

Intrinsic magnetic properties and microstructures of Bi-substituted M-type SrBaLa hexaferrite powders

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In this study, M-type hexagonal $\text{Sr}_{0.4}\text{Ba}_{0.3}\text{La}_{0.3}\text{Fe}_{12-x}\text{Bi}_x\text{O}_{19}$ ($0 \leq x \leq 0.4$) magnetic powders were synthesized by the solid state reaction method. The phase composition and magnetic properties of the magnetic powders were characterized by an X-ray diffractometer (XRD) and a vibrating sample magnetometer (VSM), respectively. The results of XRD show that all samples exhibit a well-defined M-type hexaferrite phase when Bi content (x) ≤ 0.2 , while for the magnetic powder with $x \geq 0.3$, the XRD patterns show the M-type strontium hexaferrite structure and two peaks of BiFeO_3 as a second phase are observed. The saturation magnetization (M_s) and remanent magnetization (M_r) first increase with Bi content (x) from 0 to 0.1, and then decrease when Bi content (x) ≥ 0.1 . The coercivity (H_c) decreases quickly with Bi content (x) from 0 to 0.1, then begins to increase with Bi content (x) from 0.1 to 0.3, and when $x > 0.3$ the coercivity (H_c) decreases significantly.

Key words: Hexagonal ferrite powders, Bi substitution, X-ray diffraction, Magnetic properties.

Introduction

Strontium hexaferrite $\text{SrFe}_{12}\text{O}_{19}$ is one of M-type hexaferrites. M-type hexaferrites have large saturation magnetization, high coercivity, high Curie temperature, large uniaxial magnetic anisotropy and excellent chemical stability. These materials have been extensively investigated due to their technological applications in permanent magnets, high-density magnetic recording media and microwave devices [1]. In the M-type hexaferrite structure, the Fe^{3+} ions occupy five different crystallographic sites such as three octahedral ($2a$, $12k$ and $4f_2$), one tetrahedral site ($4f_1$), and one bipyramidal site ($2b$). In addition, $2a$, $2b$ and $12k$ are spin up sites, while $4f_1$ and $4f_2$ are spin down sites [2]. The magnetic moment and magneto-crystalline anisotropy of M-type hexaferrites originate from the electronic structure of Fe^{3+} ions at the five crystallographic sites [3].

A number of studies have been done to enhance the intrinsic magnetic properties of M-type Strontium hexaferrites, such as saturation magnetization and crystalline anisotropy, by ion substitution technique [4–17]. Several cations, such as La^{3+} , Pr^{3+} , Sm^{3+} , Nd^{3+} , Bi^{3+} , Al^{3+} and Cr^{3+} , and cation combinations, such as $\text{La}^{3+}\text{-Co}^{2+}$, $\text{La}^{3+}\text{-Zn}^{2+}$, $\text{La}^{3+}\text{-Cu}^{2+}$, $\text{La}^{3+}\text{-Bi}^{3+}$, $\text{Bi}^{3+}\text{-Cr}^{3+}$, $\text{Ni}^{2+}\text{-Co}^{2+}$ and $\text{Mn}^{2+}\text{-Zn}^{2+}$, have been investigated and

discussed [4–17]. Thakur et al. have studied the La^{3+} substituted strontium hexaferrite nanoparticles prepared by citrate precursor method, and found that the coercivity value increased with increase of La^{3+} content [4]. Auwal et al. have prepared the M-type hexagonal ferrites, $\text{SrBi}_x\text{Fe}_{12-x}\text{O}_{19}$ ($0.0 \leq x \leq 1.0$) by a co-precipitation assisted ceramic route, and studied the Mössbauer analysis and cation distribution of Bi^{3+} substituted M-type hexaferrites [8]. Yang et al. have studied the M-type hexaferrite $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}\text{Cu}_x\text{O}_{19}$ ($0 \leq x \leq 0.35$) prepared by the ceramic process and found that the remanence reached to the maximum at $x = 0.20$ and the coercivity decreased linearly with x from 0 to 0.35 [13]. Shakoor et al. have synthesized the M-type hexaferrite nanomaterials, $\text{SrFe}_{12-2x}\text{Bi}_x\text{Cr}_x\text{O}_{19}$ ($0.0 \leq x \leq 0.8$), and found that the saturation magnetization and remanence reached to the maximum at $x = 0.20$ while the coercivity reached to the minimum at $x = 0.20$ [15].

