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(54) METHOD FOR THE PREPARATION OF FERRITE CALCINED BODY

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The present invention relates to a method of making a ferrite calcined body.

BACKGROUND ART

[0002] Ferrite is a generic term for any compound including an oxide of a divalent cationic metal and trivalent iron, and ferrite magnets have found a wide variety of applications in numerous types of rotating machines, loudspeakers, and so on. Typical materials for a ferrite magnet include Sr ferrites (SrFe₁₂O₁₉) and Ba ferrites (BaFe₁₂O₁₉) having a hexagonal magnetoplumbite structure. Each of these ferrites is made of iron oxide and a carbonate of strontium (Sr), barium (Ba) or any other suitable element, and can be produced at a relatively low cost by a powder metallurgical process.

[0003] A basic composition of an (M-type) ferrite having the magnetoplumbite structure is normally represented by the chemical formula AO • 6Fe₂O₃, where A is a metal element to be divalent cations and is selected from the group consisting of Sr, Ba, Pb, Ca, and other suitable elements.

[0004] It was reported that the magnetization of a Ba ferrite could be increased by substituting Ti or Zn for a portion of Fe (see Journal of the Magnetics Society of Japan Vol. 21, No. 2 (1997), 69-72).

[0005] It is also known that the coercivity and magnetization of a Ba ferrite can be increased by substituting a rare-earth element such as La for a portion of Ba and by substituting Co or Zn for a portion of Fe (see Journal of Magnetism and Magnetic Materials, Vols. 31-34 (1983), 793-794 and Bull. Acad. Sci. USSR (Transl.) phys. Sec. Vol. 25 (1961) 1405-1408).

[0006] As for an Sr ferrite on the other hand, it was reported that the coercivity and magnetization thereof could be increased by substituting La for a portion of Sr (see IEEE Transaction on Magnetics, Vol. 26, No. 3 (1999), 1144-1148).

[0007] It was also reported that the coercivity and magnetization of an Sr ferrite could be increased by substituting La for a portion of Sr and by substituting Co and Zn for a portion of Fe (see PCT International Application No. PCT/JP98/00764 (corresponding to PCT International Publication No. WO 98/38654)).

[0008] Furthermore, it was reported that a magnet, including, as its main phase, a hexagonal ferrite such as Ba ferrite or Sr ferrite in which Sr, Ba, Ca, Co, rare-earth elements (including Y), Bi and Fe are contained, may be produced by adding some or all of those constituent elements to particles including, as their main phase, a hexagonal ferrite containing at least Sr, Ba or Ca and then calcining the mixture decisively (see PCT International Application No. PCT/JP98/04243 (corresponding to PCT International Publication No. WO 99/16087)). It was reported that a magnet having at least two Curie temperatures could be obtained and the magnetization, coercivity and variation in coercivity with temperature could be improved according to this method.

[0009] As for an Sr ferrite or a Ba ferrite, it was further reported that a high-performance ferrite magnet with excellent magnetic properties (in the loop squareness of its B-H curve among other things) could be obtained at a relatively low cost by substituting La, Ce, Pr, Nd, Sm, Eu or Gd for a portion of Sr or Ba and by substituting Co, Mn or V for a portion of Fe (see Japanese Laid-Open Publication No. 11-307331).

[0010] It was further reported that a ferrite magnet, hardly exhibiting any variation in coercivity or magnetization with temperature (i.e., showing slight decrease in magnetization in a high temperature range and little decrease in coercivity in a low temperature range) could be obtained by allowing a ferrite having an M-type magnetoplumbite structure and a ferrite having a spinel-type structure to coexist (see Japanese Laid-Open Publication No. 11-224812).

[0011] However, none of these ferrite magnets can improve the magnetic properties sufficiently and reduce the manufacturing cost significantly at the same time. Specifically, it was reported that the ferrite in which Ti or Zn was substituted for a portion of Fe exhibited slightly increased magnetization but significantly decreased coercivity. It was also reported that the ferrite in which La was substituted for a portion of Sr exhibited slightly increased coercivity and magnetization. However, the properties of such a ferrite are still not fully satisfactory. Furthermore, it was reported that the ferrite in which La was substituted for a portion of Ba or a portion of Sr and in which Co or Zn was substituted for a portion of Fe exhibited increased coercivity and magnetization. But if a rare-earth element (such as La) and Co are used in large amounts as substituents for a ferrite, then the material cost of such a ferrite increases adversely because the raw materials of these substituents are expensive. In that case, the essential feature of the ferrite magnet, which should be produced at a lower manufacturing cost than a rare earth magnet, for example, might be lost. Furthermore, the ferrite in which La, Ce, Pr, Nd, Sm, Eu or Gd was substituted for a portion of Sr or a portion of Ba and in which Co, Mn or V was substituted for a portion of Fe exhibited improved loop squareness but decreased magnetization.

[0012] On the other hand, as for the ferrite disclosed in Japanese Laid-Open Publication No. 11-224812, in which a ferrite having an M-type magnetoplumbite structure and a ferrite having a spinel-type structure coexist, ferrites representing Examples Nos. 1 to 3 thereof exhibit improved magnetic properties and temperature properties but include relatively large amounts of La and element M such as Mg, Mn, Cu, Fe, Co, Ni and Li to be added to Fe. It is also disclosed...
in that document that if a ferrite having a composition represented by Sr$_{10.8}$La$_{0.2}$Fe$_{11.8}$CO$_{0.2}$O$_{19}$ is fired within a mixture of nitrogen and oxygen gases with the partial pressure of oxygen changed, a ferrite representing Example No. 4 thereof can have the structure, in which a ferrite having an M-type magnetoplumbite structure and a ferrite having a spinel-type structure coexist, even without using a reducing atmosphere as the firing atmosphere. In that case, however, good magnetic properties are not achieved. Example No. 5 disclosed therein is a ferrite magnet to be obtained, as in the present invention, by separately preparing SrFe$_{12}$O$_{19}$ as a ferrite having an M-type magnetoplumbite structure and CoFe$_{2}$O$_{5}$ as a ferrite having a spinel-type structure, mixing these ferrites together during a pulverization process, and then making a sintered body by a normal process. In that case, the temperature coefficient of magnetization is improved but the magnetization and coercivity themselves decrease significantly due to the addition of CoFe$_{2}$O$_{5}$.

[0013] The prior art in document EP 0 353 627 A2 discloses an interdispersed two-phase ferrite composite which comprises a spinel phase having the general formula M Fe$_{2}$O$_{4}$, wherein M is at least one element that forms a spinel ferrite, and a magnetoplumbite phase having the general formula R$_{x}$P$_{1-x}$Fe$_{12}$O$_{19}$, wherein R is lanthanum, neodymium, praseodymium, samarium, europium, or a mixture of two or more thereof, P is strontium, barium, calcium, lead, or a mixture of two or more thereof, and x has a value of 0.1 to 0.4. The composite has a spinel phase: magnetoplumbite phase molar ratio of 1:25 to 10:25. Also disclosed is a carrier formed from magnetized and polymerically coated particles of the composite and an electrographic developer formed from such a carrier and a toner.

