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### (54) RARE EARTH MAGNET

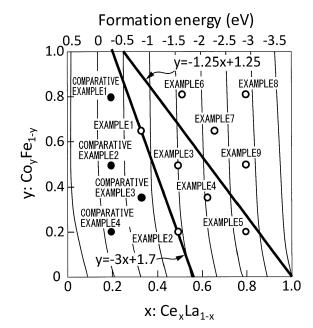
#### (57) [PROBLEM TO BE SOLVED]

To provide a rare earth magnet in which 1-5 phase is stabilized even when Ce is used for at least part of the rare earth element and part of Co is replaced with Fe, and a production method thereof.

#### [MEANS TO SOLVE THE PROBLEM]

A rare earth magnet having a composition represented by the formula:  $(Ce_xLa_{(1-x-w)}R'_w)_v(Co_y-Fe_{(1-y)})_{(100-v-z)}M_z$ , wherein R' is one or more rare earth elements other than Ce and La, M represents one or more members selected from the group consisting of a transition metal element other than Co and Fe, Ga, Al, Zn, and In, and an unavoidable impurity element, 0 < x < 1.0, 0 < y < 1.0,  $0 \le w \le 0.1$ ,  $7.1 \le v \le 20.9$ , and  $0 \le z \le 8.0$ , and satisfying, in the formula, the relationship of  $y \ge -3x + 1.7$ , and a production method thereof.

FIG. 1



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#### Description

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#### [TECHNICAL FIELD]

**[0001]** The present disclosure relates to a rare earth magnet and a production method thereof. The present disclosure relates to a rare earth magnet containing a magnetic phase having a composition represented by RT<sub>5</sub> (R is a rare earth element, and T is a transition metal element), and a production method thereof.

### [BACKGROUND ART]

**[0002]** Application of a permanent magnet is extended to a wide range of fields including electronics, information communication, medical care, machine tool field, industrial and automotive motors, etc. In addition, a requirement for reduction of carbon dioxide emission is increasing and due to, for example, spread of a hybrid car and energy saving in the industrial field as well as enhancement of power generation efficiency, it has been expected in recent years that a permanent magnet having higher properties be developed.

**[0003]** At present, an Nd-Fe-B magnet dominating the market as a high-performance magnet is used also as a drive motor magnet for HV/EHV. In response to the current trend of pursuing further size reduction and higher output of a motor, development of a new permanent magnet material is advancing.

**[0004]** As one of development of a material having a performance surpassing the Nd-Fe-B magnet, studies are being made on a rare earth magnet in which the magnetic phase is of a binary system of a rare earth element and a transition metal element.

**[0005]** For example, Patent Document 1 discloses a rare earth magnet having a composition represented by  $R(Fe_{(1-p)}Co_p)_qA_r$  (wherein R is one or more of Sm and Ce,  $0.1 \le p \le 0.6$ ,  $4 \le q \le 6$ , and 0.1 < r < 1.0), having a main phase of hexagonal  $CaCu_5$  structure, and having an interstitial atom.

#### [CITATION LIST]

#### [PATENT LITERATURE]

[0006] [Patent Literature 1] Japanese Unexamined Patent Publication) No. H4-371556

#### [SUMMARY OF INVENTION]

### [TECHNICAL PROBLEM]

**[0007]** As to the binary system of a rare earth element and a transition metal element, magnetic phases in which the molar ratio of a rare earth element and a transition metal element is 1:2, 1:5, 1:12, 2:7, 2:17, etc. are known. In the following description, these magnetic phases are sometimes referred to as 1-2 phase, 1-5 phase, 1-12 phase, 2-7 phase, 2-17 phase, etc., respectively.

[0008] In the binary system of a rare earth element and a transition metal element, it is known that when the rare earth element is Sm and the transition metal element is Co, 1-5 phase is thermally more stable than 1-2 phase, 1-12 phase, 2-7 phase and 2-17 phase. Accordingly, a rare earth magnet containing Sm and Co contains a lot of SmCo<sub>5</sub> phases.

[0009] Since Sm is high in rarity among rare earth elements, it is attempted to replace part or whole of Sm with a rare earth element lower in rarity than Sm.

[0010] In the rare earth magnet disclosed in Patent Document 1, at least part of Sm is replaced with Ce. However, (Sm, Ce)Co<sub>5</sub> is lower in saturation magnetization than SmCo<sub>5</sub>. In order to compensate for saturation magnetization reduced by substitution of Sm with Ce, at least part of Co is replaced with Fe. However, when Co is replaced with Fe, (Sm, Ce)(Co, Fe)<sub>5</sub> becomes extremely unstable, compared to (Sm, Ce)Co<sub>5</sub>. As a result, the content of 1-5 phase represented by (Sm, Ce)(Co, Fe)<sub>5</sub> in the rare earth magnet decreases significantly, and the content of 1-2 phase represented by (Sm, Ce)(Co, Fe)<sub>2</sub> increases significantly. From these fact, both saturation magnetization and anisotropy field are reduced. Accordingly, in the rare earth magnet of Patent Document 1, even when at last part of Co is replaced with Fe, in order to stabilize 1-5 phase, C and N are introduced as interstitial atoms into 1-5 phase.

[0011] However, it is difficult to introduce C and N into the core part of 1-5 phase, and therefore, it is difficult to stabilize 1-5 phase in the entire rare earth magnet. In addition, 1-5 phase having introduced thereinto C and N is readily decomposed at 400°C or more, and thus high-temperature stability is poor.

**[0012]** From these facts, the present inventors have uncovered a problem that when Ce is used for at least part of the rare earth element and part of Co is replaced with Fe, 1-5 phase and 1-2 phase become an unstable phase and a stable phase, respectively, and the rare earth magnet can hardly contain 1-5 phase. The present inventors have also uncovered

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a problem that even when C and N are introduced as interstitial atoms into the magnetic phase so as to stabilize 1-5 phase, the 1-5 phase cannot be sufficiently stabilized and 1-5 phase is decomposed at high temperatures.

**[0013]** The present disclosure has been made to solve the problems above, and an object thereof is to provide a rare earth magnet in which 1-5 phase is stabilized even when Ce is used for at least part of the rare earth element and part of Co is replaced with Fe, and a production method thereof.

### [SOLUTION TO PROBLEM]

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[0014] As a result of many intensive studies to attain the object above, the present inventors have accomplished the rare earth magnet of the present disclosure and the production method thereof. The gist thereof is as follows.

<1> A rare earth magnet having a composition represented by the formula:  $(Ce_xLa_{(1-x-w)}R'_w)_v(Co_yFe_{(1-y)})_{(100-v-z)}M_z$ , wherein R' is one or more rare earth elements other than Ce and La,

M represents one or more members selected from the group consisting of a transition metal element other than Co and Fe, Ga, Al, Zn, and In, and an unavoidable impurity element,

