

# Magnetic Properties of Divalent (Ni,Sn,Zn)– Tetravalent (Ru,Sn) Ionic Mixtures of Substituted Ba Ferrite

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The drop of coercivity, while preserving the saturation magnetic polarisation  $J_S$  of substituted M-type Ba hexaferrites with composition  $\text{BaFe}_{12-2x}(\text{Me}_1\text{Me}_2)_x\text{O}_{19}$ , was studied. Divalent  $\text{Me}_1 = \text{Ni}, \text{Zn}, \text{Sn}$  and tetravalent  $\text{Me}_2 = \text{Ru}, \text{Sn}$  ionic combinations were used in various compounds. Mössbauer spectroscopy was used to reveal sites of replacement of the  $\text{Fe}^{3+}$  ions by  $\text{Ru}^{4+}$  and  $\text{Sn}^{4+}$ . The  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Sn}^{2+}$  occupation sites were identified as well. Strong drop of coercivity difference  $\Delta H_c(x)$  near  $x = 0.1$  and slight decrease of  $\Delta H_c(x)$  close to  $x = 0.3$  was obtained for suitable coupling of  $\text{Me}_1^{2+}$  and  $\text{Me}_2^{4+}$  ions.

DOI: [10.12693/APhysPolA.126.172](https://doi.org/10.12693/APhysPolA.126.172)

PACS: 75.50.Gg, 75.50.Vv, 77.22.Ej

## 1. Introduction

For recording magnetic media and VHF electronic applications the large anisotropy of BaM hexaferrite can be diminished by substituting of  $\text{Fe}^{3+}$  ions by selected cation combinations. It is an efficient way for controlling the value of coercivity  $H_c$ , which is preserving the value of  $J_S$ , and this offers very effective media for data recording [1]. The magnetic structure and properties of substituted  $\text{BaFe}_{12-2x}(\text{Me}_1\text{Me}_2)_x\text{O}_{19}$  ferrites were studied, compared and overviewed. We found a marked reduction of  $H_c$  and slow variation of the  $J_S$ , which are related to preferential occupation of divalent and tetravalent cations in the lattice sites. One of goals of that was to develop new compounds with potential for electronic applications and with suitable properties for high density recording applications.

## 2. Experimental and methods of characterisation

The samples of  $\text{Ba}(\text{Me}_1\text{Me}_2)_x\text{Fe}_{12-2x}\text{O}_{19}$  with divalent  $\text{Me}_1 = \text{Ni}, \text{Sn}$  and tetravalent  $\text{Me}_2 = \text{Ru}, \text{Sn}$  ionic combinations were synthesized by mechanical alloying. The samples were assigned as (mx) and were annealed at  $1050^\circ\text{C} / 1.5\text{ h}$  using the Fe/Ba ratio of 10. The values of  $H_c = 350\text{ kA/m}$  and  $J_{S-m} = 80.77 \times 10^{-6}\text{ T m}^3\text{kg}^{-1}$  were measured for samples (mx) with  $x = 0$ . The other samples with  $\text{Me}_1 = \text{Ni}^{2+}, \text{Zn}^{2+}$  and  $\text{Me}_2 = \text{Sn}^{4+}$  ionic combinations assigned as (sk) were prepared using a metallorganic precursor method. The samples were subsequently annealed at temperatures  $700^\circ\text{C}$  and  $1050^\circ\text{C} / 2\text{ h}$ , using the Fe/Ba ratio of 10.8. The values  $H_c = 330\text{ kA/m}$  and  $J_{S-m} = 73.64 \times 10^{-6}\text{ T m}^3\text{kg}^{-1}$  were measured for samples (sk) with  $x = 0$ . Specific saturation polarisation  $J_{S-m}$ , and  $H_c$  were measured by a vibrating sample magnetometer Lake Shore 430 VSM in field up to 1.2 T. The phase purity and structure of samples were anal-

ysed by the Mössbauer spectra, which were obtained by a spectrometer with  $\gamma$ -ray source of  $^{57}\text{Co}$  imbedded in a Rh matrix. The Curie temperature  $T_C$  was determined from measured temperature dependences of initial susceptibility. For all samples the values of  $T_C$  were decreasing with  $x$ .

