

SPECIFICATION

Ferrite Magnet and Making Method

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TECHNICAL FIELD

This invention relates to a magnetoplumbite type hexagonal ferrite magnet and a method for preparing the same.

10

BACKGROUND ART

Hexagonal strontium and barium ferrites of the magnetoplumbite type (M type) are mainly used as oxide permanent magnet materials and they are manufactured into sintered magnets and bonded magnets.

Very important magnet properties are remanence or residual magnetic flux density (Br) and intrinsic coercivity (HcJ). The remanence (Br) of a magnet is determined by the density, degree of orientation, and saturation magnetization ($4\pi I_s$) which is determined by the crystalline structure. Br is thus expressed as

$$Br = 4\pi I_s \times \text{degree of orientation} \times \text{density}.$$

Strontium and barium ferrites of the M type have a $4\pi I_s$ value of about 4.65 kG. The density and degree of orientation are limited to about 98% of the theory at maximum even in the case of sintered magnets providing the highest values of density and orientation. Therefore, the Br of these magnets is limited to about 4.46 kG. It was substantially impossible in the prior art to obtain a Br of higher than 4.5 kG.

The inventors proposed, for example, in JP-A 11-154604, a ferrite magnet having a high remanence and a high coercivity which had never been achieved by prior art M type ferrite magnets. This ferrite magnet contains as a major phase a hexagonal magnetoplumbite type ferrite containing A, R, Fe, and M wherein A represents at least

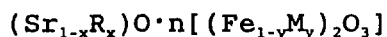


one element selected from among Sr, Ba, Ca, and Pb, A essentially containing Sr, R represents at least one element selected from among rare earth elements (inclusive of Y) and Bi, R essentially containing La, and M represents
 5 Co or a mixture of Co and Zn and wherein the proportions of the respective metal elements, each in total, are:

A: 1 to 13 at%,
 R: 0.05 to 10 at%,
 Fe: 80 to 95 at%, and
 10 M: 0.1 to 5 at%

based on the entire amount of the metal elements.

Also, JP-A 10-149910 discloses a ferrite magnet having a basic composition represented by



15 wherein R is at least one element selected from La, Nd and Pr, M is at least one element selected from Mn, Co, Ni and Zn, and letters x, y and n satisfy:

$0.05 \leq x \leq 0.5$,
 $\{x/(2.2n)\} \leq y \leq \{x/(1.8n)\}$, and
 20 $5.70 \leq n < 6.00$.

In the invention described in this reference, the Fe ion corresponding to a magnetic moment oriented in an antiparallel direction is replaced by another element (the above M) having a smaller magnetic moment than the Fe ion
 25 or being nonmagnetic in order to improve saturation magnetization, and the Sr site is replaced by another element (the above R) for electric charge compensation in order to restrain the development of a heterogeneous phase.

30 DISCLOSURE OF THE INVENTION

In the course of investigating optimum conditions under which the ferrite magnets disclosed in the above patent references are manufactured, the inventors has found that magnetic properties are largely affected by firing
 35 conditions, when the Fe site is replaced by Co, Zn, etc. and the Sr site is replaced by a rare earth element.

Namely, it has been found that even such fluctuations in firing conditions that do not cause magnetic properties to vary to a noticeable extent in the case of ferrite magnets which do not contain Co, Zn, etc. and rare earth elements, 5 can cause magnetic properties to vary to a noticeable extent in the case of ferrite magnets which contain Co, Zn, etc. and rare earth elements. Specifically, as shown in FIG. 5, a substantial drop of coercivity occurs when the oxygen partial pressure in the firing atmosphere 10 fluctuates, and particularly when the oxygen partial pressure becomes lower than in air. It has also been found that coercivity largely varies when the firing temperature fluctuates.

In manufacturing ferrite magnets, the oxygen partial 15 pressure in the firing atmosphere perpetually fluctuates during the firing step, due to the absorption of oxygen concomitant with decomposition and combustion of the binder and dispersant and the absorption and release of oxygen concomitant with changes of the valence of constituent 20 elements and structural changes. Since the spectrum of fluctuation largely differs depending on various conditions including the composition of a material to be fired, the amount of the material admitted into a firing furnace, and the type and amount of additive, it is difficult to control 25 such that the oxygen partial pressure is always kept constant. Also, the firing temperature fluctuates with various factors including the distance of a material to be fired from a heat source, the height of the material to be fired from a furnace bottom, and the gas flow within the 30 furnace which changes with the loading situation of the material to be fired. It is then difficult to control such that the temperature transition pattern is always kept constant. Therefor, in the case of ferrite magnets of the composition whose properties are sensitive to fluctuations 35 in the oxygen partial pressure and the temperature during the firing step, it is difficult for the magnet to

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consistently develop their intrinsic high coercivity.

Especially continuous furnaces, which are effective in improving the yield during mass-scale manufacture, allow for greater fluctuations in the oxygen partial pressure and the temperature transition pattern than batchwise furnaces. For example, the temperature transition pattern in the batchwise furnace includes definite heating, holding and cooling steps whereas in some continuous furnaces, the pattern substantially lacks the holding step and a direct transition from the heating step to the cooling step takes place. Also, in furnaces requiring a low cost for firing, for example, furnaces of the type utilizing the burning of fuel for heating such as gas burning furnaces, oxygen is consumed during the burning of fuel. Then the oxygen partial pressure in the furnace fluctuates drastically. Therefore, when continuous furnaces, burning furnaces and continuous furnaces of the burning furnace type are used, a need exists for a ferrite magnet which is insensitive to fluctuations in the oxygen partial pressure and the temperature during the firing step.

The invention has been made under the above-mentioned circumstances, and its object is to manufacture a ferrite magnet having a high remanence and a high coercivity while suppressing the variation of magnetic properties due to fluctuations in firing conditions.

This and other objects are attained by the invention which is defined below as (1) to (1).

(1) A ferrite magnet having hexagonal ferrite as a major phase, comprising A, R, Fe, M and Si as metal elements, wherein A represents at least one element selected from the group consisting of Sr, Ba, Ca and Pb; R represents at least one element selected from rare earth elements (inclusive of Y) and Bi; and M represents the element Co or

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a mixture consisting of Co and at least one element selected from the group consisting of Mn, Al, Cr and Ni, wherein the proportion of Co in M is at least 10 at %; and wherein the content of SiO₂ is 1.3 to 2.0 mol% when the contents of metal
 5 oxides are determined provided that the metal elements are present as oxides, and the atomic ratio given by

$$(A + R - (Fe+M)/12)/Si$$

is from 1.1 to 1.9.

(2) The ferrite magnet of (1) wherein the proportions
 10 of metal elements A, R, Fe, and M, each in total, are:

A: 1 to 13 at%,

R: 0.05 to 10 at%,

Fe: 80 to 95 at%, and

M: 0.1 to 5 at%

15 based on the entire amount of the metal elements.

(3) The ferrite magnet of (1) or (2) which has at least two distinct Curie temperatures, which fall in the range of 400 to 480°C and differ from each other by at least 5°C.

20 (4) The ferrite magnet of any one of (1) to (3), wherein the ferrite composition is represented by the following formula (I):



wherein $0.04 \leq x \leq 0.9$,

25 $0.04 \leq y \leq 1.0$,

$0.8 \leq x/y \leq 5$, and

$0.7 \leq z < 1$.

(5) A method for preparing the ferrite magnet of any one of (1) to (4), comprising the step of firing a molded
 30 body of a raw material powder to form a sintered magnet, during which step the oxygen partial pressure in the firing

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atmosphere fluctuates.

(6) The method of (5) wherein the oxygen partial pressure in the firing atmosphere lowers below 0.15 atm. for at least a duration in the firing step.

5 (7) A method for preparing the ferrite magnet of any one of (1) to (4), comprising the step of firing a molded body of a raw material powder to form a sintered magnet, during which step firing temperature fluctuates.

10 (8) The method of any one of (5) to (7) wherein at least one compound containing at least one of the magnet constituent elements is added to a calcined material or particles containing hexagonal ferrite as a major phase, followed by molding and sintering.

