

Optimum preparation conditions of Fe-deficient Ca-based M-type ferrite

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We investigated synthesis conditions and magnetic properties of Fe-deficient Ca-based hexagonal ferrites, $\text{Ca}_{1-x}\text{La}_x\text{Fe}_y\text{O}_{19-o}$ ($x = 0.1-0.3$, $y = 2.0-10$), and found the formation of M-type ferrite at $x = 0.1-0.3$ and $y = 7.0-9.0$ above 1200°C . Samples of $y = 2.0-6.0$ showed deviation from the initial compositions since molten calcium-rich oxide (possibly CaFe_2O_4) leaked out from the samples above 1200°C . The X-ray diffraction pattern of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{8.0}\text{O}_{19-o}$ sintered at 1250°C demonstrates the single phase of M-type hexagonal ferrite. The saturation magnetization of this sample was $68.0 \text{ Am}^2/\text{kg}$ at room temperature and its Curie temperature was about 400°C , which is slightly lower than that of the Sr-based M-type ferrite (460°C).

Keywords: hexagonal ferrites, M-type, calcium compound

1. Introduction

M-type ferrite is a type of hexagonal ferrite. Its chemical formula is expressed as $\text{M}^{2+}\text{Fe}^{3+}_{12}\text{O}_{19}$ ($\text{M}^{2+}=\text{Ba}^{2+}, \text{Sr}^{2+}$). The M-type ferrite has high saturation magnetization and high coercivity and is mainly used as a permanent magnet. The Curie temperatures of $\text{BaFe}_{12}\text{O}_{19}$ and $\text{SrFe}_{12}\text{O}_{19}$ are 450°C and 460°C , respectively.¹⁻⁴⁾

The unit cell of M-type ferrite is composed of two kinds of block units, where a R-block and a S-block are stacked up alternately (RSR*S*). The symbol * means 180° rotation of the corresponding block around the c -axis.^{1, 3), 4)} The M-type ferrite has ions of $2(\text{MFe}_{12}\text{O}_{19})$ in the unit cell (RSR*S*), as shown in Fig. 1.

The S-block with the chemical formula of $(2\text{Fe}_3\text{O}_4)^{2+}$ is identical to the cubic spinel structure. Two close-packed large oxygen anion layers (O layers) build the framework of the S-block. One octahedral (up-spin) and two tetrahedral (down-spin) sites exist for small Fe^{3+} cations in the S-block.^{1, 3), 4)}

The R-block contains another kind of close-packed large ion layer with $\text{M}^{2+}:\text{O}^{2-} = 1:3$ (M-O layers). The R-block with the chemical formula of $(\text{MFe}_6\text{O}_{11})^{2-}$ is made up of three large-ion layers where one M-O layer is sandwiched between two O layers. A trigonal-bipyramidal (up-spin) site is just on the M-O layer in the R-block. Two octahedral (down-spin) sites are between the M-O and O layers in the R-block. There are three octahedral (up-spin) sites just on the block border between the S- and R-blocks.^{1, 3), 4)}

Because an Fe^{3+} ion has the magnetic moment of $5 \mu_B$, the total magnetization at zero temperature can be estimated from the numbers of the up and down spins with the assumption of a collinear magnetic structure. Typical M-type ferrite has eight up spins and four down spins as shown in Fig. 1. Hence, the net magnetization per formula unit is $(8-4) \times (5 \mu_B) = 20 \mu_B$.^{1, 4)}