[0014] The prior art in document JP H-11-224812 (A) discloses a magnet powder and a sintered magnet of hexagonal ferrite composition of magnetic plumbite type M phase. More concretely, the ferrite contains A and R, wherein A denotes elements selected out of Sr, Ba, Ca and Pb and must contain Sr, Ca or Ba, and R denotes elements selected from rare earth elements (including Y) and Bi. At this point, it is ascertained by an X-ray diffraction method that an M-type ferrite phase and a spinel ferrite phase are coexistent with each other in the sintered magnet. The sintered magnet has two different Curie points. The sintered magnet has physical properties where the absolute value of a temperature coefficient of a coercive force is 0.25% / °C or less at a temperature of -50 to 50 °C, and the absolute value of temperature characteristics of saturation magnetization is 0.18% / °C in a temperature range of a room temperature (25 °C) to +125 °C.

[0015] The prior art in document EP 0 940 824 A1 discloses a magnetic powder and a sintered magnet comprising a primary phase of a hexagonal ferrite containing A, Co and R (where A represents Sr, Ba or Ca, and R represents at least one element selected from the group consisting of rare earth elements (including Y) and Bi), and have at least two different Curie temperatures, wherein the two different Curie temperatures are present within a range from 400 to 480 °C, and an absolute value of a difference therebetween is 5 °C or more.

[0016] In order to overcome the problems described above, a primary object of the present invention is to provide a ferrite magnet that can be produced at a low manufacturing cost and that can still exhibit improved magnetic properties and a method of making such a ferrite magnet.

DISCLOSURE OF INVENTION

[0017] This object is achieved by the subject matter of claim 1. Preferred embodiments are subject of the dependent claims.

(1) A method of making a ferrite calcined body according to the present invention comprises the steps of:

preparing a material powder mixture by mixing: a material powder of at least one compound that is selected from the group consisting of SrCO$_{3}$, BaCO$_{3}$, PbO and CaCO$_{3}$; an oxide material powder of at least one element to be selected from the group consisting of the rare-earth elements (including Y) and Bi, the oxide material powder always including La$_2$O$_3$; and a material powder of Fe$_2$O$_3$;

calcining the material powder mixture at a temperature of 1,100 °C to 1,450 °C, thereby forming a ferrite calcined body having an M-type magnetoplumbite structure and a composition represented by the general formula:

$$(1-x)\text{A}O \cdot (x/2)\text{R}_2\text{O}_3 \cdot n\text{Fe}_2\text{O}_3$$

where A is at least one element selected from the group consisting of Sr, Ba, Pb and Ca; R is at least one element selected from the group consisting of the rare-earth elements (including Y) and Bi and always includes La; 0.05 ≤ x < 0.3; and 5.0 ≤ n ≤ 6.5;

preparing another material powder mixture by mixing an oxide material powder of at least one element selected from the group consisting of Co, Ni, Mn and Zn and a material powder of Fe$_2$O$_3$;

calcining the material powder mixture at a temperature of 700 °C to 1,450 °C, thereby forming a ferrite calcined

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body having a spinel-type structure and a composition represented by the general formula:

$$MO \cdot Fe_2O_3$$

where M is at least one element selected from the group consisting of Co, Ni, Mn and Zn; and

preparing a calcined body mixed powder by adding the ferrite calcined body having the spinel-type structure at 0.2 wt% to 6.2 wt% to the ferrite calcined body having the M-type magnetoplumbite structure.

(2) The method of (1), wherein the oxide of the element M is partially or fully replaced with a hydroxide of the element M.

(3) The method of one of (1), and (2), wherein a sulfate of the element A or a sulfate of the element R is added to the material powder mixture.

(4) The method of one of (1) to (3), wherein at least one of the step of preparing the material powder mixture, the step of preparing the mixed solution, and the step of pulverizing the ferrite calcined body includes adding $B_2O_3$ and/or $H_3BO_3$.

(5) According to a not-claimed embodiment of the present teaching, an oxide magnetic material includes a ferrite having a hexagonal M-type magnetoplumbite structure as a main phase, the material comprising:

- A, which is at least one element selected from the group consisting of Sr, Ba, Pb and Ca;
- R, which is at least one element selected from the group consisting of the rare-earth elements (including Y) and Bi and which always includes La; and Fe,

wherein the ratio of the constituents A, R and Fe of the oxide magnetic material is represented by

$$\text{Formula 1: } (1-x) AO \cdot (x/2) R_2O_3 \cdot n Fe_2O_3,$$

where $0.05 \leq x \leq 0.3$, and

$$5.0 \leq n \leq 6.5,$$

wherein another oxide magnetic material, including a ferrite having a spinel-type structure as a main phase, is added at 0.2 wt% to 6.2 wt% to the oxide magnet material including the ferrite having the hexagonal M-type magnetoplumbite structure as its main phase, the oxide magnetic material to be added being represented by:

$$\text{Formula 2: } MO \cdot Fe_2O_3$$

where M is at least one element selected from the group consisting of Co, Ni, Mn and Zn.

(6) According to a further not-claimed embodiment of the present teaching, a ferrite magnet powder comprises the oxide magnetic material of (5).

(7) According to a further not-claimed embodiment of the present teaching, a method of making a ferrite calcined body comprises the steps of:

- preparing a mixed solution, in which a chloride of at least one element that is selected from the group consisting of Sr, Ba, Pb and Ca, a chloride of at least one element R that is selected from the group consisting of the rare-earth elements (including Y) and Bi and that always includes La, and a chloride of Fe are dissolved and which satisfies pH<6;
- calcining the mixed solution by spraying the mixed solution into an atmosphere that has been heated to a temperature of 800 °C to 1,400 °C, thereby forming a ferrite calcined body having an M-type magnetoplumbite structure and a composition represented by the general formula:

$$\text{Formula 1: } (1-x) AO \cdot (x/2) R_2O_3 \cdot n Fe_2O_3.$$
where A is at least one element selected from the group consisting of Sr, Ba, Pb and Ca; R is at least one element selected from the group consisting of the rare-earth elements (including Y) and Bi and always includes La; 0.05 ≤ x < 0.3; and 5.0 ≤ n ≤ 6.5;

preparing another material powder mixture by mixing an oxide material powder of at least one element selected from the group consisting of Co, Ni, Mn and Zn and a material powder of Fe₂O₃;

calcining the material powder mixture at a temperature of 700 °C to 1,450 °C, thereby forming a ferrite calcined body having a spinel-type structure and a composition represented by the general formula:

MO • Fe₂O₃

where M is at least one element selected from the group consisting of Co, Ni, Mn and Zn; and

preparing a calcined body mixed powder by adding the ferrite calcined body having the spinel-type structure at 0.2 wt% to 6.2 wt% to the ferrite calcined body having the M-type magnetoplumbite structure.

(8) According to a further not-claimed embodiment of the present teaching, a method of making a ferrite calcined body comprises the steps of:

- pulverizing the calcined body, formed by the method of (1) or (7), to obtain a ferrite pulverized powder having a mean particle size of 0.2 μm to 2.0 μm when the size is measured by an air permeability method; and
- calcining the ferrite pulverized powder again at a temperature of 900 °C to 1,450 °C.

(9) According to a further not-claimed embodiment of the present teaching, in the method of one of (2), (7) and (8) a sulfate of the element A or a sulfate of the element R is added to the mixed solution.