15 (9) The method of (8) wherein the at least one of the magnet constituent elements is at least one element selected from the elements R and M.

FUNCTION AND RESULTS

According to the invention, the elements R and M are added to magnets in order to acquire a high remanence and a high coercivity. The inventors have discovered that
5 ferrite magnets having the elements R and M added thereto experience very large variations in magnetic properties due to fluctuations in the firing conditions (including the oxygen partial pressure in the firing atmosphere and firing temperature) as compared with prior art ferrite magnets
10 free of the elements R and M, as seen from the experimental results in FIG. 5. It has been found that for suppressing such variations in magnetic properties, it is quite effective to optimize the silicon content and the atomic ratio $\{A+R-(Fe+M)/12\}/Si$.

15 As previously described, ferrite magnets containing the elements R and M are known in the art. However, it is unknown that the variations in magnetic properties due to fluctuations in firing conditions become exaggerated when the elements R and M are added. It is also unknown that in
20 order to suppress the variations in magnetic properties, the silicon content and the atomic ratio $\{A+R-(Fe+M)/12\}/Si$ have to be controlled so as to fall within the ranges prescribed by the invention.

Also the inventors have found that when a method of
25 obtaining a magnet by pre-forming a calcined material having as the major phase a hexagonal ferrite containing at least element A, adding at least one element of the magnet constituent elements, especially at least one element selected from elements R and M, and then firing (to be
30 referred herein as post-addition method) is used, the influence of fluctuations in firing conditions during the firing step becomes outstanding. It has been found that the control of the silicon content and the atomic ratio $\{A+R-(Fe+M)/12\}/Si$ according to the invention is effective
35 especially in this case. The ferrite magnet produced by the post-addition method usually has two or more Curie

temperatures. The magnet containing Co as the element M and having two or more Curie temperatures is improved in magnetic properties over the magnet of the same composition, but having only one Curie temperature.

5 The post-addition method is described in JP-A 11-195516 which was laid open on July 21, 1999 or after the filing of the basic application (Japanese Patent Application No. 11-193348) on which the present application is based. However, it is not described in the publication
10 that the variations in magnetic properties due to fluctuations in firing conditions become further exaggerated when the post-addition method is used, and that the silicon content and the atomic ratio $\{A+R-(Fe+M)/12\}/Si$ are controlled so as to fall within the ranges prescribed
15 by the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing the magnetic properties of sintered magnets as a function of the oxygen partial
20 pressure in the firing atmosphere.

FIG. 2 is a graph showing the magnetic properties of sintered magnets as a function of the firing temperature.

FIG. 3 is a graph showing the magnetic properties of sintered magnets as a function of the atomic ratio
25 $\{A+R-(Fe+M)/12\}/Si$.

FIG. 4 is a graph showing the magnetic properties of sintered magnets as a function of CaO content.

FIG. 5 is a graph showing the coercivity H_{cJ} of sintered magnets as a function of the oxygen concentration
30 in the firing atmosphere.

FIG. 6 is a diagram illustrating how to determine two Curie temperatures.

BEST MODE FOR CARRYING OUT THE INVENTION

35 Sintered magnet

The ferrite magnet of the invention has hexagonal

magnetoplumbite type (M type) ferrite as a major phase, and contains A, R, Fe, M, and Si as metal elements. Element A represents at least one element selected from among Sr, Ba, Ca and Pb. Element R represents at least one element
5 selected from rare earth elements (inclusive of Y) and Bi. Element M represents at least one element selected from among Co, Mn, Al, Cr and Ni. In the inventive magnet, when the contents of metal oxides are determined provided that the metal elements are present as oxides, the content
10 of SiO₂ is 1.3 to 2.0 mol%, preferably 1.4 to 1.9 mol%, and the atomic ratio given by

$$\{A + R - (Fe+M)/12\}/Si$$

is from 1.1 to 1.9, preferably from 1.2 to 1.7.

According to the invention, the content of silicon is
15 above a specific level, A+R is in excess of (Fe+M)/12, and the degree of excess is correlated to the silicon content. These choices minimize the rate of variation of magnetic properties when the oxygen partial pressure or temperature fluctuates, and in particular, significantly suppress a
20 reduction of coercivity under a low oxygen partial pressure. In contrast, if the content of SiO₂ is too low, magnetic properties can largely vary when fluctuations in the oxygen partial pressure and/or firing temperature occur during the firing step. Inversely, if the content of SiO₂
25 is too high, the proportion of a nonmagnetic component such as glass component in the magnet becomes high, resulting in poor magnetic properties, especially a low remanence. If the atomic ratio {A+R-(Fe+M)/12}/Si is too high or too low, magnetic properties can largely vary when fluctuations in
30 the oxygen partial pressure and/or firing temperature occur during the firing step.

When the contents of metal elements in the magnet are determined by converting the metal elements into their
ordinary oxides, iron oxide, strontium oxide, barium oxide,
35 calcium oxide, rare earth (RE) oxide, bismuth oxide, cobalt oxide, manganese oxide, aluminum oxide, chromium oxide and

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silicon oxide are calculated as Fe_2O_3 , SrO , BaO , CaO , RE_2O_3 (except Pr_6O_{11} for Pr, CeO_2 for Ce, and Tb_4O_7 for Tb), Bi_2O_3 , CoO , MnO , Al_2O_3 , Cr_2O_3 , and SiO_2 , respectively.

5 In the inventive magnet, the atomic ratio R/M is preferably from 0.7 to 1.5. When M is divalent, $M = R$ is preferred from the standpoint of valence equilibrium as will be described later. By incorporating R in excess of M, the effects of the invention are augmented.

10 The effects of the invention become outstanding when the inventive magnet has at least two distinct Curie temperatures which fall in the range of 400 to 480°C and differ from each other by an absolute value of at least 5°C. The magnet is structured so as to have a plurality of Curie temperatures, thereby significantly improving the squareness H_k/H_cJ and enabling to reduce the contents of expensive Co and R.

20 The Curie temperature (T_c) is the temperature at which a magnetic material changes from ferromagnetism to paramagnetism. T_c is measured by several methods. Particularly in the case of a magnet material having a plurality of T_c , a magnetization-temperature curve is depicted while the temperature of a sample under test is changed by means of a heater, from which T_c is determined. For the measurement of magnetization, a vibrating sample magnetometer (VSM) is often used because there is easily available a space for installing the heater in proximity to the sample under test.

30 The sample under test may be a powder or a sintered body although the powder must be bound with a heat resistant adhesive or binder. In order that the entire sample be uniformly heated during measurement, it is preferred to make the size of the sample as small as possible and to set a relatively low rate of heating insofar as the accuracy of measurement of magnetization is insured.

The sample may be anisotropic or isotropic. In the

event of an anisotropic sample, it is preferably magnetized in the direction of c axis which is the axis of easy magnetization before measurement is done in the direction of c axis. In the event of an isotropic sample,

5 magnetization is measured in the same direction as the magnetization direction. Magnetization of a sample is conducted by applying a magnetic field having a sufficient strength greater than 1 T. In general, a sample is magnetized at room temperature, and the magnetization of

10 the sample is measured while raising the temperature. Measurement is made preferably in the absence of a magnetic field or under a weak magnetic field of lower than 0.1 T if applied. This is because upon measurement under a strong magnetic field applied, a paramagnetic component can be

15 detected above the Curie temperature so that the Curie temperature becomes indefinite.

FIG. 6 illustrates an example where two Curie temperatures appear. FIG. 6 is a graph of temperature T on the abscissa and magnetization σ on the ordinate, showing a

20 σ - T curve in proximity to Curie temperatures. The σ - T curve is upward convex near the temperature at which a sharp decline of magnetization starts. As the temperature is raised from this point, the magnetization σ changes as follows. First, the magnetization rapidly decreases with a

25 rise of temperature. Then the σ - T curve turns to be downward convex so that the decline of magnetization becomes moderate. Next, the σ - T curve turns to be upward convex again so that the magnetization rapidly decreases. Thereafter, the σ - T curve turns to be downward convex again

30 so that the decline of magnetization becomes moderate. Finally the magnetization reaches zero. Herein, three tangents at the inflection points on this σ - T curve, that is, the points where the curve turns from upward convex to downward convex or from downward convex to upward convex,

35 are designated I, II and III from the lower temperature

side. The intersection between tangent I and tangent II gives a Curie temperature T_{c1} on the lower temperature side, and the intersection between tangent III and the abscissa gives a Curie temperature T_{c2} on the higher
 5 temperature side. Where more than two Curie temperatures exist, the respective Curie temperatures can be determined from the σ -T curve by a similar procedure.

