

Synthesis of non-magnetic-ion-substituted Ca-based M-type ferrite

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We investigated the synthesis conditions and magnetic properties of non-magnetic-ion-substituted Ca-based hexagonal ferrites, $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{8.0-2x}\text{Mg}_x\text{Ti}_x\text{O}_{19-o}$ ($x = 0.1-3.5$) and $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{y-x}\text{Al}_x\text{O}_{19-o}$ ($x = 1.0-5.0$, $y = 8.0-10$). We found that Mg-Ti-substituted Ca-based M-type ferrites formed at $x = 0.1$ and 0.2 at above 1225°C . The sample at $x = 0.1$ showed the crystallographic single phase of M-type ferrite. The minimum Curie temperature of the Mg-Ti-substituted samples was 367°C . Also, we found that the Al-substituted Ca-based M-type ferrites had the main phase of M-type ferrite in all samples. As the amount of substituted Al increased, the saturation magnetization and the Curie temperature decreased, and the coercivity increased. As the amount of substituted Al increased by $\Delta x = 1$, the Curie temperature decreased by $\Delta T_C = 50-70^\circ\text{C}$. Al-substituted samples of $x = 1.0$ and 2.0 sintered at 1300°C had the single phase of M-type ferrite.

Keywords: hexagonal ferrites, M-type, calcium compound, non-magnetic ions, Mg-Ti, Al

1. Introduction

M-type ferrite is a type of hexagonal ferrite. Its chemical formula is expressed as $\text{M}^{2+}\text{Fe}^{3+}_{12}\text{O}_{19}$ ($\text{M}^{2+}=\text{Ba}^{2+}$, 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⁾ It is also possible to tune the magnetic properties of the pure M-type ferrites by the substitution of non-magnetic ions such as $\text{Mg}^{2+}\text{-Ti}^{4+}$, $\text{Zn}^{2+}\text{-Ti}^{4+}$, and Al^{3+} .⁵⁾⁻¹⁰⁾

On the other hand, we had investigated the synthesis conditions of Ca-based M-type ferrite in our previous study.¹¹⁾ In the study, the sintering temperature of the highest magnetization sample was 1250°C and the analyzed composition was approximately $\text{Ca}:\text{La}:\text{Fe} = 0.8:0.2:9.0$. The saturation magnetization of the 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 .

In this study, we investigated the synthesis conditions and magnetic properties of non-magnetic-ion-substituted Ca-based M-type ferrites. The substitution of non-magnetic ions for Fe^{3+} can decrease the Curie temperature of a ferrite, which gives the opportunity for new application. For instance, Shimizu *et al.* put forward the non-magnetic-ion-substituted spinel ferrites with relatively low Curie temperatures as the implant material for the magnetic induction hyperthermia therapy.¹²⁾⁻¹³⁾

We employed $\text{Mg}^{2+}\text{-Ti}^{4+}$ and Al^{3+} as non-magnetic substituting elements in the Ca-based M-type ferrite. The resources of these elements are rich as well as those of Ca and Fe.¹⁴⁾ Also, Ca, Mg, Ti, and Al are less toxic than Ba, which is helpful in terms of producing a safer material.

2. Experimental Procedure

Samples were prepared by a conventional ceramic method. We used CaCO_3 , La_2O_3 , $\alpha\text{-Fe}_2\text{O}_3$, and (MgO , TiO_2) or Al_2O_3 as starting materials. They were mixed in a desired proportion, $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{8.0-2x}\text{Mg}_x\text{Ti}_x\text{O}_{19-o}$ ($x = 0.1-3.5$), or $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{y-x}\text{Al}_x\text{O}_{19-o}$ ($x = 1.0-4.0$, $y = 8.0-10$). 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 $1 \text{ mm}\phi$ 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 $T_s = 1200-1300^\circ\text{C}$ for 5 h. The crystal structure of the