(10) According to a further not-claimed embodiment of the present teaching, a method of making a magnet powder comprises the steps of:

- preparing a calcined body mixed powder by adding 0.3 wt% to 1.5 wt% of CaO, 0.2 wt% to 1.0 wt% of SiO₂, 0 wt% to 5.0 wt% of Cr₂O₃, and 0 wt% to 5.0 wt% of Al₂O₃ to the calcined body obtained by the method of one of (3) to (9), and
- pulverizing the calcined body mixed powder to obtain a ferrite pulverized powder having a mean particle size of 0.2 μm to 2.0 μm when the size is measured by an air permeability method.

(11) According to a further not-claimed embodiment of the present teaching, a method of making a magnet powder comprises the steps of:

- preparing a calcined body mixed powder by adding 0.3 wt% to 1.5 wt% of CaO, 0.2 wt% to 1.0 wt% of SiO₂, 0 wt% to 5.0 wt% of Cr₂O₃, and 0 wt% to 5.0 wt% of Al₂O₃ to the calcined body obtained by the method of one of (3) to (9), and
- pulverizing the calcined body mixed powder to obtain a ferrite pulverized powder having a mean particle size of 0.2 μm to 2.0 μm when the size is measured by an air permeability method.

(12) According to a further not-claimed embodiment of the present teaching, a magnetic recording medium comprises the ferrite magnet powder of (6).

(13) According to a further not-claimed embodiment of the present teaching, a magnetic recording medium comprises the magnet powder obtained by the method of (10) or (11).

(14) According to a further not-claimed embodiment of the present teaching, a bonded magnet comprises the ferrite magnet powder of (6).

(15) According to a further not-claimed embodiment of the present teaching, a bonded magnet is made of the magnet powder obtained by the method of (10) or (11).

(16) According to a further not-claimed embodiment of the present teaching, a sintered magnet comprises the ferrite magnet powder of (6).

(17) According to a further not-claimed embodiment of the present teaching, a sintered magnet is made of the
magnet powder obtained by the method of (10) or (11).

(18) According to a further not-claimed embodiment of the present teaching, a method for producing a magnet comprises the steps of

subjecting the magnet powder, obtained by the method of (10) or (11), to a heat treatment, and

making a bonded magnet of the magnet powder that has been subjected to the heat treatment.

(19) According to a further not-claimed embodiment of the present teaching, in the method of (18) the heat treatment is carried out at a temperature of 700 °C to 1,100 °C.

(20) According to a further not-claimed embodiment of the present teaching, a sintered magnet is made of the ferrite magnet powder of (6) and which includes CaO, SiO₂, Cr₂O₃, and Al₂O₃ at the percentages of:

0.3 wt% to 1.5 wt% (CaO),
0.2 wt% to 1.0 wt% (SiO₂),
0 wt% to 5.0 wt% (Cr₂O₃), and
0 wt% to 5.0 wt% (Al₂O₃), respectively.

(21) According to a further not-claimed embodiment of the present teaching, a method for producing a sintered magnet comprises the steps of

preparing a magnet powder by the method of (10) or (11), and

condensing, mulling, compacting and sintering the magnet powder, where the magnet powder is compacted with or without a magnetic field applied thereto.

(22) According to a further not-claimed embodiment of the present teaching, a method for producing a sintered magnet comprises the steps of

preparing a magnet powder by the method of (10) or (11), and

condensing, mulling, drying, crushing, compacting and sintering the magnet powder, where the magnet powder is compacted with or without a magnetic field applied thereto.

(23) According to a further not-claimed embodiment of the present teaching, in the method of (21) or (22) the step of pulverizing or the step of mulling includes the step of adding a dispersant at a solid matter ratio of 0.2 wt% to 2.0 wt%.

(24) According to a further not-claimed embodiment of the present teaching, a rotating machine comprises the magnet of one of (14) to (17) and (20).

(25) According to a further not-claimed embodiment of the present teaching, a magnetic recording medium comprising a thin-film magnetic layer that includes the oxide magnetic material of (5).

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a graph showing a relationship between the mole fraction x and the remanence \( B_r \) and a relationship between the mole fraction x and the coercivity \( H_{cJ} \) in a sintered magnet according to the present invention, which is represented by \((1 - x) \text{SrO} \cdot (x/2) \text{La}_2\text{O}_3 \cdot n \text{Fe}_2\text{O}_3 + y \text{CoFe}_2\text{O}_4\) (where \(0 \leq x \leq 0.5\), \(0 \leq y \leq 0.25\), \(y/x = 0.5\) and \(n=5.8\)).

FIG. 2 is a graph showing a relationship between the mole ratio \(y/x\) and the remanence \( B_r \) and a relationship between the mole ratio \(y/x\) and the coercivity \( H_{cJ} \) in a sintered magnet according to the present invention, which is represented by \((1-x) \text{SrO} \cdot (x/2) \text{La}_2\text{O}_3 \cdot n \text{Fe}_2\text{O}_3 + y \text{CoFe}_2\text{O}_4\) (where \(x=0.2\), \(0 \leq y \leq 0.22\), \(0 \leq y/x \leq 1.1\) and \(n=5.8\)).
Hereinafter, embodiments of the present invention will be described with reference to the accompanying drawings.

According to the present invention, element R (which is at least one element selected from the group consisting of the rare-earth elements (including Y) and Bi which always includes La) is substituted for a portion of element A in a ferrite having a hexagonal M-type magnetoplumbite structure $\alpha$-Fe$_2$O$_3$ and a ferrite having a spinel-type structure $\text{MFe}_2\text{O}_4$, where element M is at least one element selected from the group consisting of Sr, Ba, Pb and Ca). The present inventors initially produced a state in which the charge compensation was achieved only incompletely, i.e., just substituted element R for a portion of element A in a ferrite having a hexagonal M-type magnetoplumbite structure $\alpha$-Fe$_2$O$_3$ (where A is at least one element selected from the group consisting of Sr, Ba, Pb and Ca) and a ferrite having a spinel-type structure $\text{MFe}_2\text{O}_4$, where element M is at least one element selected from the group consisting of Co, Ni, Mn and Zn, is added to the ferrite having the hexagonal M-type magnetoplumbite structure.

In the prior art, it was believed that when divalent ions of Co, Zn or other suitable element are substituted for a portion of Fe and when trivalent ions of La or other suitable element are substituted for a portion of Ba or Sr, these substitutions may be carried out separately but are preferably carried out simultaneously in view of charge compensation. It was also believed that these substitutions should be done by both substituents at a predetermined ratio to achieve the charge compensation. However, as opposed to such a misconception prevalent in the pertinent art, the present inventors initially produced a state in which the charge compensation was achieved only incompletely, i.e., just substituted element R for a portion of element A to obtain a ferrite with a hexagonal M-type magnetoplumbite structure in which no heterogeneous phases such as ortho-ferrite (RFeO$_3$) or hematite ($\alpha$-Fe$_2$O$_3$) were created, and then added a ferrite having a spinel-type structure, including element M, to such a ferrite. The present inventors discovered that similar effects were also achieved, and yet the amount of the element M to be added could be reduced significantly, compared to the conventional method with the charge compensation, to acquire the basic idea of the present invention.

