

## Synthesis and Magnetic Properties of Na-La-Co System M-type Ferrite

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**In this study, we investigated the synthesis of Na-La system M-type ferrite with different mole ratios. Some part of Fe in the M-type ferrite was substituted by Co, and variation of fraction of the M-type ferrite as function of mole ratio was investigated. Sample with/without Co-substitution composed of multiphases of M-type ferrite and other phases. Fraction of M-type ferrite in the samples was depending on mole ratio in the raw material. Curie temperatures of Co-free and Co-substituted M-type ferrite were approximately 432 °C and 428 °C, respectively. Saturation magnetisation of the Co-free Na<sub>0.5</sub>La<sub>0.5</sub> system M-type ferrite was approximately 72.5 emu/g.**

**Keywords :** hard ferrite, ferrite permanent magnet, alkali-metal-based M-type ferrite, Co-substituted M-type ferrite

### 1. Introduction

Although, the sintered ferrite magnets has lower  $(BH)_{\max}$  value, which is figure of merit of permanent magnet, with respect to rare-earth (RE) - transition metal (TM) - based magnet. Cost-performance and chemical stability of the ferrite magnet is superior to RE-TM magnet because the ferrite mainly consists of iron oxide (hematite). Such advantages enable ferrite sintered magnets to maintain the highest production volume among all widely used permanent magnets. For the applications of industrial motors, electric vehicle driving motors, and generators the RE-TM-based magnets have been widely used. However, because of unstable market price of RE metals, ferrite magnets are increasingly replacing the RE-TM magnets for those applications, for which enhancing performance of the ferrite is demanded. The conventional ferrite magnet with magnetoplumbite structure is Sr-ferrite magnet. In the late 1990s, research was conducted on substituting Sr and Fe in SrFe<sub>12</sub>O<sub>19</sub> compositions with various elements. Simultaneous substitution of Co<sup>2+</sup> and La<sup>3+</sup> ions for Fe<sup>3+</sup> and Sr<sup>2+</sup> ions, respectively, in Sr-ferrite

has been reported to improve the magnetocrystalline anisotropy and temperature coefficients of coercivity at low temperature [1-7]. In 2007, it was reported that Ca-La-Co system ferrite magnets exhibited higher magnetocrystalline anisotropy and improved temperature coefficients of coercivity at low temperature than Sr-La-Co system sintered ferrite magnets due to more substitution of Co in the former [8-11]. Even the Ca-La-Co system ferrite magnets still have insufficient performance for replacing RE-TM-based magnets in those applications. Under this circumstances, alkali metal (Na) - based M-type ferrite has attracted much attention for this purpose. Table 1 represents comparison of the saturation magnetisation ( $M_s$ ), Curie temperature, and anisotropy field for various M-type ferrite magnets. Although overall intrinsic properties of the Na<sub>0.5</sub>La<sub>0.5</sub>Fe<sub>12</sub>O<sub>19</sub> are inferior to the conventional materials, the higher  $M_s$  at 0 K of the Na<sub>0.5</sub>La<sub>0.5</sub>Fe<sub>12</sub>O<sub>19</sub> is noteworthy. If  $M_s$  of the Na<sub>0.5</sub>La<sub>0.5</sub>Fe<sub>12</sub>O<sub>19</sub> can be maintained higher at room temperature, this leads to higher remanence. Thus, this materials can be a promising candidate for high performance future ferrite. Synthesis of Na-La system ferrite has been undergone mostly by solid state reaction, and it was revealed that preparation of M-type single phase material was hardly achieved [15-20]. In this study, we investigated the dependence of fraction of M-type phase in the synthesized sample on the mole ratio in the raw materials. Effect of Co-substitution for Fe in the M-type Na-La system

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**Table 1.** Saturation magnetisation, Curie temperature and anisotropy field of various M-type ferrites.

