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Single crystal synthesis and magnetic properties of Co²⁺-substituted and non-substituted magnetoplumbite-type Na-La ferrite

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Abstract

Single crystals of magnetoplumbite-type Na-La ferrite with and without Co doping were grown by the flux method. Wave length dispersive X-ray analysis reveals that Na and La are present in the ratio of Na/La = $0.25 - 0.41$, and Co is successfully substituted for Fe. Magnetization measurements using single crystals indicate uniaxial magnetic anisotropy in these materials. A metamagnetic transition for the hard-axis magnetization was observed in non Co²⁺-substituted samples at around 7 kOe due to the magnetic free energy double minima originating from the Fe²⁺ ion. The successful introduction of Co²⁺ enhances the uniaxial magnetic anisotropy favorable for permanent magnets.

Keywords:
magnetoplumbite-type Na-La ferrite, magnetocrystalline anisotropy, ferrite magnet, single crystal

1. Introduction

Magnetoplumbite(M)-type ferrite $A\mathrm{Fe}_{12}\mathrm{O}_{19}$ (A = Sr, Ba, Pb, $\cdots$) with the space group $P6_3/mmc$ undergoes a ferrimagnetic transition at $T = 720–740$ K and is a crucial magnetic material, particularly for hard magnets. The magnetism in the material originates from the Fe³⁺ ($3d^5$, $S = 5/2$, 5 μ_B) ions located on the $2a$-O, $2b$-B, and $12k$-O sites with majority spins, and on the $4f_1$-T and $4f_2$-O sites with minority spins, where the ion positions are given in terms of the Wyckoff positions and oxygen coordinations (O: octahedral, B: bipyramidal, and T: tetragonal). The total ordered moments amount to 20 μ_B for each formula unit.

Ion substitution effects on M-type ferrite magnets have been studied with the aim of improving remanence and coercivity, which are important measures for hard magnets. The most notable achievement is the enhancement of coercivity by co-substituting La and Co for Sr and Fe, respectively, in $\mathrm{SrFe}_{12}\mathrm{O}_{19}$ (SrM) [1], which is a prototypical material for high-performance ferrite magnets. The major factor of the enhanced coercivity in La-Co co-substituted SrM (La-Co SrM) is attributed to the enhancement of the magnetocrystalline anisotropy (MA) of the base material due to the unquenched angular momentum of Co²⁺. La³⁺ is substituted for Sr²⁺ to compensate for the extra charge generated by substituting Co²⁺ for Fe³⁺. Recently, focus has shifted to La-Co CaM, the calcium analogue of La-Co SrM, owing to its better performance compared to La-Co SrM[2].

The uniaxial MA increases with increasing Co²⁺ concentration in La-Co SrM [3]. However, Co²⁺ concentration is not the only factor affecting MA in La-Co co-substituted M-type ferrite. One example is the MA in La-Co CaM, which depends not only on the Co²⁺ concentration but also on the Ca to La ra-

tio [4]. Another example is the dependence of the MA on the concentration of La³⁺ x in $\mathrm{Sr}_{1-x}\mathrm{La}_x\mathrm{Fe}_{11.6}\mathrm{Co}_{0.4}\mathrm{O}_{19}$ ($0.4 \leq x \leq 1$) [5]. As these A site cations are non-magnetic, they do not affect the MA directly. The comparison of M-type ferrites with Co substituted by various A cations would give valuable information to reveal the mechanism of how the A cations affect the MA. Single-crystal measurements are crucial in estimating the intrinsic MA of materials. However, such measurements have been limited for La-Co SrM [5, 6] and La-Co CaM [4]. Here, we focus on Co²⁺-substituted M-type Na-La ferrite.

