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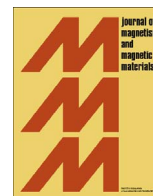
Tailoring structure and magnetic characteristics of strontium hexaferrite via Al doping engineering

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ABSTRACT

Emerging structure and magnetic properties of Al^{3+}-modified $SrFe_{12}O_{19}$ M-type hexaferrite system ($SrAl_xFe_{12-x}O_{19}$) had been studied in detail via doping engineering. With Al^{3+} ion nominal content ranging from 0 to 4 ($0 \leq x \leq 4$), the lattice parameters decrease due to the substitution of Fe^{3+} ions by smaller Al^{3+} ions, and the magnetization shows a continuous reduction with the increasing of Al content. For the coercivity, its value initially increases, reaching a maximum value of 16,876.9 Oe at $x=3$, and then reduces with the Al content further increase. When all the Fe^{3+} ions ($x=4$) are replaced by Al^{3+} ions, the net magnetic moment will be closed to zero, that will weaken the exchange interaction between Fe^{3+} ions, resulting in decrease of coercivity sharply and transformation ferrimagnetism into anti-ferrimagnetism. The mechanism of the improvement of the magnetic properties induced by Al doping is discussed in the present work.

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1. Introduction

M-type strontium hexaferrite ($SrFe_{12}O_{19}$) crystallizes in the hexagonal magnetoplumbite-type structure with the space group of $P6_3/mm$, which is of great scientific and technological importance. Owing to their large crystalline anisotropy and high intrinsic coercivity, it is extensively used in the production of permanent magnets and fabrication of certain microwave devices. Moreover, it also has been widely used in the magneto-optic and high density recording media [1,2].

M-type $SrFe_{12}O_{19}$ as a hard ferrites material have attracted extensive interests since its discovery in 1950s, its unit cell consists of two $SrFe_{12}O_{19}$ molecules which contains 64 ions over 11 different symmetry sites. The 24 Fe^{3+} ions are distributed over three octahedral sites 2a, 12k and 4f, one tetrahedral site 4f and one bipyramidal site 2b. Fe^{3+} ions located at the 2a, 2b and 12k sites are spinning upward; the others are spinning downward [3–5]. Doping engineering has been widely utilized to optimize the band structures of bulk and nanoscale materials, facilitating the implementation of various multifunctional materials and devices [6–15]. The intrinsic magnetic properties of $SrFe_{12}O_{19}$ can be modified through the substitution of Fe^{3+} ions by suitable cations. These magnetic properties are strongly dependent on the distribution of the substituted cations at those different crystallographic sites according to their site preference.

The substitution of Fe^{3+} ions by other cations has been extensively studied by various researchers, nonmagnetic Al^{3+} ion has attracted more extensive attention and been widely researched in recent years. Al substituted M-type hexaferrite is firstly solved by Bertaut in 1959 [16], and with the development of science and technology, the coercivity of barium hexaferrite with Al substitution, which is prepared by mechanical alloying and subsequent heat treatment, increases up to 9300 Oe [17]. In addition, Al substituted strontium hexaferrite can also be synthesized using electro-spinning, with coercivity of 7750 Oe [18]. These experimental results illustrate that Al doping plays a significant role in increasing coercivity of M-type hexaferrite.

Magnetic systems undergoing transitions to ordered ferromagnetic, anti-ferromagnetic and ferromagnetic states are reported to show irreversibility, indicated by the difference between their field cooled (FC) and zero-field cooled (ZFC) magnetization [19–21]. The irreversible FC and ZFC magnetic behavior is one of the characteristic features of superparamagnetism [22–24], other characteristic properties of a spin glass include the relaxation of magnetization and the presence of a cusp in the low field ZFC magnetization as well as in the thermal variation of ZFC curves.