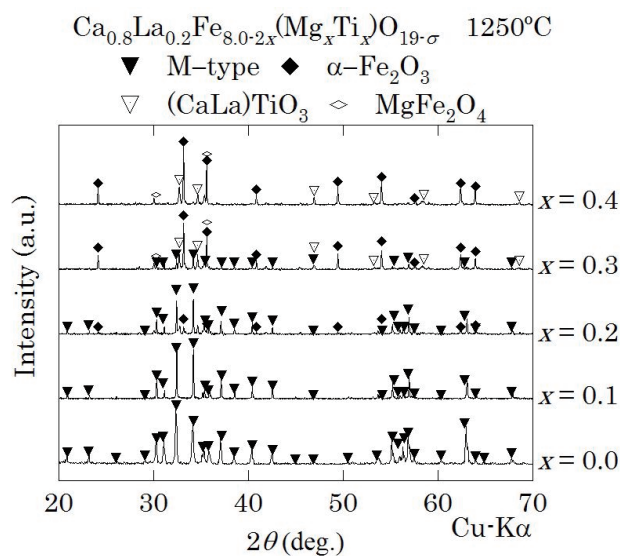


Fig. 1 X-ray diffraction patterns of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{8.0-2x}\text{Mg}_x\text{Ti}_x\text{O}_{19-o}$ ($x = 0.0-0.4$) sintered at 1250°C .

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 Energy Dispersive X-ray spectrometry (EDX). 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

3-1 Mg-Ti substituted Ca-based M-type ferrite

Figure 1 shows the X-ray diffraction patterns of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{8.0-2x}\text{Mg}_x\text{Ti}_x\text{O}_{19-\sigma}$ ($x = 0.0-0.4$) sintered at 1250°C. The main phase is M-type ferrite for the samples with $x \leq 0.2$. The sample at $x = 0.2$ also showed the minority $\alpha\text{-Fe}_2\text{O}_3$ phase. The sample at $x = 0.3$ was made up of the mixed phases of $\alpha\text{-Fe}_2\text{O}_3$, M-type ferrite, MgFe_2O_4 , and $(\text{CaLa})\text{TiO}_3$. The samples at $x \geq 0.4$ consisted of $\alpha\text{-Fe}_2\text{O}_3$, MgFe_2O_4 , and $(\text{CaLa})\text{TiO}_3$ phases, but didn't contain M-type ferrite phase. The chemical composition of the perovskite compound of $(\text{CaLa})\text{TiO}_3$ can be various forms such as $\text{Ca}_{0.2}\text{La}_{0.53}\text{TiO}_3$, $\text{Ca}_{0.4}\text{La}_{0.4}\text{TiO}_3$, and $\text{Ca}_{0.12}\text{La}_{0.58}\text{TiO}_3$.^{15,16} It is difficult to determine the chemical composition exactly because the lattice constant of $(\text{CaLa})\text{TiO}_3$ is similar to that of CaTiO_3 . Since Ca and La cations became starting materials to form the perovskite compounds, M-type ferrite was not formed.

Figure 2 shows the room-temperature saturation magnetization of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{8.0-2x}\text{Mg}_x\text{Ti}_x\text{O}_{19-\sigma}$ ($x = 0.0-0.4$) sintered at 1200–1300°C. Here, the saturation magnetization of the sample at $x = 0.0$ is that of sample prepared with the optimum preparation conditions in the previous study.¹¹ The saturation magnetization decreased with increasing the amount of Mg-Ti substitution. The gradual decrease of the magnetization indicated the formation of Mg-Ti substituted M-type ferrite at $x = 0.1$ and $1225^\circ\text{C} \leq T_s \leq 1250^\circ\text{C}$. The substitution of non-magnetic Mg^{2+} and Ti^{4+} for magnetic Fe^{3+} can decrease total magnetic moment. Even at the same substitution rate of $x=0.1$, however, the samples with $T_s=1200^\circ\text{C}$ and 1300°C showed low magnetizations. The decrease of the magnetization was more obvious at $x=0.2$ and $T_s \geq 1225^\circ\text{C}$ in spite that the main phase was the M-type phase. It should be noted that the synthesis condition of Ca-based M-type ferrite is so delicate that the M-type structure can easily be broken.¹¹ Since the sample at $x = 0.2$ and $T_s = 1200^\circ\text{C}$ didn't contain M-type ferrite phase, the saturation magnetization became much smaller than those of the $x = 0.2$ samples with higher sintering temperatures.

