Journal of Alloys and Compounds 734 (2018) 130–135

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Fabrication of M-type ferrites with high La-Co concentration through Ca^{2+} doping

Li Yuping [a, b, *], Bao Daxin [c], Wang Zhangzhong [a, b], Yujing Zhang [a, b], Chen Lizhao [a, b], Zha Guangcheng [a, b], Wu Mengling [a, b]

[a] *School of Materials Science and Engineering, Nanjing Institute of Technology, Nanjing, 211167, China*
[b] *Jiangsu Key Laboratory of Advanced Structural Materials and Application Technology, Nanjing, 211167, China*
[c] *Hengdian Group DMEGC Magnetics Co., LTD., Jinhua, 322118, China*

ARTICLE INFO

Article history:
Received 7 September 2017
Received in revised form
2 November 2017
Accepted 4 November 2017
Available online 7 November 2017

Keywords:
Sintered ferrite magnet
Ca^{2+} doping
Grain growth
La-Co substitution

ABSTRACT

Ca^{2+} doped $Sr_{0.45\text{-}x}Ca_xLa_{0.55}Fe_{11.6}Co_{0.4}O_{19}$ ($x = 0$, 0.15, 0.3, and 0.45) ferrites were fabricated through a conventional ceramic process. The influences of Ca^{2+} doping on the microstructure and magnetic properties of ferrites were investigated. Ca^{2+} doping could mitigate the presence of impurity phase ($CoFe_2O_4$) in ferrites. Single phase M-type ferrites could be fabricated when $x \geq 0.3$. Additional Co^{2+} ions entered the crystal lattice and preferentially occupied the $4f_2$ site with Ca^{2+} doping. This effect greatly improved the remanence (B_r) and intrinsic coercivity (H_{cj}) when x increased from 0 to 0.3. The average grain size of sintered ferrites slightly increased with the amount of doped Ca^{2+} ions. This behavior led to the deterioration of H_{cj} when x increased from 0.3 to 0.45. Consequently, ferrite prepared with $x = 0.3$ presented the highest maximum energy product ($(BH)_{max}$) of 5.24MGOe. This performance is much higher than that of conventional La-Co substituted Sr-ferrites.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

M-type hexagonal ferrites with the chemical formula $AFe_{12}O_{19}$ (where A is Sr, Ba, Ca or Pb) were first discovered in the 1950s. These ferrites have since attracted considerable interest because of their outstanding chemical and thermal stability and high performance-to-price ratio, as well as their additional advantage of highly abundant raw-material resources [1–3]. M-type hexagonal ferrites are widely used in a multitude of applications, such as automotive, office machine, audiovisual equipment and household appliance, etc [4–6]. Recently, with the development of magnetic devices towards miniaturization and lightweight, demands of high performance M-type hexagonal ferrites increase dramatically. Thus, numerous studies have utilized different synthesis methods, including sol-gel, hydrothermal synthesis and modified ceramic methods to fabricate M-type hexagonal ferrites with improved microstructure and magnetic properties [7–10]. Furthermore, the intrinsic magnetic properties of M-type hexagonal ferrites have been tailored through the partial substitution of Sr^{2+} with rare earth elements such as La^{3+}, Ce^{3+}, Sm^{3+} and Nd^{3+}, or Fe^{3+} by transition metal elements such as Co^{2+}, Zn^{2+}, Mn^{2+}, Cu^{2+} and Ni^{2+} [11–17].

Simultaneous substitution with La-Co is the most effective approach to improve the magnetic properties of hexagonal ferrites. La-Co substitution can improve the intrinsic coercivity (H_{cj}) of ferrites by approximately 26.5% [6]. And this improvement is associated with the enhancement in magnetic anisotropy by the unquenched angular momentum of Co^{2+}. However, the different ionic radii of Sr^{2+}, Fe^{3+}, La^{3+} and Co^{2+} cause lattice distortion and crystal collapse. These effects ultimately hinder the entry of La^{3+} and Co^{2+} into lattice. Impurity phases, such as $LaFeO_3$, $CoFe_2O_4$, hematite Fe_2O_3, etc., are usually detected in Sr-ferrites fabricated with high La-Co concentration [6,18]. Meanwhile, substitution with excessive La-Co will cause the magnetic properties of conventional SrLaCo ferrites to deteriorate. For example, the H_{cj} of $Sr_{1\text{-}x}La_xFe_{12\text{-}y}Co_yO_{19}$ ferrites deteriorates when Co concentration increases to $y = 0.25$ [3]. Therefore, the relationship between the magnetic properties and La-Co contents of SrLaCo ferrites is an important research topic.

