Flux growth of magnetoplumbite-type strontium ferrite single crystals with La-Co co-substitution

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Abstract

The Na₂O flux method was successfully applied in the single crystal synthesis of the magnetoplumbite-type strontium ferrite with La-Co co-substitution (Sr_{1-x}La_xFe_{12-y}Co_yO₁₉), which is a familiar base material for commercial permanent magnets. The initial amount of Na₂O flux was fixed in the molar ratio of Na/(Sr+La) = 5.17. Composition analysis revealed discordance between La and Co concentrations ($x > y$) in the obtained crystals, indicating that the extra charge introduced by the Co²⁺ substitution for Fe³⁺ is not compensated by La³⁺ for Sr²⁺. In the present growth condition, the necessary amount of La is nearly twice that of Co ($y/x \simeq 0.55$), suggesting valence instability of an appreciable amount of Fe³⁺ to Fe²⁺. Single crystalline magnetization measurements showed that the substitution markedly enhances the magnetic anisotropy and slightly raises the saturation magnetization. Remaining problems, which should be resolved before the experimental determination of the Co site occupation, are also discussed.

Keywords: magnetoplumbite-type strontium ferrite, single crystal, magnetic anisotropy, La-Co co-substitution

1. Introduction

Magnetoplumbite-type (M-type) strontium ferrite, SrFe₁₂O₁₉ (will be called SrM), has been one of important base materials for the permanent magnet because of its high cost performance and chemical stability in spite of much smaller producible magnetic flux than rare-earth based permanent magnets. The M-type crystal structure has hexagonal symmetry with space group $P6_3/mmc$, in which there are five crystallographically inequivalent Fe sites; $2a$, $2b$, $4f_1$, $4f_2$, and $12k$ with different oxygen coordinations (see Table 1). All Fe ions are trivalent with the $S = 5/2$ spin quantum number corresponding to the spin moment of $5 \mu_B$. The magnetic moments direct uniaxially along c axis, with majority spin at $2a$, $2b$, and $12k$ and minority spin at $4f_1$ and $4f_2$, resulting in

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a ferrimagnetic spin structure with $20 \mu_B$ per formula unit (f.u.) at the ground state.

The simultaneous substitution of La and Co in SrM (will be denoted by La-Co SrM) resulted in marked improvement in the magnetic performance [1]. The improved performance has been discussed along with enhancement in the magnetocrystalline anisotropy expected from the single ion anisotropy of Co^{2+} ($3d^6$) with residual angular momentum [2]. Since crystal field splitting of $3d$ orbitals in oxides is dominated by oxygen coordination, it is essential to determine experimentally Co site occupation to reveal the origin of the anisotropy. Although a number of works have already been done, a consensus on the Co site occupation has not been achieved; for example, $2a$ and $4f_2$ by conventional methods including Mössbauer spectroscopy [3, 4, 5], $4f_1$ and $4f_2$ by nuclear magnetic resonance (NMR) [6], $2a$, $4f_1$, and $12k$ by a combined study of extended X-ray absorption fine structure (EXAFS), neutron diffraction, and X-ray magnetic circular dichroism (XMCD) [7].

The disagreement is primarily ascribed to the presence of a huge number of unknown parameters which should be determined in the experimental analyses, in addition to unsubstantiated assumptions. For example, the extra charge resulted from the La^{3+} substitution has often been assumed to be compensated entirely by Co^{2+} . However, this assumption disagrees with a recent phase diagram study [8], which indicates that Fe_2O_3 and LaFeO_3 are included as second phases even when the preparation is started from the equal amounts of La and Co raw materials [9]. Generally, second phases are poorly crystallized and the amount is often too poor to be detected by X-ray diffraction (XRD). The real chemical formula of La-Co SrM should be $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$ with $x > y$. In this case, the charge variation associated with the La^{3+} substitution is likely to be compensated by not only the Co^{2+} substitution but also the reduction of Fe^{3+} to Fe^{2+} . Thus, the as-mixed nominal values are inappropriate as the actual compositions.

Single crystals, free from second phases, are more appropriate for reducing unknown parameters in experimental analyses. Single crystals of $\text{SrFe}_{12}\text{O}_{19}$ and its related materials have been synthesized by various methods such as a floating zone method under high oxygen pressure [10], a traveling solvent floating zone method [11], and flux methods with various flux [12, 13, 14, 15]. Since $\text{SrFe}_{12}\text{O}_{19}$ melts incongruently in ambient atmosphere [16], the flux method is suitable to obtain single crystals in ambient conditions. Although single crystals in which either the Sr or Fe site is replaced by another element have been synthesized [17, 18], to the best of our knowledge, doubly substituted single crystals have not been reported so far.

