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Mössbauer and X-ray diffraction study of Co^{2+} – Si^{4+} substituted M-type barium hexaferrite $\text{BaFe}_{12-2x}\text{Co}_x\text{Si}_x\text{O}_{19\pm\gamma}$

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ABSTRACT

Using X-ray powder diffractions, Mössbauer spectroscopy, and magnetic measurements, the effect of dopants ($\text{Co}^{2+} + \text{Si}^{4+}$) on the fine structure and magnetic properties of M-type barium hexaferrite prepared by hydroxide and carbonate precipitations has been studied. It has been shown that the magnetic properties of M-type barium hexaferrite can be controlled by heterovalent substitution $2\text{Fe}^{3+} \rightarrow \text{Co}^{2+} + \text{Si}^{4+}$.

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1. Introduction

Barium hexaferrite with magnetoplumbite structure M-type BHF is a hard magnetic material. It is characterized by high values of coercivity (H_c) and remanent magnetization (B_r) due to a strong uniaxial magnetocrystalline anisotropy [1,2]. Barium hexaferrite is widely used as a material for new permanent magnets [1–3], high-density data recording and storage systems [4,5], MW devices [6], electromagnetic energy absorbers in the high-frequency range [7–9], or biomedical hyperthermia inductors [10,11]. The requirements for the values of coercivity (H_c) depend on the application of BHF. Characteristic values of coercivity for permanent magnets are 480–640 kA/m and more, for magnetic recording 200–280 kA/m and for biomedical applications as low as possible. The value of the magnetization (M_s) must be high independent of application. Therefore, the preparation of BHF with high M_s and controlled H_c is a problem of today. In recent years, this problem is solved by heterovalent substitution of Fe^{3+} according to the scheme $2\text{Fe}^{3+} \rightarrow \text{Me}^{2+} + \text{Me}^{4+}$, where Me^{2+} and Me^{4+} are ferromagnetic and nonmagnetic ions respectively [12–19]. Such substitution ensures electrical neutrality in the BHF structure. The substitution $2\text{Fe}^{3+} \rightarrow \text{Co}^{2+} + \text{Ti}^{4+}$ is the most studied [12–18]. It is favorable for smooth decrease in H_c with increasing degree of substitution. Depending on the nature of

dopants, the magnetization (M_s) of BHF can be unchanged [14], slightly decreased [12], or increased [17].

It is known [1,2,19] that the magnetization of BHF is determined by antiferromagnetic ordering of magnetic ions Fe^{3+} . The distribution of ferromagnetic cations over nonequivalent positions in the M-type BHF structure also affects the magnetization [2,20]. The distribution of cations in ferrites depends on the synthesis conditions and the nature of dopants [1,2,20]. In this work, ($\text{Co}^{2+} + \text{Si}^{4+}$) ions were chosen as dopants.

It is known that silica (SiO_2) can be used as an inorganic matrix to prepare glass ceramics based on BHF [21,22] and as a material for encapsulating magnetic particles of BHF [23]. However, the effect of substitution of Si^{4+} ions for Fe^{3+} ions is scantily studied [24].

The aim of this work is the investigation of the effect of heterovalent substitution of ($\text{Co}^{2+} + \text{Si}^{4+}$) ions for Fe^{3+} ions on the crystal structure and magnetic properties of M-type barium hexaferrite.

2. Experimental methods

High purity $\text{Ba}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$, $\text{Co}(\text{NO}_3)_2$ and $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$ were used as initial reagents. The starting hydroxide–carbonate precipitates were obtained by two-step precipitation. The ingredients were precipitated at constant pH. pH was monitored with an I-160 MI ionometer and controlled with a BAT-15 automatic titration unit.

In the first step of precipitation, hydroxides of Fe(III) and Si(IV) were co-precipitated with a water solution of ammonia at pH=4.3. Precipitates were washed in distilled water to remove NH_4^+ ions. In the second step of precipitation, Co(II) and Ba(II) carbonates were co-precipitated with a solution of sodium

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carbonate at pH=9. The resulting precipitates were washed free from the mother solution using distilled water until no NO_3^- and Cl^- ions in the washed solution were detected. Powders were dried at 353 K and heat-treated at 1273 K for 2 h.