It should be noted that even though the charge compensation is not the issue, the respective substituents still need to be added at the best ratio because the magnetic properties might deteriorate depending on the ratios defined for those elements. Thus, according to the present invention, the respective substituents are added in predetermined amounts and the manufacturing process, composition and additives are optimized to add them at the best ratio. In this manner, the present inventors improved the magnetic properties successfully.

Also, compared to the conventional method in which element R is substituted for a portion of element A and element M is substituted for a portion of Fe simultaneously or a situation where none of these substitutions is done, the ferrite calcined body has a decreased crystal grain size in the oxide magnetic material prepared according to the method of the present invention where just the substitution of element R for a portion of element A is done, which is one of the features of the present invention. For example, if the calcining process is carried out at 1,300 °C, the resultant ferrite calcined body such that even when the ferrite calcined body is used as a ferrite magnet powder, there is almost no need, or even absolutely no need, to pulverize the ferrite calcined body.

The oxide magnetic material is obtained by adding a ferrite having a spinel-type structure, represented by:

\[
\text{Formula 1: } (1-x) \text{A}_2\text{O}_3 \cdot (x/2) \text{R}_2\text{O}_3 \cdot n \text{Fe}_2\text{O}_3.
\]

to a ferrite having a substantially M-type magnetoplumbite structure, which is represented by:

\[
\text{Formula 2: } \text{MFe}_2\text{O}_4 (=\text{MFe}_2\text{O}_4)
\]
The oxide magnetic material of the present invention may be provided as any of various forms including a calcined body, a magnet powder, a bonded magnet, a sintered magnet and a magnetic recording medium.

When Sr is selected as the element A, the magnetic properties are improved more significantly than the situation where Ba, Pb or Ca is selected as the element A. For that reason, Sr is preferably selected as the element A as an indispensable component. Depending on the specific application, however, it may be more advantageous to select Ba, for example, to reduce the cost.

The magnetic properties are improved most significantly when La is selected as the element R. Thus, only La is preferably selected as the element R. Depending on the specific application, however, it may be advantageous to add La as an indispensable element and at least one of the rare-earth elements (including Y) and Bi as an optional element to reduce the cost.

As described above, the element M is at least one element selected from the group consisting of Co, Ni, Mn and Zn. When Zn is selected as the element M, the saturation magnetization increases. On the other hand, when Co, Ni or Mn is selected as the element M, the anisotropic magnetic field increases. Particularly when Co is selected, the anisotropic magnetic field increases significantly. The anisotropic magnetic field represents a theoretical upper limit of coercivity. Thus, to increase the coercivity, it is important to increase the anisotropic magnetic field.

In the Formula 1, x and n represent mole fractions and satisfy the inequalities 0.05 ≤ x ≤ 0.3 and 5.0 ≤ n ≤ 6.5, respectively. A preferable range of x is 0.05 ≤ x ≤ 0.3 and a more preferable range thereof is 0.05 ≤ x ≤ 0.25. On the other hand, a preferable range of n is 5.5 ≤ n ≤ 6.5 and a more preferable range thereof is 5.8 ≤ n ≤ 6.3.

In the Formula 1, if x is too small, non-magnetic phases, including the element A, increase. But if n is too large, hematite and other phases increase to deteriorate the magnetic properties.

If the spinel-structure ferrite is added in too a small amount, then the effects to be achieved by the addition are not so dramatic as to improve the magnetic properties sufficiently. However, if the amount of the ferrite added is excessive, then the magnetic properties will deteriorate and the cost will rise as well. In addition, heterogeneous phases such as ortho-ferrite and hematite are created while the ferrite represented by Formula 1 is being produced, and the grain growth of those phases may be caused during the second calcining process and/or the heat treatment by sintering, thus further deteriorating the magnetic properties.

On the other hand, if n is too small, non-magnetic phases, including the element A, increase. If necessary, at most about 3 wt% of any other compound (e.g., a compound including Si, Ca, Pb, Al, Ga, Cr, etc.) may be added. If necessary, a boron compound (such as B_2O_3 or H_3BO_3) may be added to the powder. Also, a sulfate of at least one element, which is selected from the group consisting of Sr, Ba, Pb, Ca, Y, the rare-earth elements, Bi and Fe, may also be added.

In this manner, the rare-earth elements including Y and/or Bi may be added as their oxide powders. Alternatively, powders or solutions of compounds (e.g., carbonates, hydroxides, nitrates and chlorides) that will be oxides in a subsequent calcining process may also be added. As another alternative, a compound, which is made up of at least two elements to be selected from the group consisting of Sr, Ba, Pb, Ca, the rare-earth elements (including Y), Bi and Fe, may also be added.

If necessary, a boron compound (such as B_2O_3 or H_3BO_3) may be added to the powder. Also, a sulfate of at least one element, which is selected from the group consisting of Sr, Ba, Pb, Ca, Y, the rare-earth elements, Bi and Fe, may be used as a portion of the material powder. By using any of these additives, the reactivity to the ferrite phase with the M-type magnetoplumbite structure during the calcining process can be improved and the grain growth can be minimized, thus improving the magnetic properties. These effects are achieved particularly noticeably when the Formula 1 satisfies n ≥ 6, in which range it was believed that no single-phase ferrite with the M-type magnetoplumbite structure could be obtained and no good magnetic properties should be achievable.

If necessary, about 3 wt% of another compound such as BaCl_2 may be added to the powder.

If necessary, at most about 3 wt% of any other compound (e.g., a compound including Si, Ca, Pb, Al, Ga, Cr, etc.) may be added.
Sn, In, Co, Ni, Ti, Mn, Cu, Ge, V, Nb, Zr, Li, Mo, Bi and/or a rare-earth element (including Y) may be added to the material powder mixture. Also, the material powder mixture may further include very small amounts of impurities such as inevitable components.

It should be noted that the process step of preparing a material powder mixture herein refers to not only a situation where such a material powder mixture is prepared from the beginning but also a situation where a material powder mixture, prepared by somebody else, is purchased and used and a situation where a material powder mixture made by somebody else is added to the mixture.

Next, the material powder mixture is heated to a temperature of 1,100 °C to 1,450 °C by using a batch furnace, a continuous furnace, or a rotary kiln, for example, thereby producing a ferrite compound having an M-type magnetoplumbite structure through a solid-phase reaction. This process will be referred to herein as "calcining" and a compound obtained by this process will be referred to herein as a "calcined body". The calcining process may be carried out for a period of time of about 1 second to about 10 hours, preferably from 0.5 hour to 3 hours. In the calcining process, as the temperature rises, a ferrite phase is gradually formed through the solid phase reaction. The formation of the ferrite phase is completed at about 1,100 °C. If the calcining process is finished at a temperature lower than about 1,100 °C, then unreacted hematite will be left to deteriorate the resultant magnet properties. The effects of the present invention are achieved if the calcining temperature exceeds 1,100 °C. However, the effects of the present invention are relatively modest if the calcining temperature is in the range of 1,100 °C to 1,150 °C, but increases as the calcining temperature exceeds this range. However, if the calcining temperature is higher than 1,350 °C, then various inconveniences might be created. For example, crystal grains might grow so much that it would take a lot of time to pulverize the powder in the subsequent pulverizing process step. In view of these considerations, the calcining temperature is preferably in the range of 1,150 °C to 1,350 °C.