In this article, we report single crystal growth of La-substituted SrM (will be abbreviated as La SrM) and La-Co SrM using the Na_2O flux method and magnetic properties of the obtained crystals.

Table 1: Crystallographic Fe sites in $\text{SrFe}_{12}\text{O}_{19}$ with space group $P6_3/mmc$ and magnetic moment directions at the sites.

Wyckoff notation	oxygen coordination	moment direction
$2a$	octahedral	$\uparrow$
$2b$	bipyramidal	$\uparrow$
$4f_1$	tetrahedral	$\downarrow$
$4f_2$	octahedral	$\downarrow$
$12k$	octahedral	$\uparrow$

2. Experiments

We grew single crystals of $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$ (La SrM) and $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$ (La-Co SrM) by the Na_2O flux method in a platinum crucible [18]. Na_2CO_3 (purity 99.99%), SrCO_3 (99.9%), La_2O_3 (99.9%), Fe_2O_3 (99.99%), and Co_3O_4 (99.9%) were weighted and mixed well in an agate mortar for several hours. In the present synthesis condition, the initial amount of the Na_2O flux was fixed in a molar ratio $\text{Na}/(\text{Sr}+\text{La}) = 5.17$. When making La-Co SrM, we mixed the same amounts of La and Co in atomic percent. The mixture, set in a Pt crucible, was heated in a furnace with a molybdenum disilicide heater under ambient atmosphere. The mixture was kept at 1450°C for 12 h, cooled down to 1000°C in the rate of $2.5^\circ\text{C}/\text{h}$, and followed by furnace-cooling below 1000°C to room temperature. Obtained single crystals were typically in the dimension of $5 \times 5 \times 0.1$ mm³, in which hexagonal shapes were seen on the surface. The crystals were separated by dissolving residual in diluted hydrochloric acid, and followed by annealing in air at 1200°C for 6 days.

A part of obtained crystals were crushed into powder to measure XRD (X'Pert PRO Alpha-1, PANalytical) to confirm a single phase of the M-type ferrite and to estimate lattice constants. As an example, the XRD pattern of a powdered sample ($\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$ with $x = 0.378$ and $y = 0.212$) is shown in Fig. 1. Compositions of metallic elements, x and y , were analyzed using wavelength-dispersive X-ray (WDX) spectrometer (INCA Wave 500, Oxford Instruments) attached to a scanning electron microscope (S-3500H, Hitachi), which can separate thoroughly Co and Fe spectra. Characteristic X-rays, Sr- $L\alpha$, La- $L\alpha$, Fe- $K\alpha$, and Co- $K\alpha$, were examined at an acceleration voltage of 25 kV. The X-ray intensities were calibrated by using single crystals of $\text{SrFe}_{12}\text{O}_{19}$, LaAlO_3 , and metallic Co as reference materials. Intensities measured at at least three points in each sample were averaged to determine the compositions. The ratio of $(\text{Fe}+\text{Co})/(\text{Sr}+\text{La})$ always exceeds 12 because temperature fluctuation of the pentaerythritol (PET) analyzing crystal leads to unavoidable peak drift of the Sr- $L\alpha$ line with a relatively long wavelength ($= 6.86 \text{ \AA}$), resulting in underestimation (2–3%) of the Sr intensity. Here we show the concentration in the form of $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$ assuming $(\text{Fe}+\text{Co})/(\text{Sr}+\text{La}) = 12$. We also

applied WDX to check the possible inclusion of Na in the crystals. A trace of Na signal was occasionally detected, but did not indicate convincingly appreciable inclusion of Na in the crystals.

Magnetization (M) was measured at 5 K in fields (H) up to 70 kOe using a SQUID magnetometer (MPMS, Quantum Design) installed in the LTM center of Kyoto University. Magnetization for the easy axis ($H \perp c$) and the hard axis ($H \parallel c$) was independently measured for the identical crystal. The demagnetization correction was done by taking into account the sample shape. The anisotropy constant, K_1 , in the dimension of energy was estimated by integrating the area surrounded by the easy- and hard-axis M - H curves. Here, we discuss the anisotropy in the form of the anisotropy field, $H_A = 2K_1/M_s$ where M_s is the saturation magnetization, which is compared with literature data estimated by the singular point detection (SPD) method for polycrystalline samples [19]. The Curie temperature, T_C , was determined from the magnetization measured by a vibrating sample magnetometer (VSM-5, Toei Industry).