Recently, it has been reported that the magnetic properties of SrLaCo ferrites can be further improved through Ca^{2+} doping. And

---

[*] Corresponding author. School of Materials Science and Engineering, Nanjing Institute of Technology, Nanjing, 211167, China.
E-mail address: y.p.li@163.com (L. Yuping).

https://doi.org/10.1016/j.jallcom.2017.11.050
0925-8388/© 2017 Elsevier B.V. All rights reserved.

this improvement is associated with the increase of magnetocrystalline anisotropy of the ferrites [19–21]. We previously synthesized $Sr_{0.15}Ca_{0.35}La_{0.5}Fe_{11.6}Co_{0.4}O_{19}$ ferrite with high H_{cj} (approximately 5600Oe) through an improved ceramic process [22]. However, this new synthesis method, which is based on the conventional ceramic process, requires an additional reheating-remilling treatment. Furthermore, the influences of Ca^{2+} doping on the microstructure and magnetic performance of SrLaCo ferrites require further investigation. In the present study, Sr-ferrites with high La-Co concentration are fabricated through conventional ceramic process and Ca^{2+} doping. The effects of Ca^{2+} doping on the site occupation of Fe^{3+}/Co^{2+} in M-type ferrites are discussed. Moreover, the detailed effects of Ca^{2+} doping on the microstructure and magnetic properties have also been investigated.

2. Experimental

Ferrite samples were fabricated through the ceramic process. $SrCO_3$ (98.2% purity), $CaCO_3$ (99.2% purity), La_2O_3 (99.8% purity), Fe_2O_3 (99.7% purity), and CoO (99.8% purity) were used as the starting materials. They were mixed together in the chemical composition of $Sr_{0.45\text{-}x}Ca_xLa_{0.55}Fe_{11.6}Co_{0.4}O_{19}$ ($x = 0$, 0.15, 0.3 and 0.45) through wet ball milling in water for 4 h, with a rotation velocity of 65 rpm and a ball-to-powder mass ratio of 16:1. The mixed powder was dried at 100 °C for 3 h, and then calcined in a muffle furnace at 1250 °C for 1 h in air. The calcined samples were pulverized into powder with an average size of about 5 μm by a vibration mill. After that, the powder was wet-milled in water with proper amount of common sintering additives (e.g. H_3BO_3, SiO_2 and CaO) for 25 h, with a rotation velocity of 65 rpm and a ball to powder mass ratio of 16:1. For all runs of milling experiments, the powder in each batch was 500 g, and the powder to water mass ratio was 1:1.5. The finely milled slurry was pressed into disk-shaped green compacts with$\Phi 40 \times 15$ mm under 300 MPa in the magnetic field of 1.5T. Finally, the green compacts were sintered at 1190 °C for 2 h in air.

The phase characterization of the calcined samples was studied by X-ray diffraction (XRD), and also studied by room-temperature transmission Mössbauer spectrometry. The microstructures of the sintered ferrites were observed by a Hitachi S-3000N scanning electron microscopy (SEM). The magnetic properties of the sintered ferrites were measured by a B-H loop recorder (model MATS-2000, National Institute of Metrology of China).

3. Results and discussion

Fig. 1 shows the XRD patterns of samples calcined at 1250 °C for 1 h in air. The crystalline structures and phases analysis of the $Sr_{0.45\text{-}x}Ca_xLa_{0.55}Fe_{11.6}Co_{0.4}O_{19}$ ($x = 0$, 0.15, 0.3 and 0.45) powder were characterized. In addition to the major presence of M-type ferrite phase, a small amount of secondary $CoFe_2O_4$ phase is present in the sample prepared with $x = 0$. M-type ferrites with high La-Co concentration often exhibit such unsatisfactory cation substitution [6,18], which is attributed to the lattice distortion and crystal collapse of the M-type phase during substitution. The peaks of rare earth compounds (e.g. La_2O_3, $LaFeO_3$) are hardly detectable in the sample with $x = 0$, suggesting that La^{3+} concentration in the M-type phase is higher than that of Co^{2+}. The relative intensities of peaks that correspond to the $CoFe_2O_4$ phase decrease as Ca^{2+} increases. In addition, when $x = 0.3$ and 0.45, the signs of $CoFe_2O_4$ phase are almost not detected, and all X-ray diffraction peaks correspond to a single M-type ferrite phase. It suggests that Ca^{2+} doping facilitates the substitution of Fe^{3+} (or Fe^{2+}) by Co^{2+}. To investigate the effect of different Ca contents on the lattice parameters of ferrites, a refinement analysis of the XRD patterns is conducted, and the detailed data are listed in Table 1. As Ca content increases, the lattice parameter "a" negligibly changes, whereas the lattice parameter "c" decreases monotonically. These changes can be attributed to the smaller ionic radius of Ca^{2+} (1.06 Å) compared with that of Sr^{2+} (1.32 Å). The small ionic radius of Ca^{2+}decreases the distance between staking layers in the c-direction.

