

Research trends for the high-performance La-Co substituted M type ferrite magnets

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1. Introduction

The hexagonal Sr-M type ferrite magnet has been widely used in applications such as the motor for car electrical equipments and for air conditioners and refrigerators. Recently, the magnetic properties of ferrite magnet has been improved by substituting La and Co for Sr and Fe atoms, respectively. The La-Co substituted M-type ferrites (Sr-La-Co M-type ferrite and Ca-La-Co M-type ferrite, to which we will refer as ‘SLC-M’ and ‘CLC-M’ hereafter)¹⁾⁻³⁾ are known to have the higher magnetic crystalline anisotropy compared with Sr-M type ferrite. In this study, the occupation sites of cobalt ions in the La-Co substituted M-type ferrite compound were analyzed by the neutron diffraction, the extended X-ray absorption fine structure (EXAFS) and the X-ray magnetic circular dichroism (XMCD) to understand the relationship between the local structure and the improvements of magnetic characteristics in the La-Co substituted M-type ferrite, and furthermore, microstructure of CLC-M sintered ferrite magnets were analyzed by Spherical Aberration Corrected Scanning Transmission Electron Microscopy (Cs-STEM) to get guiding principles for improving magnetic property.

2. Cation distribution analysis of La-Co M-type ferrites by neutron diffraction, EXAFS and XMCD^{4), 5)}

We investigated the site distribution of the cobalt ions in SLC-M ($\text{Sr}_{0.7}\text{La}_{0.3}\text{Co}_{0.3}\text{Fe}_{11.3}\text{O}_{19}$) and CLC-M ($\text{Ca}_{0.5}\text{La}_{0.5}\text{Co}_{0.3}\text{Fe}_{10.1}\text{O}_{19}$, $a \approx 19$) by neutron diffraction and EXAFS measurements. Fig. 1 shows the one half of unit cell for Sr-M ($\text{SrFe}_{12}\text{O}_{19}$, space group: $P6_3/mmc$). The five different sublattices for the ferric ions are denoted using Wyckoff's notation as follows: 12k, 2a, 4f₂ (octahedral sites), 4f₁ (tetrahedral site) and 2b (bipyramidal site). In this study, we estimated the local structure on the assumption that cobalt ions simultaneously occupy some of the five ferric ion sites. It was suggested that cobalt ions are partitioned in the 2a, 4f₁ and 12k sites in the ratio of 1:2:2 for SLC-M. Meanwhile, it was suggested that cobalt ions are partitioned in the 2a, 4f₁ and 12k sites in the ratio of 2:6:2 for CLC-M.

Fig. 2 shows the X-ray absorption near edge structure (XANES) spectra and the XMCD spectra at the Fe K-edge for Sr-M, SLC-M and CLC-M. The ferric ions at the tetrahedral site (A site) of the spinel ferrite give a pre-edge peak around $E \approx 7.11$ keV in the XANES spectrum⁶⁾. The pre-edge peak is observed in the XANES spectra at the Fe K-edge for Sr-M, SLC-M and CLC-M. The M type ferrite has a ferrimagnetic structure, that is, eight ferric ions with the up-spin at 2a, 2b, 12k and four ferric ions with the down-spin at 4f₁, 4f₂ exist in a unit cell. The pre-edge peak originates from the ferric ions of the down spin at the tetrahedral site, 4f₁. The intensity of the XMCD spectrum peak at the pre-edge peak is smaller for CLC-M than for Sr-M and SLC-M. This suggests that the contributions of the ferric ions in the down spin site to a magnetic moment decreases, suggesting that the ferric ions at the tetrahedral site 4f₁ is replaced by more elements of a smaller or no magnetic moment for CLC-M compared to Sr-M and SLC-M.

3. Microstructural analysis of Ca-La-Co M-type sintered ferrite magnets by Cs-STEM⁷⁾

We investigated composition and microstructure at the vicinity of grain boundary by Cs-STEM for CLC-M sintered body. Table 1 shows EDX analysis results for multiple-junction phases of CLC-M sintered body with additives : (a) CaCO_3 :0.0 mass%, SiO_2 :0.34 mass%, (b) CaCO_3 :1.25 mass%, SiO_2 :0.68 mass%. It was confirmed that there are Ca-Si based oxides, which consists of Si, Ca, La and Fe, at multiple-junction phases of sintered body by adding only SiO_2 instead of both CaCO_3 and SiO_2 which are sintering aids for ferrite magnets. And then it was almost confirmed that the abundance ratio of Si, Ca, La and Fe at multiple-junction phases is 30 : 60 : 2 : 5.

