



## Research articles

Effect of Bi<sub>2</sub>O<sub>3</sub>, MnCO<sub>3</sub> additives on the structure and magnetic properties of M-type Sr-hexaferrites

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## ABSTRACT

The effects of additives Bi<sub>2</sub>O<sub>3</sub> and MnCO<sub>3</sub> on the structural and magnetic properties of M-type Sr-hexaferrites (SrFe<sub>12</sub>O<sub>19</sub>) prepared by a conventional solid-state reaction method were studied. The saturation magnetization value of undoped SrFe<sub>12</sub>O<sub>19</sub> is 71.8 emu/g; it increases to 72.6 emu/g and 74.2 emu/g with Bi<sub>2</sub>O<sub>3</sub> doping of 0.5 wt% and 1.0 wt%, respectively. However, abnormal grain growth occurs and the coercivity (H<sub>c</sub>) decreases significantly in the 1 wt% Bi<sub>2</sub>O<sub>3</sub>-doped sample. Co-doping of 0.5 wt% Bi<sub>2</sub>O<sub>3</sub> + 0.5 wt% MnCO<sub>3</sub> is effective, because a higher saturation magnetization (73.1 emu/g) than that of undoped SrFe<sub>12</sub>O<sub>19</sub> could be achieved with a relatively large coercivity of ~3.3 kOe. Based on the lattice parameter calculation, Bi<sup>3+</sup> preferably substitutes into Fe<sup>3+</sup> sites rather than Sr<sup>2+</sup> sites in M-type Sr-hexaferrite. The enhanced saturation magnetization can be attributed to the selective substitution of nonmagnetic Bi<sup>3+</sup> into the down-spin Fe<sup>3+</sup> site (4f<sub>1</sub> or 4f<sub>2</sub>).

## 1. Introduction

M-type Ba- or Sr-hexaferrites, BaFe<sub>12</sub>O<sub>19</sub> (BaM), or SrFe<sub>12</sub>O<sub>19</sub> (SrM) have been used as permanent magnets for several decades due to their useful hard magnetic properties and favorable performance/price ratio. Because of the increasing demand for ferrite magnets in global industries, including the automobile and home appliances industries, enhancement of their magnetic performance is economically important. The crystalline structure of M-type hexaferrite is comprised of alternate stacks of spinel (S, Fe<sub>6</sub>O<sub>8</sub>) and hexagonal (R, SrFe<sub>6</sub>O<sub>11</sub>) layers in the form of RSR'S\*, where \* denotes 180° rotation around the hexagonal c-axis [1]. In the unit cell, 24 Fe<sup>3+</sup> ions occupy five crystallographically inequivalent sites: one tetrahedral (4f<sub>1</sub>), three octahedral (12k, 2a, 4f<sub>2</sub>), and one hexahedral (2b) site. The spins of Fe<sup>3+</sup> ions in these sites are ferromagnetically coupled through the superexchange interaction via the oxygen ions that make the spins in 2a, 12k, and 2b sites parallel to the crystallographic c-axis and antiparallel to those in 4f<sub>1</sub> and 4f<sub>2</sub> sites. The net magnetic moment from SrFe<sub>12</sub>O<sub>19</sub> occupying half of the unit cell is 20μ<sub>B</sub>.

There have been many attempts to enhance the hard magnetic properties of M-type Sr-hexaferrites (SrM) by substitution of Sr or Fe sites with other cations [2–11]. Among them, the most successful approach is based on a significant enhancement in crystalline anisotropy without reducing saturation magnetization (M<sub>s</sub>), by co-substitution of Ca, La, Co, which is expressed by the formula Sr<sub>1-x-y</sub>Ca<sub>x</sub>La<sub>y</sub>Fe<sub>12-z</sub>Co<sub>z</sub>O<sub>19-a</sub> [5]. However, the doping of high-cost

elements, such as La and Co into ferrite magnets, significantly increases their price. Hence, an enhancement of the hard magnetic properties by doping elements of lower material cost than La or Co is an important concern in the research and development of ferrite magnets. Recently, the substitution effects of Bi<sup>3+</sup> ions into the hexaferrite structure have been reported [12–15]. In their research, the substitutional sites of Bi<sup>3+</sup> ions in the compound are assumed to be either a Fe<sup>3+</sup> [12,13] or Sr<sup>2+</sup> (or Ba<sup>2+</sup>) site [14,15]. The doping of Bi is known to promote grain growth in the solid-state reaction. In this research, we first tried to clarify the substitution site of Bi by lattice parameter analysis on two series of SrM samples with formulae Sr<sub>1-x</sub>Bi<sub>x</sub>Fe<sub>12</sub>O<sub>19</sub> and SrFe<sub>12-x</sub>Bi<sub>x</sub>O<sub>19</sub>. Then, we tried to enhance the magnetic properties of SrFe<sub>12</sub>O<sub>19</sub> by doping with Bi-based additives.

