Vol. **113** (2008) *ACTA PHYSICA POLONICA A* No. 1

Proceedings of the CSMAG'07 Conference, Košice, July 9–12, 2007

Electromagnetic Properties of Substituted Barium Hexaferrites

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Substituted M-type ferrite $BaFe_{12-2x}(Me_1Me_2)_xO_{19}$, $0 \leq x \leq 0.6$ was prepared by both mechanical alloying and precursor method, where $Me_1 =$ Co, Ni, Zn, Sn and Me_2 =Ru, Ti, Zr, Sn. Magnetic phase purity, change of saturation polarization, Curie temperature, coercivity and magnetic susceptibility was studied as function of x. Attention was focused to results obtained for $(NiRu)_x$, $(ZnRu)_x$, and $(SnRu)_x$ mixtures with low doping ratio x.

PACS numbers: 75.50.–y, 75.50.Vv, 81.20.Ev, 81.20.Ka

1. Introduction

M-type Ba–hexaferrite exhibits high specific saturation polarization J_{s-m}, strong uniaxial crystalline anisotropy K_1 and large coercivity H_c. The strong uniaxial anisotropy of Ba–hexaferrite can be reduced by substitution of iron by other cations or mixture of cations. One aim of such substitution was to decline the magnetization of one of the sublattices from antiferromagnetic axis, i.e. to decline it from collinear and anticollinear ordering, respectively. The magnetocrystalline anisotropy becomes planar for a critical doping ratio x_c in some cases; these planar hexaferrites therefore become to be interesting materials for magnetic recording and microwave absorption devices. It is an efficient way for controlling the value of H_c, while preserving the value of J_{s-m}. Various substitutions are possible in $BaFe_{12}O_{19}$ composition — big divalent cations on Ba^{2+} site and small trivalent cations, or divalent Me_1^{2+} together with tetravalent Me_2^{4+} ions combinations on the

Fe^{3+} sites [1–5]. Substitutions of Fe ions have a big influence, directly affecting the magnetic structure.

The magnetic structure and properties of substituted M-type Ba–hexaferrites with composition $BaFe_{12-2x}(Me_1Me_2)_xO_{19}$ were studied. Divalent Me_1 = Co, Ni, Sn, Zn and tetravalent Me_2 = Ru, Ti, Zr, Sn ion combinations were used in various compounds. The phase purity of the samples was evaluated by temperature dependence of initial susceptibility $\chi(T)$ and specific saturation polarization $J_{s-m}(T)$ [6] and it was verified by the Mössbauer spectroscopy and X-ray diffraction. The particle size and shape was observed under a transmission electron microscopy (TEM). The particles of all ferrite samples exhibit a plate-like, nearly hexagonal shape with diameter between 0.3 and 1.1 μm.

2. Theory

The intrinsic properties arise from the M-crystal structure — five distinct Fe-sublattices, which are coupled by super-exchange allowing only parallel (↑) or antiparallel (↓) orientation. The magnetic moments of the iron ions are arranged in parallel to hexagonal *c*-axis, but with opposite spin directions of the sublattices. Their mutual orientation is given by the known Gorter model: 12k (↑), $4f_1$ (↓), $4f_2$ (↓), 2a (↑) and 2b (↑). Three sites named 12k, 2a, and $4f_2$ have octahedral coordination, $4f_1$ has tetrahedral and 2b site has a fivefold (bipyramidal) coordination. The resulting theoretical magnetic polarization J at a temperature T of $BaFe_{12}O_{19}$ per formula unit (f.u.) can be approximated by simple summation according to formula

$$J(T) = 6m_{12\mathrm{k}}(T) - 2m_{4\mathrm{f1}}(T) - 2m_{4\mathrm{f2}}(T) + 1m_{2\mathrm{a}}(T) + 1m_{2\mathrm{b}}(T), \tag{1}$$

where m_n is the magnetic moment of Fe^{3+} ion in n–th sublattice. Assuming a magnetic moment of $5\mu_\mathrm{B}$ (Bohr magneton) per Fe^{3+} ion at 0 K we get a net polarization of $20\mu_\mathrm{B}$ per f.u. for the pure $BaFe_{12}O_{19}$ at this temperature. It is in agreement with the observed saturation polarization for the pure compound J_s. According to Eq. (1) one can expect a change of the net magnetic polarization when the Fe^{3+} ions in the spin-down sublattices ($4f_1$,$4f_2$) and/or spin up sublattices (12k, 2a, 2b) are substituted.