In the first report on the synthesis of M-type Na-La ferrite, the ratio of Na to La was assumed to be 1 : 1 under the idea that the average valence of the A site is +2 [7]. The introduction of Co²⁺ seems impossible. Detailed X-ray diffraction analysis using a single crystal, however, revealed that La and Na are not equally distributed on the A site. The amount of La exceeds that of Na, i.e., the actual chemical composition of M-type Na-La ferrite is $\mathrm{Na}_{0.3}\mathrm{La}_{0.7}\mathrm{Fe}^{3+}_{11.6}\mathrm{Fe}^{2+}_{0.4}\mathrm{O}_{19}$ [8]. This suggests that the Fe²⁺ can be replaced by Co²⁺. To the best of our knowledge, no studies on Co²⁺-substituted M-type Na-La ferrite have been reported. In this paper, we perform a comprehensive study on Co²⁺-substituted and non-substituted M-type Na-La ferrite. Our study comprises of single crystal growth, chemical characterization, and magnetic measurements.

2. Experiments

Single crystals of Co²⁺-substituted and non-substituted M-type Na-La ferrite were synthesized by the Na₂O flux method. $\mathrm{Na}_2\mathrm{CO}_3$, $\mathrm{La}_2\mathrm{O}_3$, $\mathrm{Fe}_2\mathrm{O}_3$ and $\mathrm{Co}_3\mathrm{O}_4$ were weighed in the atomic ratio of Na : La : Fe : Co = 0.75 : 1.25 : 12 - α : α, where $\alpha = 0 – 0.7$. The powders were grounded and placed in Pt crucibles followed by heat treatment. The samples were heated at 1400°C

for 12 h and cooled to 1200°C at the rate of 2.5–7.5 °C/h. The crystals were then separated from flux by boiled distilled water and diluted hydrochloric acid. A part of the obtained crystals was crushed into powder for X-ray diffraction (XRD) measurements with X'Pert PRO Alpha-1, PANalytical to confirm a single phase of the M-type ferrite and estimate the lattice constants. The compositions of metallic elements Na, La, Fe, and Co were analyzed using a wavelength-dispersive X-ray (WDX) spectrometer (INCA Wave 500, Oxford Instruments) attached to a scanning electron microscope (S-3500H, Hitachi), which can resolve the Fe and Co spectra. Characteristic X-rays were examined at an acceleration voltage of 25 kV. The X-ray intensities were calibrated using single crystals of NaCl, LaAlO$_3$, SrFe$_{12}$O$_{19}$, and metallic Co as reference materials. Signals were averaged at three points in each sample to determine the compositions. The Curie temperature, T_C, was determined from the temperature dependence of magnetization measured using a vibrating sample magnetometer (VSM-5, Toei Industry). Magnetization isotherms were measured for single crystals along the easy ($H \parallel c$) and hard ($H \perp c$) axes using a SQUID magnetometer (MPMS, Quantum Design) in the temperature and field range of $T = 5 - 300$ K and $H = 0 - 70$ kOe, respectively. The demagnetization correction was performed by accounting for the sample shape. The anisotropic field H_A was evaluated as an indicator of MA. H_A is usually defined as the field where the hard axis magnetization saturates. However, it is difficult to determine a definite point because the hard-axis magnetization of La-Co co-substituted M-type ferrites is sometimes concave [4, 6]. For simplicity, here we estimated the anisotropic field as $H_A = K/2M_s$, where K is the area spanned by the easy and hard axis magnetizations, and M_s the saturation magnetization.

3. Results and Discussion

We successfully obtained single crystals in the form of shiny platelets with a size of $0.5 \times 0.5 \times 0.1$ mm^3. The powder XRD of the obtained single crystals shows the typical pattern of the M-type ferrite for all specimens. The lattice constants a and c (Table I) are comparable to the literature values of $a = 5.883$ Å and $c = 22.955$ Å [8].