Fig. 3 shows HAADF-STEM image on intergranular grain boundary for CLC-M sintered body with additives : CaCO_3 :1.25 mass%, SiO_2 :0.68 mass%. We found that the step-terrace structure of Ca-Si based oxides are formed at the surface of the M-type ferrite grain, and the maximum width of intergranular grain boundary is nearly equal to half the edge length along z-axis, which is 1.15 nm, of M-type ferrite unit cell. This suggests that M-type ferrite grains were magnetically isolated by the presence of Ca-Si based oxide phases at intergranular grain boundary.

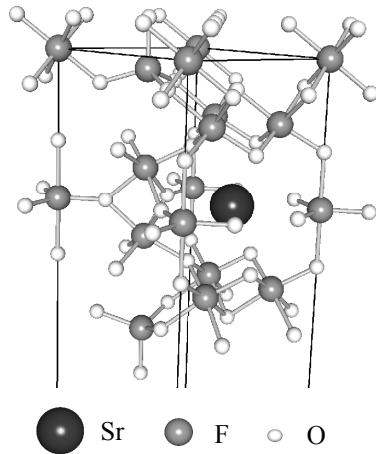


Fig.1 One half of unit cell of the Sr-M type hexaferrite (SrFe₁₂O₁₉, space group: P6₃/mmc).

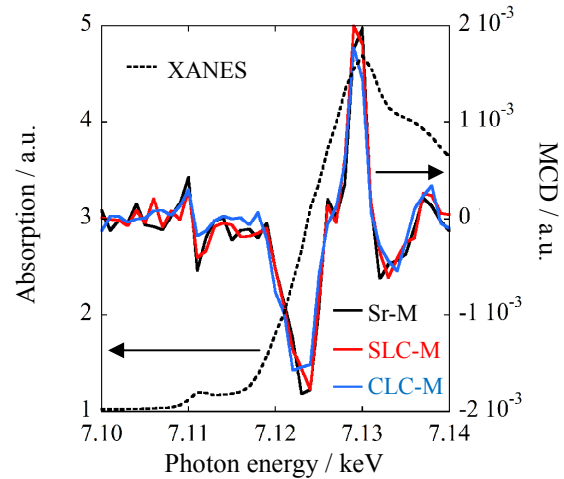


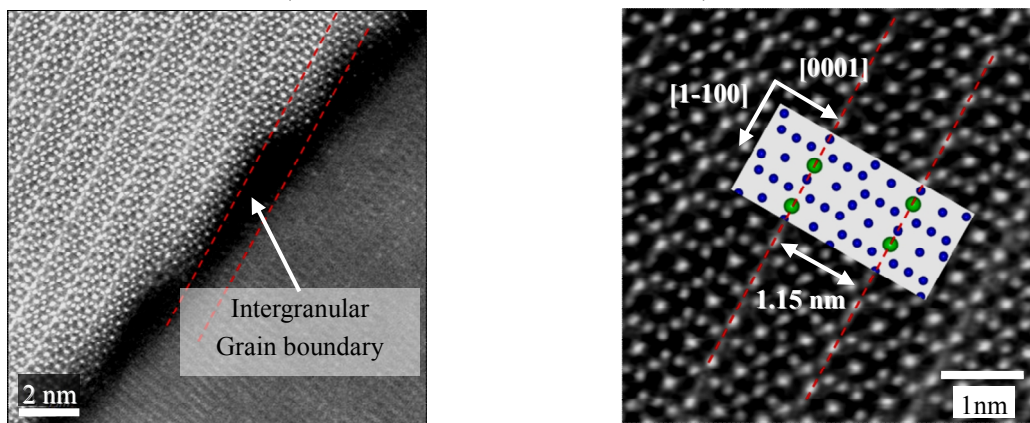
Fig. 2 The XANES and hard X-ray MCD spectra for the Sr-M and the La-Co substituted M type ferrite.

Table 1 EDX analysis results for multiple-junction phases of CLC-M sintered body with additives.
(a) CaCO₃:0.0 mass%, SiO₂:0.34 mass% (b) CaCO₃:1.25 mass%, SiO₂:0.68 mass%

	Si (at%)	Ca (at%)	La (at%)	Fe (at%)
1	29.3	64.1	2.7	3.9
2	27.7	67.2	1.6	3.5
3	32.4	60.2	2.0	5.4
4	29.7	60.4	3.3	6.6
5	30.9	63.9	1.3	3.9
Ave.	30.0	63.1	2.2	4.7

	Si (at%)	Ca (at%)	La (at%)	Fe (at%)
1	30.2	63.5	1.2	5.1
2	30.9	62.0	1.5	5.6
3	30.7	63.3	1.7	4.3
4	30.1	62.2	1.9	5.8
5	31.7	60.5	1.1	6.7
Ave.	30.7	62.3	1.5	5.5

Fig. 3 HAADF-STEM image on intergranular grain boundary for CLC-M sintered body with additives. (CaCO₃:1.25 mass%, SiO₂:0.68 mass%)



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