## 2. Experimental procedures

Stoichiometric SrFe<sub>12</sub>O<sub>19</sub> (SrM) and Bi-substituted SrM with formulae Sr<sub>1-x</sub>Bi<sub>x</sub>Fe<sub>12</sub>O<sub>19</sub> (x = 0, 0.1, 0.2) and SrFe<sub>12-x</sub>Bi<sub>x</sub>O<sub>19</sub> (x = 0, 0.1, 0.2) were prepared by conventional solid-state reaction processes. The precursor powders of Fe<sub>2</sub>O<sub>3</sub> (99%), SrCO<sub>3</sub> (99.5%), and Bi<sub>2</sub>O<sub>5</sub> (99.9%) were weighed in accordance with the cation ratios of the formulae. The respective weighed mixtures were ball-milled in water, dried, and pre-calcined in air at 1100 °C for 4 h. The calcined powders were ground, ball-milled again in water, dried, palletized at a pressure of 7.5 MPa, and sintered at temperatures of 1250 °C for 2 h in air. The additives including Bi<sub>2</sub>O<sub>3</sub>, MnCO<sub>3</sub>, CaCO<sub>3</sub>, and SiO<sub>2</sub> were mixed in the

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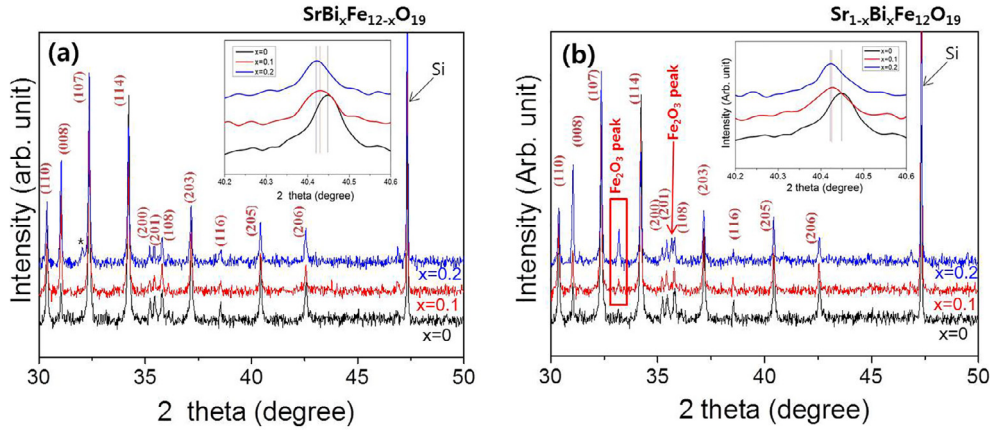


Fig. 1. XRD patterns of the hexaferrite powders of (a)  $\text{SrBi}_x\text{Fe}_{12-x}\text{O}_{19}$  ( $0 \leq x \leq 0.2$ ) and (b)  $\text{Sr}_{1-x}\text{Bi}_x\text{Fe}_{12}\text{O}_{19}$  ( $0 \leq x \leq 0.2$ ) calcined at  $1250^\circ\text{C}$ .

second ball-milling process. The sample density was calculated based on the weight and geometric dimensions of the disk-shaped samples. X-ray diffraction (XRD, D8 Advance, Bruker) with a  $\text{Cu K}\alpha$  radiation source ( $\lambda = 0.154056 \text{ nm}$ ) were used for crystalline phase analysis. All the XRD powder samples were mixed with 30 wt% of Si powders for verifying mechanical peak position error during  $\theta - 2\theta$  scan. Microstructural observation on the fractured surface of the sintered samples was conducted by Field emission scanning electron microscopy (FE-SEM, JSM-7610F, JEOL). Magnetization curves were measured using a vibrating sample magnetometer (VSM, LakeShore 7410) at 298 K with a sweeping magnetic field within  $\pm 25 \text{ kOe}$ . For the VSM measurement, pieces of the sintered bulk sample weighing about 0.1 g were used.

### 3. Results and discussion

Fig. 1(a) and (b) show the XRD patterns of the calcined powders of  $\text{SrBi}_x\text{Fe}_{12-x}\text{O}_{19}$  ( $0 \leq x \leq 0.2$ ) and  $\text{Sr}_{1-x}\text{Bi}_x\text{Fe}_{12}\text{O}_{19}$  ( $0 \leq x \leq 0.2$ ) respectively. All diffraction peaks for SrM samples are indexed on the basis of a hexagonal magnetoplumbite crystal structure with space group  $P6_3/mmc$ . All samples were checked against the reference Si (220) peak positions indicating no mechanical peak position error during the  $\theta - 2\theta$  scan. Patterns of  $\text{SrBi}_x\text{Fe}_{12-x}\text{O}_{19}$  samples with  $x = 0$  and 0.1 in Fig. 1(a) show single M-type phases without any secondary phase peaks. An unknown peak (\*) with low intensity at  $2\theta \approx 32^\circ$  is observed in the  $x = 0.2$  sample. Meanwhile, in the  $\text{Sr}_{1-x}\text{Bi}_x\text{Fe}_{12}\text{O}_{19}$  samples, a low intensity peak of the secondary phase  $\text{Fe}_2\text{O}_3$  appears at  $x = 0.1$ , and increases in intensity at  $x = 0.2$ . The peak shift by Bi substitution around the (205) peak of SrM is presented in the inset of each figure. In both cases, the peak at  $x = 0.1$  shifts toward the left, while any further shift at  $x = 0.2$  is negligible.