The WDX results are also summarized in Table I. The chemical formula is written as Na$_x$La$_y$Fe$_z$Co$_w$O$_{19}$ by normalizing the metallic ion component to $x + y + z + w = 13$. It is notable that the amounts of Na are significantly less than that of La in all batches, and agree with the value suggested by XRD analysis [8]. The assumption that equal amounts of Na and La are present is not necessarily true due to the common appearance of Fe^{2+}, which compensates the charge balance of A site in M-type ferrite [9, 10]. The ratio of Na to La varies for each sample, suggesting a range of solubilities. We also found that $x + y$ exceeds 1 by about 0.05 for all samples. A similar nonstoichiometry has been pointed out in an analogue M-type Ca-La ferrite [11, 12, 13]. Two models for the nonstoichiometry in M-type Ca-La ferrite have been proposed: occupation of a part of Ca^{2+} at Fe sites [12, 14], and the presence of stacking faults in A/O packing [15]. However, no conclusive evidence

for either model has been found yet. WDX on #2–4 suggests the presence of Co in M-type Na-La ferrite, indicating the successful substitution of Co for Fe. The valence of Co must be +2 from magnetism arguments, as discussed later. Co amount in the obtained samples increase according to α, while the actual Co composition w is reduced from α. The magnitude of α and w in #3 and #4 are reversed, probably because the crystalline temperature, which may affect the yield composition, changes with different initial chemical compositions. The maximum Co concentration is about $w = 0.3$, comparable to La-Co SrM [6] and La-Co CaM [4].

T_Cs for #1–4 are 700–710 K, which are comparable to the previous report for M-type Na-La ferrite [7] and M-type Ca-La ferrite [13], and lower compared to typical M-type ferrites (720 – 740 K). The reduced T_C may be attributed to the interruption of the super-exchange interaction between ferric ions by Fe^{2+} and/or Co^{2+}.
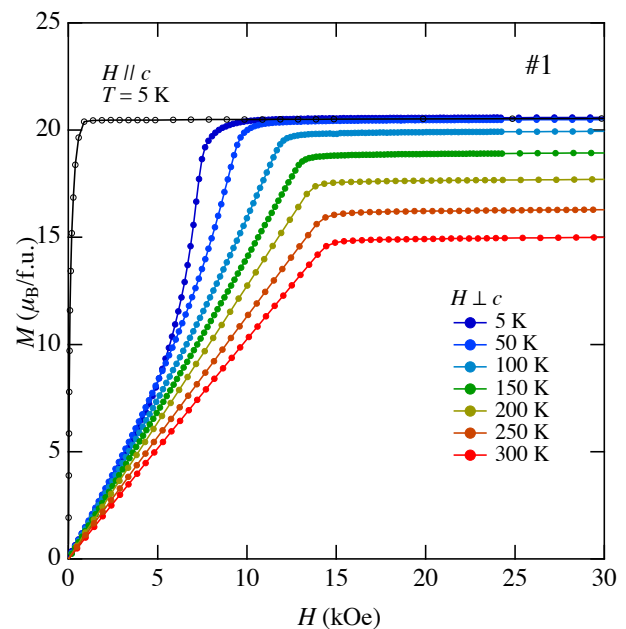

Figure 1: Magnetization curves for the M-type Na-La ferrite (#1). Spin-flip transition for hard axis at $T = 5$ K was observed at around 7 kOe.

Figure 1 shows the magnetization M curves of #1. M for $H \parallel c$ ($M_\parallel$) immediately saturates, whereas M for $H \perp c$ ($M_\perp$) linearly increases at low field, indicating uniaxial MA. It is notable that $M_\perp$ at $T = 5$ K shows a rapid increase at around $H = 7$ kOe, indicating a spin-flip transition. A similar magnetization process has been observed for M-type Ca-La ferrite [13]. The initial slope increases with temperature, suggesting the increase of MA. The spin-flip transition disappears with increasing temperature. This anomalous magnetic behavior is attributed to the presence of Fe^{2+}, as discused below.

The free energy of a ferromagnet with uniaxial symmetry is phenomenologically expressed as

$$E = K_1\sin^2\theta + K_2\sin^4\theta + K_3\sin^6\theta + \cdots - HM_s\cos(\theta - \phi), \quad (1)$$

Table 1: Chemical composition, lattice constants and Curie temperature of single crystal of $Na_xLa_yFe_zCo_wO_{19}$.