In this study, we investigated the synthesis conditions

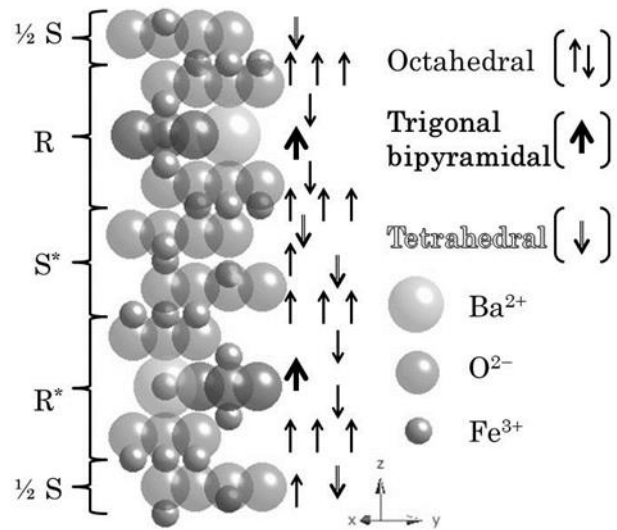


Fig. 1 Spin alignment in the unit cell of the M-type ferrite.

of Ca-based M-type ferrites. Ca is one of the alkaline earth elements. It is attractive to substitute Ca ions for Ba or Sr ions in the hexagonal ferrite because Ca is rich in resources.⁵⁾ Also, the use of Ca, which is less toxic than Ba, is helpful in terms of producing a safer material.

The synthesis of Ca-based hexagonal ferrites is, however, extremely difficult because the M-type composition sample with $\text{Ca}:\text{Fe} = 1:12$ tends to melt and decompose into $\alpha\text{-Fe}_2\text{O}_3$, CaFe_4O_7 , and CaFe_2O_4 .⁶⁻⁸⁾

On the other hand, the Ca-based M-type hexaferrite can be synthesized by adding a small amount of La in oxygen atmosphere.^{9), 10)} This Ca-based M-type ferrite exists as a ternary oxide of $\text{CaO-La}_2\text{O}_3\text{-Fe}_2\text{O}_3$ because there is no M-type $\text{CaFe}_{12}\text{O}_{19}$ in the binary $\text{CaO-Fe}_2\text{O}_3$ phase diagram as mentioned above. Most of the previous studies, however, treated La_2O_3 as an additive

to $\text{CaFe}_{12}\text{O}_{19}$.⁹⁾⁻¹²⁾ The systematic research was limited at ratio of $\text{Fe}/(\text{Ca}+\text{La}) > 10$ although Fang reported that they obtained the M-type phase by reducing the amount of Fe.¹³⁾ So, the synthesis conditions in air remain unclear. The synthesis condition of the Ca-based M-type ferrite was not systematically surveyed below $\text{Fe}/(\text{Ca}+\text{La}) = 9$. Therefore, we studied three synthesis conditions: the composition ratio of Ca:La, the ratio of (Ca+La):Fe, and the sintering temperature.

2. Experimental Procedure

Samples of Ca-based M-type ferrite were prepared by a conventional ceramic method. We used CaCO_3 , La_2O_3 , and $\alpha\text{-Fe}_2\text{O}_3$ as starting materials. They were mixed in a desired proportion, $\text{Ca}_{1-x}\text{La}_x\text{Fe}_y\text{O}_{19-\sigma}$ ($x = 0.1-0.3$, $y = 2.0-10$). The powder was ball-milled for 24 h. The mixed powder was pressed into a pellet shape and pre-calcined in air at 900°C . The sintered sample was pulverized in a mortar and then milled into fine powder with a planetary ball mill (Fritsch, P-7 Premium line with 1 mm ϕ zirconia balls and a 45 ml zirconia container) for 10 min. at 1100 rpm. The processed powder was dried and then pressed into disks. The disks were sintered at 1100 to 1300°C for 5 h. Parts of some sintered samples at $y \leq 6$ were molten above 1250°C . We removed the molten portion adhering to the pellet and employed the remaining part as a sample for measurements. The crystal structure of the sample was examined by powder X-ray diffraction (XRD) analysis with Cu-K α radiation. The magnetization was measured with a vibrating sample magnetometer (Tamakawa TM-VSM2130HGC) and a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-XL). The composition was analyzed by the use of an Electron Probe Micro Analyzer (EPMA) (JEOL, JXA-8200). Here, the composition of oxygen was not examined because the analyses of light elements are less accurate than those of heavy elements.