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The spins are frozen in random directions due to lack of long-range magnetic interactions. In addition, low field magnetic behavior of some ferromagnetic and ferromagnetic oxides indicated that their spin-glass-like magnetic properties originate from the magnetocrystalline anisotropy [25]. In other words, the magnetic behavior similar to that of cluster spin glass could also be explained based on the magneto-crystalline anisotropy of the compound. Though, conventional spin glasses and materials show spin-glass-like features such as superparamagnetic systems, cluster spin glass systems, superconducting oxides, the ordered magnetic systems, show thermomagnetic irreversibility between the FC and ZFC magnetization and cusp in their ZFC susceptibilities, the origin of such a behavior is not yet properly understood [21].

In this paper, we report the synthesis and characterization of Al-substituted $SrFe_{12}O_{19}$ samples with various Al^{3+}/Fe^{3+} ratios prepared by glycin-nitrate method. And the improvement of coercivity of $SrFe_{12}O_{19}$ is realized by Al substitution. Microscopicmechanisms of the variety of magnetic properties are discussed by XRD and FC/ZFC measurement in the present work.

2. Experiment

M-type $SrFe_{12}O_{19}$ with and without Al doping were fabricated by glycin-nitrate method and subsequent heat treatment. The iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), strontium nitrate ($Sr(NO_3)_2$), aluminium nitrate ($Al(NO_3)_3 \cdot 9H_2O$), glycin ($C_2H_5NO_2$) powder were used as raw materials in the glycin-nitrate method process. The nitrates in the proportion of $SrFe_{12}O_{19}$, $SrAlFe_{11}O_{19}$, $SrAl_2Fe_{10}O_{19}$, $SrAl_3Fe_9O_{19}$ and $SrAl_4Fe_8O_{19}$ were dissolved in deionized water. The molar ratio of glycin to total moles of nitrate ions was adjusted at 1.5:1 and then heated in a porcelain dish. As the evaporation proceeding, the emulsion became viscous, and changed to a foamy maroon sponge. Finally it was self-ignited from the bottom and the whole combustion process finished instantaneously. The as-burnt powder was considered to be the precursor powders. And then the precursor powders were pressed into disks and sintered for 2 h in air atmosphere at 1100 °C.

The structure of the samples were characterized using a Rigaku-D-Max X-ray diffractometer (XRD) with Cu Kα radiation (λ=0.15418 nm). Composition of the sample was detected by energy dispersive X-ray spectroscopy (EDS) (JEOL JXA-8200). Measurement of magnetic properties were performed in a vibrating sample magnetometer (VSM) at room temperature with a maximum applied field of 13.75 kOe (Lake Shore 7410 vibrating sample magnetometer) and superconducting quantum interference devices magnetometer (SQUID, Quantum Design, MPMSXL-5) with temperature range of 5–380 K.

3. Results and discussion

Previous study has shown that the formation of M-type $SrFe_{12}O_{19}$ phase occurs above 700 °C synthesized by glycin-nitrate method [26], which result is similar to the formation temperature of the $BaFe_{12}O_{19}$ in glycin-nitrate method report previously [27]. However, the sample contained a lot of impurity phase of α-Fe_2O_3 at low formation temperature, which will affect the magnetic of M-type $SrFe_{12}O_{19}$. In this paper, the magnetic properties of Al-substituted $SrFe_{12}O_{19}$ samples are main discussion, so the optimum synthesis temperature of 1100 °C was selected for subsequent experiments. Fig. 1(a)–(e) show the typical XRD patterns of the precursor powders undoped and doped with various concentration of Al that sintered for 2 h at 1100 °C. All the XRD patterns are similar and consist of strong diffraction profile which is similar to that of the $SrFe_{12}O_{19}$ phase, meanwhile, some weak