In the present work, M-type hexagonal $\text{Sr}_{0.4}\text{Ba}_{0.3}\text{La}_{0.3}\text{Fe}_{12-x}\text{Bi}_x\text{O}_{19}$ ($0 \leq x \leq 0.4$) magnetic powders were synthesized by the solid state reaction method. The key aim of the present study is to study substitution effects of Bi^{3+} ions on the intrinsic magnetic properties and microstructures and of M-type SrBaLa hexaferrite powders.

Experimental Procedures

The commercial powders of SrCO_3 (99 wt%), BaCO_3 (99 wt%), La_2O_3 (99 wt%), Fe_2O_3 (99 wt%) and Bi_2O_3 (99 wt%) were used as the raw materials. A series of

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M-type hexaferrite samples with nominal formula of $\text{Sr}_{0.4}\text{Ba}_{0.3}\text{La}_{0.3}\text{Fe}_{12-x}\text{Bi}_x\text{O}_{19}$ ($0 \leq x \leq 0.4$), were prepared by the solid state reaction method. The raw materials were weighed and wet-mixed in a ball mill for 12 h. The mixed powders were dried at 130 °C for 10 hrs. And then the mixtures were calcined in a laboratory furnace at 1210 °C for 2 hrs in the air. The calcined products were comminuted into fine powders using a vibration mill. The fine powders were annealed in a laboratory furnace at 810 °C for 2 hrs and cooled down to room temperature in order to relieve the stress.

X-ray diffraction (XRD) analysis was performed by an X-ray diffractometer X'Pert PRO PANalytical using $\text{Cu K}\alpha$ radiation source of wavelength $\lambda = 1.5406 \text{ \AA}$. M - H loops of magnetic powders were measured using a vibrating sample magnetometer (VSM) in an applied magnetic field up to 7500 Oe at room temperature. From the obtained hysteresis loops, the saturation magnetization (M_s), remanent magnetization (M_r) and coercivity (H_c) were determined.

Results and Discussion

The standard powder X-ray diffraction technique in the region of $2\theta = 20$ – 80° with a step of $0.04^\circ/\text{min}$ on an X-ray diffractometer (PANalytical X'Pert Pro) using $\text{Cu K}\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$) is employed at room temperature to study the phase composition of the Bi substituted hexaferrite $\text{Sr}_{0.4}\text{Ba}_{0.3}\text{La}_{0.3}\text{Fe}_{12-x}\text{Bi}_x\text{O}_{19}$

($0 \leq x \leq 0.4$) magnetic powders. Fig. 1 shows the XRD patterns for all the samples, confirming that all samples exhibited a well-defined M-type hexaferrite phase (JCPDS card no. 80-1198) and no characteristic peaks of undesired phases when Bi content (x) ≤ 0.2 . But for the magnetic powder with $x \geq 0.3$, the XRD patterns represented the M-type strontium hexaferrite and also represented two peaks of BiFeO_3 (JCPDS card no. 86-1518) which appeared as a second phase. The presence of BiFeO_3 phase indicates that not all Bi^{3+} ions enter the M-type hexaferrite lattices when $x \geq 0.3$. The results of XRD show that the strength of the diffraction peaks changes with the increase of x . For the magnetic powders with x of 0, 0.1 and 0.4, the strongest peak is (107). For the magnetic powders with x of 0.2 and 0.3, the strongest peak is (008).