Compounds	$M_S$ (0 K) [emu/g]	$M_S$ (R.T.) [emu/g]	$T_c$ [°C]	$H_A$ [kOe]	Ref.
BaFe <sub>12</sub> O <sub>19</sub>	100.0	72.0	470	17.0	[12]
SrFe <sub>12</sub> O <sub>19</sub>	100.8	74.3	470	19.3	[12, 13]
Sr <sub>0.7</sub> La <sub>0.3</sub> Fe <sub>11.7</sub> Co <sub>0.3</sub> O <sub>19</sub>	99.9	71.8	440	22.2	[1, 2, 13, 14]
Na <sub>0.5</sub> La <sub>0.5</sub> Fe <sub>12</sub> O <sub>19</sub>	113.0	71.6	435	14.7	[17]

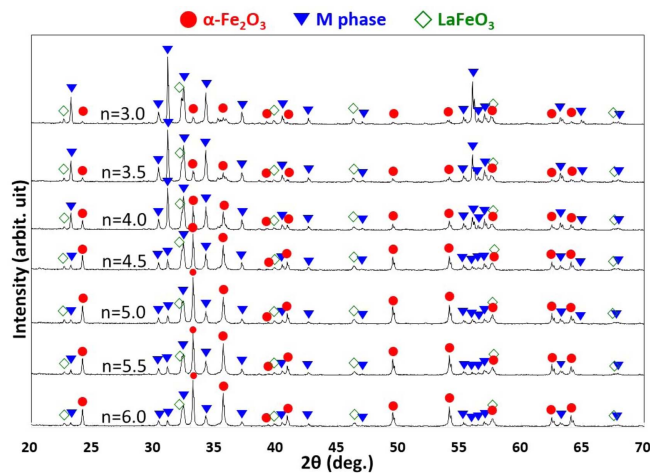
ferrite was also examined.

## 2. Experiments

Na<sub>0.5</sub>La<sub>0.5</sub>Fe<sub>2n-x</sub>Co<sub>x</sub>O<sub>19</sub> (n = 3.0 - 6.0, x = 0.0, 0.3) was prepared by solid state reaction method using raw materials of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, and Na<sub>2</sub>CO<sub>3</sub>. The raw materials were mixed in dry method to avoid the detrimental reaction between Na<sub>2</sub>CO<sub>3</sub> and water. The dried powder was further molded into pellets and calcinated in air at 1250 °C for 3 h. The calcinated powder was milled to sizes of 3-10  $\mu$ m using disk mill. Phase analysis and calculation of lattice constant of the M-type phase in the powdered sample was performed by X-ray diffraction (XRD) analysis (Cu-K $\alpha$ ). Fraction of the phases in the sample was analyzed through Rietveld refinement. The Curie temperature was measured using thermomagnetic analyzer (TMA). Magnetic characterisation of the sample was performed using vibrating-sample magnetometer (VSM) with maximum applied field of 2.5 T.

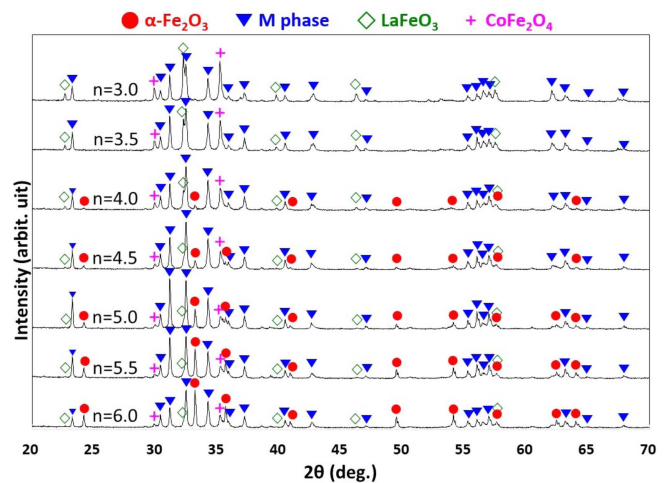
## 3. Results and Discussion

Figure 1 shows the XRD patterns of Na<sub>0.5</sub>La<sub>0.5</sub>Fe<sub>2n</sub>O<sub>19</sub> (hereafter referred to as “Co-free sample”) with varying