Where a plurality of Curie temperatures exist, the absolute value of the difference therebetween is at least
 10 5°C , and preferably at least 10°C . These Curie temperatures fall in the range of 400 to 480°C , preferably 400 to 470°C , and more preferably 430 to 460°C . It is noted that the Curie temperature of a pure M type strontium ferrite is about 465°C .

15 The ratio (σ_1/σ_{RT}) of the magnetization (σ_1) at the Curie temperature on the lowest temperature side to the magnetization (σ_{RT}) at 25°C is preferably 0.5% to 30%, more preferably 1 to 20%, and further preferably 2 to 10%. If σ_1/σ_{RT} is less than 0.5%, it is difficult to detect the
 20 Curie temperature on the higher temperature side.

It is believed that a plurality of Curie temperatures appear because the texture structure of ferrite crystals has a multi-phase structure of magnetically different M type ferrite phases. Understandably, even when a plurality
 25 of Curie temperatures exist, the single phase structure of M phase is detected by conventional x-ray diffractometry. When the post-addition method described above is employed, a plurality of Curie temperatures generally exist, and the number of Curie temperatures is two in most cases.

30 In the inventive magnet, the proportions of metal elements A, R, Fe, and M, each in total, are preferably:

A: 1 to 13 at%,
 R: 0.05 to 10 at%,
 Fe: 80 to 95 at%, and

M: 0.1 to 5 at%

based on the entire amount of the metal elements.

The more preferred range is:

A: 3 to 11 at%,

5 R: 0.2 to 6 at%,

Fe: 83 to 94 at%, and

M: 0.3 to 4 at%.

The most preferred range is:

A: 3 to 9 at%,

10 R: 0.5 to 4 at%,

Fe: 86 to 93 at%, and

M: 0.5 to 3 at%.

If the content of element A is too small, no M type ferrite would form or more nonmagnetic phases such as α -
 15 Fe_2O_3 would form. If the content of element A is too large, no M type ferrite would form or more nonmagnetic phases such as SrFeO_{3-x} would form. The proportion of strontium in A is preferably at least 51 at%, more preferably at least 70 at%, and most preferably 100 at%. If the proportion of
 20 strontium in A is too low, it would become impossible to acquire both an improvement in saturation magnetization and a significant improvement in coercivity. If the content of element R is too small, the amount of solid solution of M becomes smaller, and the magnetic property improving effect
 25 becomes insufficient. If the content of element R is too large, more nonmagnetic hetero-phases such as ortho-ferrite would form. The magnetic property improving effect becomes insufficient when the content of element M is too small or too large.

30 In the inventive magnet, the atomic ratios of A, R, Fe, and M are represented by the formula (I).



In formula (I), x, y and z are such that the atomic ratio $\{\text{A}+\text{R}-(\text{Fe}+\text{M})/12\}/\text{Si}$ may fall within the above-defined range
 35 and the atomic ratio R/M fall within the preferred range. It is preferred that x, y and z are in the range:

$$0.04 \leq x \leq 0.9,$$

$$0.04 \leq y \leq 1.0, \text{ especially } 0.04 \leq y \leq 0.5,$$

$$0.8 \leq x/y \leq 5, \text{ and}$$

$$0.7 \leq z < 1.$$

5 In formula (I), with too smaller values of x indicating smaller amounts of element R, the amount of solid solution of element M with the hexagonal ferrite cannot be increased, leading to less improvements in saturation magnetization and/or anisotropic magnetic field.

10 With too larger values of x , element R cannot substitute or form a solid solution in the hexagonal ferrite, forming an ortho-ferrite containing element R to detract from saturation magnetization. Too smaller values of y lead to less improvements in saturation magnetization and/or

15 anisotropic magnetic field. With too larger values of y , element M cannot substitute or form a solid solution in the hexagonal ferrite, and substantial losses of anisotropy constant (K_1) and anisotropy field (H_A) occur even when element M can substitute and form a solid solution. Too

20 smaller values of z increase the amount of a nonmagnetic phase containing strontium and element R to detract from saturation magnetization. Too larger values of z increase the amount of α -Fe₂O₃ phase or nonmagnetic spinel ferrite phase containing element M, also lowering saturation

25 magnetization.

 If x/y in formula (I) is outside the range, a valence equilibrium would not be established between elements R and M, with a likelihood to form hetero-phases such as W type ferrite. When element M is a divalent ion and element R is

30 a trivalent ion, $x/y = 1$ is generally set from the standpoint of valence equilibrium although an excess of R is preferred as previously mentioned. The reason why the permissible range of x/y is greater when x/y is in excess of 1 is that an equilibrium in valence is established

35 through reduction of Fe³⁺ to Fe²⁺ even if y is small.

In formula (I) representing the composition, the number of oxygen (O) atoms is 19, which stands for the stoichiometric compositional ratio given when all Ms are divalent, all Rs are trivalent, $x = y$, and $z = 1$. The
5 number of oxygen atoms varies with the type of M and R and the values of x , y , and z . There is also a possibility that oxygen vacancies be left when the firing atmosphere is reducing, for example. Furthermore, although iron is usually trivalent in the M type ferrite, there is a
10 possibility that iron change to divalent or different valence form. There is also a possibility that the element M such as cobalt change its valence. With these variances, the proportion of oxygen to the metal elements varies. Although it is assumed throughout the specification that
15 the number of oxygen atoms is 19 independent of the type of R and the values of x , y , and z , the actual number of oxygen atoms may somewhat deviate from the stoichiometric compositional ratio.

The composition of magnet can be measured by
20 fluorescent X-ray quantitative analysis, for example. The presence of the above-described major phase is confirmed by x-ray diffractometry, electron diffractometry, etc.

In order to increase the saturation magnetization and coercivity of the magnet, element A is preferably at least
25 one of strontium (Sr) and calcium (Ca) and most preferably strontium. The proportion of Sr+Ca in A is preferably at least 51 at%, more preferably at least 70 at%, and most preferably 100 at%.

Element R is preferably at least one of lanthanoids,
30 more preferably at least one of light rare earth elements, further preferably at least one of lanthanum (La), neodymium (Nd), and praseodymium (Pr), especially with lanthanum being essential. The proportion of lanthanum in R is preferably at least 40 at%, more preferably at least
35 70 at%. For improved saturation magnetization, it is most preferable to use only lanthanum as R. This is because

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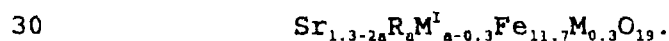
lanthanum is the highest when the limit of R forming solid solution with hexagonal M type ferrite is compared.

Therefore, if the proportion of lanthanum in R is too low, the amount of solid solution of R cannot be increased and as a consequence, the amount of solid solution of M cannot be increased too, mitigating the magnetic property improving effect. The combined use of bismuth (Bi) is advantageous in production because the calcining temperature and sintering temperature can be lower.

Element M must contain cobalt. The proportion of cobalt in M is at least 10 at% and more preferably at least 20 at%. If the proportion of cobalt in M is too low, the improvement in coercivity becomes insufficient.

Boron oxide B_2O_3 may be contained in the magnet. Inclusion of B_2O_3 is effective for lowering the calcining and sintering temperatures, which is advantageous in manufacture. The content of B_2O_3 is preferably up to 0.5% by weight of the entire magnet powder. Too high contents of B_2O_3 would lower saturation magnetization.

