

Microstructural and magnetic studies on the Cr substituted M-type CaSrLa hexaferrite magnets

Yujie Yang*, Juxiang Shao and Fanhou Wang

Computational Physics Key Laboratory of Sichuan Province, School of Physics and Electronic Engineering, Yibin University, Yibin 644007, P. R. China

A series of Cr substituted M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ ($0 \leq x \leq 1.05$) magnets were prepared by the conventional solid state reaction method. The properties of the samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and a permanent magnetic measuring system. At Cr substitution (x) ≤ 0.60 , XRD patterns of the magnetic powders show the M-type strontium hexaferrite phase with $\alpha\text{-Fe}_2\text{O}_3$ as a second phase. When Cr substitution (x) ≥ 0.60 , there are magnetoplumbite phase patterns with only a small trace of $\alpha\text{-Fe}_2\text{O}_3$ phase. The images of the magnets show that the hexagonal structures are formed, and the particle size keeps unchanged with increasing Cr substitution (x). The remanence (B_r) decreases with Cr substitution (x) from 0.00 to 1.05. The intrinsic coercivity (H_{ci}) increases with Cr substitution (x) from 0.00 to 1.05. While the magnetic induction coercivity (H_{cb}) first increases with Cr substitution (x) from 0 to 0.75 and then decreases at Cr substitution (x) ≥ 0.75 .

Key words: X-ray diffraction, Magnetic properties, M-type Hexaferrites, Cr substitution.

Introduction

M-type hexaferrite materials have drawn a considerable attention to the researchers for their versatile properties such as high anisotropy field, high coercivity, resistant corrosion and chemical stability [1, 2]. M-type hexaferrite has hexagonal symmetry with the space group the $P6_3/mmc$. The structure of M-type strontium hexaferrite of has dual layer containing two formula units of $\text{SrFe}_{12}\text{O}_{19}$. There are 2 Sr^{2+} ions, 38 O^{2-} ions and 24 Fe^{3+} ions. The Fe^{3+} ions are distributed in five crystallographic sites, namely one bipyramidal site (2b), one tetrahedral site ($4f_1$) and three octahedral (2a, 12k and $4f_2$). Ions at 2a, 2b and 12k possess spin up while $4f_1$ and $4f_2$ possess spin down [3].

To make the M-type hexaferrite suitable for different applications, ions can be used to tailor the magnetic properties. Several authors have done studies to substitute ions, such as La-Co, La-Zn, La-Cu, Nd-Zn, Nd-Co, Mn-Zn, Co-Zr, Ni-Ti, La^{3+} , Nd^{3+} , Pr^{3+} , Co^{2+} , Cu^{2+} , Mn^{3+} , Al^{3+} , Bi^{3+} , Ti^{4+} and Cr^{3+} [4-21]. In the M-type hexaferrite, rare metal ions could substitute the strontium ions, while transition metal ions could substitute the ferric ions. M-type hexagonal ferrites have been synthesized by several methods, such as the sol-gel method [22], the citrate precursor method [23], the chemical co-precipitation method [24], the solid state

reaction method [25] and the hydrothermal method [26]. Among these methods, the solid state reaction method is employed to synthesize the hexagonal ferrites due to its simplicity, highly productive, low cost and well controllable grain size [27].

In this article, the M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ magnets have been prepared by the conventional solid state reaction method. The aim of this work is to investigate the impact of Cr substitution on the microstructural and magnetic properties for Cr substituted M-type CaSrLa hexaferrite magnets.

Experimental Procedure

A series of Cr substituted M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ ($0 \leq x \leq 1.05$) magnets have been synthesized by the conventional solid state reaction method. Raw materials (CaCO_3 , SrCO_3 , La_2O_3 , Cr_2O_3 and Fe_2O_3) were powders of analytical grade, and were weighted according to the chemical formula. These powders were wet-mixed in a ball mill at a rotate speed of 80 rpm for 9 hrs with steel balls as milling media. Then the mixed powders were dried in a drying oven in the air. And then these powders were pre-sintered in a laboratory furnace at 1255 °C for 2 hrs in the air. Next, the pre-sintered samples were shattered to particles using a vibration mill and sieved (150 meshes), and then wet-milled with suitable additives (CaCO_3 , Al_2O_3 , SiO_2 and H_3BO_3) for 16 hrs in a ball-mill. The finely milled slurry was compacted into disc-shaped pellets (30 mm diameter, about 15 mm thickness) under 330 MPa in the magnetic field of 750 kA/m, which was parallel to the pressing

*Corresponding author:
Tel : +86 831 3531171
Fax: +86 831 3531161
E-mail: loyalty-yyj@163.com

direction. All the pressed pellets were sintered in a laboratory furnace at 1180 °C for 1.5 hrs in the air. At last, in order to measure the magnetic properties of the sintered pellets, the sintered samples were polished in the faces perpendicular to the pressing direction.