The samples were characterized by X-ray diffractometry (XRD) using a DRON-3M diffractometer ($\text{CuK}\alpha$ radiation, exposure at each point 10 s). SiO_2 (2θ standard) and certified intensity standard Al_2O_3 [25] were used as external standards. For X-ray phase analysis, a JCPDS database was used. The crystal structure parameters were refined by X-ray full-profile analysis.

The size of BHF particle (nm) was estimated from the broadening of the X-ray reflections 110 and 220. BHF calcined at 1773 K for 5 h was used as a standard. The diffraction peak broadening β was calculated from the formula: $\beta = \sqrt{B^2 - b^2}$, where B is the total linear broadening of the line, and b is instrumental broadening. The particle size was calculated from the Scherrer formula $D = 0.9\lambda / \beta_{hkl} \cos(\theta_{hkl})$ [3].

The Mössbauer spectra (MSs) were recorded at room temperature with a spectrometer working in the mode of constant accelerations with the use of ^{57}Co in Cr matrix. The speed scale was calibrated using α -Fe lines. MSs were fitted by the least-square method using Univem-2 software [26].

The magnetic properties of BHF powders were measured in the range of magnetic fields $H=0$ –800 kA/m at room temperature with a ballistic magnetometer.

3. Results and discussion

XRD shows that in the range $x=0$ –0.3 $\text{BaFe}_{12-2x}\text{Co}_x\text{Si}_x\text{O}_{19\pm\gamma}$ samples are single-phase ones and have a hexagonal M-type magnetoplumbite structure (space group $P6_3/mmc$). In addition to M-type BHF phase, a $\text{BaFe}_{18}\text{O}_{27}$ phase with hexagonal W-type structure also appears at $x > 0.3$ (Fig. 1). Fig. 2 shows the concentration dependence of the unit cell parameters of M-type BHF. The decrease in V of doped M-type BHF in the homogeneity region ($x=0$ –0.3) on the substitution of $\text{Fe}_{\text{CN}6}^{2+,6,\text{HS}}$ ions ($r=0.645 \text{ \AA}$) [27] by Co^{2+} and Si^{4+} ions ($r_{\text{Co}_{\text{CN}6}^{2+}}=0.735 \text{ \AA}$, $r_{\text{Si}_{\text{CN}6}^{4+}}=0.400 \text{ \AA}$, $\bar{r}=0.567 \text{ \AA}$) obeys the Vegard rule. This indicates the formation of substitutional solid solutions [28]. The increase in V for $x > 0.3$ may be due to increase in the ratio $\text{Ba}^{2+}/\text{Fe}^{3+}$ content ($r_{\text{Ba}_{\text{CN}8}^{2+}}=1.420 \text{ \AA}$, $r_{\text{Fe}_{\text{CN}6}^{3+}}=0.645 \text{ \AA}$) in M-type BHF compared with nominal composition (1/12–2x) due to the formation of the second phase, $\text{BaFe}_{18}\text{O}_{27}$. It is known that solid solution has M-type BHF structure in the range $\text{Ba}/\text{Fe}=1/12$ – $1/8$ [29–33].

The concentration dependence of the unit cell parameters of BHF is of a complex character (Fig. 2b) due to the complexity of its crystal structure.

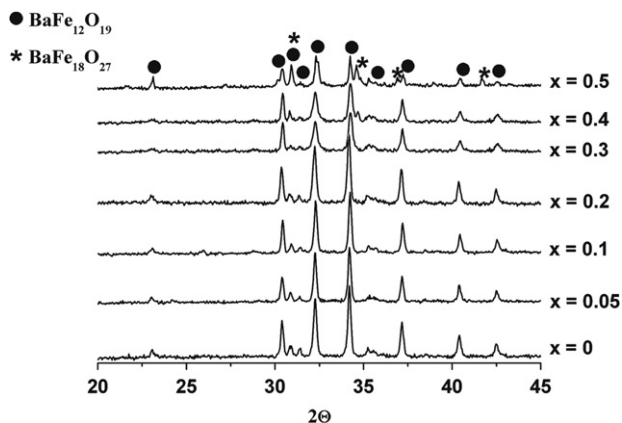


Fig. 1. Diffractograms of $\text{BaFe}_{12-2x}\text{Co}_x\text{Si}_x\text{O}_{19\pm\gamma}$ samples calcined at 1273 K.