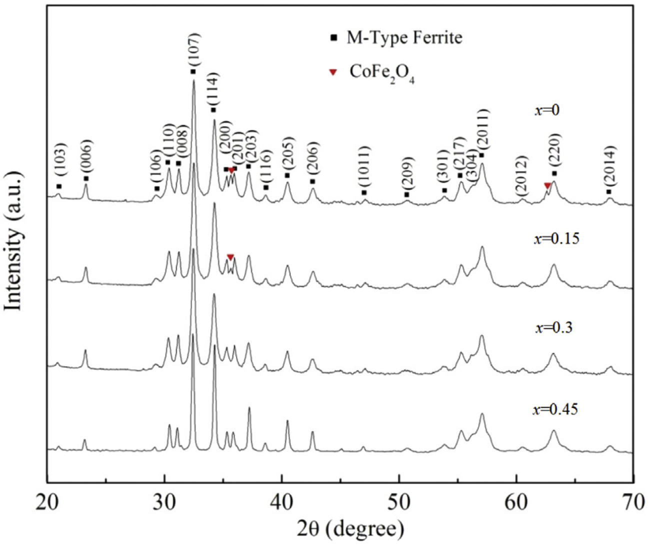

Fig. 1. XRD patterns of the samples calcined at 1250 °C for 1 h.

Fig. 2 shows the room-temperature transmission Mössbauer spectra of $Sr_{0.45\text{-}x}Ca_xLa_{0.55}Fe_{11.6}Co_{0.4}O_{19}$ ($x = 0$, 0.15, 0.3 and 0.45) samples calcined at 1250 °C for 1 h in air. In La–Co substituted ferrites, the substitution of La^{3+} for Sr^{2+} results in the presence of Fe^{2+}, instead of Fe^{3+}, at the 2a site [23]. Thus, the contribution of Fe^{2+} is fitted in the sample spectra and fitting results are summarized in Table 2. The spectrum of the ferrite with $x = 0$ is well fitted with the contribution of the dominant M-type ferrite phase and a small portion of $CoFe_2O_4$ phase. The weight percentage of impurity ($CoFe_2O_4$), which is calculated on the basis of relative area (R_A) of $CoFe_2O_4$ contribution, is about 4.4 wt.% (Table 2). It is slightly higher than that calculated from XRD patterns (Table 1). This difference can be attributed to differences in the test and calculation methods used. When x increases from 0 to 0.3, the relative intensity of the $CoFe_2O_4$ contribution decreases, whereas that of M-type ferrite phase contributions correspondingly increases. Moreover, when $x = 0.3$ and 0.45, $CoFe_2O_4$ contributions are absent from the Mössbauer spectrum. This result is in good agreement with the XRD results shown in Fig. 1. As seen in Table 2, the relative intensity of the $4f_2$ contribution of M-type ferrite phase decreases as x increases from 0 to 0.3, and negligibly changes as x further increases to 0.45. This result indicates that Fe^{3+} ion occupations in the crystal are affected by the presence of doped Ca^{2+} ions. Previous studies have shown that Co^{2+} substitutes for Fe^{3+} in different sites in ferrites with different compositions. For example, Co^{2+} ions occupy the $4f_1$ site in Co-Zr doped $BaCo_xZr_xFe_{(12\text{-}2x)}O_{19}$ ferrites [24], the 12k or 2a site in Co-Al doped Ba-Sr ferrites [25], and the $4f_2$ and 2a site for SrLaCo ferrites [6,23,26]. The results of the present study show that high amounts of Co^{2+} ions enter the crystal lattice and mainly occupy the $4f_2$ site as x increases from 0 to 0.3, causing the $4f_2$ contribution to decrease. This conclusion is in agreement with that of Morel et al. [6,23,26]. Additionally, the quadrupole splitting (QS) of $4f_2$ contribution continuously increases, while those of other contributions slightly vary when x increases from 0 to 0.45 (Fig. 3). This result might be attributed to the replacements of Sr^{2+}/Fe^{3+} by Ca^{2+}/Co^{2+}. These substitutions cause a perturbation of both

Download English Version:

https://daneshyari.com/en/article/7994647

Download Persian Version:

https://daneshyari.com/article/7994647

Daneshyari.com