The hexaferrite diffraction peaks were characterized by using a PANalytical X'Pert Pro diffractometer in continuous mode with Cu K α radiation. Images of the sintered samples were investigated by a Hitachi S-4800 field emission scanning electron microscopy (FE-SEM). Magnetic properties of the sintered samples were measured at room temperature by a permanent magnetic measuring system (NIM-2000HF, made by the National Institute of Metrology of China).

Results and Discussion

XRD patterns of the Cr substituted M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ magnetic powders are presented in Fig. 1. These peaks of XRD patterns are similar to the peaks in standard pattern (JCPDS: card no. 80-1198). As Cr substitution (x) ≤ 0.60 , minor impurity peak is emerged, and is identified as $\alpha\text{-Fe}_2\text{O}_3$

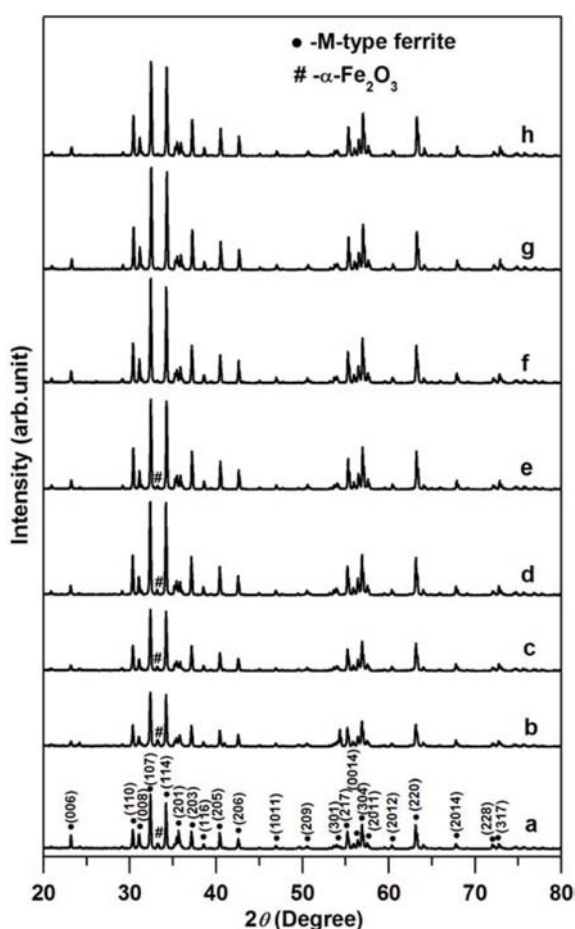


Fig. 1. XRD patterns of the Cr substituted M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ magnetic powders with Cr substitution (x) of: (a) 0.00, (b) 0.15, (c) 0.30, (d) 0.45, (e) 0.60, (f) 0.75, (g) 0.90 and (h) 1.05.

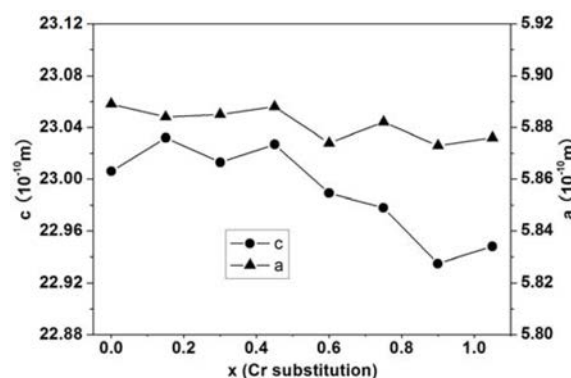


Fig. 2. Variation of lattice parameters c and a for the M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ magnetic powders with Cr substitution (x) from 0.00 to 1.05.