3. Results

3.1. $Sr_{1-x}La_xFe_{12}O_{19}$ (La SrM)

WDX analysis manifested that La was successfully doped in single crystalline La SrM. In the present work, the upper limit of the La concentration, x , is ~ 0.4 . This is roughly consistent with $x < 0.5$ at 1300°C in a literature [20]. Although La SrM has been synthesized in the range of $0 \leq x \leq 1$, rapid cooling is necessary for higher La concentrations.

Figure 2 shows typical easy- and hard-axis magnetization curves measured at 5 K for selected samples ($x = 0$ and 0.395). The easy-axis magnetization is insensitive to the substitution, whereas the hard-axis component saturates at a lower field for $x = 0.395$, indicating reduced anisotropy in La SrM. The hard-axis magnetization bends slightly on approaching the saturation, which can be interpreted phenomenologically as the appearance of higher order terms in the anisotropy energy.

As seen in Fig. 3 (a), the lattice constant, a , increases slightly with x , whereas c markedly decreases, which is ascribed to the smaller ionic volume of La^{3+} than Sr^{2+} . Figure 3 (b) shows the saturation magnetization, M_s , at 5 K. The dashed line represents the calculated magnetization for La SrM based on the GGA+ U method [21]. In a literature [22], M_s decreases monotonically with x . In our case, such a tendency is not convincing because of the limited number of data. In contrast to M_s , the anisotropy field, H_A , drastically decreases with x as seen in Fig. 3 (c). On the other hand, it should be noted that H_A for the other end compound, $LaFe_{12}O_{19}$, is enhanced up to 40 kOe (at the lowest temperature) [23]. This means that H_A takes a minimum at a certain x , as actually observed at $x \sim 0.5$ [24]. Although the origin of this characteristic variation has not been elucidated, it may be related to the appearance of Fe^{2+} with unquenched orbital momentum and occupation sites of Fe^{2+} : The enhancement in $LaFe_{12}O_{19}$ was attributed to Fe^{2+} appeared at $2a$ [23, 25]. On the other hand, at small x , it

Figure 1: (Color online) X-ray diffraction pattern for powdered single crystals of $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$ with $x = 0.378$ and $y = 0.212$. The basal plane of the powder are preferentially oriented.

Figure 2: (Color online) Typical magnetization curves for easy- (red) and hard-axes (blue) at 5 K for $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$ with $x = 0$ and 0.395.

Table 2: Parameters obtained for single crystalline $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$. Values in [] indicate nominal La compositions before the heat treatment.

Sample	x	a (Å)	c (Å)	M_s ($\mu_B/\text{f.u.}$)	H_A (kOe)	T_C (K)
SrM	0 [0]	5.8818(5)	23.0332(7)	20.05(12)	17.50	738
La1	0.192(1) [0.15]	5.8823(5)	23.0222(1)	20.02(6)	11.27	730
La2	0.261(3) [0.20]	5.8824(3)	23.0206(4)	20.17(5)	10.28	724
La3	0.395(1) [0.46]	5.8830(4)	23.0151(2)	19.69(7)	7.77	720

was claimed that Fe^{2+} occupy the sites other than $2a$ and negatively contribute to the anisotropy [24]. ^{57}Fe Mössbauer study on La SrM, however, suggests Fe^{2+} ions present only at $2a$ [22]. (Recent NMR study supports this [26].) A single crystalline Mössbauer study would give a hint to this issue. The Curie temperature, T_C , decreases with x (Fig. 3 (d)), similarly to other substituted systems. For La SrM, T_C varies linearly between 740 K for $\text{SrFe}_{12}\text{O}_{19}$ and 695 K for $\text{LaFe}_{12}\text{O}_{19}$ [27].