**Fig. 1.** (Color online) XRD patterns of Na<sub>0.5</sub>La<sub>0.5</sub>Fe<sub>2n</sub>O<sub>19</sub> (n = 3.0 - 6.0) ferrites.

mole ratio. It was revealed that samples with n = 3.0 - 6.0 consisted of magnetoplumbite phase (hereafter referred to as “M-phase”) and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Small amount of perovskite-type LaFeO<sub>3</sub> was also contained in the samples. It appeared that intensity of the M-phase increased with decreasing mole ratio. While, intensity of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase decreased as the mole ratio decreased. Samples prepared with n = 3.0 - 6.0 were multiphase material rather than M-type single phase. Figure 2 shows the XRD patterns of Na<sub>0.5</sub>La<sub>0.5</sub>Fe<sub>2n-x</sub>Co<sub>x</sub>O<sub>19</sub> (x = 0.3) (hereafter referred to as “Co-substituted sample”) with varying mole ratio. Intensity of the M-phase increased with decreasing mole ratio, showed peak at n = 4.5, and then decreased. While, intensity of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase decreased as the mole ratio decreased. Intensity of the LaFeO<sub>3</sub> and CoFe<sub>2</sub>O<sub>4</sub> phases slightly increased as the mole ratio decreased. It appeared that CoFe<sub>2</sub>O<sub>4</sub> phase was detected in the Co-substituted sample, and the CoFe<sub>2</sub>O<sub>4</sub> phase was considered to be formed by the excess Co after substituting Fe in the M-type phase. The formation of CoFe<sub>2</sub>O<sub>4</sub> spinel is known to form also in conventional M-type ferrite such as Ca-La-Co system, when added Co was excessive [8]. The present results indicated that M-type single phase sample was not prepared by varying mole ratio and Co-substitution. Further investigation by optimizing the ratio of Na to La, Co-substitution, and calcination condition



**Fig. 2.** (Color online) XRD patterns of Na<sub>0.5</sub>La<sub>0.5</sub>Fe<sub>2n-x</sub>Co<sub>x</sub>O<sub>19</sub> (x = 0.3, n = 3.0 - 6.0) ferrites.

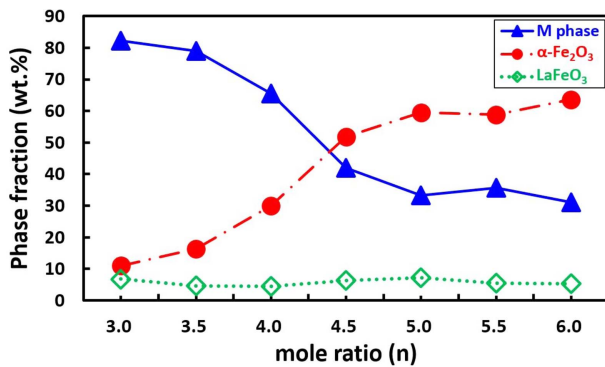


Fig. 3. (Color online) Fraction of the phases in  $\text{Na}_{0.5}\text{La}_{0.5}\text{Fe}_{2n}\text{O}_{19}$  ( $n = 3.0 - 6.0$ ) ferrites (Rietveld method).

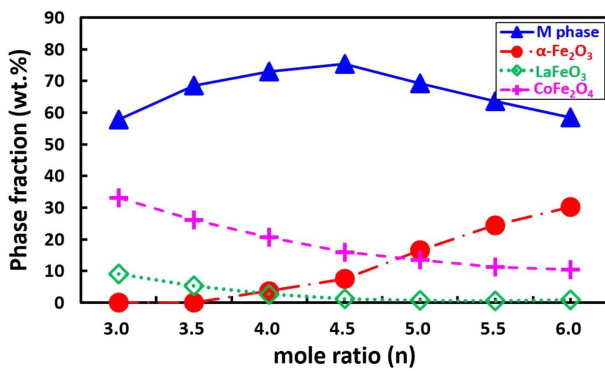


Fig. 4. (Color online) Fraction of the phases in  $\text{Na}_{0.5}\text{La}_{0.5}\text{Fe}_{2n-x}\text{Co}_x\text{O}_{19}$  ( $x = 0.3, n = 3.0 - 6.0$ ) ferrites (Rietveld method).