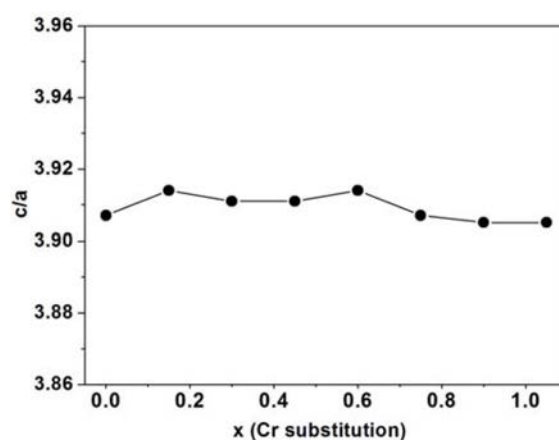


Fig. 3. Variation of c/a ratios for the M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ magnetic powders with Cr substitution (x) from 0.00 to 1.05.

phase. The presence of $\alpha\text{-Fe}_2\text{O}_3$ could be due to the incomplete reaction under synthesis conditions. As Cr substitution (x) ≥ 0.60 , all the peaks match well with the M-type hexaferrite (JCPDS: card no. 80-1198), and the magnetic powders show the magnetoplumite structure, and only a small trace of $\alpha\text{-Fe}_2\text{O}_3$ is observed. The well-defined sharp peaks in the XRD patterns indicate the polycrystalline behavior with good crystallinity. The lattice parameters are calculated from the XRD data [28].

Fig. 2 shows variation of lattice parameters c and a for the M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ magnetic powders with Cr substitution (x). Lattice parameters c and a were fluctuated with a slightly decreasing trend. This can be attributed to the fact that the ionic radius of Cr^{3+} ions (0.63 Å) is slightly smaller than that of Fe^{3+} ions (0.64 Å). The variation of c/a ratios for the M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ magnetic powders as a function of Cr substitution (x) is shown in Fig. 3. It is clear that c/a ratios of the magnetic powers with increasing Cr substitution (x) almost remain constant. It has been reported that the c/a ratios could be used to quantify

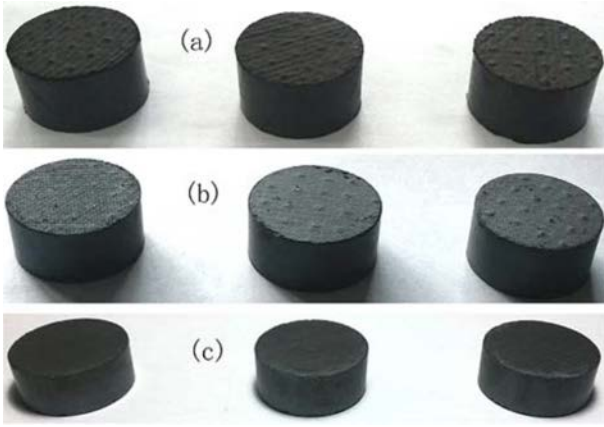


Fig. 4. Morphologies of disc shaped compacts before and after sintering: (a) green compacts with $\Phi 30 \times 16$ mm, (b) sintered compacts with about $\Phi 26.8 \times 13$ mm and (c) polished sintered compacts with about $\Phi 26.8 \times 10$ mm.

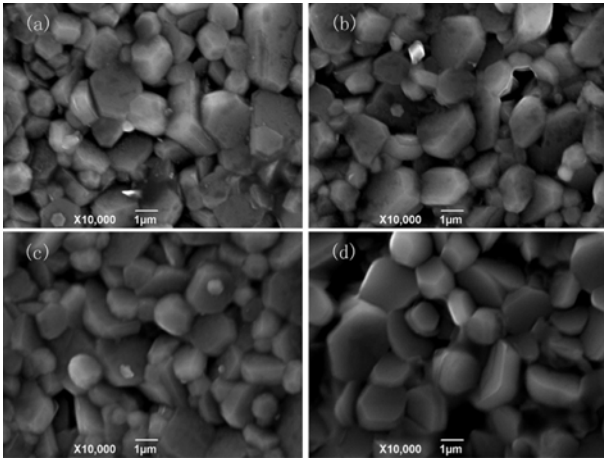


Fig. 5. Representative FESEM micrographs of the M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ magnets with Cr substitution (x) of: (a) 0.00, (b) 0.30, (c) 0.60 and (d) 1.05.

the structure type of hexagonal ferrites [29]. The c/a ratios with different Cr substitution (x) range from 3.905 to 3.911, and indicate the M-type hexaferrites.