The magnet powder may contain at least one of sodium (Na), potassium (K), and rubidium (Rb). The total content of Na, K, and Rb is preferably up to 3% by weight of the entire magnet powder when they are calculated as Na_2O , K_2O , and Rb_2O , respectively. Too large contents of these elements would lower saturation magnetization. Provided that these elements are represented by M^I , the ferrite contains M^I , for example, in the form of



Preferably, letter a is $0.3 < a \leq 0.5$. Too larger values of a would give rise to problems that the saturation magnetization lowers and more of element M^I evaporates

during firing.

In addition to the above elements, there may be contained, for example, Ga, In, Li, Mg, Cu, Ti, Zr, Ge, Sn, V, Nb, Ta, Sb, As, W, and Mo in oxide form. The contents of these elements, calculated as the oxide of stoichiometric composition, are up to 5% by weight of gallium oxide, up to 3% by weight of indium oxide, up to 1% by weight of lithium oxide, up to 3% by weight of magnesium oxide, up to 3% by weight of copper oxide, up to 3% by weight of titanium oxide, up to 3% by weight of zirconium oxide, up to 3% by weight of germanium oxide, up to 3% by weight of tin oxide, up to 3% by weight of vanadium oxide, up to 3% by weight of niobium oxide, up to 3% by weight of tantalum oxide, up to 3% by weight of antimony oxide, up to 3% by weight of arsenic oxide, up to 3% by weight of tungsten oxide, and up to 3% by weight of molybdenum oxide.

Preparation method

Next, a method of preparing the magnet is described.

The method of the invention includes the step of firing a molded body of a raw material powder to form a sintered magnet.

The method of preparing a raw material powder is not critical. For example, the raw material powder may be prepared through solid phase reaction by calcination or by a co-precipitation method or hydrothermal synthesis method. Reference is mostly made to a method involving the calcining step, hereinafter.

Starting materials are mixed and then calcined into a calcined body. The calcined body is disintegrated or pulverized into a powder, that is, the raw material powder. The raw material powder is molded and then fired.

Even when the oxygen partial pressure in the firing atmosphere and/or the firing temperature (holding temperature) fluctuates during the firing step, the inventive magnet having the above-defined composition undergoes minimized variations of magnetic properties,

especially a minimized variation of coercivity, concomitant therewith. The effects of the invention become more outstanding when the oxygen partial pressure in the firing atmosphere is up to 0.15 atm., especially up to 0.10 atm.

5 Then the invention is suited on use of a continuous gas furnace in which the oxygen partial pressure lowers. Also the invention is successful in minimizing the variations of magnetic properties, especially the variation of coercivity, even when the holding temperature fluctuates

10 over the range of 60°C, for example.

Next, the preferred conditions under which the inventive magnet is manufactured are described.

The starting materials used are oxide powders, or powders of compounds which convert into oxides upon firing,

15 for example, carbonates, hydroxides, and nitrates. The mean particle diameter of the starting materials is not critical although a mean particle diameter of about 0.1 to 2 μm is preferred. Among others, iron oxide is preferably in the form of a fine powder whose primary particles

20 preferably have a mean particle diameter of up to 1 μm , especially up to 0.5 μm . As the starting material containing element A, a hydroxide or carbonate is preferably used since it is highly stable during storage.

Calcination is generally carried out in an oxidizing

25 atmosphere, for example, air. Calcining conditions are not critical although the holding temperature is usually 1,000 to 1,350°C and the holding time is 1 second to 10 hours, especially 1 second to 3 hours. The calcined body has a ferrite structure of substantially the magnetoplumbite type

30 and its primary particles preferably have a mean particle diameter of up to 2 μm , more preferably up to 1 μm , further preferably 0.1 to 1 μm , most preferably 0.1 to 0.5 μm . The mean particle diameter may be measured by means of a scanning electron microscope.

35 In the practice of the invention, SiO_2 is preferably

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used as the starting material for providing silicon. SiO_2 may be mixed with other starting materials prior to calcination or subsequent to calcination or in divided portions prior and subsequent to calcination. The effects
5 of the invention are obtained insofar as SiO_2 is added prior to firing. To further enhance the effects of the invention, at least a portion, preferably all, of SiO_2 is preferably added subsequent to calcination.

All of starting material compounds other than SiO_2
10 need not be mixed prior to calcination. A method of adding portions or all of the respective compounds subsequent to calcination is acceptable.

The method of adding starting material compounds other than SiO_2 subsequent to calcination, that is, post-
15 addition method involves the step of first preparing a calcined material having hexagonal ferrite containing at least element A as the major phase. Next, compounds to be later added (post-additives) are added to the calcined material after the calcined material is pulverized or
20 during pulverization. The mixture is then molded and fired. To produce a magnet having a plurality of Curie temperatures as mentioned above, the compounds to be later added are selected such that the post-additives contain at least one element selected from elements R and M,
25 preferably at least both of elements R and M.

The amount of post-additives is preferably 1 to 100% by volume, more preferably 5 to 70% by volume, most preferably 10 to 50% by volume based on the calcined material. An oxide of R may be used as the compound
30 containing element R although the R oxide has the problem that it can be leached away during wet molding since its solubility in water is relatively high. Also the R oxide can cause weighing errors because it is hygroscopic. For this reason, a carbonate or hydroxide of R is preferred as
35 the R compound. The post-additives of other elements may be added in the form of oxides or compounds capable of

converting into oxides upon firing, such as carbonates and hydroxides.

The time when the post-additives are added may be after calcination and before sintering. Preferably the post-additives are added during the pulverizing step to be described later. Instead of adding to the calcined material, the post-additives may be added to the particles having hexagonal ferrite containing at least element A as the major phase, produced by the co-precipitation method or hydrothermal synthesis method.

With respect to element R or M, at least 30%, especially at least 50% of its entirety contained in the magnet is desirably added as the post-additive. With respect to the remaining elements, the amounts to be added as post-additives are not particularly limited. The post-additives preferably have a mean particle size of about 0.1 to 2 μm .

The amounts of post-additives are described in more detail. For example, when it is desired to produce a sintered magnet containing

$\text{Sr:La:Fe:Co} = 0.8:0.2:11.8:0.2$,
raw materials are admixed in a ratio:

$\text{Sr:Fe} = 0.8:9.6 (= 1:12)$,
the admixture is calcined, post-additives are added to the calcined material in a ratio:

$\text{La:Fe:Co} = 0.2:2.2:0.2$,
and the mixture is fired, whereby a sintered magnet of the desired composition is obtained.

Alternatively, raw materials are admixed in a ratio:
 $\text{Sr:Fe} = 0.8:11.8 (= 1:14.75)$,
the admixture is calcined (resulting in a two-phase state of M type strontium ferrite and $\alpha\text{-Fe}_2\text{O}_3$), post-additives are added to the calcined material in a ratio:

$\text{La:Co} = 0.2:0.2$,
and the mixture is fired, whereby a sintered magnet of the desired composition is obtained.

The reason why a sintered magnet produced by the post-addition method has a plurality of Curie temperatures, though not well understood, is explained as follows. Upon sintering, reaction takes place between calcined material particles having a M type ferrite phase and post-additives. During the process, there are formed M type ferrite portions having high La and Co concentrations and M type ferrite portions having low La and Co concentrations. Specifically, assuming that La and Co in the post-additives diffuse toward the center of calcined material particles during sintering, it is believed that the concentrations of La and Co in crystal grains after sintering tend to be higher in skin portions than in central portions. Since the Curie temperature depends on the percent substitutions of La and Co, especially the percent substitution of La, it is believed that the presence of a plurality of Curie temperature reflects the presence of a concentration distribution of La and Co within crystal grains.

Next, the molding step and the preceding step of pulverization are described.

For the molding of the raw material powder, a wet shaping method is preferably utilized. Wet shaping is carried out using a molding slurry containing a raw material powder, water as a dispersing medium, and a dispersant. In order to enhance the effect of the dispersant, a wet pulverizing step preferably precedes the wet shaping step. When calcined powder is used as the raw material powder, a dry coarse pulverizing step for coarsely pulverizing or disintegrating the calcined powder preferably precedes the wet pulverizing step because the calcined powder is generally granular. It is noted that when the raw material powder is prepared by a co-precipitation or hydrothermal synthesis method, the dry coarse pulverizing step is generally omitted and the wet pulverizing step is not essential although the wet pulverizing step is preferably provided in order to further

increase the degree of orientation. In the following description, reference is made to the embodiment wherein calcined particles are used as the raw material powder and the dry coarse pulverizing step and wet pulverizing step
5 are employed.