	0 <x<1.0,< td=""></x<1.0,<>					
20	0 <y<1.0,< td=""></y<1.0,<>					
25	0≤w≤0.1,					
	7.1≤v≤20.9,					
30	and					
	0≤z≤8.0,					
35	and satisfying, in the formula, the relationship of $y \ge -3x + 1.7$ . <2> The rare earth magnet according to item <1>, further satisfying, in the formula, the relationship of $y \le -1.25x + 1.25$ . <3> The rare earth magnet according to item <1> or <2>, wherein x satisfies $0.3 \le x \le 0.9$ . <4> The rare earth magnet according to item <1> or <2>, wherein x satisfies $0.6 \le x \le 0.9$ .					
40	<5> The rare earth magnet according to any one of items <1> to <4>, wherein y satisfies 0.1≤y≤0.9. <6> The rare earth magnet according to any one of items <1> to <4>, wherein y satisfies 0.1≤y≤0.7. <7> The rare earth magnet according to any one of items <1> to <4>, wherein y satisfies 0.3≤y≤0.9. <8> The rare earth magnet according to any one of items <1> to <4>, wherein y satisfies 0.3≤y≤0.7. <8> The rare earth magnet according to any one of items <1> to <4>, wherein y satisfies 0.3≤y≤0.7. <9> A method for producing a rare earth magnet, comprising:					
45	preparing a molten metal having a composition represented by the formula: $(Ce_xLa_{(1-x-w)}R'_w)_v(Co_y-Fe_{(1-y)})_{(100-v-z)}M_z$ , wherein R' is one or more rare earth elements other than Ce and La, M represents one or more members selected from the group consisting of a transition metal element other than Co and Fe, Ga, Al, Zn, and In, and an unavoidable impurity element,					
50	0 <x<1.0,< td=""></x<1.0,<>					
	0 <y<1.0,< td=""></y<1.0,<>					
55	0≤w≤0.1,					

## $7.1 \le v \le 20.9$

and

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## $0 \le z \le 8.0$ ,

and satisfying, in the formula, the relationship of y≥-3x+1.7, and 10 quenching the molten metal at a rate of  $1\times10^2$  to  $1\times10^7$  K/sec to obtain a ribbon.

- <10> The method according to item <9>, wherein in the formula, the relationship of y≤-1.25x+1.25 is further satisfied.
- <11> The method according to item <9> or <10>, wherein x satisfies 0.3≤x≤0.9.
- <12> The method according to item <9> or <10>, wherein x satisfies 0.6≤x≤0.9.
- <13> The method according to any one of items <9> to <12>, wherein y satisfies  $0.1 \le y \le 0.9$ .
- <14> The method according to any one of items <9> to <12>, wherein y satisfies  $0.1 \le y \le 0.7$ .
- <15> The method according to any one of items <9> to <12>, wherein y satisfies 0.3≤y≤0.9.
- <16> The method according to any one of items <9> to <12>, wherein y satisfies 0.3≤y≤0.7.

#### 20 [ADVANTAGEOUS EFFECTS OF INVENTION]

[0015] According to the present disclosure, a rare earth magnet where Ce and La are caused to be present together in a rare earth magnet having a binary system of a rare earth element and a transition metal element and the 1-5 phase is thereby stabilized even when part of Co is replaced with Fe, and a production method thereof, can be provided.

#### [BRIEF DESCRIPTION OF DRAWINGS]

#### [0016]

[Fig. 1] Fig 1 is a diagram illustrating the results of Table 1 together in a formation energy map.

[Fig. 2] Fig. 2 is a diagram illustrating the results of Table 1 together in a total magnetic moment map.

[Fig. 3] Fig. 3 is a schematic diagram of an apparatus used for a strip casting method.

[Fig. 4] Fig. 4 is a diagram illustrating the XRD analysis results regarding samples of Examples 1 to 5.

[Fig. 5] Fig. 5 is a diagram illustrating the XRD analysis results regarding samples of Comparative Examples 1 to 4.

[Fig. 6] Fig. 6 is a diagram illustrating the results of calculating formation energy of various magnetic phases.

[Fig. 7] Fig. 7 is a diagram illustrating the XRD analysis results regarding samples of Examples 6 to 9.

#### [DESCRIPTION OF EMBODIMENTS]

40 [0017] The embodiments of the rare earth magnet of the present disclosure and the production method thereof are described in detail below. However, the embodiments described below should not be construed to limit the rare earth magnet of the present disclosure and the production method thereof.

[0018] In a rare earth magnet with a binary system of a rare earth element and a transition metal element, when the transition metal element is Co, 1-5 phase is stabilized. When the rare earth element of 1-5 phase is a rare earth element other than a light rare earth element, such as Sm, Nd, Pr, Dy and Tb, the 1-5 phase exhibits good saturation magnetization. [0019] Sm, Nd, Pr, Dy, Tb, etc. are high in rarity, compared with a light rare earth element such as Ce, and therefore, Sm, Nd, Pr, Dy, Tb, etc. is replaced with Ce (hereinafter, sometimes referred to as "Ce substitution"). The saturation magnetization of 1-5 phase is reduced by Ce substitution. In order to compensate for the reduction of saturation magnetization, Co is replaced with Fe (hereinafter, sometimes referred to as "Fe substitution"). Fe substitution enhances saturation magnetization but lets 1-5 phase be an unstable phase and 1-2 phase be a stable phase, and the content of 1-5 phase in the rare earth magnet decreases. Compared with 1-5 phase, the 1-2 phase is poor in both saturation magnetization and anisotropy field.

[0020] For this reason, when Ce is used as the rare earth element, it has been conventionally difficult to obtain a rare earth magnet containing 1-5 phase.

[0021] The present inventors have found that in the case where part of Co is replaced with Fe in a rare earth magnet, when Ce and La are caused to be present together, CeFe<sub>2</sub> phase can be rendered unstable and (Ce, La)(Co, Fe)<sub>5</sub> phase can be rendered stable. The present inventors have also found that the ratio (molar ratio) of Ce and La and the

ratio (molar ratio) of Co and Fe, at which 1-5 phase is stabilized, can be estimated from the magnetic phase formation energy (Formation Energy). Incidentally, (Ce, La)(Co, Fe)<sub>5</sub> phase indicates a phase where in the  $CeCo_5$  phase, part of Ce is replaced with La and part of Co is replaced with Fe.

[0022] In the present description, the "1-5 phase" indicates a phase where when the magnetic phase is represented, for example, by (Ce, La)(Co, Fe)<sub>t</sub> phase, t is from 4 to 6 in the entire magnetic phase. Here, t being 4 to 6 means that incomplete 1-5 phase may be contained in part of the magnetic phase. For this reason, t is preferably from 4.5 to 5.5. Accordingly, "a magnetic phase represented by (Ce, La)(Co, Fe)<sub>t</sub> (wherein t is from 4 to 6, preferably from 4.5 to 5.5)" and "a magnetic phase containing (Ce, La)(Co, Fe)<sub>5</sub> phase" have the same meaning.

**[0023]** The rare earth magnet of the present disclosure, which has been accomplished based on the findings, etc. described hereinbefore, and the production method thereof are described below.

<<Rare Earth Magnet>>

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[0024] The rare earth magnet of the present disclosure has a composition represented by the formula:  $(Ce_{x^{-1}} La_{(1-x-w)}R'_{w})_{v}(Co_{y}Fe_{(1-y)})_{(100-v-z)}M_{z}$ . This formula represents the entire composition of the rare earth magnet of the present disclosure.

**[0025]** In the formula above, Ce stands for cerium, La stands for lanthanum, R' represents one or more rare earth elements other than Ce and La, Co stands for cobalt, and Fe stands for iron. M represents one or more members selected from the group consisting of a transition metal element other than Co and Fe, Ga, Al, Zn, and In, and an unavoidable impurity element. Ga stands for gallium, Al stands for aluminum, Zn stands for zinc, and In stands for indium. The transition metal element is an element between Group 3 element and Group 11 element in the periodic table.

**[0026]** x and w are content ratios (molar ratio) of Ce and R', respectively, assuming the entire rare earth site represented by  $Ce_xLa_{(1-x-w)}R'_w$  is 1. In the rare earth site, La is the remainder after removing Ce and R'.