Fig. 4 shows the morphologies of disc shaped pellets before and after sintering. Fig. 4(a-c) exhibits the green pellets with $\Phi 30 \times 16$ mm, sintered pellets with about $\Phi 26.8 \times 13$ mm and polished sintered pellets with about $\Phi 26.8 \times 10$ mm, respectively. Representative FE-SEM micrographs of the M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ magnets with Cr substitution (x) of 0.00, 0.30, 0.60 and 1.05 are shown in Fig. 5. It has been found that the hexagonal structures are formed in the sintered magnets, the grain particles have uniformly distributed, the particle size keeps unchanged with increasing Cr substitution (x).

The representative demagnetizing curves of the M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ magnets with Cr substitution (x) of 0.00, 0.30, 0.60 and 1.05 are shown in Fig. 6. The remanence (B_r), the intrinsic coercivity (H_{ci}), magnetic induction coercivity (H_{cb})

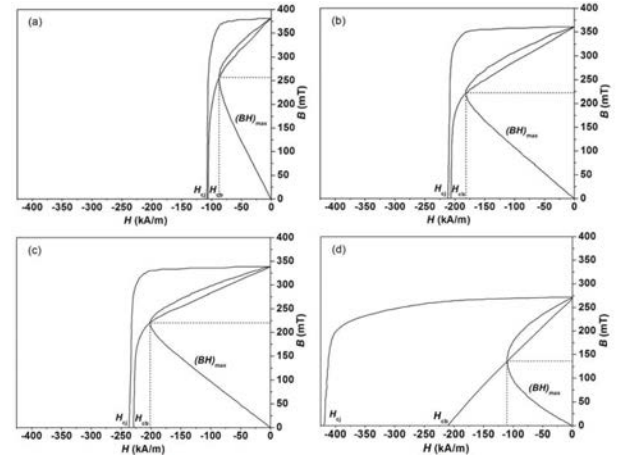


Fig. 6. Typical demagnetizing curves of the M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ magnets with Cr substitution (x) of: (a) 0.00, (b) 0.30, (c) 0.60 and (d) 1.05.

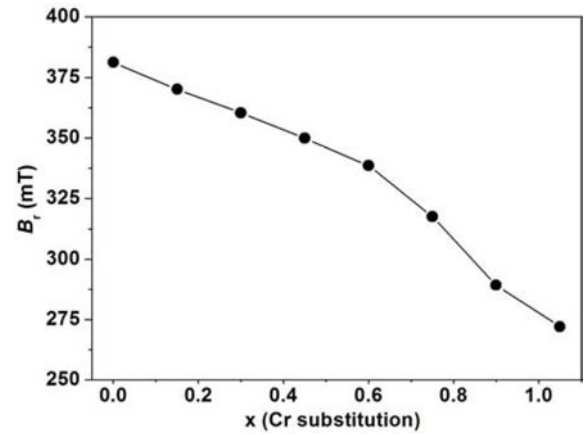


Fig. 7. Effect of Cr substitution (x) on the remanence (B_r) for the M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ magnets.

and maximum energy product $[(BH)_{\max}]$ have been calculated from the demagnetizing curves. Fig. 7 shows the effect of Cr substitution (x) on the remanence (B_r) for the M-type hexaferrite $\text{Sr}_{0.4}\text{Ba}_{0.3}\text{La}_{0.3}\text{Fe}_{12-x}\text{Bi}_x\text{O}_{19}$ magnets. As seen from Fig. 7, B_r of the magnets shows a continuous decrease with the increase of Cr substitution (x) from 0.00 to 1.05. For the M-type hexaferrite, the magnetic moments of Fe^{3+} ions are arranged collinearly due to the existence of superexchange interaction. It has been reported that Cr^{3+} ions prefer to distribute on spin up Fe sites known as 2a and 12k [30, 31]. Thus, the decrease of B_r for the magnets with Cr substitution (x) from 0.00 to 1.05 can be attributed to the following two reasons. Firstly, the doping of higher magnetic moment Fe^{3+} ($5 \mu_B$) by lower magnetic moment Cr^{3+} ($3 \mu_B$) results in the decrease of bulk magnetic moment. Secondly, More Cr^{3+} doping leads to the weakening of superexchange interaction of type $\text{Fe}_A^{3+}\text{-O-Fe}_B^{3+}$, which causes to magnetic collinearity to collapse. This results in the decrease of B_r for the magnets.