and so on is needed to obtain M-type single phase material. Figure 3 and Figure 4 show variation of the phases fraction measured by Rietveld refinement for Co-free and Co-substituted sample with varying mole ratio. For Co-free sample the highest fraction (82.3 wt.%) of M-type ferrite was obtained at  $n = 3.0$ . Meanwhile, for Co-substituted sample the maximum fraction was slightly lower compared to Co-free sample; the highest fraction was 75.3 wt.% at  $n = 4.5$ . Figure 5 shows variation of the lattice parameter  $a$  and  $c$ , the axial ratio  $c/a$ , and the unit cell volume for Co-free and Co-substituted sample with varying mole ratio. The value of  $a$  for the M-type ferrite crystal was almost unchanged regardless of the mole ratio for the Co-free and Co-substituted samples, while,  $c$ ,  $c/a$ , and the unit cell volume of the M-type ferrite crystal in the Co-substituted sample were slightly smaller than those of the crystal in the Co-free sample. Figure 6 shows the TMA results for the Co-free and Co-substituted samples with  $n = 3.0$ . Only one magnetic phase with  $T_c = 432$  °C was detected in the Co-free sample, and this phase is believed to be M-type ferrite. For the Co-substituted sample, two magnetic phases with  $T_c = 428$  °C and 670 °C are detected, these phases are M-type ferrite and

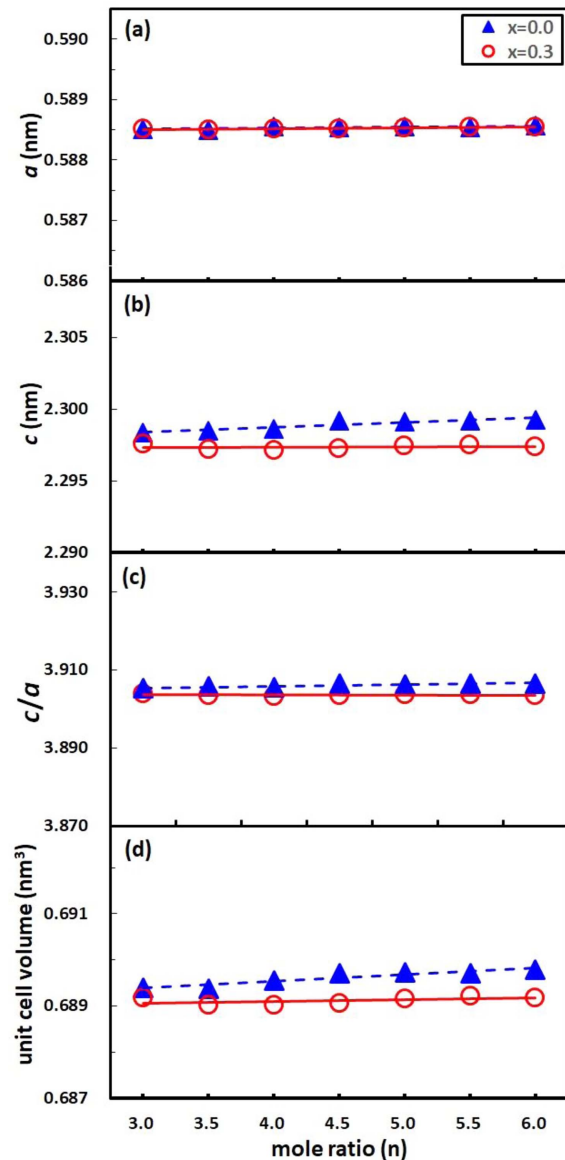
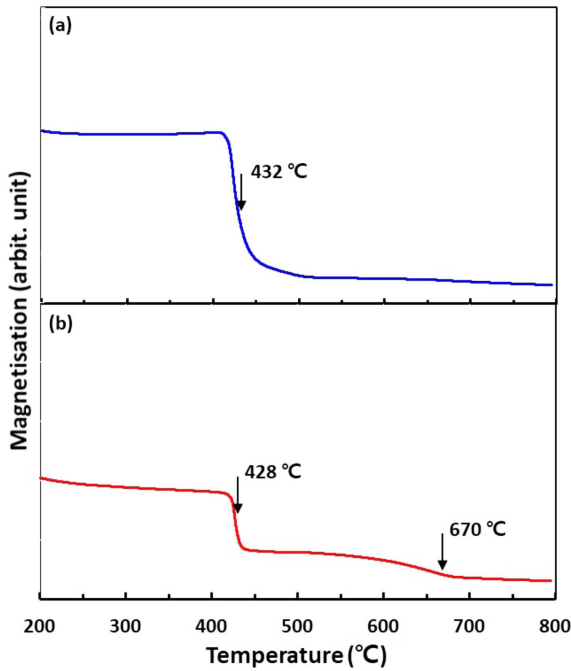
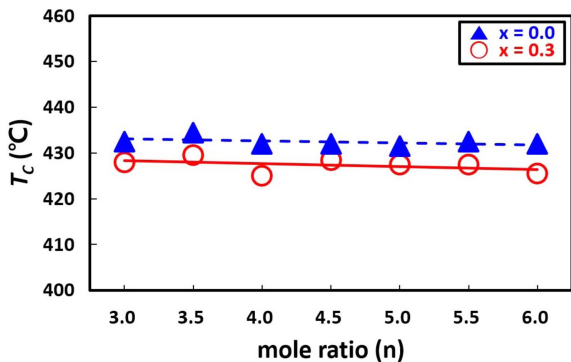