	α	x	y	z	w	x/y	Fe^{2+}	a (Å)	c (Å)	T_C (K)
#1	0	0.27	0.79	11.94	0	0.34	0.46	5.8845	22.9541	710
#2	0.3	0.34	0.82	11.72	0.12	0.41	0.20	5.8849	22.9449	702
#3	0.7	0.24	0.79	11.76	0.21	0.30	0.31	5.8858	22.9616	704
#4	0.5	0.21	0.83	11.65	0.31	0.25	0.27	5.8848	22.9416	700

where K_n is $2n$-th expansion coefficient and θ and ϕ represent the angles between the magnetization vector and the magnetic field with respect to the symmetry axis c, respectively. When the higher-order terms can be neglected, the magnetization process for the hard axis ($\phi = \pi/2$) becomes linear up to saturation. On the other hand, the magnetization shows a jump, which is named as a first-order magnetization process in the literature [16], under the condition that double minima of energy at $\theta = 0$ and $\pi/2$ exist.

Microscopically, the free energy double minima may originate from the single ion anisotropy of Fe^{2+}. Recently, Inoue et al. presented calculation results for the electronic structure of Fe^{2+}-O^{2-} clusters. The results exhibit double minima at c and the basal plane of d^6 configuration (Fe^{2+}) in M-type ferrite when Fe^{2+} enters the $2a$-O site [17]. Taking into consideration the observation of Fe^{2+} at the $2a$-O site by Mössbauer spectroscopy in $Sr_{1-x}La_xFe_{12}O_{19}$ and $LaFe_{12}O_{19}$ [18], in which the presence of Fe^{2+} is obvious from their chemical composition, the spin-flip transition in M-type Na-La ferrite may originate from the double minima of the free energy owing to the presence of Fe^{2+} at the $2a$-O site. Fe^{2+} may be present at the tetrahedral site ($4f_1$-T), based on bond valence sum analysis [8]. The determination of the Fe^{2+} sites in M-type Na-La ferrite is a subject for future study.

The temperature variation of anomalous magnetization also supports that its origin from Fe^{2+}. Anomalous MA due to Fe^{2+} at low temperature has been observed in $Sr_{1-x}La_xFe_{12}O_{19}$ [9] and $LaFe_{12}O_{19}$ [10]. H_A is dramatically enhanced for $LaFe_{12}O_{19}$ and less enhanced for $Sr_{1-x}La_xFe_{12}O_{19}$ with $0 < x < 0.75$ [9] at low temperatures, while H_A for these samples are almost temperature-independent and comparable to that of SrM at around room temperature. Two explanations have been proposed for the disappearance of MA due to Fe^{2+} at room temperature: One is the energy scale of spin-orbit coupling of Fe^{2+} (approximately 100 K), which is consistent with the spin flip transition disappearing around 100 K. The other explanation is the hopping of Fe^{2+} in M-type ferrite at increased temperatures, which reduces the MA effect [19].