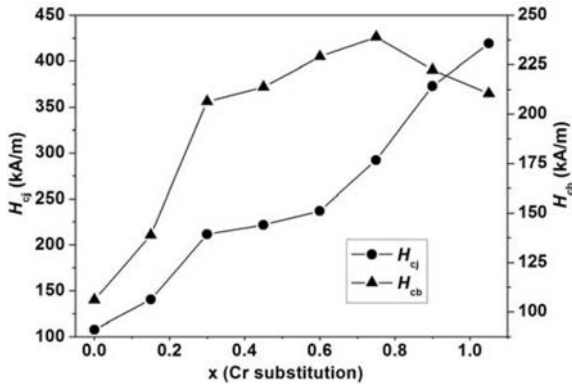


Fig. 8. Effects of Cr substitution (x) on the intrinsic coercivity (H_{cj}) and magnetic induction coercivity (H_{cb}) for the M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ magnets.

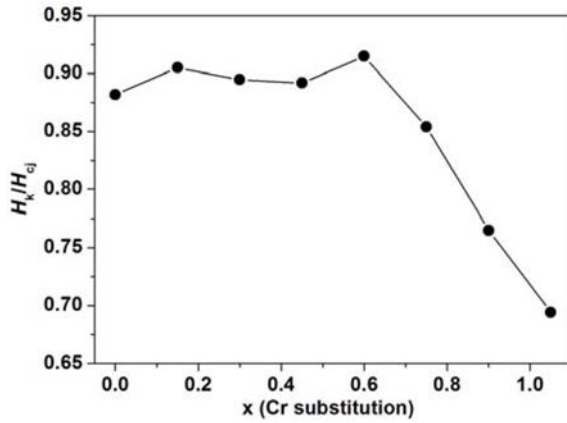


Fig. 9. Effect of Cr substitution (x) on the H_k/H_{cj} ratios for the M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ magnets.

Fig. 8 shows effects of Cr substitution (x) on the intrinsic coercivity (H_{cj}) and magnetic induction coercivity (H_{cb}) for the M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ magnets. It is found that H_{cj} of the magnets increases with Cr substitution (x) from 107.8 kA/m at $x = 0.00$ to 419.3 kA/m at $x = 1.05$, while H_{cb} of the magnets first increases with Cr substitution (x) from 0.00 to 0.75, and then decreases with Cr substitution (x) from 0.75 to 1.05. According to the Stoner-Wohlfarth theory, the coercivity in hexaferrite can be estimated by the following formula [32]:

$$H_c = 0.64 \frac{2K}{M_s} \quad (1)$$

where K is the magnetocrystalline anisotropy constant and M_s is the saturation magnetization. Thus, according to the formula (1), the increase of H_{cj} can be mainly attributed to the decrease of remanence (B_r) with Cr substitution (x) from 0.00 to 1.05 as shown in Fig. 7. The effect of Cr substitution (x) on the H_k/H_{cj} ratios for the M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ magnets is shown in Fig. 9. The H_k/H_{cj} ratio is one of the important indicators of the magnetic properties for

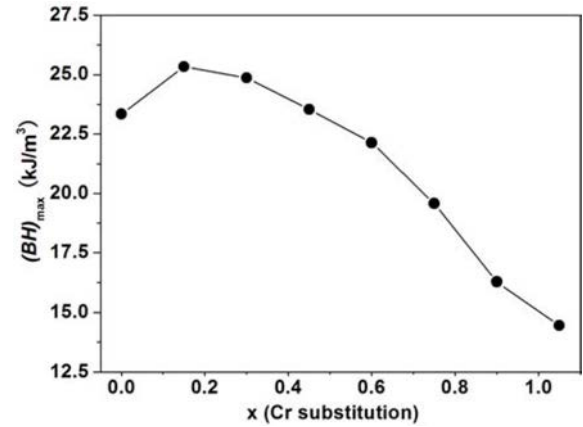


Fig. 10. Effect of Cr substitution (x) on the maximum energy product $[(BH)_{\max}]$ for the M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ magnets.