Fig. 5. (Color online) Variations of (a, b) lattice constant, (c)  $c/a$ , and (d) unit cell volume of M phase in  $\text{Na}_{0.5}\text{La}_{0.5}\text{Fe}_{2n-x}\text{Co}_x\text{O}_{19}$  ( $x = 0.0, 0.3, n = 3.0 - 6.0$ ) ferrites as a function of mole ratio.

$\text{CoFe}_2\text{O}_4$ -type spinel, respectively. The  $T_c$  (670 °C) of  $\text{CoFe}_2\text{O}_4$ -type phase in the Co-substituted sample appears to be considerably higher than  $T_c$  (520 °C) of the stoichiometric  $\text{CoFe}_2\text{O}_4$  spinel [21]. The higher  $T_c$  of the  $\text{CoFe}_2\text{O}_4$ -type spinel in the Co-substituted sample may be attributed to the off-stoichiometric composition away from the 1 : 2 : 4 stoichiometry. Figure 7 shows variation of the Curie temperature of M-type ferrite in Co-free and Co-substituted samples with varying mole ratio. As shown in Figure 7,  $T_c$  of the M-type ferrite in the Co-free and Co-substituted samples was constant regardless of varying mole ratio. It was also found that  $T_c$  of the M-

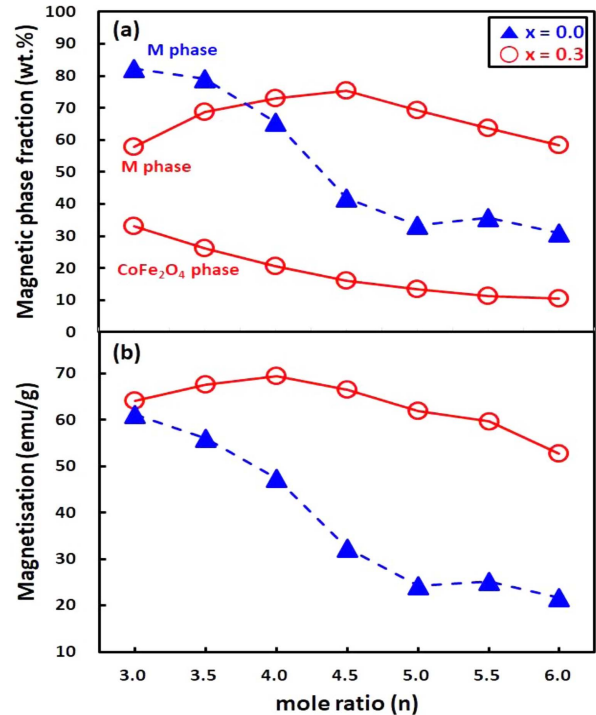


**Fig. 6.** (Color online) TMA curves of  $\text{Na}_{0.5}\text{La}_{0.5}\text{Fe}_{2n-x}\text{Co}_x\text{O}_{19}$  ((a)  $x = 0.0$ ,  $n = 3.0$ , (b)  $x = 0.3$ ,  $n = 3.0$ ).



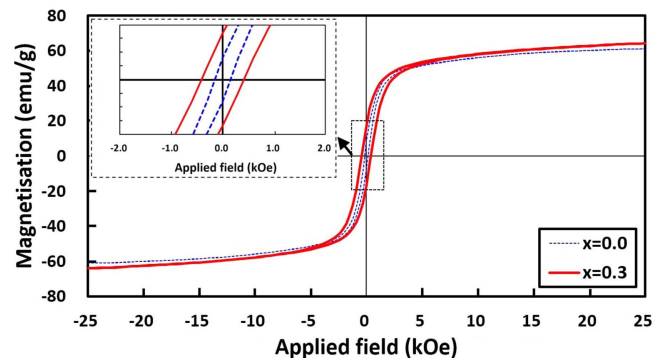