For the series of  $\text{Sr}_{1-x}\text{Bi}_x\text{Fe}_{12}\text{O}_{19}$  and  $\text{SrFe}_{12-x}\text{Bi}_x\text{O}_{19}$  samples ( $x = 0, 0.1, 0.2$ ), the lattice parameters  $a$  and  $c$ , and the cell volume, are listed in Table 1. Lattice parameters  $a$  and  $c$  were calculated from the  $d_{hkl}$  values corresponding to the (107) and (114) peaks as follows:

Table 1

Sample composition  $x$ , cell parameters ( $a$ ,  $c$ ),  $c/a$ , and cell volume of the Bi-substituted hexaferrites.

Samples	$x$	$a$	$c$	$c/a$	Vol.
$\text{SrFe}_{12-x}\text{Bi}_x\text{O}_{19}$	0	5.879	23.030	3.918	689.3
	0.1	5.880	23.032	3.917	689.7
	0.2	5.881	23.035	3.917	689.9
$\text{Sr}_{1-x}\text{Bi}_x\text{Fe}_{12}\text{O}_{19}$	0	5.879	23.030	3.918	689.3
	0.1	5.882	23.039	3.917	690.2
	0.2	5.881	23.035	3.917	690.0

$$d_{hkl} = \left\{ \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2} \right\}^{-1/2} \quad (1)$$

where  $d_{hkl}$  is the interplanar spacing, and  $h$ ,  $k$ , and  $l$  are the Miller indices. In both case of  $\text{SrBi}_x\text{Fe}_{12-x}\text{O}_{19}$  and  $\text{Sr}_{1-x}\text{Bi}_x\text{Fe}_{12}\text{O}_{19}$  samples, the cell volumes of Bi-substituted SrM ( $x = 0.1, 0.2$ ) are larger than that of the non-substitute SrM ( $x = 0$ ). The increase of cell volume by Bi substitution is understandable considering the relative ionic sizes ( $\text{Sr}^{2+}$  (0.113 nm),  $\text{Bi}^{3+}$  (0.103 nm), and  $\text{Fe}^{3+}$  (0.064 nm)). On the assumption that the cell volume changes depending on their relative ionic radius when the Bi ion substitutes either Fe or Sr ions, this result implies that Bi preferably substitutes into the Fe site rather than Sr site in the M-type structure.

Based on the result that Bi ions substitute into Fe sites of SrM, the effect of Bi-based additives on SrM is investigated. Generally, the doping elements Bi and Ca have a low firing temperature character that promotes grain growth [12–15]. Meanwhile, the additive Si suppresses grain growth effectively [16–19]. However, the  $M_S$  of the hexaferrites significantly decreases with increasing the doping amount of  $\text{SiO}_2$  because the Si diffusion into the matrix can destroy the ferrimagnetic order of the hexaferrite. Hence, generally in the ferrite magnet, higher  $H_C$  can be obtained while sacrificing  $M_S$ . Alternatively, Mn can be considered as a sintering additive. It substitutes into the  $\text{Fe}^{3+}$  site of SrM, which suppresses the grain growth of hexaferrites without compensating for  $M_S$  within a limited doping range [9,10]. In this research, various combinations of co-doping elements with Bi were used to enhance the hard magnetic properties of SrM.

Fig. 2 presents the XRD patterns of SrM samples with various combinations of additives. No secondary phase peaks are found in any of the samples. Abnormal increases in the peak intensity at  $31^\circ$ , corresponding to the (008) plane of SrM, are observed for the samples containing either 1 wt%  $\text{Bi}_2\text{O}_3$  or 1 wt%  $\text{CaCO}_3$ . It can be attributed to the powder sample preparation where the orientation of hexagonal planes around (00 $l$ ) becomes normal to the XRD specimen holder surface. It is more likely to happen in the samples with an abnormal grain growth [19,20].

Fig. 3(a)–(i) show the SEM micrographs of SrM samples doped with various additives sintered at  $1250^\circ\text{C}$ . The morphology of the as-milled powder after first calcination at  $1100^\circ\text{C}$  was presented in the previous research [19]. While as-milled particles have rounded shape with average grain size of  $0.68 \mu\text{m}$ , the sintered samples shows faceted grains with increased grain size. The SrM samples without any additives (Fig. 3(a)) show relatively porous microstructures with grain sizes in the range of  $1\text{--}3 \mu\text{m}$ . Grain growth occurs with increasing amount of  $\text{Bi}_2\text{O}_3$  doping from 0.5 wt% to 1.0 wt% (Fig. 3(b) and (c)). When 0.5 wt%  $\text{MnCO}_3$  is co-doped with 0.5 wt%  $\text{Bi}_2\text{O}_3$  (Fig. 3(d) and (e)), the grain growth is relatively suppressed compared to that in the  $\text{Bi}_2\text{O}_3$  solely doped samples (Fig. 3(b) and (c)). When 0.5 wt%  $\text{SiO}_2$  is co-doped with

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