Structural and magnetic properties of $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}(\text{Cu}_{0.5}\text{Co}_{0.5})_x\text{O}_{19}$ hexaferrites prepared by the solid-state reaction method

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Abstract. Hexaferrite $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}(\text{Cu}_{0.5}\text{Co}_{0.5})_x\text{O}_{19}$ ($0 \leq x \leq 0.50$) magnetic powders and magnets were synthesized by the solid-state reaction method. The phase compositions of magnetic powders were investigated by X-ray diffraction. The single magnetoplumbite phase is obtained in magnetic powders with x from 0 to 0.40. At $x = 0.50$, CoFe_2O_4 , and $\alpha\text{-Fe}_2\text{O}_3$ were observed. The morphology of the materials was characterized by a field-emission scanning electron microscopy. The particles were hexagonal platelets. Magnetic properties of the materials were measured by a permanent magnetic measure equipment. The remanence of the materials increases with x from 0 to 0.50. However, the intrinsic coercivity and magnetic induction coercivity of the materials increase with x from 0 to 0.15, and decreases when x varies from 0.15 to 0.50. Accordingly, the maximum energy product of the materials first increases with x from 0 to 0.35, and then decreases when x exceeds 0.35.

Keywords. Hexagonal ferrites; La–CuCo substitution; magnetic properties; X-ray diffraction.

1. Introduction

Hexagonal ferrites with the chemical formula of $\text{MFe}_{12}\text{O}_{19}$ ($\text{M} = \text{Ba}, \text{Sr}, \text{Pb}$) have been widely used as permanent magnets, microwave devices, magneto-optics, and magnetic recording media owing to relatively low price, high coercivity, large magnetocrystalline anisotropy, and outstanding chemical stability [1]. In order to fulfill various applications, many attempts have been made to improve magnetic properties of the hexagonal ferrites by adding or doping some elements. Liu *et al* [2] have studied the influences of La^{3+} substitution on the structure and magnetic properties of M-type strontium ferrites. Yang *et al* [3] have reported the effects of La–Co substitution on the structural and magnetic properties of La–Co-substituted Sr–Ca hexaferrites synthesized by the solid-state reaction method. Shen *et al* [4] have studied the effects of La–Zn substitution on the magnetic properties of strontium ferrite nanofibres. Qiao *et al* [5] have studied the magnetic properties of strontium hexaferrites with La–Cu substitution prepared by the SHS method. Abbas *et al* [6] have carried out a study of Sm-substituted SrM magnets sintered using hydrothermally synthesized powders. Wang *et al* [7] have reported a study of Sm-substituted SrM magnets sintered using hydrothermally synthesized powders. Choi *et al* [8] have studied the site occupancy and anisotropy distribution of Al-substituted Ba–ferrite with high coercivity. Yang and Liu [9] have prepared Ca^{2+} -doped hexagonal ferrites

$\text{Sr}_{0.65-x}\text{Ca}_x\text{La}_{0.35}\text{Fe}_{11.32}\text{Co}_{0.28}\text{O}_{18.435}$ ($0 \leq x \leq 0.45$) by the solid-state reaction method and have found that the remanence, intrinsic coercivity, and magnetic induction coercivity first increase with the Ca content (x) from 0 to 0.20, and then decrease when the Ca content (x) continues to increase.

On the other hand, as a result of the recent decrease in the supply of rare earth metals, research into magnetic materials that are not based on rare earth metals has boomed. In the market, CuO powder is cheaper than Co_2O_3 powder. The price of CuO powder is about 1/5 of the price of Co_2O_3 powder. In order to reduce the cost of M-type hexaferrites, La–CuCo-substituted M-type hexaferrites was prepared and have studied the influence of La–CuCo content on the microstructure and magnetic properties. Therefore, in this paper, the La–CuCo-substituted M-type strontium hexaferrites are synthesized by the solid-state reaction method. The effects of La–CuCo content on the structural and magnetic properties of the $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}(\text{Cu}_{0.5}\text{Co}_{0.5})_x\text{O}_{19}$ ($0 \leq x \leq 0.50$) hexagonal ferrites have been studied systematically.