Figure 3 shows the temperature dependence of magnetization of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{8.0-2x}\text{Mg}_x\text{Ti}_x\text{O}_{19-\sigma}$ at $0.0 \leq x \leq 0.2$. The Curie temperature decreased with increasing the amount of Mg-Ti substitution. The non-magnetic

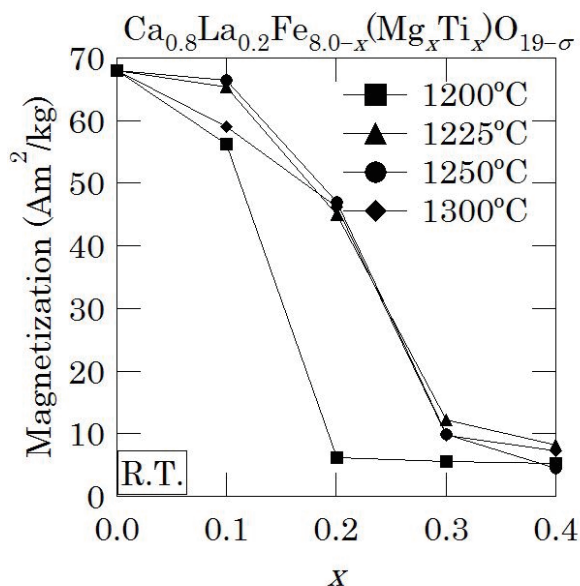


Fig. 2 Saturation magnetization at room temperature of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{8.0-2x}\text{Mg}_x\text{Ti}_x\text{O}_{19-\sigma}$ ($x = 0.0-0.4$) sintered at 1200, 1225, 1250°C and 1300°C.

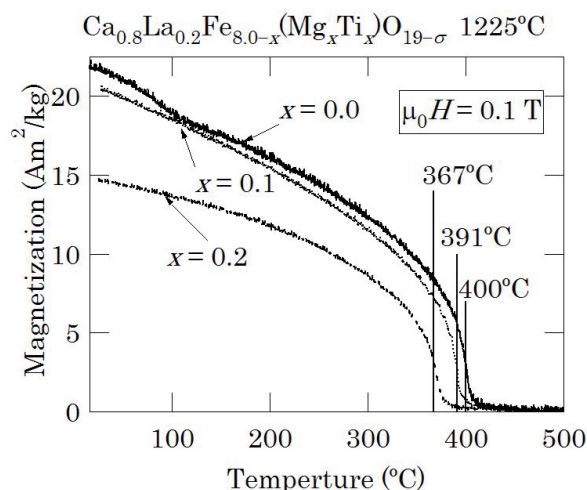


Fig. 3 Temperature dependence of magnetization of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{8.0-2x}\text{Mg}_x\text{Ti}_x\text{O}_{19-\sigma}$ ($x = 0.1$ and 0.2) sintered at 1225°C and $x = 0.0$ sintered at 1250°C.

Mg^{2+} and Ti^{4+} ions decrease the number of the connection between magnetic iron ions ($\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{3+}$) in Mg-Ti substituted Ca-based M-type ferrite at $x \leq 0.2$.

3-2 Al substituted Ca-based M-type ferrite

Figure 4 shows X-ray diffraction patterns of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{8.0-x}\text{Al}_x\text{O}_{19-\sigma}$ ($x = 1.0-4.0$) sintered at 1250°C. The main phase is M-type ferrite for these samples although minority phases of CaFe_4O_7 and CaAl_4O_7 are also observed. The formation of CaFe_4O_7 can be caused by the deficiency of Fe cations to form the M-type structure. Therefore, we attempted to increase the amounts of $(\text{Fe}+\text{Al})/(\text{Ca}+\text{La})$ to 10.

Figure 5 shows X-ray diffraction patterns of

$\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{10-x}\text{Al}_x\text{O}_{19-\sigma}$ ($x = 1.0-4.0$) sintered at 1300°C . The samples of $x = 1.0$ and 2.0 are in the single phase of M-type ferrite, but the samples of $x = 3.0$ and 4.0 have the main M-type ferrite phase and the minority CaFe_4O_7 phase. Here, it should be noted that high temperature sintering is necessary for formation of