**Fig. 7.** (Color online) Variations of Curie temperature of M phase in  $\text{Na}_{0.5}\text{La}_{0.5}\text{Fe}_{2n-x}\text{Co}_x\text{O}_{19}$  ( $x = 0.0, 0.3$ ,  $n = 3.0 - 6.0$ ) ferrites as a function of mole ratio.

type ferrite in the Co-free sample was consistently higher than that of the phase in the Co-substituted sample. The lower  $T_c$  of the M-type ferrite in the Co-substituted sample may be attributed to two effects; Co-substitution may leads to both the change of lattice parameter of the crystal and the formation of some  $\text{Fe}^{3+}\text{-O}^{2-}\text{-Co}^{2+}$  bonds. Super-exchange interaction of the  $\text{Fe}^{3+}\text{-O}^{2-}\text{-Co}^{2+}$  bond, which determines  $T_c$  of the ferrite, may be weaker compare to that of the  $\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{3+}$  bond in the Co-free sample, thus leading to reduction of  $T_c$  [22, 23]. Figure 8 shows variation of the magnetic phase fraction and saturation magnetisation of the Co-free and Co-substituted samples with varying mole ratio. Figure 8(a) is

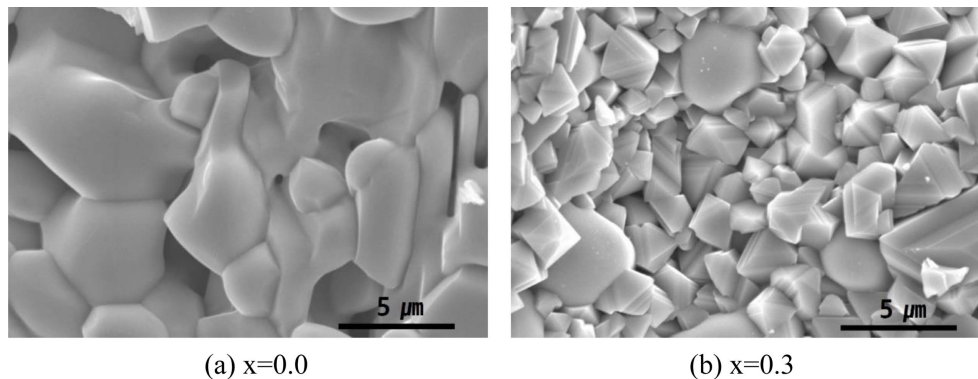


**Fig. 8.** (Color online) Variations of (a) magnetic phase fraction and (b) magnetisation of  $\text{Na}_{0.5}\text{La}_{0.5}\text{Fe}_{2n-x}\text{Co}_x\text{O}_{19}$  ( $x = 0.0, 0.3$ ,  $n = 3.0 - 6.0$ ) ferrites as a function of mole ratio.