[0027]  $\dot{y}$  is the content ratio (molar ratio) of Co, assuming the entire iron group site represented by  $Co_yFe_{(1-y)}$  is 1. In the iron group site, Fe is the remainder after removing Co.

**[0028]** v and z are contents (at%) of rare earth site and M, respectively, assuming the rare earth magnet of the present disclosure as a whole is 100 at%. In the formula above, the content (at%) of the iron group site is 100-v-z, and therefore in the rare earth magnet as a whole, the iron group site is the remainder after removing rare earth site and M.

[0029] The constituent elements of the rare earth magnet represented by the formula above are described below.

<Ce>

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**[0030]** Ce is a rare earth element and is an element essential for the rare earth magnet of the present disclosure, because it develops properties as a permanent magnet. Ce is a light rare earth element and is therefore low in rarity, compared with a medium rare earth element and a heavy rare earth element. In conventional rare earth magnets, when a light rare earth element such as Ce is used alone, it has been difficult to contain 1-5 phase in the rare earth magnet. However, in the rare earth magnet of the present disclosure, 1-5 phase is stabilized by causing Ce and La to be present together, and 1-5 phase can thereby contain in the rare earth magnet.

[0031] In the present description, the rare earth element includes 17 elements of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. Of these, Sc, Y, La, and Ce are a light rare earth element, Pr, Nd, Pm, Sm, Eu, and Gd are a medium rare earth element, and Tb, Dy, Ho, Er, Tm, Yb, and Lu are a heavy rare earth element. Incidentally, in general, the rarity of the heavy rare earth element is high, and the rarity of the light rare earth element is low. The rarity of the medium rare earth element is between the heavy rare earth element and the light rare earth element.

45 <La>

**[0032]** In the rare earth magnet, La is present together with Ce, and this makes  $CeFe_2$  phase unstable and  $(Ce, La)(Co, Fe)_5$  phase stable. Consequently, in the rare earth magnet, the content of  $CeFe_2$  phase decreases, and the content of  $(Ce, La)(Co, Fe)_5$  phase increases. Saturation magnetization and anisotropy field are higher in 1-5 phase than in 1-2 phase. Furthermore, in 1-5 phase, when the kind of the rare earth element is the same, as the content of Fe is larger, the saturation magnetization is higher. Based on these facts, the saturation magnetization reduced by Ce substitution can be compensated for by increasing the content of  $(Ce, La)(Co, Fe)_5$  phase.

<R'>

**[0033]** R' is one or more rare earth elements other than Ce and La. The rare earth magnet of the present disclosure is obtained by causing Ce and La to be present together. It is difficult for raw materials of Ce and La not to contain the rare earth element R' other than Ce and La at all.

[0034] However, when the value of w in the rare earth site represented by  $Ce_xLa_{(1-x-w)}R'_w$  is from 0 to 0.1, the properties of the rare earth magnet of the present disclosure can be regarded as substantially the same as those when w is 0. [0035] Excessively increasing the purity of raw materials of Ce and La entails a rise in the production cost, and therefore the value of w may be 0.01 or more, 0.02 or more, 0.03 or more, 0.04 or more, or 0.05 or more. On the other hand, the value of w may be low as long as the purity of raw materials of Ce and La is not excessively increased, and the value of w may be 0.09 or less, 0.08 or less, 0.07 or less, or 0.06 or less.

<Rare Earth Site>

[0036] The total content of Ce, La, and R' is indicated by the content v (at%) of the rare earth site represented by  $Ce_xLa_{(1-x-w)}R'_w$ .

[0037] The rare earth magnet of the present disclosure has a binary system of a rare earth element and a transition metal element. Known magnetic phases having such a binary system include 1-2 phase, 1-5 phase, 1-12 phase, 2-7 phase, 2-17 phase, etc. The order of these magnetic phases when arranged in descending order of rare earth element content (in descending order of rare earth concentration) is 1-2 phase, 2-7 phase, 1-5 phase, 2-17 phase, and 1-12 phase. [0038] In the rare earth magnet of the present disclosure, the content v (at%) of the rare earth site is determined so as to contain 1-5 phase.

[0039] When the value of v is 7.1 at% or more, a magnetic phase smaller in the rare earth element content than 1-5 phase, that is, 2-17 phase and 1-12 phase, etc., is less likely to be formed, as a result, 1-5 phase is readily stabilized. From the viewpoint of making formation of a magnetic phase smaller in the rare earth element content than 1-5 phase difficult, the value of v is preferably 9.0 at% or more, more preferably 12.0 at% or more, still more preferably 14.0 at% or more, yet still more preferably 16.0 at% or more, even yet still more preferably 17.0 at% or more. With the value of v in such a range, the content of the iron group site can be reduced. As a result,  $\alpha$ -Co phase,  $\alpha$ -Fe phase, and  $\alpha$ -(Co, Fe) phase are less likely to be formed as well. Incidentally,  $\alpha$ -(Co, Fe) phase indicates a phase where part of Co of  $\alpha$ -Co phase is replaced with Fe.

**[0040]** On the other hand, when the value of v is 20.9 at% or less, a magnetic phase larger in the rare earth element content than 1-5 phase, that is, 1-2 phase and 2-7 phase, etc., is less likely to be formed, as a result, 1-5 phase is readily stabilized. From the viewpoint of making formation of a magnetic phase larger in the rare earth element content than 1-5 phase difficult, the value of v is preferably 20.0 at% or less, more preferably 19.0 at% or less, still more preferably 18.0 at% or less.

<Co>

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**[0041]** As described above, the rare earth magnet of the present disclosure has a binary system of a rare earth element and a transition metal element. As the transition metal element, the magnet contains Co together with the below-described Fe. The rare earth element and the transition metal element can form an intermetallic compound phase (1-5 phase) at a molar ratio of 1:5. In the case of employing Co as the transition metal element, in order to stabilize the 1-5 phase, Co is essential in the rare earth magnet of the present disclosure. When Co is essential, it is easy for the rare earth magnet to contain 1-5 phase. In addition, Co can also enhance the Curie point of the rare earth magnet.

**[0042]** However, as the transition metal element contained in the rare earth magnet of the present disclosure, Fe is essential, in addition to Co. The reason therefor is described below.

<Fe>

[0043] As described above, 1-5 phase is higher in the saturation magnetization and anisotropy field than 1-2 phase. Furthermore, in 1-5 phase, when the kind of the rare earth element R is the same, RFe<sub>5</sub> phase is higher in the saturation magnetization than RCo<sub>5</sub> phase. The rare earth magnet of the present disclosure contains both Ce and La as the rare earth element, and therefore even when part of Co of the RCo<sub>5</sub> phase is replaced with Fe, 1-2 phase is not stabilized but 1-5 phase remains stable. In this way, the content of 1-5 phase having high saturation magnetization and high anisotropy field can be increased in the rare earth magnet.

<Iron Group Site>

**[0044]** The total content of Co and Fe described hereinbefore is indicated by the content of the iron group site represented by  $Co_yFe_{(1-y)}$ . Since the iron group site is the remainder after removing rare earth site and M, when denoting v at% as the content of rare earth site and z at% as the content of M, the content of the iron group site is represented by (100-v-z) at%.

[0045] In the rare earth magnet of the present disclosure, binary elements of a rare earth element and a transition

metal element are the main component, and therefore M is a subcomponent contained in the range not compromising the effects of the rare earth magnet of the present disclosure. M is described later.