The lattice parameters a and c , and unit cell volume (V_{cell}) of the M-type hexagonal $\text{Sr}_{0.4}\text{Ba}_{0.3}\text{La}_{0.3}\text{Fe}_{12-x}\text{Bi}_x\text{O}_{19}$ magnetic powders with Bi content (x) from 0 to 0.4 have been calculated from the XRD data using the following equations [18]:

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

$$V_{\text{cell}} = \frac{\sqrt{3}}{2} a^2 c \quad (2)$$

where d_{hkl} is the inter-planer spacing value, and the values of h , k and l are the Miller indices. The calculated values of lattice parameters a and c , and unit cell volume (V_{cell}) for all the samples with different Bi content (x) are listed in Table 1. As seen from Table 1, lattice parameters a and c , the c/a ratio and the unit cell volume (V_{cell}) increase with the increase of Bi content (x). Mozaffari et al. have reported that the substitution of higher ionic radii element should result in the increase of lattice parameters [19]. These variations can mainly be explained on the basis of the ionic radius of the substituted ions. The ionic radii of Bi^{3+} ions ($1.03 \text{ \AA}$) are larger than that of Fe^{3+} ions ($0.645 \text{ \AA}$). The lattice parameter ratio c/a may be used to quantify the structure type, and the magnetoplumbite structure could be assumed if the ratio is lower than 3.98 [20]. The c/a ratios for the magnetic powders with different Bi content (x) range from 3.915 to 3.925, which are well within the

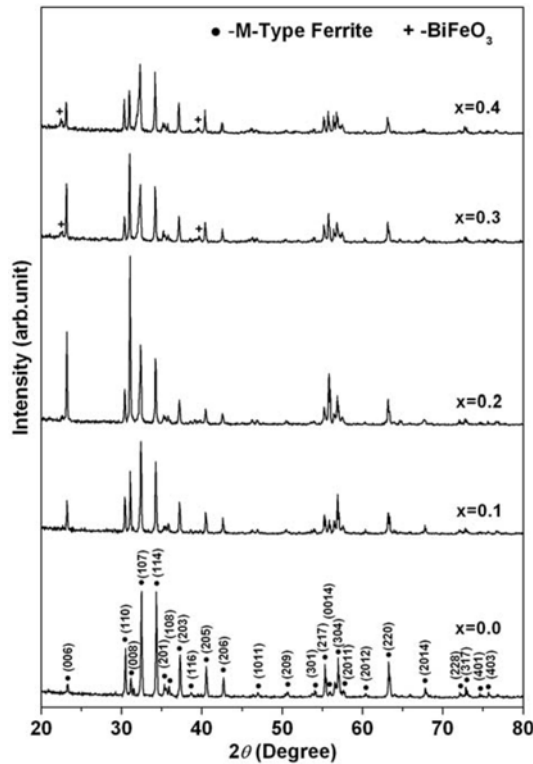


Fig. 1. The XRD patterns of the M-type hexaferrite $\text{Sr}_{0.4}\text{Ba}_{0.3}\text{La}_{0.3}\text{Fe}_{12-x}\text{Bi}_x\text{O}_{19}$ magnetic powders with different Bi content (x) from 0 to 0.4.

Table 1. Lattice parameters c and a , ratio of c/a , and unit cell volume (V_{cell}) for M-type hexaferrite $\text{Sr}_{0.4}\text{Ba}_{0.3}\text{La}_{0.3}\text{Fe}_{12-x}\text{Bi}_x\text{O}_{19}$ magnetic powders with different Bi content (x) from 0 to 0.4.

Bi content (x)	c ($\text{\AA}$)	a ($\text{\AA}$)	c/a	V ($\text{\AA}^3$)
0	22.954	5.863	3.915	683.3
0.1	23.007	5.875	3.916	687.7
0.2	23.038	5.880	3.918	689.8
0.3	23.072	5.886	3.920	692.2
0.4	23.107	5.887	3.925	693.5