3.2. $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$ (La-Co SrM)

In WDX analysis of the identical La-Co SrM sample, we observed both La and Co signals, indicating successful La-Co co-substitution in SrM. The WDX-determined La concentration, x , is plotted against the Co concentration, y , in Fig. 4, where always $x > y$. The upper limits were $x \simeq 0.5$ and $y \simeq 0.3$. It is likely that rapid cooling is necessary to obtain samples with large x and y [8] similarly to La SrM. The present WDX analysis confirmed that the charge compensation between La^{3+} and Co^{2+} is not fulfilled. Tenaud et al. [9] reported a ratio of $y/x = 0.75$ as the upper limit for powder samples. Our y/x values are rather close to 0.55 (except LaCo6 marked with an asterisk). These different values may be ascribed to different sample preparation conditions; the surface area exposed to air is limited in the flux method. These results strongly suggest that Fe^{3+} is partly reduced to Fe^{2+} in La-Co SrM. In LaCo6 , y is accidentally small. The presence of the La SrM series implies that y can vary without changing x . In other words, $y/x = 0.55$ is the upper limit in the present sample preparation condition. In a preliminary experiment, we have confirmed that the value of y/x increases with increasing oxygen partial pressure.

Figure 5 shows easy- and hard-axis magnetization curves for La-Co SrM. The easy-axis magnetization is insensitive to the substitution, whereas the hard-axis component for the substituted sample bends at higher fields and saturates at a higher field than that of the non-doped case, demonstrating directly that the anisotropy is enhanced associated with the La-Co substitution. The present result, together with the data for La SrM, indicates that the anisotropy is enhanced as a result of the Co substitution not by the appearance of Fe^{2+} . The

Table 3: Parameters obtained for single crystalline $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$. Values in [] indicate nominal compositions before the heat treatment.

sample	x	y	a (Å)	c (Å)	M_s ($\mu_B/\text{f.u.}$)	H_A (kOe)	T_C (K)
SrM	0 [0]	0 [0]	5.8818(5)	23.0332(7)	20.05(12)	17.50	738
LaCo1	0.055(2) [0.04]	0.032(1) [0.04]	5.8819(2)	23.0261(4)	19.83(9)	17.22	726
LaCo2	0.139(1) [0.10]	0.077(3) [0.10]	5.8821(3)	23.0239(3)	20.07(5)	19.46	715
LaCo3	0.242(2) [0.15]	0.108(7) [0.15]	5.8824(4)	23.0211(1)	20.33(8)	18.62	711
LaCo4	0.289(4) [0.20]	0.152(2) [0.20]	5.8829(2)	23.0148(2)	20.19(16)	21.57	724
LaCo5	0.367(4) [0.35]	0.212(6) [0.35]	5.8837(1)	23.0089(1)	20.22(10)	24.36	717
LaCo6	0.511(5) [0.50]	0.161(2) [0.50]	5.8837(1)	22.9997(3)	19.38(20)	22.17	712
LaCo7	0.472(3) [0.80]	0.266(4) [0.80]	5.8840(1)	23.0002(1)	20.39(10)	25.57	700

160 origin of the curved magnetization is of interest and would be essential to explain the anisotropy enhancement. It is highly probable that this observation is related to a Co-doping induced magnetic structural change, for example, the appearance of non-collinear components, which should be revealed experimentally.

165 Crystal and magnetic parameters obtained for La-Co SrM are summarized in Table 3 and Fig. 6. The data in Fig. 6 are plotted against the La concentration, x , which satisfies $y/x = 0.55$ in most cases; the data of LaCo6 will be omitted when referring to x dependence. The lattice parameter, a , depends slightly on x , whereas c decreases with x (Fig. 6 (a)). The volume shrinkage is ascribed to the
170 La substitution. Naively, the increase in M_s with x (Fig. 6 (b)) suggests that the moment at the minority spin sites is reduced by the substitution. The marked reduction of M_s for LaCo6 may be due to the appearance of a larger amount of Fe^{2+} , which contributes negatively to M_s similarly to La SrM. In contrast to the La SrM case, H_A increases monotonically with increasing x (Fig. 6 (c)) as
175 was reported in literatures [28, 29, 30]. Thus, the Co substitution cancels the negative contribution of Fe^{2+} to enhance the anisotropy.

4. Discussion

The original motivation of the single crystal preparation is to resolve the controversial situation and determine unambiguously the Co site occupation
180 in La-Co SrM with the use of well-characterized crystals. However, during the course of the present study, we noticed that the following issues should be resolved before proceeding to the problem of the Co site occupation.