3. Results and discussion

Figure 2 shows the room-temperature saturation magnetization of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_y\text{O}_{19-\sigma}$ ($y = 2.0-9.5$) sintered at $1200-1300^\circ\text{C}$. The saturation magnetization was high for the samples sintered above 1250°C with $y = 3.0-8.0$. However, deviations from the initial compositions seems to take place below $y = 6.0$ because molten oxides separated out from these initially poor-iron samples, as shown in the inset of Fig. 2. Actually, the EPMA measurement of the sample with the initial composition of $y = 4.0$ sintered at 1250°C showed the average atomic ratio of Ca:La:Fe = 0.76:0.24:8.53, demonstrating a great deviation from the initial composition. The composition of the molten oxides is possibly close to Ca:Fe = 1:2 because CaFe_2O_4 has the lowest melting point of 1216°C in the CaO- Fe_2O_3 system.⁶⁾⁻⁸⁾ The maximum saturation magnetization is $68.0 \text{ Am}^2/\text{kg}$ for the sample with the

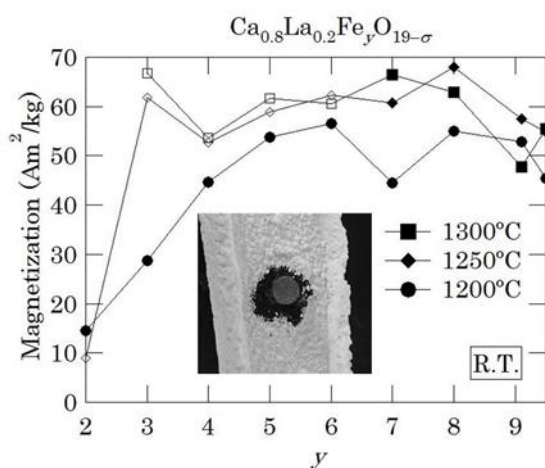


Fig. 2 Saturation magnetization at room temperature of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_y\text{O}_{19-\sigma}$ ($y = 2.0-9.5$) sintered at 1200 , 1250°C and 1300°C . Open markers indicate the samples whose molten portion was removed.

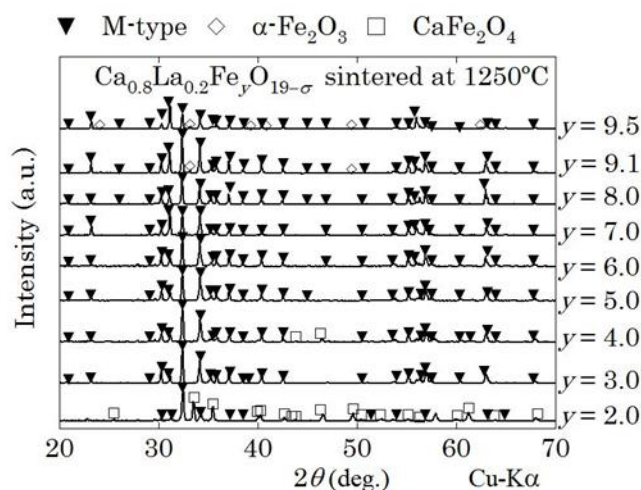


Fig. 3 X-ray diffraction patterns of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_y\text{O}_{19-\sigma}$ ($y = 2.0-9.5$) sintered at 1250°C .