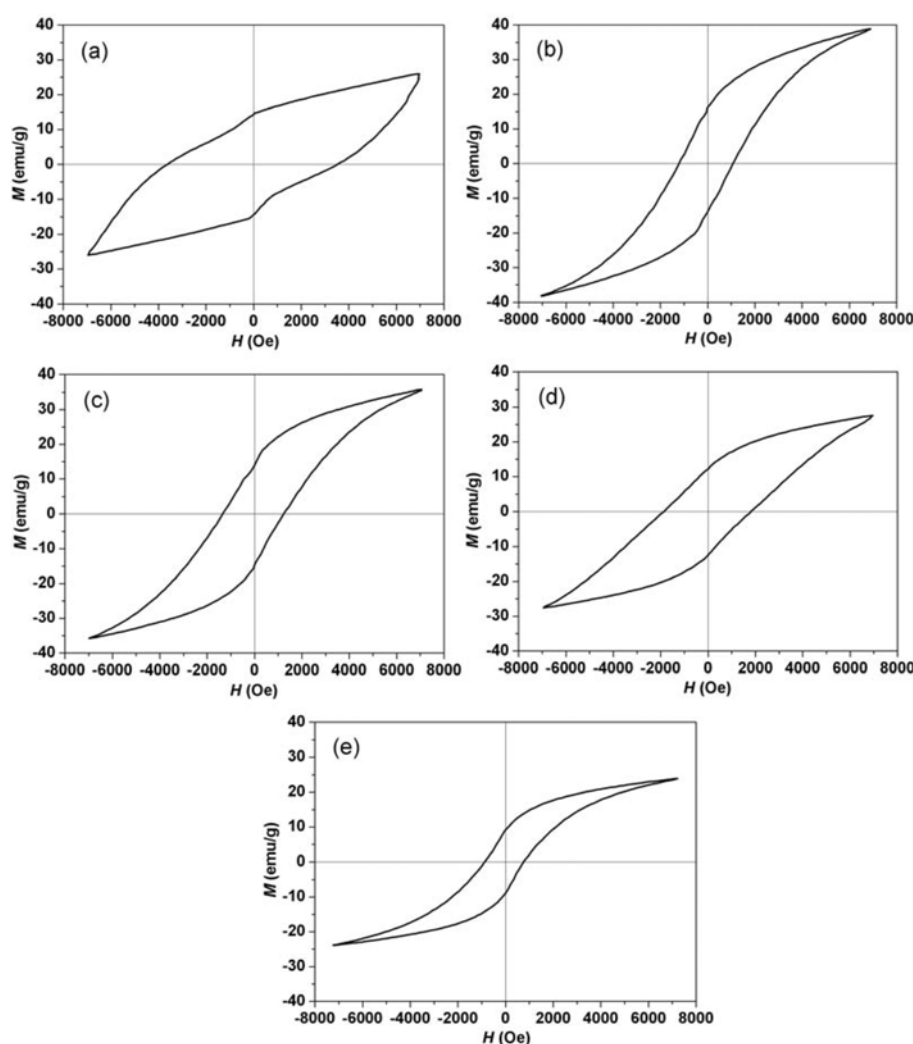


Fig. 2. Magnetic hysteresis loops of the M-type hexaferrite $\text{Sr}_{0.4}\text{Ba}_{0.3}\text{La}_{0.3}\text{Fe}_{12-x}\text{Bi}_x\text{O}_{19}$ magnetic powders for compositions of (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$, and (e) $x = 0.4$.

Table 2. Data of M_r , M_s , H_c and M_r/M_s of the M-type hexaferrite $\text{Sr}_{0.4}\text{Ba}_{0.3}\text{La}_{0.3}\text{Fe}_{12-x}\text{Bi}_x\text{O}_{19}$ magnetic powders with different Bi content (x) from 0 to 0.4.

Bi content (x)	M_r (emu/g)	M_s (emu/g)	H_c (Oe)	M_r/M_s
0	14.28	25.93	3572	0.551
0.1	15.04	38.50	1146	0.391
0.2	14.36	35.73	1289	0.402
0.3	12.33	27.51	1845	0.448
0.4	8.99	23.91	817	0.376

ratio range of magnetoplumbite structures.