- (i) Fe^{2+} site occupation: If the presence of Fe^{2+} were undoubtable, the site occupation of Fe^{2+} should be determined. The possible single ion anisotropy
185 of Fe^{2+} , which depends on local symmetry, would be important similarly

to that of Co^{2+} . Some ^{57}Fe Mössbauer studies such as Ref. [4] claimed that Fe^{2+} occupy $2a$ in La-Co SrM. However, in ^{57}Fe Mössbauer measurements performed for our single crystalline La-Co SrM, we have not obtained convincing evidence on the presence of Fe^{2+} [31]. Needless to say, the amount and site occupation of Fe^{2+} correlate significantly with the total magnetization.

(ii) Valence and spin state of Co: Generally it is assumed that the doped Co is in the divalent high-spin state ($S = 3/2$; $3 \mu_B$). If the Fe valence were unstable as mentioned above, why not for Co? It is probable that the Co valence depends on the occupation site. In addition, symmetry and magnitude of the crystal field, which determines orbital splitting and the spin state, should depend on the site too. Indeed, ^{59}Co -NMR study has revealed the presence of an anomalously low-frequency signal [6], suggesting small or no moment at the Co site, in addition to high frequency signals coming from high-spin Co^{2+} [26]. Particularly, the origin of the low-frequency ^{59}Co signal should be elucidated at the beginning. Needless to say, if Co were in the trivalent state, the story on the appearance of Fe^{2+} should severely be modified.

(iii) Magnetic structure: One of reasonable interpretations of the bended magnetization curve observed for not only La-Co SrM but also La SrM is the appearance of non-collinear components in the magnetic structure. So far, most experimental analyses aiming to determine the Co site occupation such as Rietveld refinement of neutron diffraction and XMCD profiles relies on the collinear ferrimagnetic structure in La-Co SrM. If not, the conclusions derived from such experimental analyses would be affected seriously. Neutron diffraction experiments with the use of single crystals would be helpful to solve this problem.

(iv) Co moment direction with respect to host Fe moment: In most experimental analysis, the magnetic moment of doped Co was assumed to be parallel to the host Fe^{3+} moment. Williams et al. [32], however, pointed out the possibility that Co moments occupied at $4f_2$ and $2b$ are antiparallel to host Fe^{3+} moments in $\text{BaFe}_{12-2x}(\text{CoTi})_x\text{O}_{19}$. Such a possibility cannot be neglected in La-Co SrM. Experimentally, it is quite tough to determine these relative directions without the knowledge of the Co site occupation. First-principle calculations may give a hint on this topic.

These factors correlate significantly with each other, implying that all of them should be examined simultaneously to identify the Co site occupation. Although we have not pointed out above, possible deficiency of Fe and O atoms may make the problem further complicated.

5. Summary

We successfully synthesized single crystals of La and La-Co substituted M-type strontium ferrite by the Na_2O flux method. For $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$, crystals

were obtained up to $x \simeq 0.50$. The magnetic anisotropy is reduced with increasing x in the small x region. The origin of this behavior remains to be explained. For $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$, the co-substitution does not necessarily mean the equal amounts of La and Co, implying appreciable instability of the 3d-metal valence. The upper limit of the La concentration and the Co/La ratio in the present growth condition are $x \simeq 0.50$ and $y/x \simeq 0.55$, respectively. The y/x ratio is likely to depend on the sample preparation condition. The hard-axis magnetization of the La-Co substituted crystals increases non-linearly. The anisotropy is enhanced and the saturation magnetization, M_s , increases slightly with the La-Co substitution. To optimize magnetic properties, precise x and y dependencies should be explored. Efforts to identify the Co site occupation are now under way using single crystals.

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Figure 3: (Color online) (a) La concentration (x) dependencies of lattice constants, a and c , (b) saturation magnetization, M_s , (c) the anisotropy field, H_A , and (d) Curie temperature, T_C . The dashed line in (b) represents the calculated magnetization [21]. In (c), literature data [24] are also included (open squares). The dashed line in (d) represents the interpolation between T_C for $\text{SrFe}_{12}\text{O}_{19}$ and that for $\text{LaFe}_{12}\text{O}_{19}$.

Figure 4: (Color online) WDX-determined Co concentration, y , plotted against La concentration, x , for $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$.

Figure 5: (Color online) Easy- and hard-axis magnetization curves for $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$ with $x = y = 0$ (SrM) and $x = 0.367, y = 0.212$ (LaCo5) at 5 K.

Figure 6: (Color online) La concentration (x) dependence of lattice constants, a (solid circles) and c (solid squares) (a), the saturation magnetization, M_s (b), the anisotropy field, H_A (c), and the Curie temperature, T_C (d) for $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$. Dashed lines are the guide for the eye.