## 3. Results and discussion

The  $J_S$ ,  $T_C$  and  $H_c$  values arise from the M-type structure with five distinct Fe sublattices, which are coupled by super-exchange coupling. Three sites named  $\uparrow 12k$ ,  $\uparrow 2a$  and  $\downarrow 4f_2$  have octahedral coordination,  $\downarrow 4f_1$  has tetrahedral and  $\uparrow 2b$  site has a bipyramidal coordination with lattice momentum orientation spin-up, or spin-down. Mössbauer spectra at room temperature for  $\text{Ba}(\text{Me}_1\text{Me}_2)_x\text{Fe}_{12-2x}\text{O}_{19}$  samples with  $\text{Me}_1 = \text{Ni}, \text{Sn}, \text{Zn}$  and  $\text{Me}_2 = \text{Ru}, \text{Sn}$  ionic combinations were measured. The spectra were corresponding to all five different sites. According to analyses of spectra, previous researches [2–5] and taking into account the difference of ionic radii between  $\text{Me}_1^{2+}$  and  $\text{Me}_2^{4+}$  ions, we assume that  $\text{Ni}^{2+}$  and  $\text{Sn}^{2+}$  ions replace  $\text{Fe}^{3+}$  ions in  $4f_2$  and  $2a$  sites while

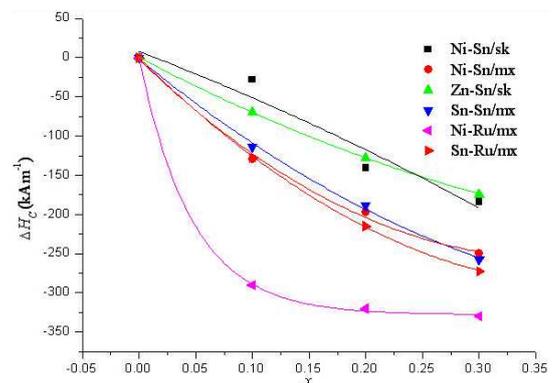


Fig. 1. Change of coercivity difference  $\Delta H_c(x)$  as a function of  $x$  for the samples  $(\text{Me}_1\text{Ru})_x$ ,  $(\text{Me}_1\text{Sn})_x$  (mx) and  $(\text{Me}_1\text{Sn})_x$  (sk).

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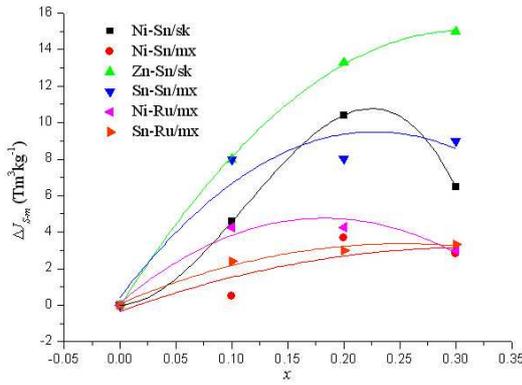


Fig. 2. Change of specific polarisation  $\Delta J_{S-m}$  as a function of  $x$  for  $(\text{Me}_1\text{Ru})_x$ ,  $(\text{Me}_1\text{Sn})_x$  (mx) and  $(\text{Me}_1\text{Sn})_x$  (sk) samples.

$\text{Sn}^{4+}$  and  $\text{Ru}^{4+}$  ions replace  $\text{Fe}^{3+}$  ions in tetrahedral  $4f_1$  and bipyramidal 2b sites. Regarding the  $(\text{ZnSn})_x$  samples, the  $\text{Zn}^{2+}$  ion has a strong preference for  $4f_1$  sites and  $\text{Sn}^{4+}$  ion preferably replaces  $\text{Fe}^{3+}$  ions in 2b and then in sites  $4f_2$  and 2a, see Table. The main aim of substitution was to decline the magnetisation of one of the sublattices from antiferromagnetic axis, in order to make the magnetocrystalline anisotropy to become planar for a critical doping ratio  $x_C$  in some cases; while preserving the value of  $J_S$ . The coercivity difference  $\Delta H_c(x) = H_c(x) - H_c(0)$ , where  $H_c(0)$  is the coercivity of a sample with  $x = 0$ , was chosen as evaluation criterion of anisotropy variation. The  $\Delta H_c(x)$  reflects the change of  $H_c$  comparing to the pure BaM ferrite. The variation of  $\Delta H_c(x)$  for selected  $(\text{Me}_1\text{Me}_2)_x$  substituent ions, prepared by mechanical alloying (mx), and for the metallorganic precursor method (sk) is presented in Fig. 1. The strong fall of  $\Delta H_c(x)$  near  $x = 0.1$  and slight decrease of  $\Delta H_c(x)$ , observed near  $x = 0.3$  for  $(\text{NiRu})_x$  confirms the planar anisotropy at a small doping. The  $(\text{SnRu})_x$  mixture produces a visibly smaller change of  $\Delta H_c$  compared to  $(\text{NiRu})_x$ . The  $(\text{SnSn})_x$  and  $(\text{NiSn})_x$  mixtures (mx) have roughly similar decrease of  $\Delta H_c$ , compared to  $(\text{SnRu})_x$ . The  $\Delta H_c$  variation of  $(\text{ZnSn})_x$  and  $(\text{NiSn})_x$  substituted ferrites (sk) showed that  $\Delta H_c$  decreases relatively slowly in comparison with  $(\text{Me}_1\text{Ru})_x$  and  $(\text{Me}_1\text{Sn})_x$  samples (mx). It is well known, that the 2b sublattice is a main contributor to the magnetocrystalline anisotropy and hence  $H_c$ . We attribute the rapid change of  $\Delta H_c(x)$  and anisotropy in  $(\text{Me}_1\text{Ru})_x$  and  $(\text{Me}_1\text{Sn})_x$  to preferential occupation of 2b site by  $\text{Ru}^{4+}$  and  $\text{Sn}^{4+}$  ions. We observed that not only  $\text{Me}^{4+}$  ions, but also divalent  $\text{Me}^{2+}$  (Ni, Zn, Sn) ions have an influence on  $\Delta H_c$  reduction. The effect of  $\text{Me}_1^{2+}$  ions is, however, less significant.