By adding the spinel-type structure ferrite to the M-type magnetoplumbite ferrite calcined body and then subjecting the calcined body to the pulverization process step of pulverizing and/or crushing it, a ferrite magnet can be obtained. The mean particle size thereof is preferably 2.0 μm or less, more preferably 0.2 μm to 1 μm. An even more preferable range of the mean particle size is 0.4 μm to 0.9 μm. These mean particle sizes were measured by an air permeability method.

To obtain a more uniform ferrite magnet powder, the resultant ferrite magnet powder may be re-calcined and further pulverized and/or crushed.

Since the respective ferrite structures have already been produced by the first-stage calcining process, the calcining temperature of the second-stage calcining process may be lower than that of the first-stage calcining process. Thus, the second-stage calcining process may be carried out within a temperature range of 900 °C to 1,450 °C. To minimize the growth of crystal grains, the second-stage calcining temperature is preferably 900 °C to 1,200 °C. The calcining temperature may range from about 1 second to about 10 hours, preferably 0.5 hour to 3 hours.

It should be noted that a bonded magnet may also be obtained by compounding the ferrite magnet powder with any of various types of binders such as a rubber with some flexibility or a hard and lightweight plastic after subjecting the magnet powder to a heat treatment. In that case, the magnet powder is milled with such a binder and then the mixture is compacted. During the mulling process, any of various known dispersants and surfactants is preferably added at a solid matter ratio of 0.2 wt% to 2.0 wt%. The compaction process is carried out by a method such as injection molding, extrusion molding or roll molding with or without a magnetic field applied thereto.

The heat treatment is carried out to remove the crystal strain that has been caused in the particles of the calcined body during the pulverization process of the calcined body. By conducting the heat treatment at a temperature of 700 °C or more, the crystal strain in the particles of the calcined body is relaxed and the coercivity is recovered. However, if the heat treatment is carried out at a temperature of 1,100 °C or more, then the grains of the powder start to grow and the coercivity decreases. On the other hand, the magnetization increases along with the coercivity up to a temperature of 1,000 °C. However, once this temperature is exceeded, the degree of alignment decreases, so does the magnetization. This is probably because the powder particles should be fused with each other. In view of these considerations, the heat treatment is preferably carried out at a temperature of 700 °C to 1,100 °C for 1 second to 3 hours. A more preferable range of the heat treatment temperature is 900 °C to 1,000 °C.

It should be noted that if the ferrite magnet powder is heat-treated, milled with any of various known binders and then applied, an applied magnetic recording medium can be obtained.

Hereinafter, a method for producing a ferrite magnet will be described.

First, an M-type magnetoplumbite ferrite calcined body and a spinel-type structure ferrite calcined body are prepared by the method described above. Next, the spinel-type structure ferrite calcined body is added to the M-type magnetoplumbite ferrite calcined body. Thereafter, the calcined body is subjected to a fine pulverization process using a vibrating mill, a ball mill and/or an attritor so as to be pulverized into fine powder particles having a mean particle size of 0.4 μm to 0.9 μm as measured by the air permeability method. The fine pulverization process is preferably carried out as a combination of dry pulverization (i.e., coarse pulverization to a size of greater than 1 μm) and wet pulverization (i.e., fine pulverization to a size of 1 μm or less).
To obtain a more uniform ferrite magnet powder, the resultant ferrite magnet powder may be re-calcined and further pulverized and/or crushed at this point in time. In the fine pulverization process, to improve the magnetic properties, CaO, SiO₂, Cr₂O₃ and Al₂O₃ (specifically, 0.3 wt% to 1.5 wt% of CaO, 0.2 wt% to 1.0 wt% of SiO₂, 0 wt% to 5.0 wt% of Cr₂O₃ and 0 wt% to 5.0 wt% of Al₂O₃) may be added to the calcined body. The wet pulverization process may be carried out with an aqueous solvent such as water or any of various non-aqueous solvents. As a result of the wet pulverization process, slurry is produced as a mixture of the solvent and the powder of the calcined body. Any of various known dispersants or surfactants is preferably added to the slurry at a solid matter ratio of 0.2 wt% to 2.0 wt%. During this fine pulverization process, about 1 wt% or less of another compound including Bi₂O₃, for example, may also be added.

Thereafter, in a wet compaction process, the slurry is compacted with or without a magnetic field applied thereto, while the solvent is removed from the slurry. Alternatively, in a dry compaction process, the slurry may be subjected to drying, crushing and other process steps, and then compacted with or without a magnetic field applied thereto. After the compaction process, the compact is subjected to various known manufacturing processing steps including degreasing, sintering, finishing, cleaning and testing to obtain a ferrite magnet as a final product. The sintering process may be carried out in the air at a temperature of 1,100 °C to 1,250 °C for 0.5 hour to 2 hours, for example. The sintered magnet to be obtained by the sintering process may have a mean particle size of 0.5 μm to 2.0 μm, for example.

A rotating machine is characterized by including a ferrite magnet produced by the method described above. Thus, the specific structure thereof may be the same as that of a known rotating machine.

Also, a thin-film magnetic layer for use in a magnetic recording medium is preferably formed by a sputtering process. The ferrite magnet described above may be used as a target for the sputtering process. Alternatively, oxides of respective elements may also be used as targets. By subjecting the thin film, formed by the sputtering process, to a heat treatment, a thin-film magnetic layer of ferrite can be obtained.

A method for producing a ferrite magnet is characterized by preparing a magnetic body including, as a main phase, a ferrite having an M-type magnetoplumbite structure and represented by (1-x) AO • (x/2) R₂O₃ • n Fe₂O₃ (where A is at least one element selected from the group consisting of Sr, Ba, Pb and Ca and R is at least one element selected from the group consisting of the rare-earth elements (including Y) and Bi and always includes La) and then adding a spinel-type structure ferrite thereto during a fine pulverization process. Thus, even if the ferrite having the M-type magnetoplumbite structure is a mother material with a constant composition, a ferrite magnet, exhibiting any desired combination of magnetic properties that fall somewhere within a broad range, can be easily obtained by appropriately changing the amounts of the additives during the fine pulverization process. Thus, the present invention is very effectively applicable for use in a manufacturing process of producing ferrite magnets with a wide variety of magnetic properties.

**Example 1**

First, various material powders, including an SrCO₃ powder, an La₂O₃ powder and an Fe₂O₃ powder, were mixed together such that a composition (1-x) SrO • (x/2) La₂O₃ • n Fe₂O₃ would satisfy x=0.2 and n=5.8. The resultant material powder mixture was pulverized with a wet ball mill for four hours, dried, and then sieved. Thereafter, the powder was calcined in the air at 1,300 °C for three hours, thereby obtaining a calcined body magnet powder.

The calcined body magnet powder was analyzed by an X-ray diffraction method. As a result, an M-type ferrite single phase was identified but no ortho-ferrite phases or hematite phases were identifiable.

