of BaO, 10.0 mol percent of CoO, 6.6 mol percent of ZnO and 66.7 mol percent of Fe<sub>2</sub>O<sub>3</sub> contained, according to an X-ray examination, two hexagonal crystal phases, one having a *c*-axis of about 32.8 Å. and an *a*-axis of about 5.9 Å. and one having a *c*-axis of about 43.5 Å. and an *a*-axis of about 5.9 Å.

The rings of a composition corresponding to 18.2 mol percent of BaO, 9.9 mol percent of CoO, 6.6 mol percent of ZnO and 65.3 mol percent of Fe<sub>2</sub>O<sub>3</sub> contained, according to an X-ray examination, two hexagonal crystal phases, one having a *c*-axis of about 43.5 Å. and an *a*-axis of about 5.9 Å. and one having a *c*-axis of about 52.3 Å. and an *a*-axis of about 5.9 Å.

The rings of a composition corresponding to 11.8 mol percent of BaO, 8.8 mol percent of CoO, 2.9 mol percent of ZnO and 76.4 mol percent of Fe<sub>2</sub>O<sub>3</sub> and corresponding to 13.3 mol percent of BaO, 10.0 mol percent of CoO, 3.3 mol percent of ZnO and 73.4 mol percent of Fe<sub>2</sub>O<sub>3</sub> contained, according to an X-ray examination, two hexagonal crystal phases, one having a *c*-axis of about 32.8 Å. and an *a*-axis of about 5.9 Å. and one

having a *c*-axis of about 43.5 A. and an *a*-axis of about 5.9 A.

It was determined in the above-described manner that all hexagonal crystal phases which occur in this example have a preferred plane of magnetization at right angles to the hexagonal *c*-axis.

Properties of these rings are specified in Table 3.

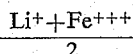
Table 3

Composition, Mol Percent				Sintering Temp., °C.	10 mc./s. $\mu'$	80 mc./s.		260 mc./s.		500 MHzs	
BaO	CoO	ZnO	Fe <sub>2</sub> O <sub>3</sub>			$\mu'$	$\tan \delta$	$\mu'$	$\tan \delta$	$\mu'$	$\tan \delta$
15.7	6.9	3.5	73.9	1,330	3.8	3.4	0.04	3.5	0.13	3.2	0.33
17.3	6.9	3.4	72.4	1,330	8.9	8.2	0.065	8.0	0.14	7.4	0.35
15.5	6.9	5.2	72.4	1,330	8.8	7.2	0.08	8.6	0.30	7.5	0.46
17.1	6.8	5.1	71.0	1,330	8.8	9.2	0.04	11.1	0.27	8.7	1.00
15.4	8.5	5.1	71.0	1,330	6.8	7.3	0.04	8.3	0.15	7.7	0.60
16.9	8.5	5.1	69.5	1,330	7.8	7.2	0.03	9.9	0.18	7.4	0.70
16.8	10.1	5.0	68.1	1,300	6.0	7.6	0.03	8.5	0.24	7.3	0.54
18.3	10.0	5.0	66.7	1,300	9.5	8.8	0.03	9.7	0.09	9.3	0.46
16.7	10.0	6.6	66.7	1,300	8.2	7.6	0.03	9.0	0.12	8.2	0.48
18.2	9.9	6.6	65.3	1,300	8.6	8.4	0.03	8.7	0.12	8.5	0.47
11.8	8.8	2.9	76.4	1,300	9.5	8.5	0.19	6.2	0.53	4.7	0.76
13.3	10.0	3.3	73.4	1,300	8.5	6.5	0.06	5.9	0.15	5.7	0.32

While I have described my invention in connection with specific embodiments and applications, other modifications thereof will be readily apparent to those skilled in this art without departing from the spirit and scope of the invention as described in the appended claims.

What is claimed is:

1. A ferromagnetic material having a composition corresponding to about 2 to 21 mol percent of AO, 5 to 45% of MeO, and about 52 to 83% of Fe<sub>2</sub>O<sub>3</sub> in which A is a metal selected from the group consisting of barium, strontium, lead and calcium, and Me is a bivalent ion selected from the group consisting of Fe<sup>++</sup>, Mn<sup>++</sup>, Co<sup>++</sup>, Ni<sup>++</sup>, Zn<sup>++</sup>, Mg<sup>++</sup>, Cu<sup>++</sup>, and the bivalent complex

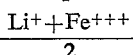


and consisting essentially of at least two crystal phases selected from the group of compositions consisting of:

A. Crystals having the composition

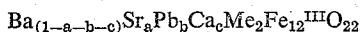


in which *y* has a value up to 0.4, A is a bivalent ion selected from the group consisting of Ba<sup>++</sup>, Sr<sup>++</sup>, and Pb<sup>++</sup>, and Me is a bivalent ion selected from the group consisting of Fe<sup>++</sup>, Mn<sup>++</sup>, Co<sup>++</sup>, Ni<sup>++</sup>, Zn<sup>++</sup>, Mg<sup>++</sup>, and the bivalent metal complex



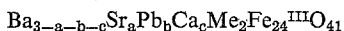
said crystals having a *c*-axis of 32.8 A. and an *a*-axis of 5.9 A. in the hexagonal system;

B. Crystals having the composition

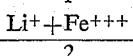


in which *a* has a value up to 0.5, *b* has a value up to 0.25, and *c* has a value up to 0.25, Me is a bivalent ion selected from the group consisting of Fe<sup>++</sup>, Mn<sup>++</sup>, Co<sup>++</sup>, Ni<sup>++</sup>, Zn<sup>++</sup>, Mg<sup>++</sup>, and Cu<sup>++</sup>, said crystals having a rhombohedral structure with a *c*-axis in the hexagonal system of about 43.5 A. and an *a*-axis of about 5.9 A.