replot of the results in Figure 3 and 4 for better discussion. As seen in Figure 8(b), for Co-free sample the magnetisation increased with decreasing mole ratio. On the other hand, for Co-substituted sample the magnetisation increased with decreasing mole ratio, showed peak at  $n = 4.0$ , and then slightly decreased. Based upon the measured phase fraction and magnetisation value, saturation magnetisation of the Na-La system M-type ferrite was estimated. Estimating the  $M_S$  value of the M-type ferrite in the Co-substituted sample is complicated because it contained additional magnetic phase ( $\text{CoFe}_2\text{O}_4$  spinel)



**Fig. 9.** (Color online) Hysteresis loops of  $\text{Na}_{0.5}\text{La}_{0.5}\text{Fe}_{2n-x}\text{Co}_x\text{O}_{19}$  ( $x = 0.0, 0.3$ ,  $n = 3.0$ ) ferrites.



**Fig. 10.** SEM micrographs showing grain structure of  $\text{Na}_{0.5}\text{La}_{0.5}\text{Fe}_{2n-x}\text{Co}_x\text{O}_{19}$  ( $x = 0.0, 0.3, n = 3.0$ ) ferrites.

together with M-type ferrite. Therefore, estimation of  $M_S$  value of the Na-La system M-type ferrite was carried out for the Co-free sample containing only single magnetic M-type phase. Considering the fraction of M-type ferrite and magnetisation value of the Co-free sample, average  $M_S$  value of the Na-La system M-type ferrite was estimated to be 72.5 emu/g. This was in good agreement with the  $M_S$  value reported previously [17] (see Table 1). Figure 9 compared the magnetic hysteresis loops of the Co-free and Co-substituted samples with  $n = 3.0$ . It appeared that magnetisation ( $M_{25}$ ) of the Co-substituted sample was slightly higher than that of the Co-free sample. This was attributed to the presence of  $\text{CoFe}_2\text{O}_4$  spinel phase with high  $M_S$  (80 emu/g) [25] in the Co-substituted sample. Coercivity of the Co-substituted sample was slightly higher than the Co-free sample. Coercivity of the ferrite is directly related to anisotropy field ( $H_A$ ) of the material. Considering the negligible change in the lattice parameter and  $T_c$  by the Co-substitution,  $H_A$  of the two samples may be almost identical. The higher coercivity of the Co-substituted sample may be attributed to finer grain size of the M-type ferrite formed in the Co-substituted sample as can be seen in Figure 10. Grain size of the M-type ferrite formed in the Co-substituted sample was finer compared to Co-free sample.

#### 4. Conclusion

Synthesized  $\text{Na}_{0.5}\text{La}_{0.5}\text{Fe}_{2n-x}\text{Co}_x\text{O}_{19}$  ( $n = 3.0 - 6.0, x = 0.0, 0.3$ ) samples consisted of multiphases of M-type ferrite and other additional phases. Fraction of M-type ferrite in the samples depended on mole ratio in the raw material. For Co-free sample the highest fraction (82.3 wt.%) of M-type ferrite was obtained at  $n = 3.0$ . For Co-substituted sample the maximum fraction was slightly lower (75.3 wt.% at  $n = 4.5$ ) compared to Co-free sample. Curie temperatures of Co-free and Co-substituted M-type

ferrite were approximately 432 °C and 428 °C, respectively. Saturation magnetisation of the Co-free  $\text{Na}_{0.5}\text{La}_{0.5}$  system M-type ferrite was approximately 72.5 emu/g.

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