Change of  $J_{S-m}(x)$  with  $x$  is expressed by the difference  $\Delta J_{S-m} = J_{S-m}(x) - J_{S-m}(0)$ , where  $J_{S-m}(0)$  is the specific saturated polarisation for  $x = 0$ . These curves for samples prepared by both methods are shown in Fig. 2. For  $(\text{Me}_1\text{Ru})_x$  and  $(\text{Me}_1\text{Sn})_x$  substitutions

the  $\Delta J_{S-m}$  values increase (or have positive increment) with  $x$ , presumably because the magnetic moments in the spin-down sites ( $4f_1$ ,  $4f_2$ ) decrease more than those in the spin-up sites (2a, 2b), see Table.

TABLE  
Ionic parameters and occupation site preference of substituted mixtures.

substituted mixture	orbit	radius	$4f_2$ octa	2a octa	$4f_1$ tetra	12k octa	2b hexa
Zn-Sn	$\text{Zn}^{2+}$	$3d^{10}$	0.074		*		
	$\text{Sn}^{4+}$	$4d^{10}$	0.071	*	*		*
Ni-Sn	$\text{Ni}^{2+}$	$3d^8$	0.072	*	*		
	$\text{Sn}^{4+}$	$4d^{10}$	0.071		*		*
Sn-Sn	$\text{Sn}^{2+}$	$4d^{10}$	0.112	*	*		
	$\text{Sn}^{4+}$	$4d^{10}$	0.071		*		*
Ni-Ru	$\text{Ni}^{2+}$	$3d^8$	0.072	*	*		
	$\text{Ru}^{4+}$	$4d^4$	0.067		*		*
Sn-Ru	$\text{Sn}^{2+}$	$4d^{10}$	0.112	*	*		
	$\text{Ru}^{4+}$	$4d^4$	0.067	$\uparrow\downarrow$	$\downarrow\uparrow$	$\uparrow^*$	*
lattice momentum ( $\mu_B$ )				$10\downarrow$	$5\uparrow$	$10\downarrow$	$30\uparrow$

#### 4. Conclusions

The expressive drop of  $H_c$ , as  $x$  increased, was related to reduction of the magnetocrystalline anisotropy, due to replacement of  $\text{Fe}^{3+}$  ions by  $\text{Ru}^{4+}$  in 2b sites for  $(\text{NiRu})_x$ . We observed that divalent ions have also an influence on  $H_c$  reduction. The  $(\text{SnRu})_x$  substitution has shown a smaller, but similar effect on the  $H_c$  decrement of samples as  $(\text{SnSn})_x$  and  $(\text{NiSn})_x$  substitutions in BaM ferrite (mx), at low value of  $x = 0.3$ . For the samples with the  $(\text{NiSn})_x$  and  $(\text{ZnSn})_x$  substitutions, prepared by the precursor method (sk), a smaller decrement of  $H_c$  was achieved up to the value of  $x = 0.3$ , probably due to smaller sized particles, produced by this method.

#### Acknowledgments

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-006211 and by the Scientific Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic and the Slovak Academy of Sciences (VEGA), projects No. VG-1/1163/12, VG-1/1325/12 and VG-1/0286/12.

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