In the dry coarse pulverizing step, pulverization is generally continued until the BET specific surface area is increased by a factor of about 2 to 10. At the end of pulverization, the particles preferably have a mean
10 particle size of about 0.1 to 1 μm and a BET specific surface area of about 4 to 10 m^2/g . The pulverizing means is not critical and use may be made of, for example, dry vibratory mills, dry attritors (media agitating mills) and dry ball mills, with the dry vibratory mills being
15 preferably used. The pulverizing time may be determined as appropriate depending on the particular pulverizing means used. When some starting materials are added subsequent to calcination, they are preferably added during the dry pulverizing step. For example, it is preferred to add at
20 least parts of SiO_2 and CaCO_3 (which converts to CaO upon firing) during the dry pulverizing step.

The dry coarse pulverization is effective for reducing coercivity H_{cB} by introducing crystal strains into the calcined particles. The drop of coercivity restrains
25 agglomeration of particles, improves dispersion and also improves the degree of orientation because of becoming magnetically soft. The particles once turned to be magnetically soft will resume intrinsic hard magnetism in the subsequent sintering step.

30 After the dry coarse pulverization, a pulverizing slurry containing the pulverized particles and water is prepared and subjected to wet pulverization. The content of the raw material powder in the pulverizing slurry is preferably about 10 to 70% by weight. The pulverizing
35 means used in wet pulverization is not particularly limited although ball mills, attritors and vibratory mills are

preferably used in most cases. The pulverizing time may be determined as appropriate depending on the particular pulverizing means used.

At the end of wet pulverization, the pulverized
5 slurry is concentrated into a molding slurry. Concentration may be effected by centrifugal separation or the like. The amount of the raw material powder contained in the molding slurry is preferably about 60 to 90% by weight.

10 In the wet shaping step, the molding slurry is shaped in a magnetic field. A compacting pressure of about 0.1 to 0.5 t/cm² and a magnetic field of about 5 to 15 kOe may be applied.

Although the use of a non-aqueous dispersing medium
15 in the molding slurry is preferred because a high degree of orientation is obtained, the present invention favors the use of an aqueous dispersing medium for reducing the burden on the environment. To compensate for a drop of degree of orientation due to the use of an aqueous dispersing
20 medium, a dispersant is preferably incorporated into the molding slurry. The dispersant used herein is preferably an organic compound having hydroxyl and carboxyl groups or a neutralized salt thereof or a lactone thereof, an organic compound having a hydroxymethylcarbonyl group, or an
25 organic compound having an enol type hydroxyl group dissociable as an acid or a neutralized salt thereof.

Understandably, when the non-aqueous dispersing medium is used, it is obtained by adding a surfactant such as oleic acid to an organic solvent such as toluene or
30 xylene as described in JP-A 6-53064. The use of such a dispersing medium allows a high degree of magnetic orientation of about 98% at maximum to be accomplished even when difficult-to-disperse ferrite particles of submicron size are used.

35 The above-described organic compounds are those having 3 to 20 carbon atoms, preferably 4 to 12 carbon

atoms, and having hydroxyl groups attached to at least 50% of the carbon atoms other than the carbon atom forming a double bond with an oxygen atom. If the number of carbon atoms is 2 or less, the effect of improving a degree of orientation becomes insufficient. Also, the effect becomes insufficient with organic compounds of at least 3 carbon atoms, but having hydroxyl groups attached to less than 50% of the carbon atoms other than the carbon atom forming a double bond with an oxygen atom. The bonding proportion of hydroxyl groups is limited for the above-described organic compounds, but not applied to the dispersants themselves. For lactones of organic compounds having hydroxyl and carboxyl groups (i.e., hydroxycarboxylic acids) as the dispersant, for example, the limited bonding proportion of hydroxyl groups is applied to the hydroxycarboxylic acids themselves, but not to the lactones.

The basic skeleton of the above organic compounds may be chain or cyclic and be saturated or contain unsaturated bonds.

Illustratively, hydroxycarboxylic acids or neutralized salts thereof or lactones thereof are preferred as the dispersant. Especially preferred are gluconic acid (C=6, OH=5, COOH=1) or a neutralized salt thereof or lactone thereof, lactobionic acid (C=12, OH=8, COOH=1), tartaric acid (C=4, OH=2, COOH=2) or a neutralized salt thereof, and glucoheptonic acid γ -lactone (C=7, OH=5). Of these, gluconic acid or a neutralized salt thereof or lactone thereof is preferable for the augmented effect of improving the degree of orientation and low cost.

Sorbose is preferable as the organic compound having a hydroxymethylcarbonyl group.

Ascorbic acid is preferable as the organic compound having an enol type hydroxyl group dissociable as an acid.

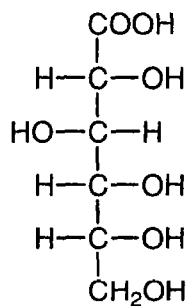
It is noted that citric acid or a neutralized salt thereof can be used as the dispersant in the practice of the invention. Citric acid has hydroxyl and carboxyl

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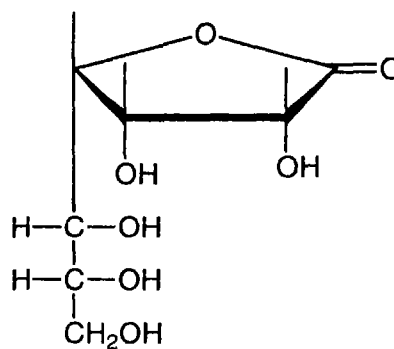
groups, but does not satisfy the requirement that hydroxyl groups are attached to at least 50% of the carbon atoms other than the carbon atom forming a double bond with an oxygen atom. Nevertheless, the effect of improving the
5 degree of orientation is ascertained.

Some of the preferred dispersants described above are illustrated below by their structure.

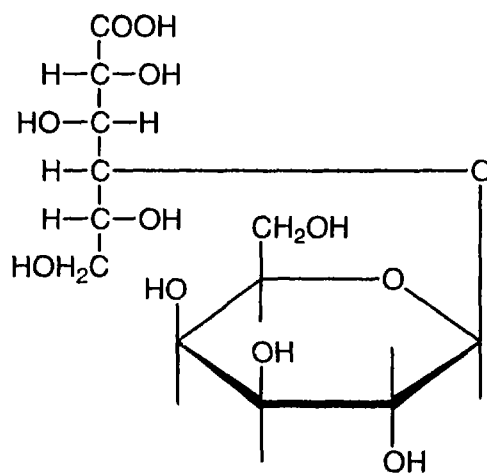
D - gluconic acid



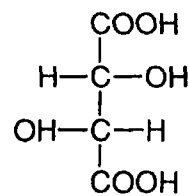
α - D - glucoheptonic acid
 γ - lactone



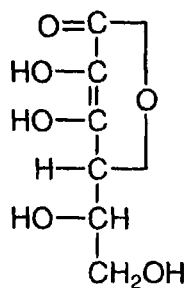
lactobionic acid



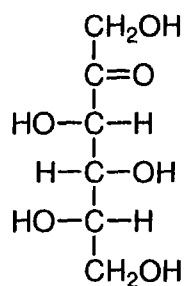
(R , R) - tartaric acid



ascorbic acid



L - (-) - sorbose



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The degree of orientation achieved by magnetic field orientation is affected by the pH value of the slurry. More particularly, at too low pH, the degree of orientation becomes lower and the remanence after sintering is affected thereby. When a compound which exhibits acid properties in an aqueous solution, for example, hydroxycarboxylic acid is used as the dispersant, the resulting slurry has a low pH. Accordingly, it is preferred to adjust the pH of the slurry as by adding a basic compound along with the dispersant.