Meanwhile, various material powders, including an Fe₂O₃ powder and a CoO powder, an NiO powder, an Mn₂O₄ powder or ZnO powder, were mixed together to satisfy a composition CoO • Fe₂O₃ (Co-S), NiO • Fe₂O₃ (Ni-S), MnO • Fe₂O₃ (Mn-S) or ZnO • Fe₂O₃ (Zn-S). The resultant material powder mixture was pulverized with a wet ball mill for four hours, dried, and then sieved. Thereafter, the powder was calcined in the air at 850 °C for three hours, thereby obtaining a spinel ferrite calcined body magnet powder.

The spinel ferrite calcined body powder was analyzed by an X-ray diffraction method. As a result, a spinel-type ferrite single phase was identified.

Next, 2.3 wt% of Co-S calcined body magnet powder (Sample No. 1), 2.3 wt% of Ni-S calcined body magnet powder (Sample No. 2), 2.2 wt% of Mn-S calcined body magnet powder (Sample No. 3), 2.5 wt% of Zn-S calcined body magnet powder (Sample No. 4), 1.1 wt% of Co-S calcined body magnet powder and 1.1 wt% of Ni-S calcined body magnet powder (Sample No. 5), 1.1 wt% of Co-S calcined body magnet powder and 1.1 wt% of Mn-S calcined body magnet powder (Sample No. 6), or 1.1 wt% of Co-S calcined body magnet powder and 1.2 wt% of Zn-S calcined body magnet powder (Sample No. 7) was added to the M-type ferrite calcined body magnet powder such that the equivalent mole fraction y of the element M in the spinel ferrite calcined body powder to be added to one mole of the M-type ferrite calcined body magnet powder satisfied y=0.1 (i.e., y/x=0.5). Also, 0.7 wt% of CaCO₃ powder and 0.4 wt% of SiO₂ powder were further added thereto. Then, using water as a solvent, the mixture was finely pulverized with a wet ball mill to a mean particle size of about 0.55 μm as measured
Thereafter, with the solvent removed from the finely pulverized slurry, the slurry was compacted under a magnetic field. The compact was sintered in the air at 1,200 °C for 30 minutes to obtain a sintered magnet.

As a comparative example, a sample to which no spinel ferrite calcined body powder was added (Comparative Example No. 1) was also prepared. 0.7 wt% of CaCO3 powder and 0.4 wt% of SiO2 powder were further added thereto. Then, using water as a solvent, the mixture was finely pulverized with a wet ball mill to a mean particle size of about 0.55 μm as measured by the air permeability method. Thereafter, with the solvent removed from the finely pulverized slurry, the slurry was compacted under a magnetic field. The compact was sintered in the air at 1,200 °C for 30 minutes to obtain a sintered magnet. Meanwhile, another sintered magnet that satisfied n=5.8 in the composition SrO • n Fe2O3 was also prepared as Comparative Example No. 2 by the same method as that described above.

The saturation magnetization ($J_s$), remanence ($B_r$) and coercivity ($H_{cJ}$) of the resultant sintered magnets were measured. The results of measurement are shown in the following Table 1. As can be clearly seen from Table 1, Samples Nos. 1 through 7, representing examples of the present invention, exhibited improved magnetic properties as compared with Comparative Example No. 1 or 2.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_s$ (T)</th>
<th>$B_r$ (T)</th>
<th>$H_{cJ}$ (kA/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.447</td>
<td>0.434</td>
<td>348</td>
</tr>
<tr>
<td>2</td>
<td>0.442</td>
<td>0.430</td>
<td>327</td>
</tr>
<tr>
<td>3</td>
<td>0.446</td>
<td>0.431</td>
<td>335</td>
</tr>
<tr>
<td>4</td>
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<td>0.444</td>
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</tr>
<tr>
<td>5</td>
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<td>0.431</td>
<td>334</td>
</tr>
<tr>
<td>6</td>
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<td>0.433</td>
<td>341</td>
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<td>0.455</td>
<td>0.440</td>
<td>256</td>
</tr>
<tr>
<td>Cmp. Exp. 1</td>
<td>0.451</td>
<td>0.437</td>
<td>251</td>
</tr>
<tr>
<td>Cmp. Exp. 2</td>
<td>0.431</td>
<td>0.418</td>
<td>245</td>
</tr>
</tbody>
</table>

**Example 2**

First, as in the first example described above, an M-type calcined body magnet powder and a Co-S calcined body magnet powder were prepared so as to satisfy $0 \leq x \leq 0.5$ and $n=5.8$ in a composition $(1-x)$ SrO • $(x/2)$ La2O3 • n Fe2O3.

The Co-S calcined body powder was added to the M-type ferrite calcined body magnet powder such that the mole fraction $y$ of Co in the Co-S calcined body powder to be added to one mole of the M-type ferrite calcined body magnet powder satisfied $0 \leq y \leq 0.25$ (i.e., $y/x=0.5$). After that, a sintered body was obtained as in the first example described above.

$B_r$ and $H_{cJ}$ of the resultant sintered magnet were measured. The results of measurement are shown in FIG. 1. As can be clearly seen from FIG. 1, $B_r$ and $H_{cJ}$ increased in a range where $0.05 \leq x \leq 0.3$ was satisfied.

**Example 3**

First, as in the first example described above, an M-type ferrite calcined body magnet powder and a Co-S calcined body magnet powder were prepared so as to satisfy $x=0.2$ and $n=5.8$ in a composition $(1-x)$ SrO • $(x/2)$ La2O3 • n Fe2O3.

The Co-S calcined body powder was added to the M-type ferrite calcined body magnet powder such that the mole fraction $y$ of Co in the Co-S calcined body powder to be added to one mole of the M-type ferrite calcined body magnet powder satisfied $0 \leq y \leq 0.22$ (i.e., $0 \leq y/x \leq 1.1$). After that, a sintered body was obtained as in the first example described above.

$B_r$ and $H_{cJ}$ of the resultant sintered magnet were measured. The results of measurement are shown in FIG. 2.
As can be clearly seen from FIG. 2, $H_{cJ}$ increased in a range where $0.2 \leq y/x \leq 0.8$ was satisfied.

**Example 4**

[0075] A calcined body magnet powder was prepared as in the first example described above except that respective materials were mixed together so as to satisfy $x=0.2$ and $4.6 \leq n \leq 7.0$ in the composition $(1-x)$ SrO • $(x/2)$ La$_2$O$_3$ • $n$ Fe$_2$O$_3$. Then, a sintered body was made of the calcined body magnet powder as in Sample No. 1 of the first example.

[0076] $B_r$ and $H_{cJ}$ of the resultant sintered magnet were measured. The results of measurement are shown in FIG. 3. As can be clearly seen from FIG. 3, $B_r$ and $H_{cJ}$ increased in a range where $5.0 \leq n \leq 6.5$ was satisfied.

**Example 5**

[0078] First, a finely pulverized slurry was prepared as in Sample No. 1 of the first example except that the slurry was finely pulverized to a mean particle size of about 1.0 $\mu$m as measured by the air permeability method. Thereafter, the slurry was dried, crushed and then thermally treated at a temperature of 500 °C to 1,200 °C, thereby preparing a ferrite magnet powder.