[0046] The iron group site is the remainder after removing rare earth site and M and since M is a subcomponent, the content of the iron group site is controlled substantially by the content v of the rare earth site. The lower limit of the content v of the rare earth site is determined as described above, and  $\alpha$ -Co phase,  $\alpha$ -Fe phase, and  $\alpha$ -(Co, Fe) phase are thereby less likely to be formed, as a result, the stability of 1-5 phase is not hindered. On the other hand, when the upper limit of the content v of the rare earth site is determined as described above, the transition metal element (Co and Fe) for forming 1-5 phase does not run short easily, as a result, the stability of 1-5 phase is not hindered.

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[0047] M represents one or more members selected from the group consisting of a transition metal element other than Co and Fe, Ga, Al, Zn, and In, and an unavoidable impurity element.

**[0048]** Among M, Ga, Al, Zn, and In and transition metal elements other than Co and Fe are elements that may be contained within the range not compromising the effects of the present invention. In addition to these elements, M may contain an unavoidable impurity element. The unavoidable impurity element indicates an impurity element that is unavoidably contained or causes a significant rise in the production cost for avoiding its inclusion, such as impurity element contained in raw materials of the rare earth magnet or impurity element mixed in the production step.

**[0049]** M other than Mn (manganese), Ti (titanium) and Zr (zirconium) (excluding an unavoidable impurity element) is present as a non-magnetic phase at an interface of the crystal grain of 1-5 phase and enhances the coercivity of the rare earth magnet by magnetically separating the crystal grain of 1-5 phase.

**[0050]** Cu among the transition metal elements and Ga, Al, Zn, and In can reduce the melting point of a crystal grain boundary of the magnetic phase. Consequently, the crystal grain boundary readily turns into a liquid phase during temperature rise, and therefore the sintering (including liquid-phase sintering) temperature can be lowered.

[0051] Mn and Ti can more stabilize 1-5 phase by replacing part of Fe in 1-5 phase.

[0052] Zr can more stabilize 1-5 phase by replacing part of rare earth element in 1-5 phase.

**[0053]** When the value of the content z of M (including an unavoidable impurity element) is 8.0 at% or less, the contents of rare earth site and iron group site are excessively decreased, and therefore when the value of z is 8.0 at% or less, the effects of the rare earth magnet of the present disclosure are not compromised. From this viewpoint, the value of z may be 7.0 at% or less, 5.0 at% or less, 3.0 at% or less, 1.0 at% or less, or 0.5 at% or less.

**[0054]** On the other hand, although the value of z may be 0 at%, it is difficult not to contain an unavoidable impurity element at all, or a significant rise in the production cost is caused. For this reason, the value of z may be 0.1at% or more, 0.2 at% or more, or 0.4 at% or more.

35 < Relationship of x and y>

**[0055]** As described above, the entire composition of the rare earth magnet of the present disclosure is represented by the formula:  $(Ce_xLa_{(1-x-w)}R'_w)_v(Co_yFe_{(1-y)})_{(100-v-z)}M_z$ . In addition, as described hereinbefore, in the rare earth magnet of the present disclosure, part of Co is replaced with Fe, nevertheless, 1-5 phase is stabilized, because part of Ce is replaced with La.

**[0056]** The stability of 1-5 phase is achieved by i) determining the value of v in the range where 1-5 phase can be formed, and ii) setting a predetermined relationship between x and y such that 1-5 phase is stabilized. Incidentally, the values of w and z are too small to provide a substantial effect on the predetermined relationship between x and y.

**[0057]** The relationship of x and y when 1-5 phase is stabilized can be determined by creating a Ce-La-Fe-Co formation energy (Formation Energy) map. The formation energy map can be created by calculating respective formation energies according to first-principle calculation when changing x and y of  $(Ce_xLa_{(1-x)})(Co_yFe_{(1-y)})_5$  phase, and applying regular solution approximation to all formation energies calculated.

[0058] As the method for first-principal calculation, a package (AkaiKKR) adopting Coherent Potential Approximation (CPA) of the Korringa-Kohn-Rostoker (KKR) method is used. More specifically, respective formation energies are calculated with respect to a total of 121 points when each of x and y of  $(Ce_xLa_{(1-x)})(Co_yFe_{(1-y)})_5$  phase is increased in steps of 10%. Then, with respect to the calculation results of these 121 points, a formation energy map is created using regular solution approximation formula. Incidentally, the regular solution approximation formula is as follows.

 $\Delta E_{RE5}(x,y) = E_{RE5}(x,y) - \{xyE_{CeCo5} + (1-x)yE_{LaCe5} + (1-x)(1-y)E_{LaFe5} + x(1-y)E_{CeFe5}\}$  wherein  $\Delta E_{RE5}(x,y)$  is change in formation energy when being x and y,

 $E_{RE5}(x,y)$  is formation energy when being x and y,

E<sub>CeCo5</sub> is formation energy of CeCo<sub>5</sub>,

E<sub>LaCe5</sub> is formation energy of LaCe<sub>5</sub>,

E<sub>LaFe5</sub> is formation energy LaFe<sub>5</sub>, and

E<sub>CeFe5</sub> is formation energy CeFe<sub>5</sub>.

**[0059]** In the thus-created formation energy map, 1-5 phase is stabilized in a small formation energy region. The boundary between the region where 1-5 phase is stabilized and the region where 1-5 phase becomes unstable produces a relationship that as x increases, y decreases, and the boundary is represented by y=-3x+1.7. In addition, the region where 1-5 phase is stabilized is a region where y is larger than in the boundary. From these facts, the region where 1-5 phase is stabilized is a region represented by  $y \ge -3x+1.7$ .

**[0060]** In the region represented by y>-3x+1.7, as both x and y are further larger, the formation energy is reduced. On the other hand, the region represented by  $y \le -1.25x+1.25$  is a region where as Ce increases, 1-5 phase is stabilized. The region where 1-5 phase is stabilized may be a region represented by  $y \le -x+1.00$ .

10 **[0061]** In the region represented by y≥-3x+1.7, since Ce and La are present together and Co and Fe are present together, it is necessary to satisfy 0<x<1 and 0<y<1.

**[0062]** In the region represented by  $y \ge -3x + 1.7$ , since the formation energy is reduced as both x and y are further larger, x may be 0.3 or more, 0.6 or more, or 0.7 or more, and y may be 0.1or more, 0.2 or more, 0.3 or more. Although not bound by theory, in particular, when y is 0.3 or more, the content of Fe decreases, making production of CeFe<sub>2</sub> phase difficult, and the enhancement of saturation magnetization can be more stabilized. On the other hand, although 1-5 phase is likely to be stabilized as the formation energy is smaller, when the formation energy is small to a certain extent, the phase is stabilized to a degree not causing a problem in practice. Accordingly, x may be 0.9 or less, 0.85 or less, or 0.80 or less, and y may be 0.9 or less, 0.8 or less, or 0.7 or less.

**[0063]** Fig. 6 shows the results of calculating formation energy Er of various magnetic phases by the same method. As seen from Fig. 6, the LaFe $_5$  phase is unstable, because the formation energy Er is positive. In addition, although the CeFe $_5$  phase formation energy Er is negative, since the CeFe $_2$  phase formation energy is lower than the CeFe $_5$  phase formation energy, CeFe $_2$  phase is more preferentially formed than CeFe $_5$  phase. It is seen also from Fig. 6 that Ce and La must be present together.