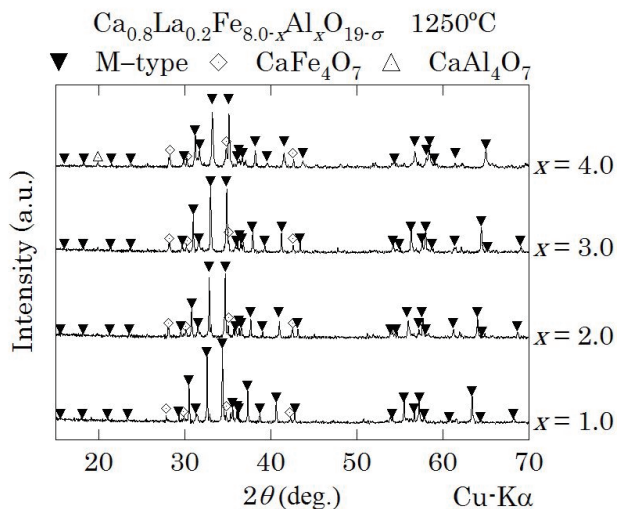


Fig. 4 X-ray diffraction patterns of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{8.0-x}\text{Al}_x\text{O}_{19-\sigma}$ ($x = 1.0-4.0$) sintered at 1250°C .

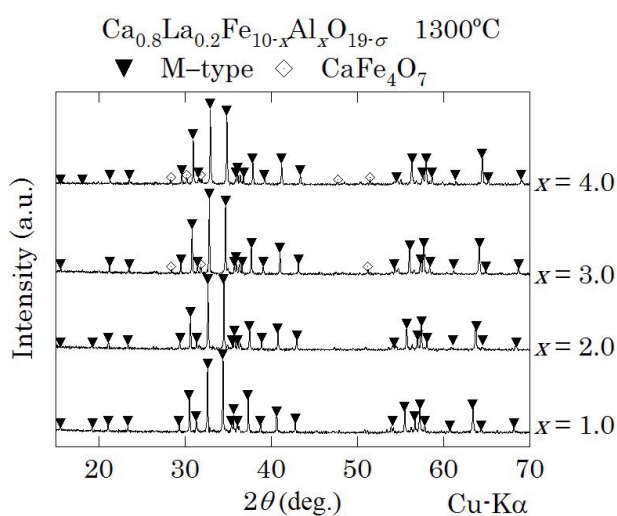


Fig. 5 X-ray diffraction patterns of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{10-x}\text{Al}_x\text{O}_{19-\sigma}$ ($x = 1.0-4.0$) sintered at 1300°C .

Table 1 Ionic radii of each coordination number of Fe and Al.

	Octahedral	Tetrahedral	Trigonal bipyramidal
Fe^{3+} (Å)	0.645	0.49	0.58
Al^{3+} (Å)	0.535	0.39	0.48

$\text{CaAl}_{12}\text{O}_{19}$.¹⁷⁾ Actually, Nagumo *et al.* reported that iron-substituted hibonite ($\text{CaAl}_{12-x}\text{Fe}_x\text{O}_{19}$) samples were synthesized at a relatively low sintering temperature of 1300°C as the amount of Al was decreased.¹⁸⁾ Therefore, it is possible that the substitution of Al may increase the suitable sintering temperature to form the single M-type phase. Also, the diffraction peaks of M-type phase shifted to the higher angle side as the substitution amount increased. Table 1 shows the ionic radii of Fe^{3+} and Al^{3+} .¹⁹⁾ Since Al^{3+} is smaller than Fe^{3+} , the lattice constants decrease with increasing the amount of Al^{3+} , as shown in Fig. 6. Therefore, the Al-substituted M-type ferrite was formed successfully.

Figure 7 shows the saturation magnetization and the coercivity at room temperature of

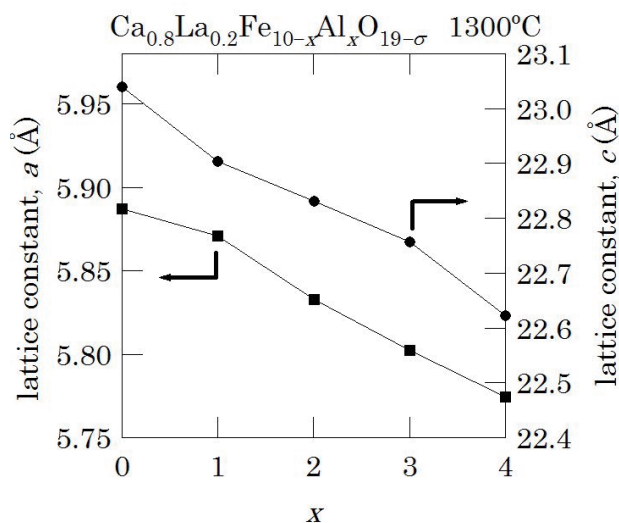


Fig. 6 Lattice constant of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{10-x}\text{Al}_x\text{O}_{19-\sigma}$ ($x = 1.0-4.0$) sintered at 1300°C .