[0079] $B_r$ and $H_{cJ}$ of the resultant powder were measured with a vibrating sample magnetometer (VSM). The results are shown in FIG. 4. As can be seen from FIG. 4, $H_{cJ}$ increased if the heat treatment was carried out at a temperature of less than 1,100 °C but decreased once that temperature was exceeded. It can also be seen that the magnetization increased along with the coercivity up to a temperature of about 1,000 °C but decreased once that temperature was exceeded.

[0080] A bonded magnet shaped for motors was made of the ferrite magnet powder and embedded in a motor instead of a bonded magnet made of the conventional material, and then the motor was operated under rated conditions. As a result, good characteristics were achieved. Also, the torque thereof was higher than that of the motor including the bonded magnet made of the conventional material.

[0081] Also, the ferrite magnet powder was used for a magnetic recording medium. As a result, a high S/N ratio was achieved at a high output.

**Example 6**

[0082] Sintered bodies were prepared as in Sample No. 1 of the first example described above except that the mixtures were finely pulverized with CaO, SiO$_2$, Cr$_2$O$_3$ and Al$_2$O$_3$ added as shown in the following Table 2. $B_r$ and $H_{cJ}$ of the resultant sintered magnets are also shown in the following Table 2:

| Table 2 |
|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| CaO (wt%) | SiO$_2$ (wt%) | Cr$_2$O$_3$ (wt%) | Al$_2$O$_3$ (wt%) | $B_r$ (T) | $H_{cJ}$ (kA/m) |
| 0.3 | 0.3 | 0 | 0 | 0.439 | 327 |
| 0.6 | 0.3 | 0 | 0 | 0.443 | 324 |
| 0.6 | 0.45 | 1.0 | 1.0 | 0.427 | 355 |
| 0.6 | 0.45 | 0 | 0 | 0.443 | 329 |
| 0.6 | 0.45 | 0.5 | 0.5 | 0.436 | 347 |
Example 7

A sintered body was prepared as in the fourth example described above except that a Co(OH)$_3$ powder was used as a Co material instead of the CoO powder. $B_r$ and $H_{cJ}$ of the resultant sintered magnet were measured. The results are shown in FIG. 5. As can be clearly seen from FIG. 5, better properties were achieved by using the Co(OH)$_3$ powder than by using the CoO powder. Specifically, when the Co(OH)$_3$ powder was used, particularly good properties were achieved in the range in which $n>6.0$ was satisfied. As for the other elements M (i.e., Ni, Mn and Zn), similar results were obtained.

The following Samples Nos. 8 through 16 were also prepared, and $B_r$ and $H_{cJ}$ of the resultant sintered magnets were measured. The results are shown in the following Table 3. The sintered magnets representing the respective samples were obtained as in Sample No. 1 of the first example described above.

Sample No. 8, obtained by adding 0.5 wt% of SrSO$_4$ as an Sr material to a portion of SrCO$_3$;

Sample No. 9, obtained by adding 1.0 wt% of SrSO$_4$ as an Sr material to a portion of SrCO$_3$;

Sample No. 10, obtained by adding 2.0 wt% of SrSO$_4$ as an Sr material to a portion of SrCO$_3$;

Sample No. 11, obtained by adding 0.2 wt% of H$_3$BO$_3$ while respective material powders were mixed together to make an M-type ferrite calcined body magnet powder;

Sample No. 12, obtained by adding 0.5 wt% of H$_3$BO$_3$ while respective material powders were mixed together to make an M-type ferrite calcined body magnet powder;

Sample No. 13, obtained by adding 1.0 wt% of H$_3$BO$_3$ while respective material powders were mixed together to make an M-type ferrite calcined body magnet powder;

Sample No. 14, obtained by using a Co(OH)$_3$ powder as a Co material instead of the CoO powder and adding 1.0 wt% of SrSO$_4$ as an Sr material to a portion of SrCO$_3$;

Sample No. 15, obtained by using a Co(OH)$_3$ powder as a Co material instead of the CoO powder and adding 0.5 wt% of H$_3$BO$_3$ while respective material powders were mixed together to make an M-type ferrite calcined body magnet powder; and

Sample No. 16, obtained by using a Co(OH)$_3$ powder as a Co material instead of the CoO powder, adding 0.5 wt% of H$_3$BO$_3$ while respective material powders were mixed together to make an M-type ferrite calcined body magnet powder, and adding 1.0 wt% of SrSO$_4$ as an Sr material to a portion of SrCO$_3$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_s$ (T)</th>
<th>$B_r$ (T)</th>
<th>$H_{cJ}$ (kA/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
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<tr>
<td>16</td>
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</tr>
</tbody>
</table>
INDUSTRIAL APPLICABILITY

[0085] According to the present invention, a ferrite having a spinel-type structure is added to a ferrite having a hexagonal M-type magnetoplumbite structure, in which a portion of Sr, for example, has been replaced with an element R that includes La at least. In this manner, a low manufacturing cost is achieved and yet the magnetic properties of the ferrite magnet can be improved.

Claims

1. A method of making a ferrite calcined body, the method comprising the steps of:

- preparing a material powder mixture by mixing: a material powder of at least one compound that is selected from the group consisting of SrCO₃, BaCO₃, PbO and CaCO₃; an oxide material powder of at least one element to be selected from the group consisting of the rare-earth elements (including Y) and Bi, the oxide material powder always including La₂O₃; and a material powder of Fe₂O₃;
- calcining the material powder mixture at a temperature of 1100°C to 1450°C, thereby forming a ferrite calcined body having an M-type magnetoplumbite structure and a composition represented by the general formula:

\[(1-x) \text{AO} \cdot \frac{x}{2} \text{R}_2\text{O}_3 \cdot n \text{Fe}_2\text{O}_3\]

where A is at least one element selected from the group consisting of Sr, Ba, Pb and Ca; R is at least one element selected from the group consisting of the rare-earth elements (including Y) and Bi and always includes La; \(0.05 \leq x < 0.3\); and \(5.0 \leq n \leq 6.5\);
- preparing another material powder mixture by mixing an oxide material powder of at least one element selected from the group consisting of Co, Ni, Mn and Zn and a material powder of Fe₂O₃;
- calcining the material powder mixture at a temperature of 700°C to 1450°C, thereby forming a ferrite calcined body having a spinel-type structure and a composition represented by the general formula:

\[\text{MO} \cdot \text{Fe}_2\text{O}_3\]

where M is at least one element selected from the group consisting of Co, Ni, Mn and Zn; and
- preparing a calcined body mixed powder by adding the ferrite calcined body having the spinel-type structure at 0.2 wt.-% to 6.2 wt.-% to the ferrite calcined body having the M-type magnetoplumbite structure.

2. The method of claim 1, characterized in that the oxide of the element M is partially or fully replaced with at hydroxide of the element M.

3. The method of one of claims 1 and 2, characterized in that a sulfate of the element A or a sulfate of the element R is added to the material powder mixture.

4. The method of one of claims 1 to 3, characterized in that at least one of the step of preparing the material powder mixture and the step of pulverizing the ferrite calcined body includes adding B₂O₃ and/or H₃BO₃.