2. Experimental

All samples of the $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}(\text{Cu}_{0.5}\text{Co}_{0.5})_x\text{O}_{19}$ hexagonal ferrites were prepared according to the solid-state reaction method. The starting materials used in this study were SrCO_3 (99% purity), La_2O_3 (99% purity), Fe_2O_3 (99% purity), CuO (99% purity) and Co_2O_3 (99% purity) powders, mixed together in the chemical composition of $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}(\text{Cu}_{0.5}\text{Co}_{0.5})_x\text{O}_{19}$, where x varied from 0 to

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0.50. Mixtures of these starting materials were charged in a ball mill together with hardened steel balls with diameter of 8 mm. The powders were milled in water for 8 h with an angular velocity of 80 rpm and a ball-to-power weight ratio of 12 : 1. The milled powders were dried, crushed, and sifted. The sifted powders were shaped into balls of about $\Phi 8$ mm, and the balls were then calcined at 1250°C for 2 h in a box furnace in air. Then the calcined balls were dry milled to particles under 100 μm using a vibration mill, then wet-milled with additives (CaCO_3 , SiO_2 , Al_2O_3 and H_3BO_3) for 14 h using a ball-mill. The finely milled slurry with a diameter of about 0.75 μm was pressed into disk-shaped compacts with $\Phi 30 \times 15$ mm by wet compacting under 310 MPa in a pulsed magnetic field of 900 kA m^{-1} , which was parallel to the pressing direction. The green compacts were sintered in a box furnace at 1185°C for 1.5 h in air.

The phase compositions of the magnetic powders were characterized by a PANalytical X'Pert Pro diffractometer in continuous mode using Cu K_α radiation. The morphology of the magnets was observed by a HITACHI S-4800 field-emission scanning electron microscopy (FESEM). Magnetic properties of the magnets were measured by a permanent magnetic measure equipment (MATS-2000, manufactured by the National Institute of Metrology of China).

3. Results and discussion

3.1 Structural properties

Figure 1 shows the X-ray diffraction (XRD) patterns of the hexaferrite $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}(\text{Cu}_{0.5}\text{Co}_{0.5})_x\text{O}_{19}$ magnetic powders with different La–CuCo substitutions (x) from 0 to 0.50. In comparison with the standard strontium ferrite JCPDS card no. 80-1198, it can be seen from figure 1 that there is a single magnetoplumbite phase in the magnetic powders with the increase of x from 0 to 0.40. For the magnetic powder with x of 0.50, CoFe_2O_4 and $\alpha\text{-Fe}_2\text{O}_3$ appear in the structure. However, the intensities of the diffraction peaks vary with the increase in x . For the magnetic powders with x of 0 and 0.20, the strongest peak is (114). For the magnetic powders with x of 0.10 and 0.15, the strongest peak is (008). For the magnetic powders with x from 0.25 to 0.50, the strongest peak is (107). The results of XRD are not in agreement with that reported by Qiao *et al* [5].

The lattice constants a and c are calculated from the values of the d_{hkl} corresponding to (107) peaks and (114) peaks according to the following formula [10]:

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

where d_{hkl} is the crystal face distance and values of h , k and l are the corresponding Miller indices.

The variation of lattice parameters a and c of the hexaferrite $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}(\text{Cu}_{0.5}\text{Co}_{0.5})_x\text{O}_{19}$ magnetic powders with different La–CuCo substitutions (x) from 0 to 0.50 is shown in figure 2. It is observed from this figure that the

Figure 1. X-ray diffraction patterns of the hexaferrite $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}(\text{Cu}_{0.5}\text{Co}_{0.5})_x\text{O}_{19}$ magnetic powders with different La–CuCo substitutions (x).

Figure 2. Lattice parameters a and c of the hexaferrite $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}(\text{Cu}_{0.5}\text{Co}_{0.5})_x\text{O}_{19}$ magnetic powders with different La–CuCo substitutions (x).

lattice parameter a remains almost constant, while the lattice parameter c linearly decreases with the increase in the dopant contents. The decrease of the lattice parameter c can be attributed to the difference in the ionic radii (Δr) of the

Figure 3. Representative FESEM images of the hexaferrite $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}(\text{Cu}_{0.5}\text{Co}_{0.5})_x\text{O}_{19}$ magnets with a La-CuCo substitution (x) of: (a) 0, (b) 0.15, (c) 0.35 and (d) 0.50.

metal ions and the number of ionic substitutions of each species. Substitution of Sr^{2+} ($r = 1.32 \text{ \AA}$) by La^{3+} ($r = 1.22 \text{ \AA}$) makes a negative difference in the ionic radii of $\Delta r = -0.10 \text{ \AA}$. However, substitution of Fe^{3+} ($r = 0.67 \text{ \AA}$) by Cu^{2+} ($r = 0.73 \text{ \AA}$) and Co^{2+} ($r = 0.74 \text{ \AA}$) makes a positive difference in the ionic radii of $\Delta r = +0.06 \text{ \AA}$ and $\Delta r = +0.07 \text{ \AA}$, respectively. Therefore, the lattice parameters c is expected to decrease.