The magnetic hysteresis loops of the M-type hexagonal $\text{Sr}_{0.4}\text{Ba}_{0.3}\text{La}_{0.3}\text{Fe}_{12-x}\text{Bi}_x\text{O}_{19}$ magnetic powders with Bi content (x) from 0 to 0.4 are shown in Fig. 2. The values of the saturation magnetization (M_s), remanent magnetization (M_r) and coercivity (H_c) were obtained from the magnetic hysteresis loops and these values are tabulated in Table 2.

Fig. 3 presents the variations in the saturation

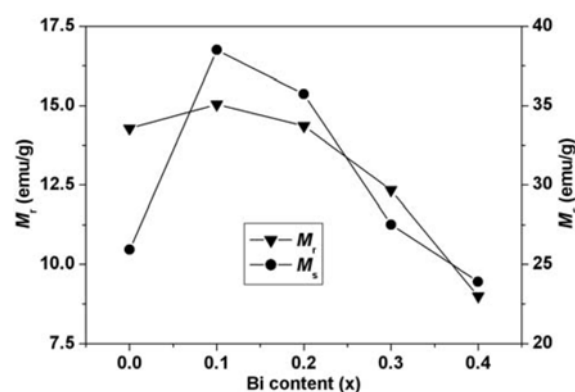


Fig. 3. Variations in the saturation magnetization (M_s) and remanent magnetization (M_r) with Bi content (x) for the M-type hexaferrite $\text{Sr}_{0.4}\text{Ba}_{0.3}\text{La}_{0.3}\text{Fe}_{12-x}\text{Bi}_x\text{O}_{19}$ magnetic powders.

magnetization (M_s) and remanent magnetization (M_r) as a function of Bi content (x) for the M-type hexagonal $\text{Sr}_{0.4}\text{Ba}_{0.3}\text{La}_{0.3}\text{Fe}_{12-x}\text{Bi}_x\text{O}_{19}$ magnetic powders. The substitution Bi^{3+} ions in $\text{Sr}_{0.4}\text{Ba}_{0.3}\text{La}_{0.3}\text{Fe}_{12-x}\text{Bi}_x\text{O}_{19}$

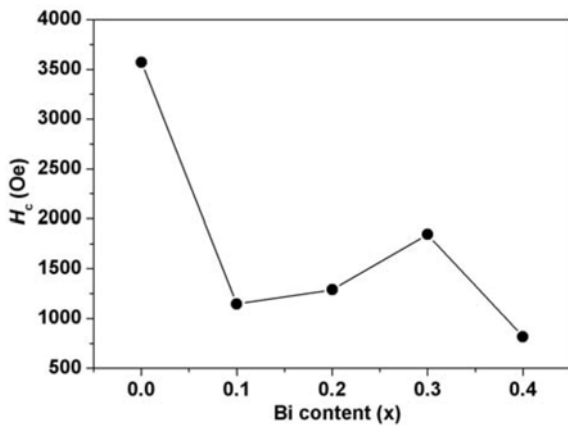


Fig. 4. Variation in the coercivity (H_c) with Bi content (x) for the M-type hexaferrite $\text{Sr}_{0.4}\text{Ba}_{0.3}\text{La}_{0.3}\text{Fe}_{12-x}\text{Bi}_x\text{O}_{19}$ magnetic powders.