**[0064]** Furthermore, structural parameters (Fe-Fe distance, Fe-Co distance, etc.) based on the lattice constants of CeCo<sub>5</sub>, LaCes, LaFe<sub>5</sub>, and CeFe<sub>5</sub> are calculated by first-principle calculation. As regards the structural parameters, when the regular solution approximation formula is used, a total magnetizing moment (Total magnetic moment) map can be created. Then, the relationship between the formation energy and the total magnetic moment can be studied. The formation energy is related to stability of 1-5 phase, and the total magnetic moment is proportional to magnetization, so that the relationship between stability of 1-5 phase and magnetization can be studied from the formation energy map and the total magnetic moment map. Incidentally, as the method for first-principle calculation, the results of calculation using KKR-CPA (AkaiKKR) package are supplemented by calculation using a Vienna first-principle simulation package (VASP) or Full potential local orbital minimum-base code (FPLO)).

[0065] In addition, the total magnetic moment map shows that a region in which the content of La is not excessively small relative to the content of Ce can be used to prevent reduction of magnetization, and this is a region represented by y≤-1.25x+1.25. Although not bound by theory, the reason therefore is believed as follows. Ce has an atomic valence of trivalence and tetravalence, and a lot of tetravalent Ce is present in the rare earth magnet. On the other hand, La has an atomic valence of only trivalence. In the case of tetravalence, 4f electrons are not localized, and magnetization is likely to disappear, but La is trivalent and since 4f electrons are localized, the magnetization is enhanced by La. From these facts, it is considered that in the case of causing Ce and La to be present together, the magnetization is more enhanced by increasing the content of La. From this viewpoint, a region represented by y≤-x+1.00 is more preferred.

<< Production Method>>

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**[0066]** The production method of a rare earth magnet of the present disclosure includes a molten metal preparation step and a molten metal quenching step. These steps are described one by one below.

<Molten Metal Preparation Step>

**[0067]** In the production method of the present disclosure, a molten metal having the same composition as the entire composition of the rare earth magnet is prepared. The composition of the molten metal is the composition immediately before completion of solidification. In the case where consumption of molten metal components occurs due to evaporation, etc. in the process of holding and/or solidifying the molten metal, the molten metal may be prepared by blending the raw materials by taking into account the consumption. In order to prevent the molten metal from oxidation, etc., the molten metal is preferably prepared in an inert gas atmosphere.

**[0068]** In the case where the consumption of molten metal components need not be taken into account, a molten metal is prepared by blending raw materials to afford a composition represented by  $(Ce_xLa_{(1-x-w)}R'_w)_v(Co_y-Fe_{(1-y)})_{(100-v-z)}M_z$ . In this formula, Ce, La, R', Co, Fe, and M are the same as the contents described for the rare earth magnet. In addition, x, w, and y as well as v and z are the same as the contents described for the rare earth magnet.

Furthermore, in this formula, as with the description of the rare earth magnet, the relationship of  $y \ge -3x+1.7$  is satisfied. The relationship of  $y \le -1.25x+1.25$  may also be satisfied.

<Molten Metal Quenching Step>

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[0069] A molten metal having the composition above is quenched at a rate of  $1\times10^2$  to  $1\times10^7$  K/sec to obtain a ribbon. This operation provides the ribbon as the rare earth magnet of the present disclosure. In the ribbon, 1-5 phase is present, and the content ratios (molar ratio) x and w as well as y in 1-5 phase are substantially the same as x and w as well as y in the molten metal. Although not bound by theory, the residual liquid in the middle of solidification, which has not turned into such 1-5 phase, forms a grain boundary phase and is present in the rare earth magnet. In other words, in the rare earth magnet of the present disclosure, 1-5 phase satisfying 0<x<1, 0<y<1 and  $y\ge-3x+1.7$ , i.e., a  $(Ce_x-La_{(1-x-w)}R'_w)(Co_yFe_{(1-y)})_t$  phase (wherein  $0\le w\le 0.1$  and  $4\le t\le 0$ , preferably  $4.5\le t\le 5.5$ ), is present. In the production method of the present disclosure, x and y are set to afford a  $(Ce_xLa_{(1-x-w)}R'_w)(Co_yFe_{(1-y)})_t$  phase (wherein  $0\le w\le 0.1$  and  $4\le t\le 0.1$ ), preferably  $4.5\le t\le 5.5$ ). Incidentally, "a  $(Ce_xLa_{(1-x-w)}R'_w)(Co_yFe_{(1-y)})_t$  phase (wherein  $0\le w\le 0.1$  and  $4\le t\le 0.1$ ) satisfying 0<x<1, 0<y<1 and 0<x<1. The same meaning as "a magnetic phase containing a  $(Ce_xLa_{(1-x-w)}R'_w)(Co_yFe_{(1-y)})_5$  phase (wherein  $0\le w\le 0.1$ ) satisfying 0<x<1, 0<y<1 and 0<x<1. The same meaning as "a magnetic phase containing a  $(Ce_xLa_{(1-x-w)}R'_w)(Co_yFe_{(1-y)})_5$  phase (wherein  $0\le w\le 0.1$ ) satisfying 0<x<1, 0<y<1 and 0<x<1. The same meaning as "a magnetic phase containing a  $(Ce_xLa_{(1-x-w)}R'_w)(Co_yFe_{(1-y)})_5$  phase (wherein  $0\le w\le 0.1$ ) satisfying 0<x<1, 0<y<1 and 0<x<1. The same meaning as "a magnetic phase containing a  $(Ce_xLa_{(1-x-w)}R'_w)(Co_yFe_{(1-y)})_5$  phase (wherein  $0\le w\le 0.1$ ) satisfying 0<x<1, 0<y<1 and 0<x<1. The same meaning as "a magnetic phase containing a  $(Ce_xLa_{(1-x-w)}R'_w)(Ce_xLa_{(1-x-w)}R'_w)(Ce_xLa_{(1-x-w)}R'_w)(Ce_xLa_{(1-x-w)}R'_w)(Ce_xLa_{(1-x-w)}R'_w)(Ce_xLa_{(1-x-w)}R'_w)(Ce_xLa_{(1-x-w)}R'_w)(Ce_xL$ 

**[0070]** As the quenching method, for example, the molten metal can be cooled at a predetermined rate according a strip casting method by using a quenching apparatus 10 illustrated in Fig. 3. In the quenching apparatus 10, raw materials are melted in a melting furnace 11 to prepare a molten metal 12 having the composition above. The molten metal 12 is supplied to a tundish 13 at a fixed supply rate. The molten metal 12 supplied to the tundish 13 is supplied to a cooling roll 14 from an end of the tundish 13 due to its own weight.

**[0071]** The tundish 13 is composed of a ceramic, etc. and can temporarily store the molten metal 12 being continuously supplied from the melting furnace 11 at a predetermined flow rate and rectify the flow of the molten metal 12 to the cooling roll 14. In addition, the tundish 13 also has a function of adjusting the temperature of the molten metal 12 immediately before reaching the cooling roll 14.

**[0072]** The cooling roll 14 is formed of a material having high thermal conductivity, such as copper or chromium, and the surface of the cooling roll 14 is subjected to chromium plating, etc. so as to prevent erosion with the high-temperature molten metal. The cooling roll 14 can be rotated in the arrow direction by a drive device (not shown) at a predetermined rotating speed. By controlling the rotating speed, the cooling rate of the molten metal can be controlled to a speed of  $1 \times 10^7$  K/sec.

**[0073]** When the cooling rate of the molten metal is  $1\times10^2$  K/sec or more, 1-5 phase is contained in the ribbon. From this viewpoint, the cooling rate of the molten metal is more preferably  $1\times10^3$  K/sec or more. On the other hand, when the cooling rate of the molten metal is  $1\times10^7$  K/sec or less, despite saturation of the effect obtained by quenching, the molten metal may not be cooled at a higher rate than necessary. The cooling rate of the molten metal may be  $1\times10^6$  K/sec or less, or  $1\times10^5$  K/sec or less.