Figure 3 displays the representative FESEM images of the hexaferrite $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}(\text{Cu}_{0.5}\text{Co}_{0.5})_x\text{O}_{19}$ magnets with La-CuCo substitutions (x) of 0, 0.15, 0.35 and 0.50. From the FESEM micrographs, it is clearly seen that the particles are hexagonal platelets and are distributed homogeneously. Besides that, the mean particle size and particle morphology of the magnets are unchanged with the increase of La-CuCo substitution.

3.2 Magnetic properties

The influence of La-CuCo substitution (x) on the remanence (B_r) of the hexaferrite $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}(\text{Cu}_{0.5}\text{Co}_{0.5})_x\text{O}_{19}$ magnets is shown in figure 4. It is obvious from this figure that B_r continuously increases with the increase in x . In the M-type hexaferrite crystals, the unit cell consists of two molecules. Within the basic structure, Fe^{3+} ions occupy five different sites: spin up sites 2a, 2b and 12k and spin down sites 4f₁ and 4f₂, where 2a, 12k and 4f₂ are octahedral sites, 4f₁ is tetrahedral site and 2b is trigonal bipyramid site. Qiao *et al* have reported that the Cu^{2+} ions probably prefers to substitute the Fe^{3+} ions in 4f₂ sites considering that the 4f₂ site is closer to the Sr-layer [5]. Mössbauer investigations of La-Co-substituted M-type hexaferrites have revealed that La^{3+} ions are located in the Sr^{2+} sites, and Co^{2+} ions are substituted for Fe^{3+} ions in the octahedral 4f₂ (mainly) and 2a sites [11–14]. The occupation of Cu^{2+} ($\sim 1 \mu_B$) and Co^{2+} ($\sim 4 \mu_B$) in 4f₂ sites decreases magnetic moment in the

Figure 4. Influence of La-CuCo substitution (x) on the remanence (B_r) of the hexaferrite $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}(\text{Cu}_{0.5}\text{Co}_{0.5})_x\text{O}_{19}$ magnets.

Figure 5. Influence of La-CuCo substitution (x) on the intrinsic coercivity (H_{cj}) and magnetic induction coercivity (H_{cb}) of the hexaferrite $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}(\text{Cu}_{0.5}\text{Co}_{0.5})_x\text{O}_{19}$ magnets.

opposite direction, and then the whole magnetic moment can be increased. However, the substitution of Co^{2+} ions in 2a sites may also decrease the magnetic moment, but the positive contribution of 4f₂ sites is more, owing to the more 4f₂ sites for sitting of Cu^{2+} and Co^{2+} ions in. This is the reason that B_r of the magnets increases with the increase in x .

Figure 5 shows the influence of La-CuCo substitution (x) on the intrinsic coercivity (H_{cj}) and magnetic induction coercivity (H_{cb}) of the hexaferrite $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}(\text{Cu}_{0.5}\text{Co}_{0.5})_x\text{O}_{19}$ magnets. As can be seen from figure 5, H_{cj} and H_{cb} increase with the increase of x from 0 to 0.15, while the values of H_{cj} and H_{cb} are found to decrease when x varies from 0.15 to 0.50. When x is up to 0.15, H_{cj} and H_{cb} reach to the maximum values of 337.5 and 301.3 kA m⁻¹, respectively. The coercivity of the magnets depends both on their magnetocrystalline anisotropy and on their microstructure.

According to the literature [15], the coercivity can be described by the following expression:

$$H_c = \alpha H_a - \frac{N(B_r + J_s^0)}{\mu_0}, \quad (2)$$

where α is the microstructure factor, N the grain demagnetization factor, H_a the magnetocrystalline anisotropy field, and J_s^0 the saturation polarization of the magnet. The factor α increases with the decrease in grain size, thus reflecting the well-known H_c -grain size dependency; the factor N is governed by the grain shape and increases when the grain shape becomes more platelet shaped. The representative FESEM micrographs shown in figure 3 exhibit that the mean particle size and particle morphology of the magnets do not change basically with the increase in x , which implies that the factors α and N remain constant. Therefore, it can be concluded that the increase of H_{cj} with x from 0 to 0.15 can be accredited to the increase of the magnetocrystalline anisotropy field with the increase in x . Asti *et al* [16] have reported that the magnetocrystalline anisotropy field increases with the increase in z in the $\text{Sr}_{1-z}\text{La}_z\text{Fe}_{12-z}\text{Co}_z\text{O}_{19}$ ($0 \leq z \leq 0.4$) ferrites. In addition, the decrease of H_{cj} with x from 0.15 to 0.50 can be attributed to two following reasons. First, an increase in the abundance of Co^{2+} ions at 2a sites, which will destroy the regular arrangement of the Fe^{3+} ions, increases with the increase in x . This causes the magnetocrystalline anisotropy field to decrease. Second, in the M-type hexaferrites, the magnetocrystalline anisotropy is mainly from the single-ion anisotropy of the Fe^{3+} ions on the $4f_2$ and $2b$ sites [17]. As mentioned above, Cu^{2+} ions occupy the $4f_2$ sites and have a negative influence on the magnetocrystalline anisotropy.