We show the magnetization of Co^{2+}-substituted system #4, representative of the Co^{2+}-substituted samples, in Fig. 2. The $M_\perp$ curves at low temperatures have finite slopes even at 70 kOe, suggesting that the magnetization does not reach saturation within the measured field range. This is indicative of the enhanced MA associated with successful Co substitution. The non-linear or convex magnetization process is similar to that observed in other La-Co co-substituted systems [4, 5, 6]. The initial slopes are almost temperature-independent, unlike those of #1. At higher temperatures, $M_\perp$ saturates within the available
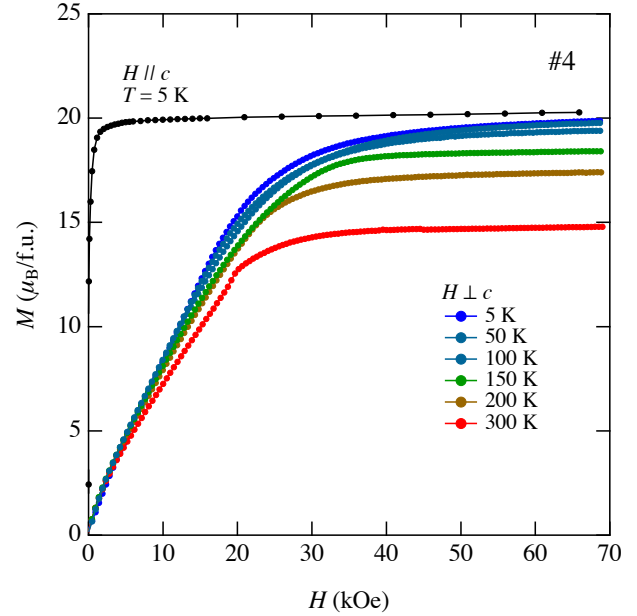

Figure 2: Magnetization for Co^{2+}-substituted Na-La M ferrite (#4).

field range.

Figure 3 shows the temperature dependences of saturation moment M_s for #1–#4. The overall temperature dependence is similar to those of the other M-type ferrites. One notable feature is that the saturation moment for #1 exceeds 20 μ_B/f.u. M_s for Co^{2+}-substituted systems is less than that of #1. The variation of M_s is not a simple function of Co^{2+} concentration, and may be affected by the complicated site occupation of Co^{2+} and Fe^{2+}.

The temperature dependences of H_A for #1 – #4 are shown in Fig. 4. H_A of SrM, which is almost temperature-independent below room temperature, is also shown for comparison. H_A of #1 is less than that of SrM for all temperatures and decreases with decreasing temperature similar to M-type Ca-La ferrite [13]. The further drop below 100 K is attributed to the spin-flip transition discussed above. On the other hand, H_A at the lowest temperature is enhanced and decreases monotonically with increasing temperature in Co^{2+}-substituted systems.

A comparison of the temperature dependence of H_A among La-Co co-substituted M-type ferrites with different A site ions demonstrates that the Co^{2+} concentration is not the sole factor affecting the enhancement of the uniaxial MA. For example, H_A of La-Co CaM with $w = 0.1$ (#2 in the reference [4]), which has a comparable amount of Co^{2+} to #2 in this study,
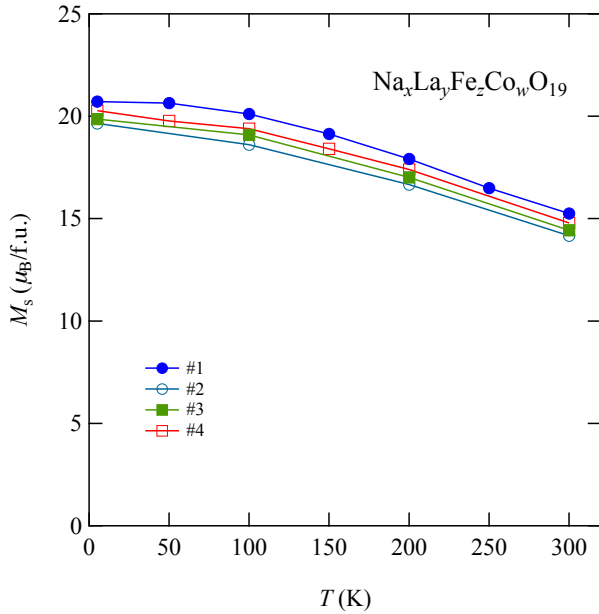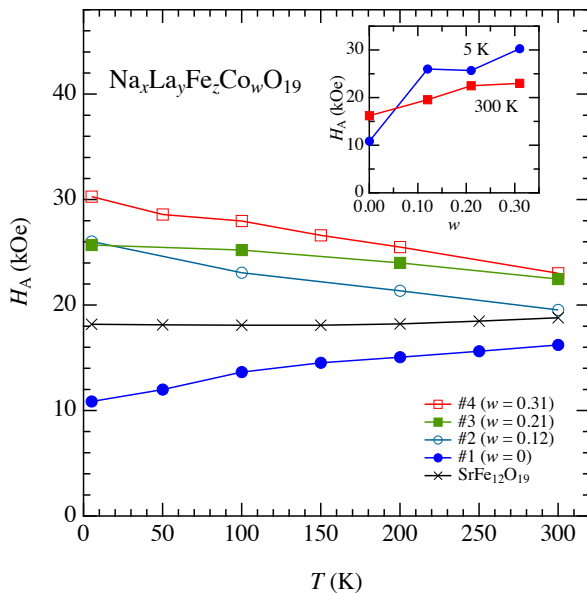
Figure 3: Temperature dependence of M_s for #1–#4.

