Journal of ELECTRONIC MATERIALS, Vol. 46, No. 7, 2017
DOI: 10.1007/s11664-017-5387-y

The Study of Microstructure and Magnetic Properties of La^{3+} doped W-Type Hexagonal Ferrites $Sr_{1-x}La_xCo_2Fe_{16}O_{27}$

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The W-type hexagonal ferrites with the composition $Sr_{1-x}La_xCo_2Fe_{16}O_{27}$ ($0 \le x \le 0.35$) magnetic powders were synthesized by the solid state method. The phase constituents, micro-morphology, and magnetic properties of the particles were investigated by x-ray diffraction (XRD), a scanning electron microscope, and a vibrating sample magnetometer. The single phase was observed in the W-type ferrites with different La content from XRD. The micro-morphology of the particles exhibits the hexagonal plate-like shape, and the particles are distributed homogeneously of W-type ferrites with different La content. The coercivity (H_c) of the particles increases with the increase of La content (x), while the saturation magnetization (M_s) of the particles first increases with x from 0 to 0.15, and then begins to decrease when x continues to increase.

Key words: W-type ferrites, the solid state method, microstructure, magnetic properties

INTRODUCTION

Generally speaking, the family of hexagonal ferrites can be classified on the basis of different chemical compositions and crystal structures. They are subdivided into six fundamental types: M, W, X, Y, Z and U.[1] The hexaferrites can be used as hard ferrite magnets, electromagnetic wave absorbers,[2] magnetic recording media,[3] and microwave devices.[4,5] For instance, the M-type ferrites have become the mainstream of hexagonal ferrites; however, the performance of them is close to their limitations, and it is so difficult to improve their magnetic properties rapidly.[6] The hexagonal Ba-M hexaferrite ($BaFe_{12}O_{19}$) thin films have been widely studied for applications in the magnetic recording industry.[7,8] The W-type hexaferrites, $BaMe_2Fe_{16}O_{27}$ (where Me is any divalent element), have a crystalline structure building up as a superposition of RSSR* S*S*; the structures of R and S (spinel block) are $SrFe_6O_{11}$ and $Me_2Fe_4O_8$, respectively, and the * means that the corresponding block has been turned 180° around the hexagonal axis.[9–12]

(Received October 25, 2016; accepted February 15, 2017; published online March 1, 2017)

In the last few years researchers have diverted their attention to substitute rare earth metal at various sites in the W-type hexagonal ferrites such as Y, Er, Ho, Sm, Gd, Ce,[13] Dy, Nd, Pr,[14] because these substitutions change the magnetic interactions and, therefore, enhance the magnetic properties.[15] Rare earth ions have typical relaxation characteristics which may affect the electromagnetic properties of ferrite magically.[16] La substitution has been found to play an important role in tailoring properties of ferrites, and; hence, it was decided to investigate the electromagnetic properties of the compound having the chemical formula $Sr_{1-x}La_xCo_2Fe_{16}O_{27}$. As far as we know, the compound studied in the present investigations is being reported for the first time.

MATERIAL AND METHODS

All samples of W-type ferrites $Sr_{1-x}La_xCo_2Fe_{16}O_{27}$ (x = 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 and 0.35) were synthesized by the solid state method. All the raw materials ($SrCO_3$ (99% purity), La_2O_3 (99% purity), Co_2O_3 (98% purity), and Fe_2O_3 (98% purity)) were used as received without further purification before the synthesized process. The raw

materials were weighted according to a stoichiometric composition of $Sr_{1-x}La_xCo_2Fe_{16}O_{27}$, where x = 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 and 0.35. Then the raw materials were added in a ball mill together, with a diameter of 8 mm. The mixtures of the raw materials were ground for 4 h with an angular velocity of 80 rpm and a ball-to-powder weight ratio of 15:1. The obtained powder was dried at 100°C for 10 h before pre-sintering at 1270°C in air for 3 h. Finally, the vibration mill was employed to crush the pre-sintered products.

The powder x-ray diffraction (XRD) patterns of the samples were recorded on x-ray diffraction (XRD) using Cu K_α radiation. The morphology and sizes of the samples were studied by a HITACHI S-4800 scanning electron microscope (SEM). Meanwhile, the saturation magnetization (M_s) and coercivity (H_c) were measured by a Riken Denshi BH-55 vibrating sample magnetometer (VSM).

RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction patterns of $Sr_{1-x}La_xCo_2Fe_{16}O_{27}$ (x = 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 and 0.35) magnetic powders pre-sintered in air at 1270°C for 3 h. Compared with the JCPDS data (PDF#55-0106), all the patterns show that the samples have single phase W-type hexaferrites and without any extra peaks compared to those observed for the standard W-type ferrites.[17] As a

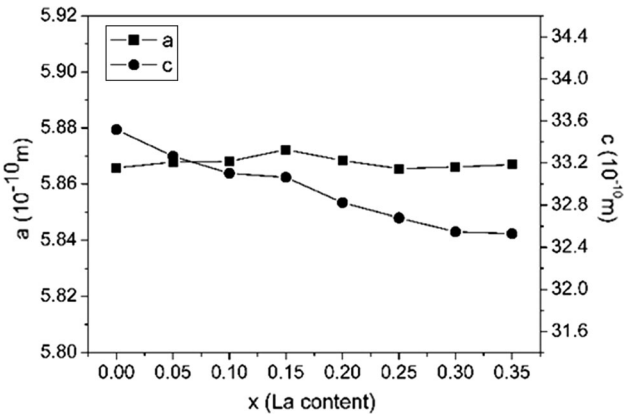

Fig. 2. Lattice parameters a and c of the hexaferrite $Sr_{1-x}La_xCo_2Fe_{16}O_{27}$ magnetic powders.

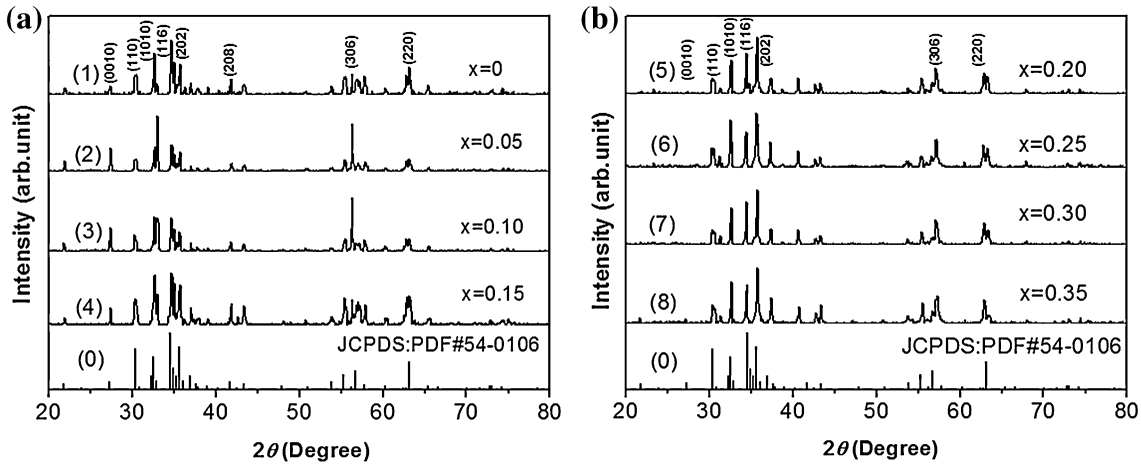

Fig. 1. X-ray diffraction patterns for the W-type ferrites $Sr_{1-x}La_xCo_2Fe_{16}O_{27}$ (a): (1)–(4) x = 0, x = 0.05, x = 0.10, x = 0.15 respectively, (b): (5)–(8) x = 0.20, x = 0.25, x = 0.30, x = 0.35 respectively, and (0) is the standard card.

Table I. Effects of La doping on the lattice constants (a and c), c/a, M_s and H_c for the W-type ferrites $Sr_{1-x}La_xCo_2Fe_{16}O_{27}$ samples

Sample (x)	c (Å) ±0.001	a(Å) ±0.001	c/a ratio	M_s (emu/g)	H_c (Oe)
0	33.517	5.866	5.714	53.23	136.11
0.05	33.265	5.868	5.669	63.83	136.97
0.10	33.102	5.868	5.641	67.25	152.87
0.15	33.064	5.872	5.631	73.08	178.12
0.20	32.823	5.868	5.594	68.62	549.84
0.25	32.68	5.866	5.571	60.57	763.85
0.30	32.548	5.866	5.549	58.29	899.06
0.35	32.530	5.867	5.545	56.29	949.43