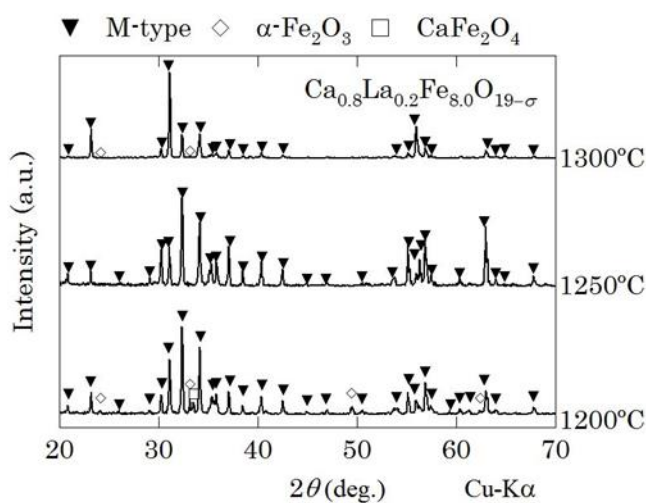


Fig. 4 X-ray diffraction patterns of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{8.0}\text{O}_{19-\sigma}$ sintered at 1200°C , 1250°C , and 1300°C .

initial composition of Ca:La:Fe = 0.8:0.2:8.0 sintered at 1250°C.

Figure 3 shows the X-ray diffraction patterns of the samples with the initial compositions of Ca:La:Fe = 0.8:0.2:y ($y = 2.0-9.5$) sintered at 1250°C. The main phase is M-type ferrite for the samples with $y \geq 3.0$.^{14), 15)} However, the compositions of the samples with $y \leq 6.0$ are different from the initial compositions because molten calcium-rich oxide (possibly CaFe_2O_4) was separated out from the samples sintered at $T \geq 1250^\circ\text{C}$. Also, there are minor $\alpha\text{-Fe}_2\text{O}_3$ peaks in the X-ray diffraction patterns of the samples with $y \geq 9.1$. Therefore, the initial composition of $y = 7.0$ or 8.0 is suitable for the preparation of Ca-based M-type ferrite.

Figure 4 shows the X-ray diffraction patterns of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{8.0}\text{O}_{19-\sigma}$ sintered at 1200°C, 1250°C, and 1300°C. The main phase of these samples is M-type ferrite. However, the sample sintered at 1200°C also has the secondary phases of CaFe_2O_4 and $\alpha\text{-Fe}_2\text{O}_3$. Since the raw material of $\alpha\text{-Fe}_2\text{O}_3$ remains, the sintering temperature of 1200°C is still insufficient for the formation of Ca-based M-type phase. On the other hand, if the sintering temperature was higher than 1300°C, the separation of molten oxides also took place, similar to that shown in the inset of Fig. 2. Therefore, the sintering temperature of about 1250°C is suitable for the preparation of Ca-based M-type ferrite.

Figure 5 shows the X-ray diffraction patterns of $\text{Ca}_{1-x}\text{La}_x\text{Fe}_{8.0}\text{O}_{19-\sigma}$ ($x = 0.1-0.3$) sintered at 1250°C. The samples of $x = 0.2$ and 0.3 have the single phase of M-type ferrite, but the sample of $x = 0.1$ has the mixed phases of M-type and $\alpha\text{-Fe}_2\text{O}_3$. The raw material of $\alpha\text{-Fe}_2\text{O}_3$ remains in the Ca-rich sample with $x < 0.2$. The lattice constants of these samples are shown in Table 1. The lattice constants of samples are close to those of SrM. On the other hand, the c -axis lattice constants are smaller than that of BaM. This is caused by the difference in the ionic radii because the ionic radii of Ca^{2+} , La^{3+} , Sr^{2+} , and Ba^{2+} are 1.12 Å, 1.16 Å, 1.26 Å, and 1.42 Å, respectively.¹⁶⁾ The Ba cations with the large ionic radius may expand the c -axis of the BaM ferrite.