Figure 4: Temperature dependence of H_A for #1–#4. The data for SrM is taken from our previous report [13]. The inset shows the w (Co^{2+} concentration) dependence of H_A for 5 and 300 K.

has the value of 18 kOe at the lowest temperature, reaches its maximum (22 kOe) at around T = 150 K and remains almost temperature-independent above the temperature. This behavior is quite different from that of #2 in this work, which shows a monotonic decrease of MA with increasing temperature. As another example, the H_A of La-Co CaM with w = 0.17 (#3 in the reference [4]) has a higher value (25 kOe) at room temperature compared to that of Co^{2+}-substituted M-type Na-La ferrite with w = 0.31, despite the fairly low Co^{2+} concentration of the former.

Here, we discuss how non-magnetic A site ions contribute to MA in La-Co co-substituted M-type ferrite. One possible mechanism is the generation of Fe^{2+}. While the direct determination of Fe^{2+} amount is not easy, the charge balance of the A site is not solely preserved by Co^{2+} compensation in La^{3+}-substituted systems; Co^{2+} and Fe^{2+} may coexist together. The low-temperature drop of H_A in La-Co CaM with w = 0.1 [4] may be accounted for by the presence of Fe^{2+}, as was observed for #1. The contribution of Fe^{2+} to MA at room temperature, however, is not significant as discussed above. The enhancement and temperature dependence of MA at around room temperature is attributed to Co^{2+}. The second mechanism for the contribution of non-magnetic A site ions to MA is via the alternation of Co^{2+} site preference. As revealed by NMR spectroscopy, Co^{2+} ions are non-uniformly distributed over the $2a$-O, $4f_1$-T and $12k$-O sites, and mainly located on the $4f_1$-T site [20]. Since H_A is correlated with the concentration of Co^{2+} on the $4f_1$-T site, Co^{2+} on the site contributes to uniaxial MA. When Co^{2+} on the $2a$-O and $12k$-O sites have unquenched orbital moments, the MA is planer-type [17]. As the MA due to Co^{2+} differs depending on the sites Co^{2+} occupies, the total MA varies with the Co^{2+} distribution even thought the Co^{2+} concentration is the same among the La-Co co-substituted M-type ferrites. The ionic size of the A cation affects the site preference of Co^{2+} owing to the inverse correlation of the c-axis length with Co^{2+} occupation of the $4f_1$-T site [20].

4. Summary

We successfully synthesized single crystals of Co^{2+}-substituted and non-substituted M-type Na-La ferrite, a possible base material for high-performance hard ferrite magnets. Chemical compositions studied by WDX revealed that the Na-La ratio is Na/La = 0.25 – 0.41, and Co^{2+} has been successfully substituted. Magnetization measurements demonstrated the uniaxial MA in these materials. The spin-flip transition observed for the non-doped sample was attributed to the double minima of Fe^{2+} ion free energy in the system. Substituted Co^{2+} enhances the uniaxial MA of M-type Na-La ferrite, which is favorable for hard magnets. The role of A site cations for MA was discussed.

Acknowledgements

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