the permanent magnets, and can intuitively indicate the rectangularity of the demagnetizing curves for the magnets [33]. As seen from Fig. 6, it is found that the ratio H_k/H_{cj} ratio first fluctuates and basically keeps constant with Cr substitution (x) from 0.00 to 0.75, and then decreases when Cr substitution (x) ≥ 0.75 . This may be the reason for the variation of H_{cb} with Cr substitution (x).

The effect of Cr substitution (x) on the maximum energy product $[(BH)_{\max}]$ for the M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ magnets is shown in Fig. 10. It can be seen that the values of $(BH)_{\max}$ first increase with Cr substitution (x) from 0.00 to 0.15, and then decrease when Cr substitution (x) ≥ 0.15 . The maximum energy product of the hexaferrite magnets can be estimated by the product between the remanent magnetization and coercivity field, and can be considered as a comparative indication of the hysteresis area.

Conclusions

The conventional solid state reaction method was used to synthesize the Cr substituted M-type hexaferrite $\text{Ca}_{0.30}\text{Sr}_{0.35}\text{La}_{0.35}\text{Cr}_x\text{Fe}_{12-x}\text{O}_{19}$ ($0 \leq x \leq 1.05$) magnets. At Cr substitution (x) ≤ 0.60 , XRD patterns of the magnetic powders show the M-type strontium hexaferrite phase with $\alpha\text{-Fe}_2\text{O}_3$ as a second phase. When Cr substitution (x) ≥ 0.60 , there are magnetoplumbite phase patterns with only a small trace of $\alpha\text{-Fe}_2\text{O}_3$ phase. The images of the magnets show that the hexagonal structures are formed, and the particle size keeps unchanged with increasing Cr substitution (x). B_r decreases with Cr substitution (x) from 0.00 to 1.05. H_{cj} increases with Cr substitution (x) from 0.00 to 1.05. While H_{cb} first increases with Cr substitution (x) from 0 to 0.75 and then decreases at Cr substitution (x) ≥ 0.75 . $(BH)_{\max}$ first increases with Cr substitution (x) from 0.0 to 0.15, and then decreases at Cr substitution (x) ≥ 0.15 .

Acknowledgments

This work was supported by National Natural Science Foundation of China (No. 51272003 and No. 51472004), Scientific Research Fund of Sichuan Provincial Education Department (No. 13ZA0918, No. 14ZA0267 and No. 16ZA0330), the Major Project of Yibin City of China (No. 2012SF034 and No. 2016GY025), Scientific Research Key Project of Yibin University (No. 2015QD13) and the Open Research Fund of Computational Physics Key Laboratory of Sichuan Province, Yibin University (No. JSWL2015KFZ04).