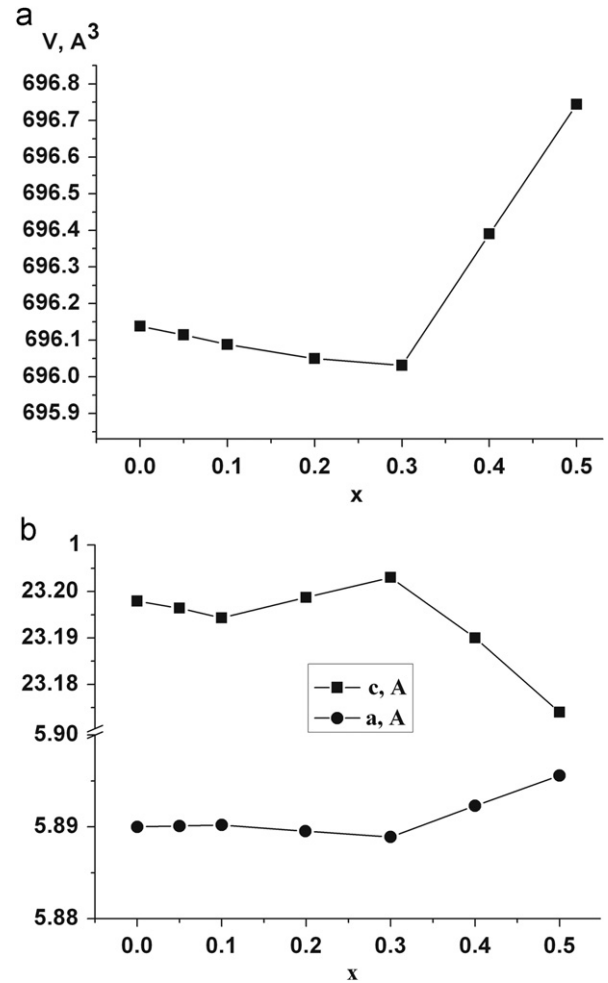


Fig. 2. Concentration dependence of the unit cell volume (a) and parameters (b) of $\text{BaFe}_{12-2x}\text{Co}_x\text{Si}_x\text{O}_{19\pm\gamma}$ samples calcined at 1273 K.

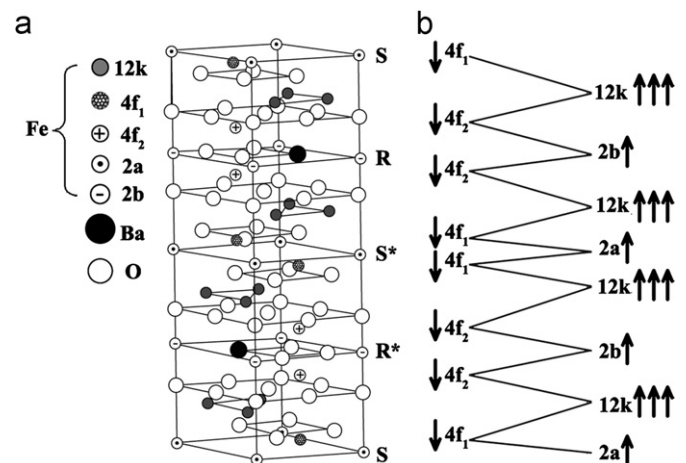


Fig. 3. Crystal (a) and magnetic (b) structures M-type $\text{BaFe}_{12}\text{O}_{19}$.

Fig. 3 shows crystal and magnetic structures M-type $\text{BaFe}_{12}\text{O}_{19}$ [34]. The structure of M-type BHF consists of spinel blocks S , S^* and hexagonal barium-containing blocks R , R^* , alternating in the direction of the c axis. S^* and R^* blocks result from rotation of S and R blocks by 180° about the c axis. The unit cell of BHF contains 10 layers of O^{2-} ions (Fig. 3). There are five

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