[0074] In order to obtain the above-described cooling rate, the temperature of the molten metal when supplied from the end part of the tundish 13 to the cooling roll 14 may be 1,300°C or more, 1,350°C or more, or 1,400°C or more and may be 1,600°C or less, 1,550°C or less, or 1,500°C or less. In addition, the peripheral velocity of the cooling roll 14 may be 10 m/s or more, 14 m/s or more, or 18 m/s or more and may be 30 m/s or less, 28 m/s or less, or 24 m/s or less.

**[0075]** The molten metal 12 having being cooled and solidified on the outer periphery of the cooling roll 14 is peeled off as a ribbon 15 from the cooling roll 14 and collected by a collection device. If desired, the ribbon 15 may be pulverized by means of a cutter mill, etc. to obtain a powder. The molten metal quenching step described hereinbefore is preferably in an inert gas atmosphere as to prevent oxidation, etc. of the molten metal.

**[0076]** The ribbon 15 has a crystal grain of 1-5 phase and a crystal grain boundary and therefore, the ribbon 15 has a function as a permanent magnet by itself. A bond magnet or sintered (including liquid-phase sintering) magnet may also be produced using the ribbon 15 or a powder obtained by pulverizing the ribbon 15.

[EXAMPLES]

**[0077]** The rare earth magnet of the present disclosure and the production method thereof are described more specifically below by referring to Examples and Comparative Examples. However, the rare earth magnet of the present disclosure and the production method thereof are not limited to the conditions employed in the following Examples.

<< Preparation of Sample>>

[0078] A sample of the rare earth magnet was prepared in the following manner.

[0079] A molten metal having the composition shown in Table 1 was prepared using an arc melting method, and the molten metal at 1,450°C was supplied to the surface of a cooling roll rotating at a peripheral velocity of 20 m/s by using

a strip casting method to prepare a ribbon. The cooling rate of the molten metal was 106 K/s.

<<Evaluation of Sample>>

<sup>5</sup> **[0080]** The ribbon was coarsely pulverized to obtain a powder, and the presence or absence of 1-5 phase was confirmed by X-ray diffraction (XRD) analysis of the powder.

**[0081]** In addition, the ribbon was coarsely pulverized and resin-embedded, and the magnetization properties were measured using a vibrating sample magnetometer (VSM) with a maximum magnetic field of 9T. The measurement was performed at normal temperature (20°C). The saturation magnetization Ms and anisotropy field Ha were calculated according to the law of approach to saturation.

[0082] The results are shown in Table 1. In Table 1, Reference Example 1 was quoted from J.J. Zhang et al., JMMM, 324(2012), pp. 3272-3275. Furthermore, in Fig. 1, a diagram showing the results of Table 1 together in a formation energy map is illustrated, and in Fig. 2, a diagram showing the results of Table 1 together in a total magnetic moment map is illustrated. The formation energy map and the total magnetic moment map were created by the methods described above. In addition, the XRD analysis results for the samples of Examples 1 to 5 and for the samples of Comparative Examples 1 to 4 are shown in Fig. 4 and Fig. 5, respectively. With respect to the analysis results of each sample of Figs. 4 and 5, the upper side displays the XRD pattern of each sample, and the lower side displays the XRD pattern of  $CeCo_5$  phase. Incidentally, in Figs. 4 and 5, the abscissa is 20, and the ordinate is X-ray intensity. The XRD analysis results for the samples of Examples 6 to 9 are shown in Fig. 7. With respect to the analysis results of each sample of Fig. 7, the upper side displays the XRD pattern of each sample, and the lower side displays the XRD pattern of  $CeCo_5$  phase. Here, the peak positions of  $CeCo_5$  phase and  $CeCo_5$  phase are substantially the same.

[Table 1]

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Absence of Ms (T) Ha (T) 3.48 2.39 2.89 4.36 7.74 3.07 9.07 3.27 1.01 1.05 1.10 1.11 96.0 0.97 0.97 0.91 5 Presence of 1-5 Phase present present present present present present present present 10 Relationship of y<-1.25x+1.25 y<-1.25x+1.25 y<-1.25x+1.25 y<-1.25x+1.25 y<-1.25x+1.25 y>-1.25x+1.25 y>-1.25x+1.25 y>-1.25x+1.25 -1.25x+1.25 y and 15 Value of -1.25x+ 1.25 0.25 0.63 0.44 0.44 0.25 0.81 0.63 0.63 20 Relationship of y and -3x+1.7 y=-3x+1.7 y>-3x+1.7 v=-3x+1.7 y>-3x+1.7 y>-3x+1.7 y>-3x+1.7 y>-3x+1.7 y>-3x+1.7 25 Value of -3x+1.7 -0.25 -0.70 -0.25 0.65 0.20 0.20 0.20 -0.70 30 Charge Composition (composition of 53.76 41.35 66.17 28.95 28.94 66.17 16.54 54 Е 16. 28.95 66.16 53.75 41.35 16.54 53.75 16.54 16 molten metal) ပ္ပ .,99 35 11.25 8.65 90.9 3.46 3.46 8.65 8.65 90.9 Ľ 40 13.83 11.24 11.24 13.84 6.05 8.65 8.65 8.64 Ce 0.35 0.65 Target Magnetic Phase of 0.65 0.50 0.20 0.80 0.20 0.80 > 45 0.35 0.65 0.50 0.65 0.80 0.50 0.50 0.80 × )-(Co0.2Fe0. 8)5 35)-Co0.35Fe0. 65)5 Ce0.65La0. 35)-Co0.65Fe0. Composition (Ce0.5La0.5 (Ce0.5La0.5 )-(Co0.5Fe0. Ce0.8La0.2) -(Co0.2Fe0. (Ce0.5La0.5 )-(Co0.8Fe0. (Ce0.8La0.2 )-(Co0.8Fe0. (Co0.65Fe0. Ce0.35La0. Ce0.65La0. Formula 35)5 35)5 50 Example 5 Example 2 Example 3 Example 6 Example 7 Example 8 Example 1 Example 4 55 [0083]

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		É	Па (т)	3.49	2.93	1.68	2.39	1.62	12.7
5		Relationship of Presence of y and Absence of Ms (T) -1.25x+1.25 1-5 Phase		0.91	96.0	1.14	1.16	1.24	78.0
10				present	none	none	none	none	present
15				y>-1.25x+1.25	y<-1.25x+1.25	y<-1.25x+1.25	y<-1.25x+1.25	y<-1.25x+1.25	y>-1.25x+1.25
20	Value of		1.25	0.25	1.00	1.00	0.81	1.00	0
25		Relationship of y and -3x+1.7		y>-3x+1.7	y<-3x+1.7	y<-3x+1.7	y<-3x+1.7	y<-3x+1.7	y>-3x+1.7
	(penu		-3x+1.7	-0.70	1.10	1.10	0.65	1.10	-1.30
30	(continued)	sition of	Fe	41.35	16.54	41.35	53.76	66.17	1
35		on (compo metal)	S	41.35	66.16	41.35	28.95	16.54	
		Charge Composition (composition of molten metal)	Га	3.46	13.85	13.84	11.24	13.84	ı
40		Charge C	Ce	13.84	3.46	3.46	6.05	3.46	1
45		ase of	y 0.50		0.80	0.50	0.35	0.20	1.00
		agnetic Ph	×	0.80	0.20	0.20	0.35	0.20	1.00
50		Target Magnetic Phase of Region	Composition Formula	(Ce0.8La0.8 )-(Co0.5Fe0. 5)5	(Ce0.2La0.8 )-(Co0.8Fe0. 2)5	(Ce0.2La0.8 )-(Co0.5Fe0. 5)5	(Ce0.35La0. 65)-(Co0.35 Fe0.65)5	(Ce0.2La0.8 )-(Co0.2Fe0. 8)5	Ce-Co5 (document)
55				Example 9	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Reference Example

**[0084]** As seen from Table 1 and Figs. 4 and 5, it could be confirmed that in Examples 1 to 5, the peak of 1-5 phase is clearly recognized from the XRD analysis results. Furthermore, as seen from Figs. 1 and 2, it could be confirmed that the formation energy map and the total magnetic moment map each created by calculation have a correlation with the results of Table 1. Incidentally, in Fig. 1, y=-3x+1.7 is a straight line passing through the values of Example 1 and Example 2, and y=-x+1.00 is a straight line passing through Example 1 and Example 3.