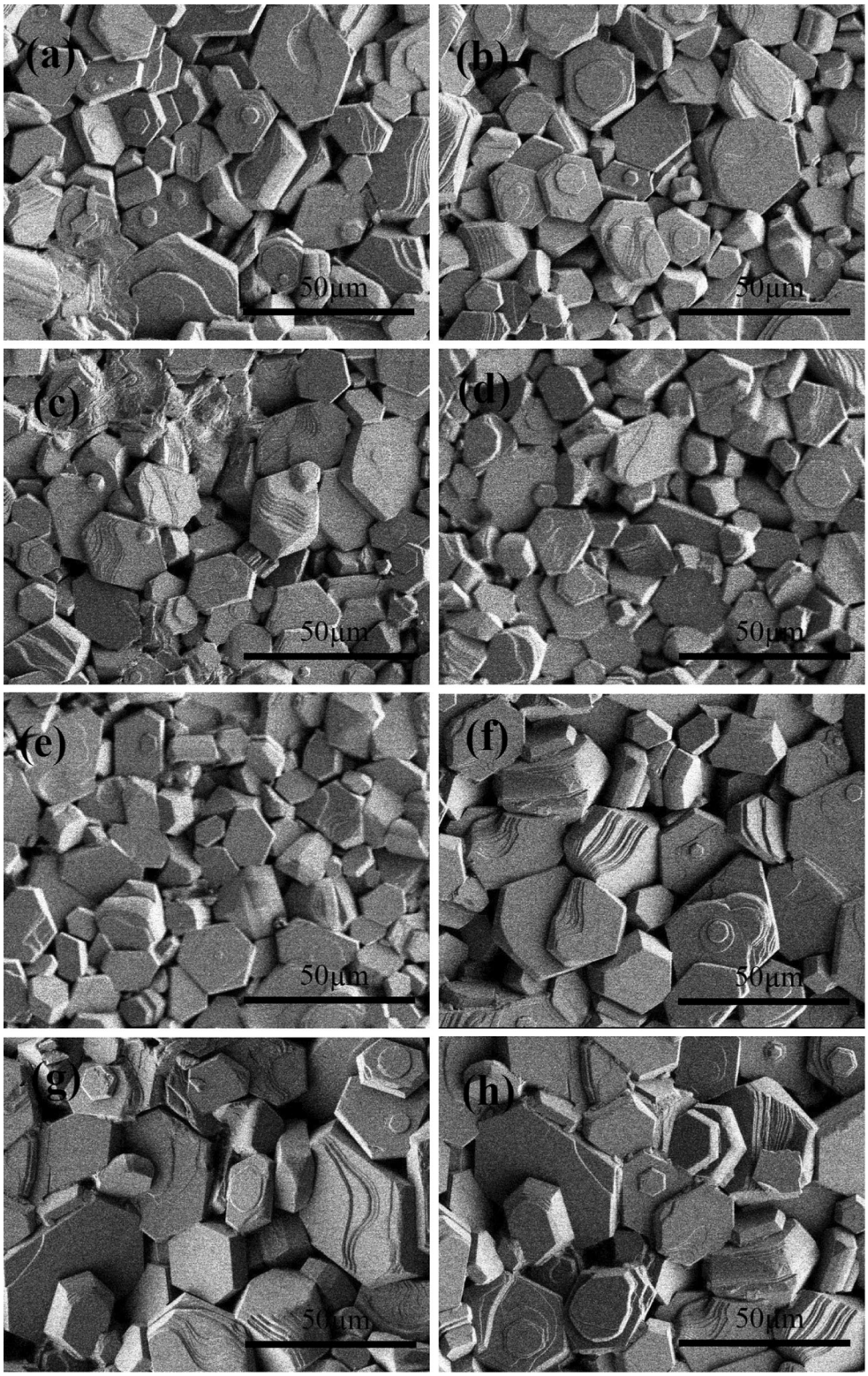

Fig. 3. SEM micrographs for the W-type ferrites $Sr_{1-x}La_xCo_2Fe_{16}O_{27}$ (a) $x = 0$ (b) $x = 0.05$ (c) $x = 0.10$ (d) $x = 0.15$ (e) $x = 0.20$ (f) $x = 0.25$ (g) $x = 0.30$ (h) $x = 0.35$.

consequence, we can draw the conclusion that single W-type ferrites are synthesized and La^{2+} has entered the lattice of hexaferrite successfully.

The lattice parameters a and c for the magnetic powders with different La contents (x) are calculated from the values of the d_{hkl} corresponding to