3. Results

Influence of substitution to net polarization, magnetostructural anisotropy and coercivity H_c was investigated as well as possible limits of such approach. Change of magnetic polarization with doping ratio x is expressed by the difference $\Delta J_{\mathrm{s-m}} = J_{\mathrm{s-m}}(x) - J_{\mathrm{s-m}}(0)$, where $J_{\mathrm{s-m}}(0)$ is the specific magnetic polarization of pure BaM ferrite ($x = 0$). This dependence for selected samples prepared by mechanical alloying (Mx) is shown in Fig. 1a. It can be seen that $\Delta J_{\mathrm{s-m}}$ increases with x for ZnRu, NiRu, and SnRu substitutions presumably, because the magnetic moments in the spin-down sublattices ($4f_1$,$4f_2$) decrease more than those in the spin-up sublattices (2a,2b) (Eq. (1)). The Ru^{4+} ions seem to increase $\Delta J_{\mathrm{s-m}}$,

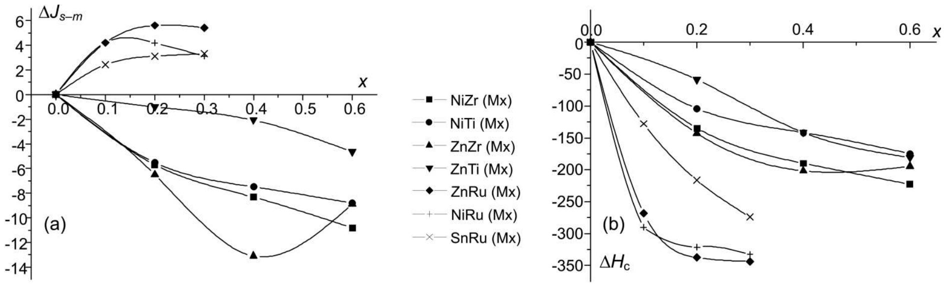

Fig. 1. Change of specific polarization $\Delta J_{\mathrm{s-m}}$ (a) and coercivity ΔH_{c} (b) as a function of x for samples (Mx).

it can also be attributed to a strong preference of Zn^{2+} to tetrahedral, Ni^{2+} and Sn^{2+} to octahedral coordination and no particular preference Ru^{4+} ions in $\mathrm{Me_1Ru}$ mixtures.

The dependence of coercivity on x is expressed by coercivity difference $\Delta H_{\mathrm{c}}(x) = H_{\mathrm{c}}(x) - H_{\mathrm{c}}(0)$, where $H_{\mathrm{c}}(0)$ is a coercivity of sample with $x = 0$. Dependence $\Delta H_{\mathrm{c}}(x)$ for selected $(\mathrm{Me_1,Me_2})_x$ substituent ions is shown in Fig. 1b. The strong fall of ΔH_{c} near $x = 0.1$ and slight decrease in ΔH_{c} observed near $x = 0.3$ for $(\mathrm{NiRu})_x$ and $(\mathrm{ZnRu})_x$ leads to the conclusion that the reached value of H_{c} starts to correspond with planar anisotropy. This value of H_{c} change ($x \approx 0.3$) is much lower than those of $x \approx 0.3 \div 0.6$ necessary for the H_{c} change of other $(\mathrm{Me_1,Me_2})_x$ ions. In order to understand the decrease in ΔH_{c} with increasing x, ionic distribution in sites should be taken into account. The fivefold site 2b has the strongest influence on the high anisotropy of $\mathrm{BaFe_{12}O_{19}}$ ferrite. Structural refinements on $(\mathrm{NiRu})_x$ and $(\mathrm{ZnRu})_x$ substitutions show that Ru^{4+} preferentially substitutes Fe^{3+} ions on 2b site for low x, and then on octahedral sites $4f_2$ and 2a (for Ni) or on the tetrahedral sites $4\mathrm{f}_1$ (for Zn).

