Structural and magnetic properties of SrFe$_{12-2x}$Ti$_x$Ru$_x$O$_{19}$

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ABSTRACT

The magnetic properties of M-type Strontium hexaferrites can be modified by partially substituting Fe ions by other metallic ions. In this work, we report on the effect of the substitution of Ti^{2+} and Ru^{4+} ions for Fe^{3+} ions on the magnetic properties of the system, and the dependence of these properties on the cationic distribution in the lattice. SrFe$_{12-2x}$Ti$_x$Ru$_x$O$_{19}$ hexaferrite samples were prepared by ball milling and sintering at 1100 °C the appropriate amounts of the starting powders. The structural and magnetic properties of the fabricated samples were investigated using X-ray diffraction, SEM, Mössbauer spectroscopy, and vibrating sample magnetometry. It was found that Ti–Ru substitution improved the crystallinity of the prepared samples slightly, and did not influence the particle size appreciably. Mössbauer spectroscopy revealed that Ti^{2+} and Ru^{4+} ions substituted Fe^{3+} ions at the 4f_2, (4f_1 + 2a) and 2b sites for x values up to 0.2, and at the 12k site for x > 0.2. The saturation magnetization increased up to x = 0.2, and then decreased for higher x values, while the coercivity decreased monotonically, recording a reduction of 70% at x = 0.3. The magnetic properties of the system were interpreted in terms of the distribution of Ti^{2+} and Ru^{4+} ions in the hexagonal lattice.

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1. Introduction

Although hexagonal ferrites had been extensively investigated since their discovery in the past decades, search for new materials with improved properties had been a field of great interest to researchers. The magnetic properties of hexaferrites such as their high saturation magnetization, large magnetocrystalline anisotropy and high coercive field [1–4], in addition to their low production cost and corrosion resistivity, had generated considerable attention to these materials. In order to satisfy the utilization requirements of this compound in recording media, permanent magnets, microwave devices and magneto-optics etc. [3–6], many studies had focused on tailoring hexaferrites with modified magnetic properties by substituting Fe^{3+} ions with divalent, trivalent and tetravalent cations or combinations of cations [4–13]. The preparation method and the type of cation substitution were found to have significant influence on the magnetic properties of strontium hexaferrite. Accordingly, several methods had been used to prepare hexaferrite particles including sol–gel method [2,5,6],

gel-combustion method [14], hydrothermal process [15], ammonium nitrate melt technique [7], ceramic route [14], co-precipitation method [3,4,16], and polymerizable complex method [9]. Ball milling method had been recently employed for the preparation of strontium ferrite powders [11–13]. This method is useful for the production of powders consisting of fine particles smaller than the single domain size.

The intrinsic magnetic properties of hexaferrites are strongly dependent on their structure. The structure of SrM hexaferrite consists of a periodic repetition of cubic spinel (S) blocks having the spinel-type structure, and hexagonal (R) blocks containing the Sr ions. The unit cell of SrFe$_{12}$O$_{19}$ is the stacking sequence RSR*S*, where R* and S* are the R and S blocks rotated by 180° about the hexagonal c-axis. The ferric ions occupy five different interstitial sites: three octahedral sites (12k, 4f_2 and 2a), one tetrahedral site (4f_1) and one trigonal bi-pyramidal site (2b) [17]. The spin-up Fe^{3+} ions in a formula unit are distributed with one ion at the 2a, one at the 2b, and six at the 12k sites, while the spin-down Fe^{3+} ions are distributed with two at the 4f_1 and two at the 4f_2 sites. Accordingly, the magnetic moment per formula can be expressed as follows:

$$\vec{m} = \overrightarrow{2a} + \overrightarrow{2b} + \overrightarrow{12k} + \overleftarrow{4f_1} + \overleftarrow{4f_2} \qquad (1)$$

Thus, the saturation moment of the SrM lattice per formula unit is given by [18]:

$$M_s = 6M_{12k}^{Fe3+} + M_{2b}^{Fe3+} + M_{2a}^{Fe3+} - 2M_{4f1}^{Fe3+} - 2M_{4f2}^{Fe3+} \qquad (2)$$

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The anisotropy field H_a for uniaxial strontium hexaferrite spherical particles can be expressed as:

$$H_a = \frac{2K_1}{M_s} \tag{3}$$

where K_1 is the magnetocrystalline anisotropy constant, and M_s is the saturation magnetization. Based on the single ion model, Xu et al. [19] found that Fe^{3+} ions at $2b$ sites have the largest positive contribution to the magnetocrystalline anisotropy constant, those at $4f_1$, $4f_2$, and $2a$ sites have relatively weak positive contributions, while those at $12k$ sites have a negative contribution. Hence, the magnetic properties of the samples could be modified in accordance with the distribution of Ti^{2+} and Ru^{4+} nonmagnetic ions at different sites in the lattice. Thus, knowledge of this distribution is essential for fabricating samples with magnetic properties suitable for specific applications, and for understanding the magnetic properties of the fabricated samples.

The present work is concerned with the fabrication of Ti–Ru substituted strontium hexaferrites using ball milling method, and investigation of the cationic distribution in the lattice and its effect on the magnetic properties of these ferrites. X-ray diffraction (XRD), scanning electron microscopy (SEM), Mössbauer spectroscopy (MS), and vibrating sample magnetometry (VSM) had been employed for this purpose.