C. Crystals having the composition:



in which *a* has a value up to 1, *b* has a value up to 0.6, and *c* has a value up to 0.3, Me is a bivalent ion selected from the group Fe<sup>++</sup>, Mn<sup>++</sup>, Co<sup>++</sup>, Ni<sup>++</sup>, Zn<sup>++</sup>, Mg<sup>++</sup>, Cu<sup>++</sup>, and the bivalent complex



said crystals having a *c*-axis of about 52.3 A. and an *a*-axis of about 5.9 A. in the hexagonal system;

D. Crystals having the composition:



said crystals having a *c*-axis of about 113.1 A. and an *a*-axis of about 5.9 A.;

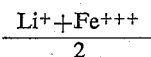
in which *a* has a value up to 1.0, *b* has a value up to 0.7, *c* has a value up to 0.6, Me is a bivalent ion selected from the group consisting of Fe<sup>++</sup>, Co<sup>++</sup>, Ni<sup>++</sup>, Zn<sup>++</sup>, Mg<sup>++</sup>, R is a bivalent ion selected from the group consisting of Mn<sup>++</sup> and Cu<sup>++</sup>, *d* has a value up to 0.6, said crystals having a rhombohedral structure with a *c*-axis in

the hexagonal system of about 113.1 A. and an *a*-axis of about 5.9 A.;

E. Crystals having the composition



in which *a* has a value up to 0.4, Me is a bivalent ion selected from the group consisting of Fe<sup>++</sup>, Mn<sup>++</sup>, Co<sup>++</sup>, Ni<sup>++</sup>, Zn<sup>++</sup>, Mg<sup>++</sup>, and the bivalent complex



said crystals having a rhombohedral structure with a *c*-axis in the hexagonal system of about 84.1 A. and an *a*-axis of about 5.9 A.

2. A ferromagnetic material as defined in claim 1 in which the material is the fired reaction product of about 8 to 21 mol percent of AO, about 5 to 21 mol percent of MeO, and about 58 to 83 mol percent of Fe<sub>2</sub>O<sub>3</sub>.

3. A ferromagnetic material as defined in claim 1 in which at least one of the hexagonal crystal phases constituting the material has a preferred plane of magnetization.

4. A ferromagnetic material as defined in claim 2 in which at least one of the hexagonal phases constituting the material has a preferred plane of magnetization.

5. A ferromagnetic material as defined in claim 2 in which at least one of the hexagonal crystal phases constituting the material has a preferred direction of magnetization.

6. A ferromagnetic material as defined in claim 3 in which the material is the fired reaction product of about 2 to 21 mol percent of AO, about *x* mol percent of CoO, up to about (45-*x*) mol percent of MeO, and about 52 to 83 mol percent of Fe<sub>2</sub>O<sub>3</sub>, wherein *x* has a value of at least 7 and not more than 45.

7. A ferromagnetic material as defined in claim 3 in which the material is the fired reaction product of 2 to 21 mol percent of AO, 18 to 45 mol percent of MeO, about 52 to 61 mol percent of Fe<sub>2</sub>O<sub>3</sub>.

8. A ferromagnetic material as defined in claim 4 in which the material is the fired reaction product of about 8 to 21 mol percent of AO, about *y* mol percent of CoO, up to (21-*y*) mol percent of MeO, and about 58 to 83 mol percent of Fe<sub>2</sub>O<sub>3</sub>, wherein *y* is at least 7 and not more than 21.

9. A ferromagnetic material as defined in claim 4 in which the material is the fired reaction product of about 15 to 21 mol percent of AO, *z* mol percent of CoO, 4 to (21-*z*) mol percent of MeO, and about 58 to 78 mol percent of Fe<sub>2</sub>O<sub>3</sub>, wherein *z* is at least 3 and not more than 17.

10. A ferromagnetic material as defined in claim 5 in which the material is the fired reaction product of about

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8 to 19 mol percent of AO,  $a$  mol percent of CoO,  $(5-a)$  to  $(20-a)$  mol percent of DO, and 69 to 83 mol percent of Fe<sub>2</sub>O<sub>3</sub>, wherein  $a$  is at least 5 and D is a bivalent ion selected from the group consisting of Fe<sup>++</sup>, Mn<sup>++</sup>, Ni<sup>++</sup>, Zn<sup>++</sup>, Mg<sup>++</sup>, Cu<sup>++</sup>, and the bivalent complex

$$\frac{\text{Li}^+ + \text{Fe}^{+++}}{2}$$

11. A ferromagnetic material as defined in claim 5 in which the material is the fired reaction product of up to 13 mol percent of AO,  $b$  mol percent of CoO,  $(c-b)$  mol percent of DO, and 69 to 83 mol percent of Fe<sub>2</sub>O<sub>3</sub>, where  $b$  is not greater than 6.5,  $c$  is not less than 6.5 and not more than 20, and  $(c-b)$  is not less than zero.

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