10 The preferred basic compounds are ammonia and sodium hydroxide. Ammonia may be added as ammonia water. The use of a sodium salt of hydroxycarboxylic acid is also effective in preventing pH lowering.

When SiO_2 and CaCO_3 are added as the raw materials, the use of hydroxycarboxylic acid or a lactone thereof as the dispersant allows SiO_2 and CaCO_3 to be carried over along with the supernatant of the slurry mainly during preparation of the molding slurry, resulting in a drop of HcJ and a loss of the desired performance. Also, if the pH of the slurry is increased as by adding the basic compound, the carry-over amount of SiO_2 and CaCO_3 is increased. By contrast, the use of a calcium salt of hydroxycarboxylic acid suppresses the carry-over of SiO_2 and CaCO_3 . It is noted that when the basic compound is added or when a sodium salt is used as the dispersant, any shortage of the SiO_2 and CaO contents in the magnet can be prevented by adding SiO_2 and CaCO_3 in excess of the desired composition. When ascorbic acid is used, the carry-over of SiO_2 and CaCO_3 is little ascertained.

30 For the above reason, the slurry is preferably at pH 7 or higher, and more preferably at pH 8 to 11.

No particular limit is imposed on the type of the neutralized salt used as the dispersant. Any of calcium, sodium and other salts may be used although a calcium salt is preferably used for the above reason. If a sodium salt is used as the dispersant or ammonia water is added, there

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arise problems including the carry-over of auxiliary components and a likelihood for a compact or sintered body to crack.

It is understood that a mixture of two or more dispersants may be used.

The amount of the dispersant added is preferably 0.05 to 3.0% by weight, more preferably 0.10 to 2.0% by weight based on the raw material powder. Too less amounts of the dispersant would achieve an insufficient improvement in the degree of orientation. With too much amounts of the dispersant, a compact or sintered body is likely to crack.

It is noted that if the dispersant is a compound ionizable in an aqueous solution, for example, an acid or metal salt, the amount of the dispersant added is calculated as an ion. That is, the addition amount is calculated as the organic moiety with the hydrogen ion or metal ion removed. When the dispersant is a hydrate, the addition amount is calculated with the water of crystallization removed. For example, when the dispersant used is calcium gluconate monohydrate, the addition amount is calculated as a gluconate ion.

Also, when the dispersant is a lactone or contains a lactone, the addition amount is calculated as a hydroxycarboxylate ion provided that the lactone opens all its rings and converts into a hydroxycarboxylic acid.

The time when the dispersant is added is not critical. The dispersant may be added during dry coarse pulverization or during preparation of a pulverizing slurry subject to wet pulverization, or in divided portions, with one portion during dry coarse pulverization and the remaining portion during wet pulverization. Alternatively, the dispersant may be added under agitation after wet pulverization. Any of these procedures results in the molding slurry containing the dispersant therein, with which the effect is accomplished. It is understood that a higher degree of orientation is obtainable when the dispersant is added

during pulverization, especially dry coarse pulverization. It is believed that a vibratory mill used for dry coarse pulverization imparts greater energy to particles and elevates the temperature of particles higher than a ball mill used for wet pulverization, so that the particles may take a sufficient state for chemical reaction to proceed. It is thus believed that if the dispersant is added during dry coarse pulverization, a more amount of the dispersant is adsorbed on surfaces of particles and as a result, a higher degree of orientation is obtainable. In fact, on measurement of the amount of the dispersant remaining in the molding slurry (which is deemed substantially equal to the adsorption amount), the ratio of the residual amount to the addition amount is higher when the dispersant is added during dry coarse pulverization than when the dispersant is added during wet pulverization. It is noted that in case the dispersant is added in divided portions, the amounts of respective portions are determined such that the total addition amount may fall in the preferred range.

After the wet shaping step, the compact is dried and heat treated in air or nitrogen, preferably at a temperature of 100 to 500°C for fully decomposing off the dispersant added. The drying and heat treating steps may be continuously carried out. If the compact is rapidly heated before it is fully dried, cracks form in the compact. It is then preferred to slowly heat the compact from room temperature to about 100°C, at which temperature range the compact is fully dried. The heat treatment is followed by firing, obtaining a sintered ferrite magnet. The holding temperature during the firing step is preferably 1,150 to 1,250°C, and more preferably 1,160 to 1,220°C, and the time of holding at the temperature is preferably 0.5 to 3 hours. As previously described, the holding step is not involved in continuous furnaces or the like, and even in that case, the ferrite magnet of the invention has satisfactory performance.

The magnet of the invention preferably has a mean crystal grain size of up to 2 μm , more preferably up to 1 μm , and most preferably 0.5 to 1.0 μm . The magnet of the invention exhibits a fully high coercivity even when the
5 mean crystal grain size is in excess of 1 μm . The crystal grain size can be measured by means of a scanning electron microscope. The resistivity is usually $10^0 \Omega\text{m}$ or higher.

It is noted that a sintered magnet can also be obtained by disintegrating the compact by a crusher or the
10 like, classifying the granules through sieves to collect a fraction of magnetic field orienting granules having a mean particle size of about 100 to 700 μm , and dry shaping the fraction in a magnetic field, followed by sintering.

Because of the inclusion of elements R and M, the
15 ferrite magnet of the invention has a high coercivity and a high remanence. More particularly, provided that the inventive magnet is of the same shape as conventional ferrite magnets free of the relevant elements, the inventive magnet, which generates a more magnetic flux
20 density, contributes to improvements in the performance of applied products, for example, the achievement of higher torque in the case of motors, and the achievement of sound quality with improved linearity due to the strengthened magnetic circuit in the case of speakers or headphones.
25 Also, if applied products may have the same function as the prior art ferrite magnets, the dimensions (thickness) of magnets can be reduced (thinner), contributing to size and weight reductions (flattening). Also, in the case of motors using wound electromagnets as the field magnet, the
30 ferrite magnets can substitute for the electromagnets, contributing to weight reduction, manufacturing process shortening and cost reduction. Because of the improved temperature properties of coercivity (H_cJ), it becomes possible to use the ferrite magnets in low-temperature
35 environments where conventional ferrite magnets have the

risk of low-temperature demagnetization (permanent demagnetization). The reliability of products used in cold districts and high altitude zones is significantly improved. Even when firing conditions are inconsistent, the invention
 5 permits ferrite magnets having excellent properties as mentioned above to be produced on a mass scale. The invention provides a great contribution to cost reduction as by permitting the use of a continuous gas furnace.

The magnet of the invention is worked into the
 10 desired shape and finds a wide variety of applications as described below.

The magnets are advantageously used in automotive motors for fuel pumps, power windows, ABS, fans, wipers, power steering, active suspensions, starters, door locks
 15 and mirrors; motors for business machines and audio-visual equipment such as FDD spindles, VCR capstans, VCR rotary heads, VCR reels, VCR loading, VCR camera capstans, VCR camera rotary heads, VCR camera zoom, VCR camera focus, tape cassette capstans, CD, LD, and MD drive spindles, CD,
 20 LD and MD loading, CD and LD optical pickups; motors for household appliances such as air conditioner compressors, refrigerator compressors, electric tools, fans, microwave oven fans, microwave oven plate rotation, mixer driving, dryer fans, shaver driving, and power toothbrushes; motors
 25 for factory automation equipment such as robot shafts, connection drives, robot drives, machine tool table drives, and machine tool belt drives; and miscellaneous units including motorcycle generators, speaker magnets, headphone magnets, magnetron tubes, MRI magnetic field generating
 30 systems, CD-ROM clamps, distributor sensors, ABS sensors, fuel/oil level sensors, and magnet latches.

EXAMPLE

Example 1

35 Powders of SrCO_3 , Fe_2O_3 , SiO_2 and CaCO_3 as raw materials were blended, mixed and pulverized for 2 hours in

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a wet attritor, dried and classified, obtaining granules.

The granules were calcined in air at 1,250°C for 3 hours, obtaining a calcined material. The composition of the calcined material as determined by fluorescent x-ray analysis is shown in Table 1-1.