Patentansprüche

1. Verfahren zum Herstellen eines kalzinierten Ferritkörpers, wobei das Verfahren die Schritte umfasst:

- das Herstellen einer Materialpulvermischung durch Mischen: eines Materialpulvers von wenigstens einer Verbindung, welche ausgewählt ist aus der Gruppe bestehend aus SrCO₃, BaCO₃, PbO und CaCO₃; eines Oxidmaterialpulvers von wenigstens einem Element, das aus der Gruppe bestehend aus den Seltenerdmetallen (einschließlich Y) und Bi ausgewählt werden soll, wobei das Oxidmaterialpulver immer La₂O₃ einschließt; und eines Materialpulvers von Fe₂O₃;
- das Kalzinieren der Materialpulvermischung bei einer Temperatur von 1100 °C bis 1450 °C, wodurch ein kalzinierter Ferritkörper mit einer Magnetoplumbit-Struktur vom M-Typ und einer Zusammensetzung gebildet wird, die durch die allgemeine Formel wiedergegeben ist:

\[(1-x) \ \text{AO} \cdot \left(\frac{x}{2}\right) R_2O_3 \cdot n \ Fe_2O_3\]

wobei A wenigstens ein Element, ausgewählt aus der Gruppe bestehend aus Sr, Ba, Pb und Ca, ist; R wenigstens ein Element, ausgewählt aus der Gruppe bestehend aus den Seltenerdmetallen (einschließlich Y) und Bi, ist und immer La einschließt; 0,05 ≤ x < 0,3; und 5,0 ≤ n ≤ 6,5;

- das Herstellen einer weiteren Materialpulvermischung durch Mischen eines Oxidmaterialpulvers von wenigstens einem Element, ausgewählt aus Co, Ni, Mn und Zn, und eines Materialpulvers von Fe₂O₃;

- das Kalzinieren der Materialpulvermischung bei einer Temperatur von 700 °C bis 1450 °C, wodurch ein kalzinierter Ferritkörper mit einer Struktur vom Spinell-Typ und einer Zusammensetzung gebildet wird, die durch die allgemeine Formel wiedergegeben ist:

\[MO \cdot Fe_2O_3\]

wobei M wenigstens ein Element, ausgewählt aus der Gruppe bestehend aus Co, Ni, Mn und Zn, ist; und

- das Herstellen eines kalzinierten Körper-Mischpulvers durch Zugeben des kalzinierten Ferritkörpers mit der Struktur vom Spinell-Typ in einer Menge von 0,2 Gew.-% bis 6,2 Gew.-% zu dem kalzinierten Ferritkörper mit der Magnetoplumbit-Struktur vom M-Typ.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass das Oxid des Elements M teilweise oder vollständig durch ein Hydroxid des Elements M ersetzt wird.

3. Verfahren nach einem der Ansprüche 1 und 2, dadurch gekennzeichnet, dass ein Sulfat des Elements A oder ein Sulfat des Elements R zu der Materialpulvermischung zugegeben wird.


Revendications

1. Procédé pour réaliser un corps de ferrite calciné, le procédé comprenant les étapes consistant à :

- préparer un mélange de poudres de matière en mélangeant : une poudre de matière constituée d’au moins un composé qui est choisi dans le groupe constitué de SrCO₃, BaCO₃, PbO et CaCO₃ ; une poudre de matière d’oxyde d’au moins un élément à choisir dans le groupe constitué des terres rares (incluant Y) et Bi, la poudre de matière d’oxyde incluant toujours La₂O₃ ; et une poudre de matière de Fe₂O₃ ;

- calciner le mélange de poudres de matière à une température de 1 100 °C à 1 450 °C, en formant ainsi un corps de ferrite calciné ayant une structure de magnétoplumbite de type M et une composition représentée par la formule générale :

\[(1-x) \ \text{AO} \cdot \left(\frac{x}{2}\right) R_2O_3 \cdot n \ Fe_2O_3\]

où A est au moins un élément choisi dans le groupe constitué de Sr, Ba, Pb et Ca ; R est au moins un élément choisi dans le groupe constitué des terres rares (incluant Y) et Bi et inclut toujours La ; 0,05 ≤ x ≤ 0,3 ; et 5,0 ≤ n ≤ 6,5 ;

- préparer un autre mélange de poudre de matière en mélangeant une poudre de matière d’oxyde d’au moins un élément choisi dans le groupe constitué de Co, Ni, Mn et Zn et une poudre de matière de Fe₂O₃ ;
- calciner le mélange de poudre de matière à une température de 700 °C à 1 450 °C, en formant ainsi un corps de ferrite calciné ayant une structure de type spinelle et une composition représentée par la formule générale :

\[
MO\cdot Fe_2O_3
\]

où M est au moins un élément choisi dans le groupe constitué de Co, Ni, Mn et Zn ; et
- préparer une poudre mixte de corps calcinés en ajoutant le corps de ferrite calciné ayant la structure de type spinelle à raison de 0,2 % en poids à 6,2 % en poids au corps de ferrite calciné ayant la structure de magnétoplombite de type M.

2. Procédé selon la revendication 1, caractérisé en ce que l’oxyde de l’élément M est partiellement ou totalement remplacé par un hydroxyde de l’élément M.

3. Procédé selon l’une des revendications 1 et 2, caractérisé en ce qu’un sulfate de l’élément A ou un sulfate de l’élément R est ajouté au mélange de poudres de matière.

4. Procédé selon l’une des revendications 1 à 3, caractérisé en ce qu’au moins une étape parmi l’étape de préparation du mélange de poudres de matière et l’étape de pulvérisation du corps de ferrite calciné inclut l’ajout de B_2O_3 et/ou de H_3BO_3.
FIG. 1

\[(1-x)\text{SrO} \cdot (x/2)\text{La}_2\text{O}_3 \cdot n\text{Fe}_2\text{O}_3 + y\text{CoFe}_2\text{O}_4\]

\[0 \leq x \leq 0.5, 0 \leq y \leq 0.25, \frac{y}{x} = 0.5, n = 5.8\]
FIG. 2

\( B_r [T] \)

\( H_{cJ} [kAm^{-1}] \)

\((1-x)\text{SrO} \cdot (x/2)\text{La}_2\text{O}_3 \cdot n\text{Fe}_2\text{O}_3 + y\text{CoFe}_2\text{O}_4\)

\( x=0.2, 0 \leq y \leq 0.22, 0 \leq y/x \leq 1.1, n=5.8 \)
FIG. 3

\[
(1-x)\text{SrO} \cdot (x/2)\text{La}_2\text{O}_3 \cdot n\text{Fe}_2\text{O}_3 + y\text{CoFe}_2\text{O}_4
\]

\[
x = 0.2, \; y = 0.1, \; y/x = 0.5, \; 4.6 \leq n \leq 7.0
\]
FIG. 4

(1-x)SrO·(x/2)La$_2$O$_3$·nFe$_2$O$_3$ + yCoFe$_2$O$_4$

$x=0.2$, $y=0.1$, $y/x=0.5$, $n=5.8$
**FIG. 5**

\[(1-x)\text{SrO} \cdot (x/2)\text{La}_2\text{O}_3 \cdot n\text{Fe}_2\text{O}_3 + y\text{CoFe}_2\text{O}_4 \]

\[x=0.2, \ y=0.1, \ y/x=0.5, \ 4.6 \leq n \leq 7.0\]
REFERENCES CITED IN THE DESCRIPTION

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