hexaferrite powders can effect M_s and M_r significantly. As shown in Fig. 3 and Table 2, the values of both M_s and M_r increase with Bi content (x) up to $x = 0.1$, and then decrease with further increase in Bi content (x). In the M-type hexaferrite, the Fe^{3+} ions occupy five different interstitial sites, i.e. tetrahedral $4f_1$ (downward spin), bipyramidal $2b$ (upward spin), and three octahedral sites $12k$ (upward spin), $4f_2$ (downward spin), and $2a$ (upward spin). For the M-type hexaferrite, the magnetic moments of Fe^{3+} ions are arranged collinearly because of the existence of super-exchange interaction. Auwal et al. [8] have reported that Bi^{3+} ions prefer to distribute on downward Fe sites known as $4f_1$ and $4f_2$. As Bi^{3+} ions at low substitution level occupy the site having spin of electrons in downward direction which results in the number of Fe^{3+} ions having spin in upward direction. Thus, the values of both M_s and M_r increase with increasing Bi content (x) when Bi content (x) ≤ 0.1 . When Bi content (x) > 0.1 , the decreases of both M_s and M_r can be attributed to the following two factors. Firstly, the non-magnetic Bi^{3+} ions cause to decrease the super-exchange interaction between the sub-lattices. The weakening of super-exchange interaction results in the reduction of both M_s and M_r . Secondly, when Bi content (x) ≥ 0.3 , the content of BiFeO_3 as a second phase increases with the increase of x . This causes both M_s and M_r to decrease. It can be seen from the Fig. 2 that the squareness of magnetic hysteresis loops varies with the increasing Bi content (x) from 0 to 0.4. The M_r/M_s ratio which is known as squareness ratio is also calculated and is listed in Table 2. It is observed from the Table 2 that M_r/M_s firstly decreases from 0.551 at $x = 0$ to 0.391 at $x = 0.1$, then increases with Bi content (x) from 0.1 to 0.3, and when $x > 0.3$ M_r/M_s decreases and reaches to 0.376 at $x = 0.4$. This indicates that Bi substitution can affect the squareness of magnetic hysteresis loops.

The variation of the coercivity (H_c) as a function of Bi content (x) for the M-type hexagonal $\text{Sr}_{0.4}\text{Ba}_{0.3}$

$\text{La}_{0.3}\text{Fe}_{12-x}\text{Bi}_x\text{O}_{19}$ magnetic powders is shown in Fig. 4. It is observed from Fig. 4 and Table 2, the coercivity (H_c) decreases quickly from 3925 Oe at $x = 0$ to 1146 Oe at $x = 0.1$, then begins to increase with Bi content (x) from 0.1 to 0.3, and when $x > 0.3$ the coercivity (H_c) decreases significantly and reaches to 817 Oe at $x = 0.4$. As is known, the coercivity (H_c) is inversely proportional to M_s theoretically and can be described by the following formula [21]:

$$H_c = \alpha \times \frac{2K}{M_s} \quad (3)$$

where α is the orientation factor, M_s is the saturation magnetization and K is the magnetocrystalline anisotropy constant. Therefore, the increase of H_c with Bi content (x) from 0 to 0.1 may be attributed to the following reason. According to the formula (3), the quickly increase of the saturation magnetization (M_s) with Bi content (x) from 0 to 0.1 leads to the decrease of the coercivity (H_c). However, the increase of H_c with Bi content (x) from 0.1 to 0.3 is mainly due to the following reason. According to the formula (3), the linearly decrease of the saturation magnetization (M_s) with Bi content (x) from 0.1 to 0.3 results in the increase of the coercivity (H_c). For Bi content (x) > 0.3 , the decrease of H_c may be due to decrease of magnetocrystalline anisotropy.

Conclusions

M-type hexagonal $\text{Sr}_{0.4}\text{Ba}_{0.3}\text{La}_{0.3}\text{Fe}_{12-x}\text{Bi}_x\text{O}_{19}$ ($0 \leq x \leq 0.4$) magnetic powders with Bi content (x) from 0 to 0.4 have been prepared by the solid state reaction method. The XRD analysis indicates that when Bi content (x) ≤ 0.2 , all samples exhibit a well-defined M-type hexaferrite phase, while for the magnetic powder with $x \geq 0.3$, the XRD patterns show the M-type strontium hexaferrite structure and two peaks of BiFeO_3 as a second phase are observed. We have systematically investigated magnetic properties of the M-type hexagonal $\text{Sr}_{0.4}\text{Ba}_{0.3}\text{La}_{0.3}\text{Fe}_{12-x}\text{Bi}_x\text{O}_{19}$ magnetic powders with different Bi content (x). M_s and M_r first increase with Bi content (x) from 0 to 0.1, and then decrease when Bi content (x) ≥ 0.1 . H_c decreases quickly with Bi content (x) from 0 to 0.1, then begins to increase with Bi content (x) from 0.1 to 0.3, and when $x > 0.3$ H_c decreases significantly.

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