Next, SiO_2 , CaCO_3 , lanthanum carbonate $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$, and cobalt oxide (a mixture of Co_3O_4 and CoO) as post-additives were added to the calcined material, and 0.6% by weight of calcium gluconate added to the mixture, followed by 20 minutes of dry pulverization in a batchwise vibratory rod mill, obtaining a coarse pulverized powder. Next, Fe_2O_3 was added to the coarse pulverized powder, followed by 40 hours of wet pulverization in a ball mill. By concentrating to a concentration of about 78%, a molding slurry was obtained.

The molding slurry was compression molded while removing water therefrom, obtaining a compact of 30 mm diameter and 18 mm high. During the compression molding, a magnetic field of about 13 kOe was applied in the compression direction. The molding pressure was 0.4 t/cm².

Next, the compact was fired into a sintered magnet and worked on the upper and lower surfaces. Then the magnetic properties and sintering properties of the sintered magnet relative to the oxygen partial pressure in the firing atmosphere were examined. Firing was carried out in a mixed gas atmosphere consisting of oxygen and nitrogen gases (1 atm.) while the oxygen partial pressure in the firing atmosphere was changed by controlling the flow rates of the gases. The heating rate and cooling rate in the firing step were 5°C/min, the firing temperature was 1,220°C, and the time of holding at the firing temperature (holding time) was 1 hour.

The composition as determined by fluorescent x-ray analysis of the sintered magnet which was evaluated for magnetic properties is shown in Table 1-2. It is understood that the composition shown in Table 1-2 is that

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of a test sample obtained by firing a molding slurry in air
at 1,000°C for 1 hour.

Table 1-1

	Content mol%									
	SrO	BaO	CaO	La ₂ O ₃	Fe ₂ O ₃	CoO	MnO	Al ₂ O ₃	Cr ₂ O ₃	SiO ₂
Calcined material	12.69	0.06	0.17	—	85.89	—	0.63	0.13	0.03	0.40

Table 1-2

Composition	Content mol%										{A+R-(Fe+M) /12}
	SrO	BaO	CaO	La ₂ O ₃	Fe ₂ O ₃	CoO	MnO	Al ₂ O ₃	Cr ₂ O ₃	SiO ₂	
E 1-1	10.11	0.12	2.66	1.28	81.09	2.61	0.62	0.08	0.10	1.33	1.23
E 1-2	10.51	0.12	2.53	1.33	80.24	2.69	0.61	0.09	0.10	1.78	1.20
CE 1-1	10.64	0.12	2.30	1.35	81.06	2.72	0.62	0.08	0.09	1.02*	1.91
CE 1-2	11.21	0.11	1.47	1.42	81.05	2.88	0.60	0.09	0.10	1.07*	1.68
CE 1-3	11.78	0.12	0.49	1.49	80.37	3.05	0.59	0.09	0.10	1.92	0.85*
CE 1-4	10.52	0.12	3.02	1.33	80.12	2.72	0.61	0.09	0.09	1.38	1.93*

*: outside the specific range

With respect to the magnets of the composition shown in Table 1-2, the relationship of magnetic properties (coercivity H_cJ , remanence B_r and squareness ratio H_k/H_cJ) to oxygen partial pressure pO_2 during firing is shown in the graph of FIG. 1.

As seen from FIG. 1, within the composition of the inventive Examples, that is, the composition in which the atomic ratio $\{A+R-(Fe+M)/12\}/Si$ and SiO_2 content fall within the specific ranges, magnetic properties at least comparable to firing in air are obtained even when firing is done in an atmosphere having an oxygen partial pressure of 0.05 atm., and little degradation of magnetic properties was ascertained even when firing is done in an atmosphere having an oxygen partial pressure of 0.01 atm. More illustratively, when the oxygen partial pressure is decreased from 0.20 atm. to 0.01 atm., a coercivity drop of more than about 400 Oe is ascertained with the composition in which either one of the atomic ratio $\{A+R-(Fe+M)/12\}/Si$ and SiO_2 content falls outside the specific range. In particular, for the comparative example composition with which a coercivity surpassing that of the inventive example composition is obtained at an oxygen partial pressure of 0.20 atm., a coercivity drop as large as about 1500 Oe as a result of a lowering of oxygen partial pressure is ascertained. In contrast, the coercivity drop associated with the inventive example composition is less than about 150 Oe, and no drop of remanence is found. These results demonstrate the effectiveness of the invention.

30 Example 2

Sintered magnets of the composition (as determined by fluorescent x-ray analysis) shown in Table 2-2 were prepared as in Example 1 except that calcined materials of the composition shown in Table 2-1 were used. The other exception is that the oxygen partial pressure in the firing atmosphere was fixed at 0.05 atm. while the firing

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temperature was varied.

Table 2-1

	Content mol%									
	SrO	BaO	CaO	La ₂ O ₃	Fe ₂ O ₃	CoO	MnO	Al ₂ O ₃	Cr ₂ O ₃	SiO ₂
Calcined material	12.69	0.06	0.17	—	85.89	—	0.63	0.13	0.03	0.40

Table 2-2

Composition	Content mol%										{A+R-(Fe+M) /12}
	SrO	BaO	CaO	La ₂ O ₃	Fe ₂ O ₃	CoO	MnO	Al ₂ O ₃	Cr ₂ O ₃	SiO ₂	
E 2	10.09	0.05	2.92	1.33	80.77	2.57	0.60	0.11	0.10	1.46	1.34
CE 2-1	10.12	0.05	2.67	1.33	81.22	2.58	0.61	0.13	0.11	1.18*	1.40
CE 2-2	10.09	0.05	2.60	1.33	81.06	2.59	0.60	0.13	0.09	1.46	1.09*

*: outside the specific range

For the magnets of the composition shown in Table 2-2, the relationship of magnetic properties to the firing temperature is shown in the graph of FIG. 2.

As seen from FIG. 2, the comparative example composition experiences large variations in coercivity when the firing temperature was changed. The inventive example composition, that is, the composition in which the atomic ratio $\{A+R-(Fe+M)/12\}/Si$ and SiO_2 content fall within the specific ranges experiences less variations in coercivity than the comparative example composition, that is, the composition in which either one of the atomic ratio $\{A+R-(Fe+M)/12\}/Si$ and SiO_2 content falls outside the specific range.

15 Example 3

Sintered magnets of the composition (as determined by fluorescent x-ray analysis) shown in Table 3-2 were prepared as in Example 1 except that calcined materials of the composition shown in Table 3-1 were used. The other exception is that the oxygen partial pressure in the firing atmosphere was fixed at 0.05 atm. and the firing temperature was fixed at 1,220°C. It is noted that the amounts of elements other than Ca were substantially equal among

25 group A of Example 3A-1, Example 3A-2 and Comparative Example 3A,

group B of Example 3B-1, Example 3B-2 and Comparative Example 3B, and

30 group C of Example 3C-1, Example 3C-2 and Comparative Example 3C,

while the amount of Ca was changed to change the quantity of A and the atomic ratio $\{A+R-(Fe+M)/12\}/Si$.