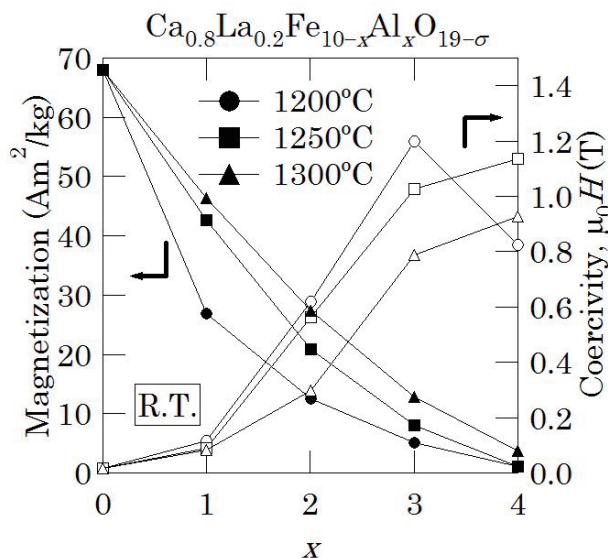


Fig. 7 Saturation magnetization and coercivity at room temperature of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{10-x}\text{Al}_x\text{O}_{19-\sigma}$ ($x = 1.0-4.0$) sintered at $1200-1300^\circ\text{C}$.

$\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{10-x}\text{Al}_x\text{O}_{19-\sigma}$ ($x = 1.0\text{--}4.0$) sintered at $1200\text{--}1300^\circ\text{C}$. The saturation magnetization decreased and the coercivity increased with increasing amount of Al. The decrease of the saturation magnetization at room temperature is caused by the substitution of non-magnetic ions (Al^{3+}) for magnetic ions (Fe^{3+}), which can decrease the intrinsic magnetic moment and the Curie temperature.

In contrast, the Al substitution increased the coercivity of the Ca-based M-type ferrite although the coercivity of the starting sample without Al was small.¹¹⁾ The Al-substitution effect on coercivity is similar to those of other M-type ferrites. For instance, Haneda and Kojima reported that $\text{BaAl}_x\text{Fe}_{12-x}\text{O}_{19}$ exhibited a large increase in coercivity and that the magnetocrystalline anisotropy field contributed greatly to the increase of coercivity.²⁰⁾ De Bitetto also found that the anisotropy field of $\text{SrO} \cdot x\text{Al}_2\text{O}_3 \cdot (6-x)\text{Fe}_2\text{O}_3$ increased as the substitution amount of Al (x) was increased.²¹⁾

The Al-substitution effects on coercivity of M-type ferrites have been attributed to the variation of magnetocrystalline anisotropy under the assumption of a single-domain model (Stoner-Wohlfarth model).^{8,10,20-21)} This assumption is plausible because the single-domain structure can be stabilized by the reduction of magnetostatic energy if the decrease of the saturation magnetization is more significant than the change of the magnetocrystalline anisotropy.²²⁻²³⁾ According to the Stoner-Wohlfarth model, the coercivity can be expressed as

$$H_c \propto K_1/M_s$$

where H_c is the coercivity, K_1 is the magnetocrystalline uniaxial anisotropy constant, and M_s is the saturation magnetization. If the decrease of K_1 is smaller than the decrease of M_s , H_c can be increased. The studies of Al substituted Sr-based M-type ferrite also showed that the saturation magnetization decreased and the coercivity increased with increasing amount of Al.^{8-10, 21)} This tendency is consistent with our result.