References

1. H.M. Khan, M.U. Islam, Y.B. Xu, M.N. Ashiq, I. Ali, M.A. Iqbal, M. Ishaque, *Ceram. Int.* 40 (2014) 6487-6493.
2. G. Qiang, Y. Jin, X.W. Lu, X.P. Cui, D.M. Deng, B.J. Kang, W.G. Yang, S.X. Cao, J.C. Zhang, *Appl. Phys. A* 122 (2016) 681-686.
3. Y.J. Yang, X.S. Liu, D.L. Jin, K. Huang, S. Gao, J. Magn. Mater. 355 (2014) 254-258.
4. Y.J. Yang, X.S. Liu, D.L. Jin, Y.Q. Ma, *Mater. Res. Bull.* 59 (2014) 37-41.
5. A. Grusková, J. Lipka, M. Papánová, J. Sláma, I. Tóth, D. Kevická, G. Mendoza, J.C. Corral, J. Šubr, *Hyperfine Interact.* 164 (2005) 27-33.
6. Y.J. Yang, X.S. Liu, *Mater. Technol.* 29 (2014) 232-236.
7. H.M. Khan, M.U. Islam, Y.B. Xu, M. Asif Iqbal, I. Ali, M. Ishaque, M.A. Khan, *J. Sol-Gel. Sci. Technol.* 75 (2015) 305-312.
8. C.A. Herme, P.G. Bercoff, S.E. Jacobo, *Mater. Res. Bull.* 47 (2012) 3881-3887.
9. Y.M. Kang, Y.H. Kwon, M.H. Kim, D.Y. Lee, J. Magn. Mater. 382 (2015) 10-14.
10. S.K. Chawla, R.K. Mudsainiyan, S.S. Meena, S.M. Yusuf, *J. Magn. Mater.* 350 (2014) 23-29.
11. J. Li, H.W. Zhang, V.G. Harris, Y.L. Liao, Y.L. Liu, *J. Alloys Compd.* 649 (2015) 782-787.
12. C.J. Li, B. Wang, J.N. Wang, *J. Magn. Mater.* 324 (2012) 1305-1311.
13. J.F. Wang, C.B. Ponton, I.R. Harris, *IEEE Trans. Magn.* 38 (2002) 2928-2930.
14. W. Abbas, I. Ahmad, M. Kanwal, G. Murtaza, I. Ali, M.A. Khan, M.N. Akhtar, M. Ahmad, *J. Magn. Mater.* 374 (2015) 187-191.
15. R. Ezhil Vizhi, V. Harikrishnan, P. Saravanan, D. Rajan Bahu, *J. Cryst. Growth* 452 (2016) 117-114.
16. A. Awadallah, S.H. Mahmood, Y. Maswadeh, I. Bsoul, M. Awawdeh, Q.I. Mohaidat, H. Juwhari, *Mater. Res. Bull.* 74 (2016) 192-201.
17. P. Sharma, R.A. Rocha, S.N. de Medeiros, A. Paesano Jr, B. Hallouche, *Hyperfine Interact.* 175 (2004) 77-84.
18. Y.J. Yang, F.H. Wang, X.S. Liu, J.X. Shao, D.H. Huang, J. Magn. Mater. 421 (2017) 349-354.
19. Y.J. Yang, F.H. Wang, X.S. Liu, J.X. Shao, S.J. Feng, D.H. Huang, M.L. Li, *J. Magn. Mater.* 422 (2017) 209-215.
20. P.A. Mariño-Castellanos, J. Anglada-Rivera, A. Cruz-Fuentes, R. Lora-Serrano, *J. Magn. Mater.* 280 (2004) 214-220.
21. S. Katlakunta, S.S. Meena, S. Simath, M. Bououdina, R. Sandhya, K. Praveena, *Mater. Res. Bull.* 63 (2015) 58-66.
22. A. Thakur, R.R. Singh, P.B. Barman, *Mater. Chem. Phys.* 141 (2013) 562-569.
23. T. Kaur, S. Kumar, B.H. Bhat, B. Want, A.K. Srivastava, S.X. Cao, J.C. Zhang, *Appl. Phys. A* 119 (2015) 1531-1540.
24. M.J. Iqbal, M.N. Ashiq, I.H. Gul, *J. Magn. Mater.* 322 (2010) 1720-1726.
25. Y.J. Yang, F.H. Wang, J.X. Shao, D.H. Huang, M.J. Wan, Q.L. Cao, *Mater. Technol.* 32 (2017) 165-170.
26. L. Zhao, X.X. Lv, Y.S. Wei, C. Ma, L.J. Zhao, *J. Magn. Mater.* 332 (2013) 44-47.
27. J. Li, H.W. Zhang, Q. Li, Y.X. Li, Q.L. Yu, *J. Rare Earths* 31 (2013) 983-987.
28. Y.J. Yang, F.H. Wang, J.X. Shao, D.H. Huang, Z.H. Gao, Q.L. Cao, M.J. Wan, *J. Mater. Res.* 301 (2015) 1844-1851.
29. T.R. Wagner, *J. Solid. State Chem.* 136 (1998) 120-124.
30. S. Ounnunkad, P. Winotai, *J. Magn. Mater.* 301 (2006) 292-300.
31. C.S. Kim, S.Y. An, J.H. Son, *IEEE Trans. Magn.* 35 (1999) 3160-3162.
32. J.X. Qiu, M.Y. Gu, H.G. Shen, *J. Magn. Mater.* 295 (2005) 263-268.
33. Z.M. Wang, *Ferrite Production Technology*, Chongqing University Press, Chongqing, 2013.