Therefore, we attribute the rapid change of anisotropy and H_{c} in $(\mathrm{NiRu})_x$ and $(\mathrm{ZnRu})_x$ compounds to preferential occupation of 2b site by Ru^{4+} cations. Moreover, we suppose that the nature of divalent cation — Ni^{2+} ($3d^8$) or Zn^{2+} ($3d^{10}$) has influence but lower on the anisotropy change. This opinion is confirmed by the fact that the cationic distribution is the same in $(\mathrm{NiRu})_x$ as in $(\mathrm{Sn}^{2+}\mathrm{Ru})_x$, but ΔH_{c} values of $(\mathrm{SnRu})_x$ are significantly lower as compared with $(\mathrm{NiRu})_x$ and $(\mathrm{ZnRu})_x$. It is probably due to Ni^{2+} or Zn^{2+} having $3\mathrm{d}^8$ or $3\mathrm{d}^{10}$ orbitals and Sn^{2+} having $3\mathrm{d}^{10}$, $4\mathrm{d}^{10}$ orbitals. This opinion could be supported by the fact, that $(\mathrm{CoRu})_x$ substitution [4] (Co^{2+} has $3\mathrm{d}^7$ orbitals) has the same effect on anisotropy as $(\mathrm{NiRu})_x$. In addition, T_{c} decreases with the substitution rate x from 442°C ($x = 0$) down to 426°C for $(\mathrm{ZnRu})_{0.3}$, 435°C for $(\mathrm{NiRu})_{0.3}$ and 420°C for $(\mathrm{CoRu})_{0.3}$. Significantly lower value of $T_{\mathrm{c}} = 389$°C was found in the case of $(\mathrm{SnRu})_{0.3}$ substitution.

Furthermore presence of secondary phases containing spinel ferrite was found in $\chi(T)$ curves at temperature above T_{c} of the hexagonal phase for $\mathrm{NiMe_2}$ sub-

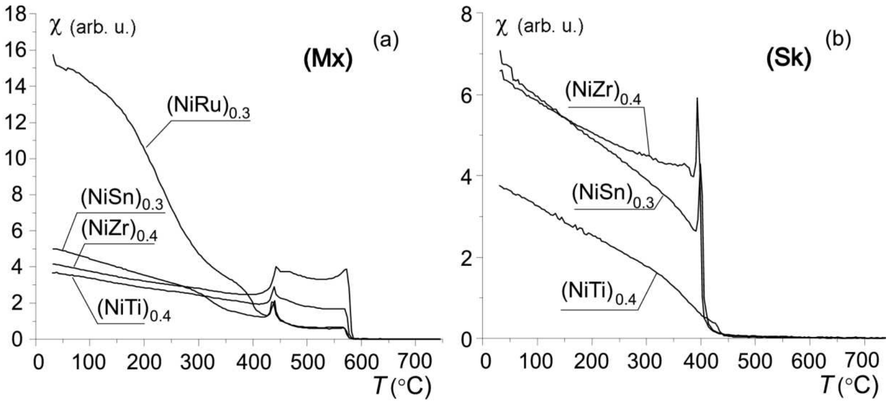

Fig. 2. Temperature dependence of magnetic susceptibility $\chi(T)$ of NiMe_2^{4+} prepared by Mx (a) and Sk (b).

stituted samples Me_2 = Ti, Zr, Sn, Ru) prepared only by mechanical alloying (Fe/Ba = 10.0), Fig. 2a. This phase was not detected by X-ray analysis; it is most likely the $\mathrm{NiFe_2O_4}$ (or magnetite $\mathrm{Fe_3O_4}$) compound, with $T_\mathrm{c} \approx 585$°C. On the other hand, no traces of spurious phases were found in BaM samples synthesized by the citrate precursor method (Sk) (Fe/Ba = 10.8) with x up to 0.4, Fig. 2b. Ni spinel ferrite was obtained by Turilli et al. [1] in Sr(NiTi) M–hexaferrite prepared by the metalorganic precursor method. Small doping rate of x was sufficient in some cases - to achieve nearly planar anisotropy in $(\mathrm{NiRu})_{0.3}$ and $(\mathrm{ZnRu})_{0.3}$ mixtures with a low temperature coeficient of H_c. Such ferrites could be very promising media for microwave devices and absorption at higher temperatures.

Acknowledgments

This work was supported by the VEGA of the Slovak Republic, the projects No. G-1/3096/06 and G-1/3189/06, respectively.

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