Figure 6 shows the temperature dependence of magnetization of $\text{Ca}_{1-x}\text{La}_x\text{Fe}_{8.0}\text{O}_{19-\sigma}$ ($x = 0.1-0.3$) sintered at 1250°C. The Curie temperatures of these samples were about 400°C, which is slightly lower than that of the Sr-based M-type ferrite (460°C).²⁾

Table 2 shows the experimental results of the chemical composition analysis of the maximum saturation magnetization sample with the initial composition of Ca:La:Fe = 0.8:0.2:8.0 sintered at 1250°C. The compositions of Ca and La are similar to the initial amounts, but the composition of Fe is slightly larger than the initial amount. Therefore, the M-type ferrite was formed with the composition of $\text{Ca}_{0.83}\text{La}_{0.17}\text{Fe}_{8.9}\text{O}_{19-\sigma}$. The difference from the initial composition may be caused by low-melting-point calcium-iron oxides such as CaFe_2O_4 that can be eluted off from the M-type grain.

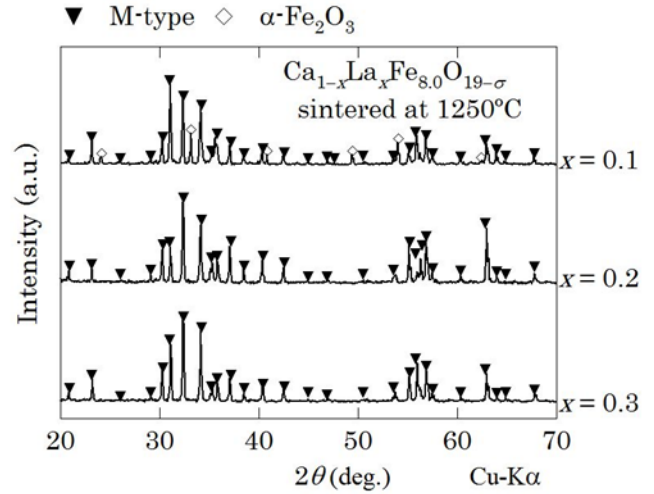


Fig. 5 X-ray diffraction patterns of $\text{Ca}_{1-x}\text{La}_x\text{Fe}_{8.0}\text{O}_{19-\sigma}$ ($x = 0.1-0.3$) sintered at 1250°C.

Table 1 Lattice constants of $\text{Ca}_{1-x}\text{La}_x\text{Fe}_{8.0}\text{O}_{19-\sigma}$ sintered at 1250°C.

		$a(\text{\AA})$	$c(\text{\AA})$
$y = 0.8$ sintered at 1250°C	$x = 0.3$	5.892	22.98
	$x = 0.2$	5.887	23.00
	$x = 0.1$	5.894	23.03
SrFe ₁₂ O ₁₉ (SrM) ¹⁴⁾		5.884	23.04
BaFe ₁₂ O ₁₉ (BaM) ¹⁵⁾		5.889	23.22

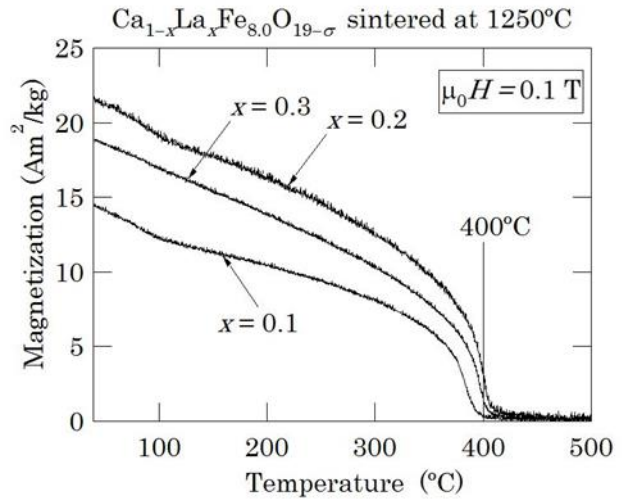


Fig. 6 Temperature dependence of magnetization of $\text{Ca}_{1-x}\text{La}_x\text{Fe}_{8.0}\text{O}_{19-\sigma}$ ($x = 0.1-0.3$) sintered at 1250°C.