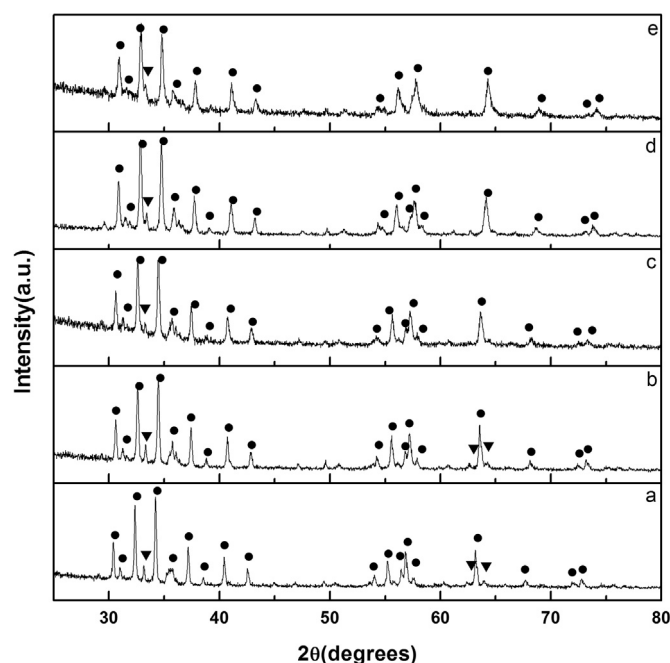Fig. 1. the XRD diffraction patterns of $SrFe_{12}O_{19}$ (a), $SrAlFe_{11}O_{19}$ (b) , $SrAl_2Fe_{10}O_{19}$ (c), $SrAl_3Fe_9O_{19}$ (d) and $SrAl_4Fe_8O_{19}$ (e) prepared by glycin-nitrate method for 2 h at 1100 °C: (●) $SrFe_{12}O_{19}$; (▼) α-Fe_2O_3.

diffraction peaks of α-Fe_2O_3 phase was discovered. It can be seen that the intensities of the three weak diffraction peaks of the α-Fe_2O_3 (marked by label ▼), decreased with increasing Al doping concentration, as shown in Fig. 1. On the other hand, it is found that the intensities of diffraction peaks in the strong diffraction profile (denoted as ●) have no obvious change, but their diffraction peak positions systematically shift towards high angle with the increasing content of Al doping. In order to more clearly observe the change of diffraction peak positions, the strong diffraction peaks, located at 63.2°, were chosen with care, as shown in Fig. 2. From Fig. 2, the diffraction peak position shift towards high angle with increasing content Al, which the diffraction peak position is from 63.2° to 64.3° in the series of sample. In addition, the shift does not lead to change in crystal structure but in lattice constants. By using the change of diffraction peak position, the lattice constant of $SrFe_{12}O_{19}$ were calculated, as shown in Fig. 2. It can be seen from Fig. 2 that the lattice constant of $SrFe_{12}O_{19}$ decreases from 0.5887 to 0.5794 nm in a-axis with increasing Al doping content. Since the ionic radius of Al^{3+} ion (0.051 nm) is smaller

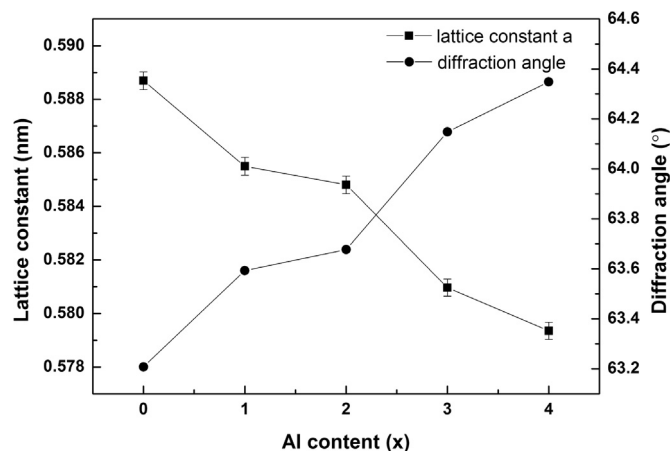Fig. 2. Plot of lattice constant a and change of diffraction peak position of $SrFe_{12}O_{19}$ with increasing Al content.