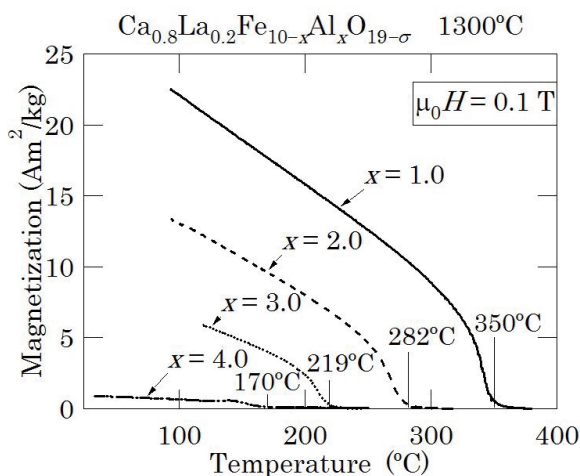


Fig. 8 Temperature dependence of magnetization of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{10-x}\text{Al}_x\text{O}_{19-\sigma}$ ($x = 1.0\text{--}4.0$) sintered at 1300°C .

Figure 8 shows the temperature dependence of magnetization of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{10-x}\text{Al}_x\text{O}_{19-\sigma}$ ($x = 1.0\text{--}4.0$) sintered at 1300°C . The Curie temperature of these samples decreased with increasing the amount of Al. As the Al substitution increased by $\Delta x = 1$, the Curie temperature decreased by $\Delta T_C = 50\text{--}70^\circ\text{C}$. The substitution of the non-magnetic Al^{3+} for Fe^{3+} causes to decrease the links of $\text{Fe}^{3+}\text{--O}^{2-}\text{--Fe}^{3+}$, and consequently weakens the superexchange interaction in the M-type structure.

Figure 9 shows the magnetization curves at 5 K (-268°C) of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{10-x}\text{Al}_x\text{O}_{19-\sigma}$ ($x = 1.0$ and 2.0) sintered at 1300°C . The saturation magnetic moment per molecule at $x = 1.0$ is estimated to be $12.5 \mu_B/\text{f.u.}$ from the magnetization at $\mu_0 H = 7$ T ($85.0 \text{ Am}^2/\text{kg}$). The EDX analysis showed the chemical formula of this sample as $\text{Ca}_{0.88}\text{La}_{0.12}\text{Fe}_{8.80}\text{Al}_{1.01}\text{O}_{15.8}$. Here, the composition ratio of oxygen is estimated from the charge balance with the concentration of Ca^{2+} , La^{3+} , Fe^{3+} , and Al^{3+} cations.

The saturation magnetic moment per molecule at $x = 2.0$ is also estimated to be $7.86 \mu_B/\text{f.u.}$ from the magnetization at $\mu_0 H = 7$ T ($55.1 \text{ Am}^2/\text{kg}$). The EDX analysis of this sample showed the chemical formula of $\text{Ca}_{0.83}\text{La}_{0.17}\text{Fe}_{7.88}\text{Al}_{1.83}\text{O}_{15.7}$.

Comparing these two results, the difference of the magnetic moment between these two samples is $4.7 \mu_B$, which is approximately close to the magnetic moment of Fe^{3+} ($5 \mu_B$). In other words, as the substitution amount of Al^{3+} increased by 1, one Fe^{3+} located at the up spin sites decreased. In other words, Al^{3+} prefers to be located at the up spin sites. Therefore, the saturation magnetization was greatly decreased even by the small amount of Al substitution.

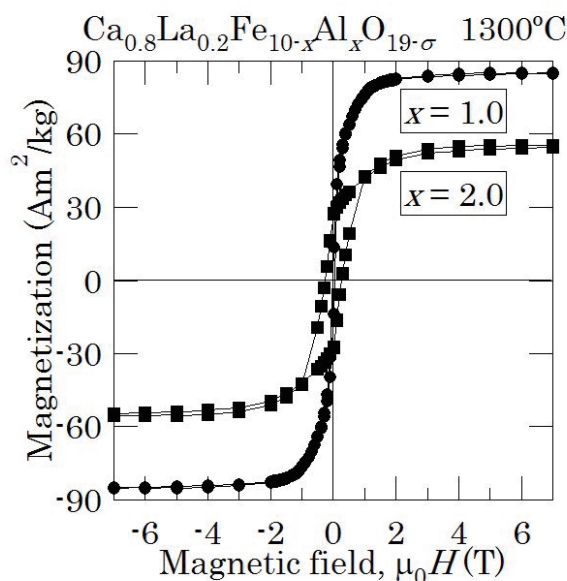


Fig. 9 Magnetization curves at 5 K (-268°C) of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{10-x}\text{Al}_x\text{O}_{19-\sigma}$ ($x = 1.0$ and 2.0) sintered at 1300°C .