The influence of La–CuCo substitution (x) on the maximum energy product $[(BH)_{\max}]$ of the hexaferrite $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}(\text{Cu}_{0.5}\text{Co}_{0.5})_x\text{O}_{19}$ magnets is shown in figure 6. It

Figure 6. Influence of La–CuCo substitution (x) on the maximum energy product $[(BH)_{\max}]$ of the hexaferrite $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}(\text{Cu}_{0.5}\text{Co}_{0.5})_x\text{O}_{19}$ magnets.

can be seen from this figure that $(BH)_{\max}$ increases from 30.31 kJ m^{-3} ($x = 0$) to 33.84 kJ m^{-3} ($x = 0.35$), and at $x = 0.35$, $(BH)_{\max}$ reaches the maximum value. When x is above 0.35, $(BH)_{\max}$ of the magnets starts to decrease. The larger the maximum energy product is, the better the magnet is. Since the maximum energy product is the maximum area in second quadrant of the hysteresis loop, the values of remanence (B_r) and magnetic induction coercivity (H_{cb}) will have their influence on it.

Figure 7 presents two typical demagnetizing curves of the hexaferrite $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}(\text{Cu}_{0.5}\text{Co}_{0.5})_x\text{O}_{19}$ magnets measured at room temperature with La–CuCo substitutions (x) of 0.15 and 0.35. As shown in figure 7a, the magnet with x of 0.15 exhibits the magnetic properties, including remanence ($B_r = 408.3 \text{ mT}$), intrinsic coercivity ($H_{cj} = 337.5 \text{ kA m}^{-1}$), magnetic induction coercivity ($H_{cb} = 301.3 \text{ kA m}^{-1}$), and maximum energy product $[(BH)_{\max} = 32.08 \text{ kJ m}^{-3}]$. As shown in figure 7b, the magnet with x of 0.35 exhibits the magnetic properties, including remanence ($B_r = 422.7 \text{ mT}$),

Figure 7. Typical demagnetizing curves of the hexaferrite $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}(\text{Cu}_{0.5}\text{Co}_{0.5})_x\text{O}_{19}$ magnets measured at room temperature with a La–CuCo substitution (x) of (a) 0.15 and (b) 0.35.

intrinsic coercivity ($H_{\text{cj}} = 240.7 \text{ kA m}^{-1}$), magnetic induction coercivity ($H_{\text{cb}} = 226.0 \text{ kA m}^{-1}$) and maximum energy product [$(BH)_{\text{max}} = 33.84 \text{ kJ m}^{-3}$].

4. Conclusions

Hexagonal ferrite $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}(\text{Cu}_{0.5}\text{Co}_{0.5})_x\text{O}_{19}$ ($0 \leq x \leq 0.50$) magnetic powders and magnets were synthesized by the solid-state reaction method. The phase compositions of magnetic powders were investigated by the XRD. The single magnetoplumbite phase is obtained in magnetic powders with x from 0 to 0.40. For the magnetic powder with x of 0.50, CoFe_2O_4 and $\alpha\text{-Fe}_2\text{O}_3$ appear in the structure. The morphology of the magnets was characterized by a FESEM. The particles are hexagonal platelets.

Magnetic properties of the magnets were measured by a magnetic properties test instrument. B_{r} of the magnets increases with the increase in x . However, H_{cj} and H_{cb} of the magnets increase with the increase in x from 0 to 0.15, and then decrease when x varies from 0.15 to 0.50. Accordingly, the maximum energy product of the magnets first increases with the increase in x from 0 to 0.35, and then begins to decrease when x is above 0.35. H_{cj} and H_{cb} of the magnets reach the maximum values at $x = 0.15$, while $(BH)_{\text{max}}$ of the magnets reaches the maximum value at $x = 0.35$.

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