Table 3-1

	Content mol%									
	SrO	BaO	CaO	La ₂ O ₃	Fe ₂ O ₃	CoO	MnO	Al ₂ O ₃	Cr ₂ O ₃	SiO ₂
Calcined material	13.54	0.15	0.41	—	84.21	—	0.65	0.09	0.12	0.83

Table 3-2

Composition	Content mol%										{A+R-(Fe+M) /12}
	SrO	BaO	CaO	La ₂ O ₃	Fe ₂ O ₃	CoO	MnO	Al ₂ O ₃	Cr ₂ O ₃	SiO ₂	
E 3A-1	9.99	0.12	3.25	1.26	80.35	2.56	0.61	0.08	0.12	1.66	1.32
E 3A-2	9.94	0.12	3.83	1.26	79.83	2.56	0.61	0.08	0.11	1.66	1.69
CE 3A	9.89	0.11	4.40	1.26	79.36	2.56	0.60	0.08	0.10	1.64	2.07*
E 3B-1	11.10	0.11	1.71	1.40	80.17	2.87	0.59	0.09	0.10	1.86	1.10
E 3B-2	11.04	0.11	2.33	1.39	79.66	2.87	0.59	0.08	0.09	1.84	1.45
CE 3B	11.16	0.11	1.06	1.41	80.73	2.88	0.60	0.09	0.11	1.85	0.74*
E 3C-1	10.58	0.12	2.07	1.35	80.94	2.73	0.62	0.09	0.10	1.40	1.19
E 3C-2	10.56	0.12	2.55	1.34	80.55	2.72	0.61	0.08	0.09	1.38	1.58
CE 3C	10.52	0.12	3.02	1.33	80.12	2.72	0.61	0.09	0.09	1.38	1.93*

*: outside the specific range

For the magnets of the composition shown in Table 3-2, the relationship of magnetic properties to the atomic ratio $\{A+R-(Fe+M)/12\}/Si$ is shown in the graph of FIG. 3, and the relationship of magnetic properties to the CaO content shown in the graph of FIG. 4.

As seen from FIG. 3, a comparison of magnetic properties among groups A, B and C reveals that a very high coercivity is obtained when the atomic ratio falls within the specific range prescribed by the invention. That is, the invention ensures that the magnet has a high coercivity when fired at a low oxygen partial pressure. Referring to the coercivity graph of FIG. 4, the CaO content of Comparative Example 3C is less than the inventive example composition of group A, but more than the inventive example compositions of groups B and C. That is, the CaO content of Comparative Example 3C is not excessive or short, as compared with the inventive example compositions.

It was believed in the prior art that the coercivity of strontium ferrite magnets is largely affected by the content of CaO as an additive. It is seen from FIGS. 3 and 4 that when fired at a low oxygen partial pressure, the coercivity widely varies depending on the atomic ratio $\{A+R-(Fe+M)/12\}/Si$ rather than the CaO content.

It was found that when Bi substitutes for part of La in the strontium ferrite magnets in the above Examples, the addition of Bi is effective for lowering the calcining temperature. That is, the calcining temperature at which optimum properties are obtainable is shifted to a lower temperature side without substantial degradation of coercivity. Similar effects to the above Examples were found when sintered magnets of the composition in which part of La was replaced by another rare earth element were prepared.

Although lanthanum carbonate and cobalt oxide were added to the calcined materials as the post-additives in the above Examples, similar effects to the above Examples

were found even when the same amounts of these compounds were added to the starting materials rather than as the post-additives. However, the effects were slightly less than the post addition.

5 The sintered magnets prepared in the above Examples were measured for Curie temperature by the following procedure. First, the sintered magnet was machined into a test sample in the form of a cylinder having a diameter of 5 mm and a height of 6.5 mm in the direction of c axis.

10 Next, the sample was magnetized at 25°C by VSM by applying a magnetic field of about 20 kOe in the direction of c axis. Next, with the magnetic field generating current flow in the VSM set zero (a magnetic field of about 50 Oe was generated by the residual magnetization of magnetic

15 poles), the residual magnetization of the sample in the direction of c axis and the temperature of the sample were measured at the same time. A σ -T curve as shown in FIG. 6 was depicted. The heating of the sample was carried out by a heater disposed around the sample. The heating rate was

20 about 10°C/min. From the σ -T curve thus obtained, Curie temperatures were determined according to the above-described procedure. As a result, the magnets prepared in the above Examples was found to have two Curie

25 temperatures, with the lower Curie temperature falling in the range of 430 to 445°C and the higher Curie temperature falling in the range of 450 to 460°C. The ratio (σ_l/σ_{RT}) of the magnetization (σ_l) at the lower Curie temperature to the magnetization (σ_{RT}) at 25°C was 2 to 10%. On analysis by x-ray diffractometry, the samples were found to have a M

30 type ferrite single phase.

Reference Example

Sintered ferrite magnets of the composition shown in Table 4 were prepared. It is noted that the strontium

35 ferrite magnet containing La and Co was prepared by the

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post-addition method. Firing was carried out in a mixed
gas atmosphere consisting of oxygen and nitrogen gases (1
atm.) while the oxygen concentration in the firing
atmosphere was changed by controlling the flow rates of the
5 gases. The oxygen concentration in the firing atmosphere
is plotted in FIG. 5. These sintered magnets were measured
for coercivity (H_cJ), with the results shown in FIG. 5.

Table 4

	Content mol%									
	SrO	BaO	CaO	La ₂ O ₃	Fe ₂ O ₃	CoO	MnO	Al ₂ O ₃	Cr ₂ O ₃	SiO ₂
LaCo-containing Sr ferrite	11.0	0.1	1.5	1.2	81.7	2.3	0.6	—	—	1.6
Sr ferrite	13.7	0.1	1.6	—	82.5	—	0.6	—	—	1.5

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As seen from FIG. 5, the coercivity of the Sr ferrite magnet containing La and Co widely varies depending on the oxygen concentration in the firing atmosphere whereas the coercivity of the prior art Sr ferrite magnet free of La and Co little depends on the oxygen concentration in the firing atmosphere. It is noted that the LaCo-containing magnet shown in FIG. 5 has an atomic ratio $\{A+R-(Fe+M)/12\}/Si$ outside the specific range prescribed by the invention.

As is evident from both the results shown in FIG. 5 and the results of the above Examples, the control of Si content and atomic ratio $\{A+R-(Fe+M)/12\}/Si$ exerts a unique effect only when applied to ferrite magnets containing elements R and M.

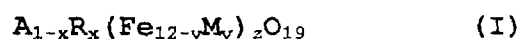
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CLAIMS:

1. A ferrite magnet having hexagonal ferrite as a major phase, comprising A, R, Fe, M and Si as metal elements, wherein A represents at least one element selected from the group consisting of Sr, Ba, Ca and Pb; R represents at least one element selected from rare earth elements (inclusive of Y) and Bi; and M represents the element Co or a mixture consisting of Co and at least one element selected from the group consisting of Mn, Al, Cr and Ni, wherein the proportion of Co in M is at least 10 at %; and wherein the content of SiO₂ is 1.3 to 2.0 mol% when the contents of metal oxides are determined provided that the metal elements are present as oxides, and the atomic ratio given by
- $$\{A + R - (Fe+M)/12\}/Si$$
- is from 1.1 to 1.9.
2. The ferrite magnet of claim 1 wherein the proportions of metal elements A, R, Fe, and M, each in total, are:
- A: 1 to 13 at%,
R: 0.05 to 10 at%,
Fe: 80 to 95 at%, and
M: 0.1 to 5 at%
- based on the entire amount of the metal elements.
3. The ferrite magnet of claim 1 or 2 which has at least two distinct Curie temperatures, which fall in the range of 400 to 480°C and differ from each other by at least 5°C.

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4. The ferrite magnet of any one of claims 1 to 3, wherein the ferrite composition is represented by the following formula (I):



- 5 wherein $0.04 \leq x \leq 0.9$,
 $0.04 \leq y \leq 1.0$,
 $0.8 \leq x/y \leq 5$, and
 $0.7 \leq z < 1$.

- 10 5. A method for preparing the ferrite magnet of any one of claims 1 to 4, comprising the step of firing a molded body of a raw material powder to form a sintered magnet, during which step the oxygen partial pressure in the firing atmosphere fluctuates.

15

6. The method of claim 5 wherein the oxygen partial pressure in the firing atmosphere lowers below 0.15 atm. for at least a duration in the firing step.

- 20 7. A method for preparing the ferrite magnet of any one of claims 1 to 4, comprising the step of firing a molded body of a raw material powder to form a sintered magnet, during which step firing temperature fluctuates.

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8. The method of any one of claims 5 to 7 wherein at least one compound containing at least one of the magnet constituent elements is added to a calcined material or particles containing hexagonal ferrite as a major phase, followed by molding and sintering.

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9. The method of claim 8 wherein the at least one of the magnet constituent elements is at least one element selected from the elements R and M.
- 5 10. The ferrite magnet substantially as hereinbefore described with reference to the examples and figures.