2. Experimental procedures

$SrFe_{12-2x}Ti_xRu_xO_{19}$ powders with x = 0.0, 0.1, 0.2, and 0.3, were prepared by ball milling method. The appropriate weights of high purity Aldrich-made metallic oxides (Fe_2O_3 99%, TiO 99.9% and RuO_2 99.9%) and strontium carbonate ($SrCO_3$ 99.9%) were used as starting materials. The molar ratio of iron to strontium was set at Fe/Sr = 11, which is the optimum ratio for obtaining a single hexaferrite phase. Mechanical milling was performed using a planetary ball-mill (Fritsch Pulverisette-7) with a ball to powder ratio of 8:1. Milling was carried out for 16 h with an angular frequency of 250 rpm. The resulting powder for each sample was pressed into a 4 cm-diameter disk under a force of 50 kN, and then sintered in air at 1100 °C for 2 h.

XRD analysis on the sintered samples was carried out using Philips X'Pert PRO X-ray diffractometer (PW3040/60) with CuKα radiation (λ = 1.54056 Å). Mössbauer spectra were collected over 512 channels using a conventional spectrometer operating in the constant acceleration mode. The γ-ray source was a 50 m Ci ^{57}Co in palladium matrix. Isomer shifts were measured relative to the centroid of the α-Fe spectrum at room temperature, and the separation between the outer lines of the spectrum was used for calibrating the velocity scale. The grain structure of the prepared samples was investigated using scanning electron microscope (SEM FEI Quanta 600). The magnetic measurements were carried out using a vibrating sample magnetometer (VSM MicroMag 3900, Princeton Measurements Corporation), with a maximum applied field of 796 kA/m. The isothermal remanent magnetization (IRM) curve was obtained by the following procedure: the sample was initially demagnetized. A small positive field was applied and then removed, and the remanence magnetization was recorded. The procedure was repeated with increasing the positive field until the saturation remanence was reached.

3. Results and discussion

3.1. Structural

Fig. 1 shows XRD patterns of $SrFe_{12-2x}Ti_xRu_xO_{19}$ samples, together with the standard pattern for hexagonal strontium ferrite ($SrFe_{12}O_{19}$) with space group $P6_3/mmc$ (ICDD file no: 033-1340) [20]. The main diffraction peaks in all XRD patterns are consistent with those for the standard pattern of M-type strontium hexaferrite. A weak reflection at 33.17° indicates the presence of a small amount of α-Fe_2O_3 phase in the sample with x = 0.3, and only traces of this phase in the sample with x = 0.2. Therefore we may conclude that Ti and Ru ions with concentrations in the range reported in this work substitute Fe^{3+} ions in the $SrFe_{12}O_{19}$ lattice without affecting its hexagonal structure appreciably.
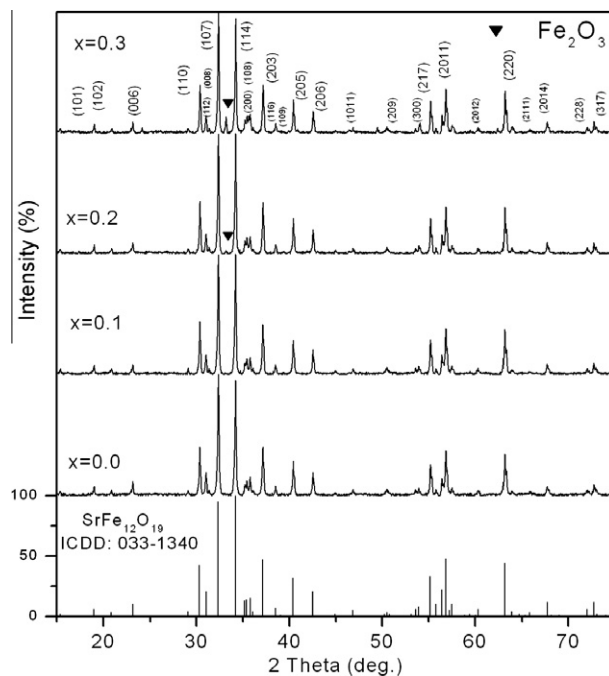

Fig. 1. Standard ICDD pattern for M-type hexagonal strontium ferrite (file no: 033-1340) and XRD patterns of $SrFe_{12-2x}Ti_xRu_xO_{19}$ with different doping concentrations.

The lattice parameters a, c were calculated from the values of inter-planer spacing d_{hkl} corresponding to the main peaks (107) and (104) according to the following equation [21]:

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

Here h, k, and l are Miller indices. The lattice parameters for this phase are listed in Table 1. These values of lattice parameters agree well with those reported for strontium hexaferrite [16,17].

The average crystallite size was determined from the positions and widths of the (114) and (107) reflections using the well-known Scherrer formula [21],

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{5}$$

where D is the crystallite size, k the Scherrer constant, λ the wavelength of radiation (1.54056 Å), β the peak width at half maximum (in radians), and θ the peak position. The average crystallite size for the pure sample was found to be 62 nm, while that for the substituted samples was in the range (70 ± 3) nm as shown in Table 1. These sizes are similar to those found for the Ti–Ru substituted BaM samples [13], and indicate that the crystallinity of the samples did not change significantly with the substitution.

On the other hand, the morphology of the grains for all samples was investigated by direct observation using scanning electron microscopy. Fig. 2 shows representative SEM images for $SrFe_{12-2x}Ti_xRu_xO_{19}$ samples with x = 0.0 and 0.3. As x increased,

Table 1
Lattice parameters and average crystallite size of $SrFe_{12-2x}Ti_xRu_xO_{19}$ samples.

x	$a = b$ (Å) ± 0.002	c (Å) ± 0.007	Average crystallite size (D) nm
0.0	5.885	23.049	62
0.1	5.885	23.052	67
0.2	5.884	23.052	72
0.3	5.882	23.049	73