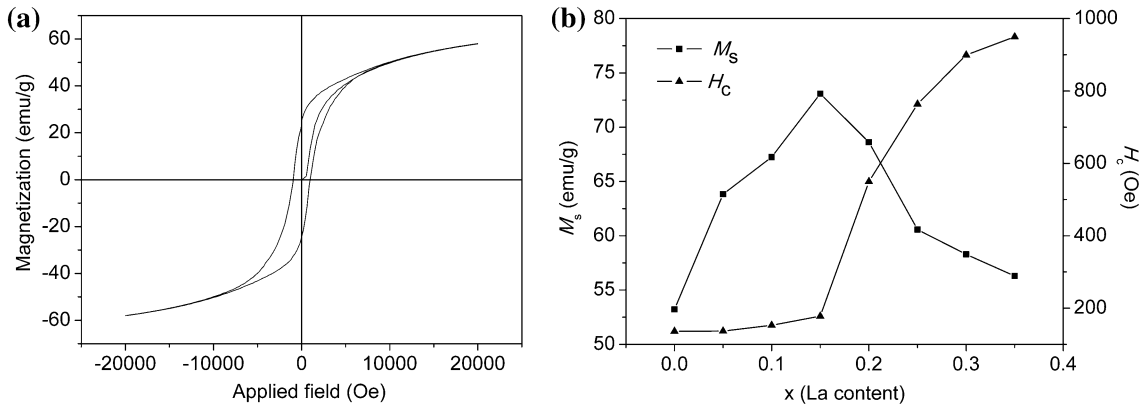

Fig. 4. Magnetic properties of W-type ferrites $Sr_{1-x}La_xCo_2Fe_{16}O_{27}$ samples: (a) magnetic hysteresis loop for W-type ferrite $Sr_{0.65}La_{0.35}Co_2Fe_{16}O_{27}$; (b) variation of saturation magnetization (M_s) and coercivity (H_c) with x increase.

(116) peaks and (202) peaks according to the equation given by:

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

where d_{hkl} is the interplaner spacing, and the values of h, k, and l are the Miller indices.

The lattice parameters a and c of the hexaferrite $Sr_{1-x}La_xCo_2Fe_{16}O_{27}$ magnetic powders with La content (x) from 0 to 0.35 are shown in Table I and Fig. 2. It is observed that the lattice parameter c of the magnetic powders decreases with an increase of x, but changes slowly between 0.1 and 0.15. However, compared with the lattice parameter c, the variation of the lattice parameter a is slight. The results are in agreement with that reported by Liu et al.[18] The variation of the lattice parameters with the increase of La content (x) is mainly due to the fact that the ionic radius of La^{3+} (1.06 Å) is smaller than that of Sr^{2+} (1.12 Å). The crystal axis ratio c/a for all samples is also listed in Table I. Due to the easy axis in W-type hexaferrites being the c-axis, it is easier to accommodate the spin directions along c-axis, which is perpendicular to the hexagonal based plane. Thus, we can observe the considerable variation in parameter c rather than in a.[19]

The SEM micrographs for W-type ferrites $Sr_{1-x}La_xCo_2Fe_{16}O_{27}$ (x = 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 and 0.35) are shown in Fig. 3. It is indicated that all the samples formed a uniform hexagonal platelet-like shape, and the orientation of the grains is random. Furthermore, the shape of the grains is very important for specific applications in different fields, and it has been reported that the platelet-shaped hexaferrite can be used as microwave absorbing coatings.[20] In addition, the average particle size of the samples changes slightly with the increase in La content (x). It is easy to see that with the increase of La content (x), the average particle size of the samples decreases and then increases and becomes more uniform.

The magnetic hysteresis loops for W-type ferrites $Sr_{1-x}La_xCo_2Fe_{16}O_{27}$ (x = 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 and 0.35) are measured and the loop for W-type ferrite $Sr_{0.65}La_{0.35}Co_2Fe_{16}O_{27}$ are shown in Fig. 4a. The saturation magnetization (M_s) and coercivity (H_c) are also listed in Table I, and the influence of La content on the saturation magnetization (M_s) and coercivity (H_c) of the W-type ferrites is shown in Fig. 4b. As can be seen from Fig. 4b, the saturation magnetization (M_s) first increases and reaches a maximum value of 73.08 emu/g at x = 0.15, then, decreases with the increase of x from 0.15 to 0.35. But, the coercivity (H_c) increases with the increase of x, however, a slight increase is discerned when $0 < x < 0.15$, then increases rapidly and reaches its maximum (949.43Oe) at x = 0.35. The priority to be replaced by La^{2+} are Sr^{2+} where found in the A sites, when the content of x is small, which can improve the M_s significantly. With the increase of the content of the rare earth ions, the La^{2+} will occupy the B sites because of the volume effect and electrostatic effect. Thereupon, the volume of A and B sites is changed, and part of Fe^{3+} will be substituted by La^{2+}, and turn the spin magnetic moment from parallel to reverse which weakens the saturation magnetization. Nevertheless, the magnetocrystalline anisotropy is enhanced due to the La^{2+} doping, thus make the coercivity increase.

CONCLUSIONS

W-type hexagonal ferrites $Sr_{1-x}La_xCo_2Fe_{16}O_{27}$ (x = 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 and 0.35) magnetic powders have been successfully synthesized by the solid state method in air. The microstructure and magnetic properties of hexaferrites were examined by the La^{2+} ions substituted Sr^{2+} ions. The single phase of the W-type ferrites phase was obtained in the hexagonal ferrite magnetic powder with the iron content (x) from 0 to 0.35. The study of SEM shows that the ferrites formed the

hexagonal structure and the particles distributed evenly. With the increases of content x, the saturation magnetization (M_s) increases first and then decreases, while the coercivity (H_c) increases continuously.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (Nos. 51072002 and 51272003), Dr. Start-up capital of Suzhou University (2016jb10), and the Natural Science Research Fund of Anhui Provincial Department of Education (KJ2016A775).

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