**[0085]** Moreover, as seen from Table 1 and Fig. 7, it was confirmed that in Examples 6 to 9, the peak of 1-5 phase is also clearly recognized from the XRD analysis results. Then, it could be confirmed from Table 1 that in the region of y≤-1.25x+1.25, saturation magnetization tends to be enhanced. In addition, it could be confirmed that when y is 0.3 or more, the enhancement of saturation magnetization is stabilized.

10 [0086] Although not bound by theory, the reason why the enhancement of saturation magnetization is stabilized in the region of y being 0.3 or more is possibly as follows. Referring to Figs. 4 and 7, in Examples 1 to 9, a peak is recognized even at a position of 2θ being 35°. This is considered to be attributable to the fact that in Examples 1 to 9, a phase other 1-5 phase is slightly present. It is then believed that when y is 0.3 or more, the content of Fe is small and consequently, the phase other than 1-5 phase has a low possibility of being CeFe<sub>2</sub>.

15 [0087] From these results, the effects of the rare earth magnet of the present disclosure and the production method thereof could be confirmed.

[REFERENCE SIGNS LIST]

#### 20 [0088]

- 10 Quenching apparatus
- 11 Melting furnace
- 12 Molten metal
- 25 13 Tundish
  - 14 Cooling roll
  - 15 Ribbon

#### 30 Claims

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A rare earth magnet having a composition represented by the formula: (Ce<sub>x</sub>La<sub>(1-x-w)</sub>R'<sub>w</sub>)<sub>v</sub>(Co<sub>y</sub>Fe<sub>(1-y)</sub>)<sub>(100-v-z)</sub>M<sub>z</sub>, wherein R' is one or more rare earth elements other than Ce and La,
 M represents one or more members selected from the group consisting of a transition metal element other than Co and Fe, Ga, Al, Zn, and In, and an unavoidable impurity element,

		0 <x<1.0,< th=""></x<1.0,<>		
40		0 <y<1.0,< td=""></y<1.0,<>		
45		0≤w≤0.1,		
		7.1≤v≤20.9,		
50	and			

and satisfying, in the formula, the relationship of  $y \ge -3x + 1.7$ .

2. The rare earth magnet according to claim 1, further satisfying, in the formula, the relationship of  $y \le -1.25x + 1.25$ .

 $0 \le z \le 8.0$ ,

- 3. The rare earth magnet according to claim 1 or 2, wherein x satisfies  $0.3 \le x \le 0.9$ .
- **4.** The rare earth magnet according to claim 1 or 2, wherein x satisfies 0.6≤x≤0.9.
- 5. The rare earth magnet according to any one of claims 1 to 4, wherein y satisfies 0.1≤y≤0.9.
  - **6.** The rare earth magnet according to any one of claims 1 to 4, wherein y satisfies  $0.1 \le y \le 0.7$ .
  - 7. The rare earth magnet according to any one of claims 1 to 4, wherein y satisfies 0.3≤y≤0.9.
  - 8. The rare earth magnet according to any one of claims 1 to 4, wherein y satisfies 0.3≤y≤0.7.
  - **9.** A method for producing a rare earth magnet, comprising:

preparing a molten metal having a composition represented by the formula:  $(Ce_xLa_{(1-x-w)}R'_w)_v(Co_y-Fe_{(1-y)})_{(100-v-z)}M_z$ , wherein R' is one or more rare earth elements other than Ce and La, M represents one or more members selected from the group consisting of a transition metal element other than Co and Fe, Ga, Al, Zn, and In, and an unavoidable impurity element,

0<x<1.0,

0<y<1.0,

 $0 \le w \le 0.1$ ,

 $7.1 \le v \le 20.9$ ,

and

 $0 \le z \le 8.0$ 

and satisfying, in the formula, the relationship of  $y \ge -3x + 1.7$ , and quenching the molten metal at a rate of  $1 \times 10^2$  to  $1 \times 10^7$  K/sec to obtain a ribbon.

- **10.** The method according to claim 9, wherein in the formula, the relationship of y≤-1.25x+1.25 is further satisfied.
  - **11.** The method according to claim 9 or 10, wherein x satisfies 0.35x≤0.9.
- **12.** The method according to claim 9 or 10, wherein x satisfies  $0.6 \le x \le 0.9$ .
  - **13.** The method according to any one of claims 9 to 12, wherein y satisfies  $0.1 \le y \le 0.9$ .
  - **14.** The method according to any one of claims 9 to 12, wherein y satisfies  $0.1 \le y \le 0.7$ .
- 50 **15.** The method according to any one of claims 9 to 12, wherein y satisfies 0.3≤y≤0.9.
  - **16.** The method according to any one of claims 9 to 12, wherein y satisfies 0.3≤y≤0.7.

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FIG. 1

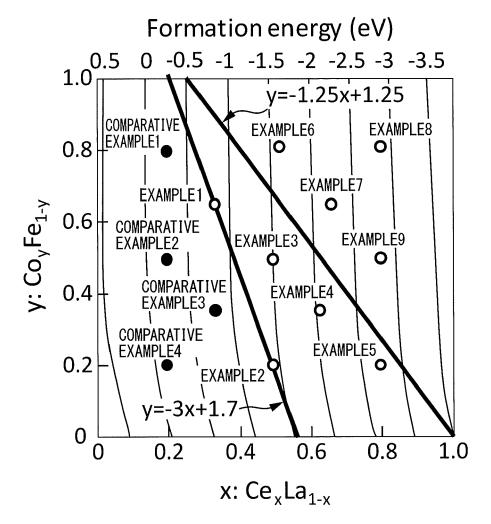
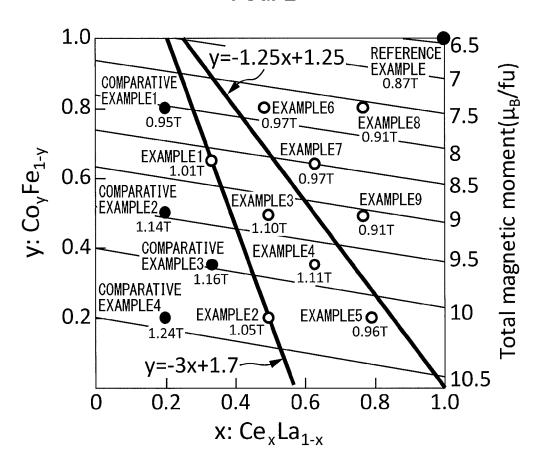