Figure 7 shows the magnetization curves at 5 K (-268°C) and 300 K (27°C) of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{8.0}\text{O}_{19-\sigma}$ sintered at 1250°C. The spontaneous magnetization at 5 K (-268°C) is estimated to be 14.7 $\mu\text{B}/\text{f.u.}$ (104 Am^2/kg) by linear extrapolation of the magnetization curve from

Table 2 The result of composition analysis of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{8.0}\text{O}_{19-\sigma}$ sintered at 1250°C .

Element	Average (at.%)
Ca	8.328
La	1.761
Fe	89.91
Fe/(Ca+La)	8.912

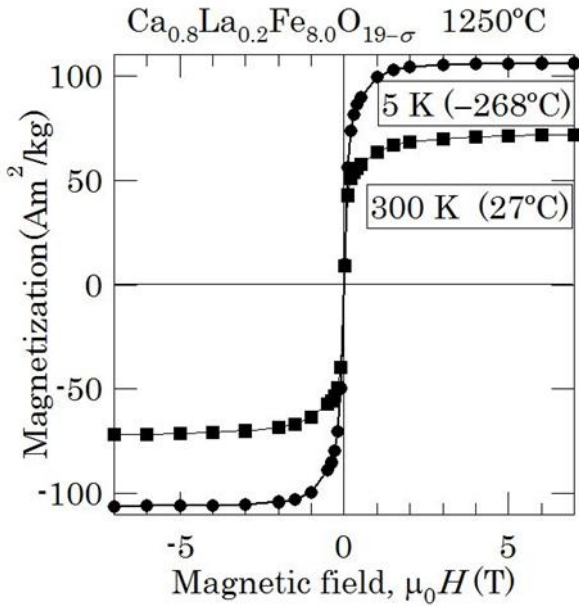


Fig. 7 Magnetization curves at 5 K (-268°C) and 300 K (27°C) of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{8.0}\text{O}_{19-\sigma}$ sintered at 1250°C .

the high field region of $2 \leq \mu_0 H \leq 7$ T.

We would like to estimate the magnetic moment of the Ca-based hexaferrite. The hexaferrite ($\text{MFe}_{12}\text{O}_{19}$; $\text{M}=\text{Ba}^{2+}, \text{Sr}^{2+}$) consists of the R-block ($[\text{MFe}_6\text{O}_{11}]^{2-}$) and the S-block ($[\text{2Fe}_3\text{O}_4]^{2+}$), as shown in Fig. 1. The spin arrangements in the R- and S-blocks are similar to each other in spite of the different block structures. There is one central up-spin site between two down-spin sites in each block. There are three up-spin sites between the R-blocks and S-blocks. Therefore, the spin distribution is such that the number of up-spin sites is twice that of the down-spin sites (up:down = 2:1).

The EPMA analysis implied that the chemical formula was approximately $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{9.0}\text{O}_{14.6}$ as shown in Table 2. Here, the composition ratio of oxygen is estimated from the charge balance with the concentration of Ca^{2+} , La^{3+} , and Fe^{3+} cations. In this chemical formula, six of nine spins are in up direction and the other three spins are in down direction with respect to the spin distribution ratio (up:down = 2:1). This estimated magnetic moment of $15 \mu_B/\text{f.u.}$ is consistent with the observed magnetization at 5 K (-268°C).

4. Conclusion

We have investigated the synthesis conditions and magnetic properties of Fe-deficient Ca-based M-type ferrite. The sintering temperature of the best sample was 1250°C and the analyzed composition was approximately Ca:La:Fe = 0.8:0.2:9.0. The saturation magnetization of the best sample was $68.0 \text{ Am}^2/\text{kg}$ at room temperature and $104 \text{ Am}^2/\text{kg}$ at 5 K (-268°C). The Curie temperature of this sample was about 400°C .

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