4. Conclusion

We have investigated the synthesis conditions and magnetic properties of non-magnetic-ion-substituted Ca-based M-type ferrites. In the Mg-Ti substitution case of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{8.0-2x}\text{Mg}_x\text{Ti}_x\text{O}_{19-\sigma}$, the single-phase sample was formed at $x = 0.1$. As the amount of substitution increased, both the saturation magnetization and the Curie temperature decreased. In the Al substitution case of $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_{y-x}\text{Al}_x\text{O}_{19-\sigma}$ samples, the single M-type phase samples were formed at $x = 1.0$ and 2.0 sintered at 1300°C . As the amount of substituted Al increased, the saturation magnetization and the Curie temperature decreased and the coercivity increased. The Al substitution seems to change the distribution of iron cations in the M-type structure and to cause to change the magnetic properties.

References

- 1) J. Smit and H. P. J. Wijn: Ferrites, pp. 182–184, pp. 193–194 (Philips Technical Library, Netherlands 1959).
- 2) S. Chikazumi: Physics of Ferromagnetism, p. 212 (Oxford University Press, Oxford, 2009).
- 3) G. W. Rathenau: *Rev. Mod. Phys.*, **25**, 297 (1953).
- 4) Ü. Özgür, Y. Alivov, and H. Morkoc: *J. Mater. Sci-Mater. EL*, **20**, 789 (2009).
- 5) S. Alablance, J. They, and D. Viven: *Mater. Res. Bull.*, **24**, 475 (1989)
- 6) V. V. Soman, V. M. Nanoti, and D. K. Kulkarni: *Ceram. Int.*, **39**, 5713 (2013).
- 7) V. V. Soman, V. M. Nanoti, D. K. Kulkarni, and V. V. Soman: *Physics Procedia*, **54**, 30 (2014).
- 8) M. Liu, X. Shen, F. Song, J. Xiang, and X. Meng: *J. Solid State Chem.*, **184**, 871 (2011).
- 9) H. Z. Wang, B. Yao, Y. Xu, Q. He, G. H. Wen, S. W. Long, J. Fan, G. D. Li, L. Shan, B. Liu, L. N. Jiang, and L. L. Gao: *J. Alloy. Compd.*, **537**, 43 (2012).
- 10) H. Luo, B. K. Rai, S. R. Mishra, V. V. Nguyen, J. P. Liu: *J. Magn. Magn. Mater.*, **324**, 2602 (2012).
- 11) M. Shigemura, K. Watanabe, K. Kakizaki, and K. Kamishima: *J. Magn. Soc. Jpn*, **41**, 10 (2017).
- 12) T. Shimizu, M. Matsui: *Sci. Technol. Adv. Mater.*, **4**, 469 (2003).
- 13) T. Shimizu, H. Asano, M. Matsui: *J. Magn. Magn. Mater.*, **310**, 1835 (2007).
- 14) F. W. Clarke and H. S. Washington: The Composition of the Earth's Crust, pp. 20–21 (United States Geological Survey, Washington, 1924).
- 15) Z. Zhang, G. R. Lumpkin, C. J. Howard, K. S. Knight, K. R. Whittle, and K. Osaki: *J. Solid State Chem.*, **180**, 1083 (2007).
- 16) The Powder Diffraction File (PDF00-055-0922) by the Internal Center for Diffraction Data (ICDD): L. Vasylechko, Semiconductor Electronic Dept., L'viv Polytechnic Natinal Univ., Ukraine. ICDD Grant-in-Aid, (2016).
- 17) H. H. Mao, M. Selleby, and B. Sundman: *CALPHAD*, **28**[3], 307 (2004).
- 18) H. Nagumo, K. Watanabe, K. Kakizaki, and K. Kamishima: *J. Magn. Soc. Jpn*, **41**, 20 (2017).
- 19) R. D. Shannon: *Acta Cryst.*, **A32**, 751 (1976).
- 20) K. Haneda and H. Kojima: *Jpn. J. Appl. Phys.*, **12**, 355 (1973).
- 21) D. J. De Bitetto: *J. Appl. Phys.*, **35**, 3482 (1964).
- 22) *Ibid.* 1, p. 68.
- 23) *Ibid.* 2, p. 455.

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