FIG. 2



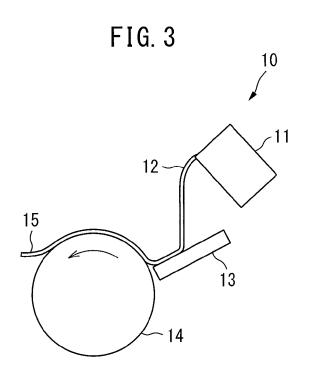


FIG. 4

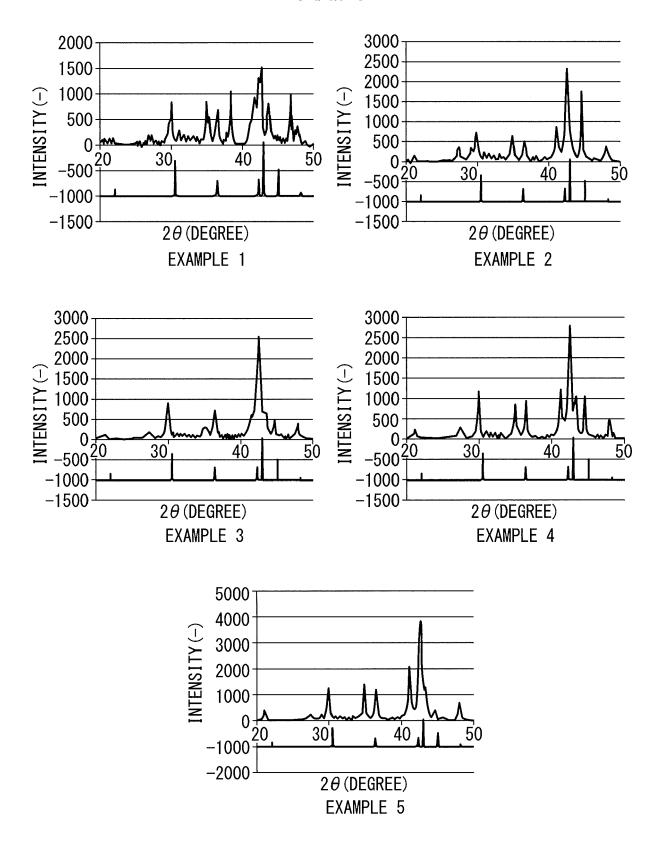
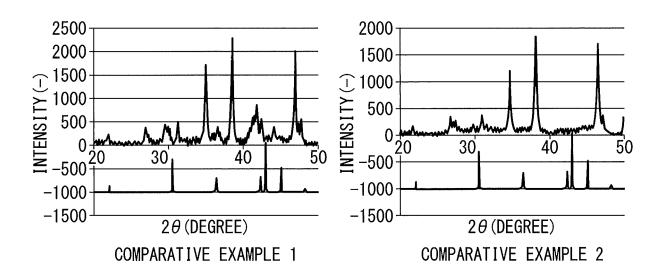


FIG. 5



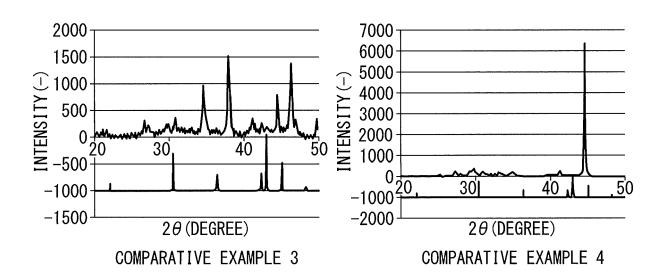


FIG. 6

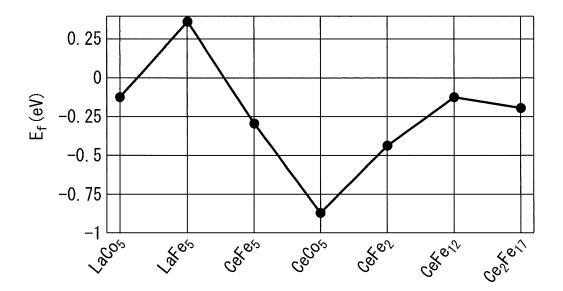
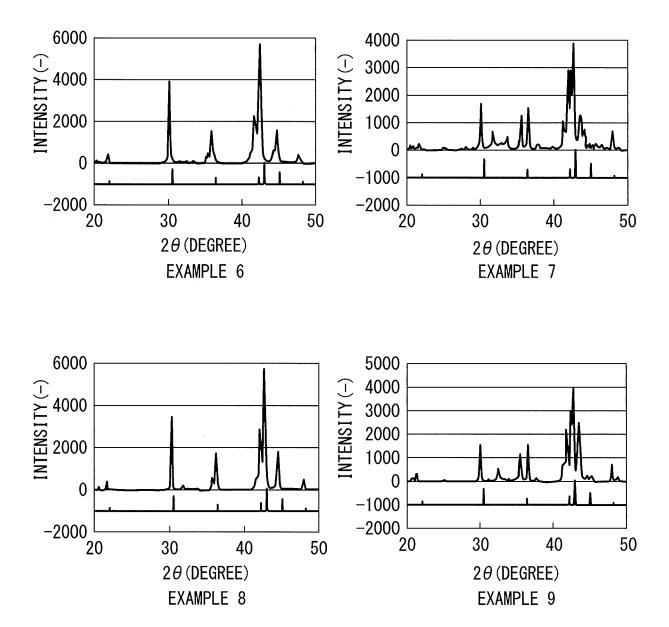


FIG. 7



**DOCUMENTS CONSIDERED TO BE RELEVANT** 



### **EUROPEAN SEARCH REPORT**

**Application Number** 

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Category	Citation of document with inc of relevant passaç		Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Х	US 4 087 291 A (GAIF 2 May 1978 (1978-05-	·02)	1-8	INV. H01F1/055
Υ	* column 1, line 57	- column 2, line 9 *	9-16	,
Υ	JP H08 191006 A (TOS 23 July 1996 (1996-6 * paragraphs [0023]	07 <b>-</b> 23)	9-16	
A	US 4 664 723 A (ISHI 12 May 1987 (1987-05 * table 1 *	I JUNICHI [JP] ET AL) -12)	1-16	
A	NL 7 217 038 A (STRM 18 June 1973 (1973-6 * example 1 *		1-16	
				TECHNICAL FIELDS
				SEARCHED (IPC)
				11011
	The present search report has be	een drawn up for all claims		
	Place of search	Date of completion of the search	<del>'</del>	Examiner
	Munich	22 February 201	9 Pr	imus, Jean-Louis
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## ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

22-02-2019

10	Patent document cited in search report		Publication date		Patent family member(s)	Publication date
	US 4087291	Α	02-05-1978	US US	4087291 A 4144105 A	02-05-1978 13-03-1979
15	JP H08191006	Α	23-07-1996	NONE		
	US 4664723	Α	12-05-1987	NONE		
20	NL 7217038	Α	18-06-1973	AT CA CH DD DE FR	325866 B 969076 A 582410 A5 100891 A5 2258780 A1 2163611 A1	10-11-1975 10-06-1975 30-11-1976 12-10-1973 28-06-1973 27-07-1973
25				GB JP JP NL	1398588 A S4866524 A S55550099 B2 7217038 A	25-06-1975 12-09-1973 16-12-1980 18-06-1973
30						
35						
40						
45						
50						
55	PORT LINE OF L					

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

#### REFERENCES CITED IN THE DESCRIPTION

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#### Patent documents cited in the description

JP H4371556 B [0006]

## Non-patent literature cited in the description

• **J.J. ZHANG et al.** *JMMM*, 2012, vol. 324, 3272-3275 **[0082]**