

## CHARACTERISTICS OF MAGNETIC PROPERTIES OF SUBSTITUTED HEXAGONAL FERRITES

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**Summary** The samples of barium hexaferrite  $\text{BaFe}_{12-2x}(\text{Me}_1\text{Me}_2)_x\text{O}_{19}$  with  $x$  from 0.0 to 0.6 were prepared by various methods. The cationic preference of mainly divalent  $\text{Me}_1 = \text{Zn, Co, Ni, Sn}$  ions and tetravalent  $\text{Me}_2 = \text{Ti, Zr, Ir, Sn, Ru}$  ions and their combinations in substituted Ba ferrites was investigated. The substitutions were performed to reduce the grain size and high magnetic uniaxial anisotropy field of the M-type Ba ferrite without affecting the magnetic polarisation. The goal is to reach the properties of ferrite proper for high-density magnetic recording and microwave absorption devices. Magnetic properties were determined as a function of the substitution level  $x$ . The specific saturation magnetic polarisation  $J_{s-m}$  and remanence  $J_{s-r}$  increased with small  $x$  due to the substitution of non-magnetic and less magnetic ions in  $4f_1$  and  $4f_2$  sites. The steep decrease of coercivity  $H_c$  with increasing  $x$  may be caused by the  $\text{Co}^{2+}$  preference of  $4f_2$  site and  $\text{Ti}^{4+}$  or  $\text{Zr}^{4+}$  ions preference of 2b and slightly in  $4f_1$  sites. The temperature coefficient of the coercivity  $TKH_c$  was very low ( $0.01\text{kA}\cdot\text{m}^{-1}\cdot^\circ\text{C}^{-1}$ ) for the Co-Zr substitutions and positive for the rest of samples.

### 1. INTRODUCTION

The paper is concerned on the synthesis of M-type barium ferrites for perpendicular recording media. Beside of their importance as permanent magnets for small actuators, they exhibit also excellent properties for applications within the centimetre- and millimetre-waves band [1, 2].

The  $\text{BaFe}_{12}\text{O}_{19}$  and related isostructural M-type hexaferrites derived by a single or double cationic substitution of  $\text{Fe}^{3+}$  ions with preservation of the formal valence are of a significant interest. Attention was focused on  $\text{Me}_1\text{--Me}_2$  combinations of substituents [3, 4], where  $\text{Me}_1 = \text{Zn, Co, Ni, Sn}$  were used as divalent ions and  $\text{Me}_2 = \text{Ti, Zr, Ir, Sn, Ru}$  as tetravalent ions. The aim of substitutions is to decline the magnetisation of one of the sub-lattices from antiferromagnetic axis, i.e. to decline from collinear and anti-collinear ordering respectively [5]. It has a remarkable influence to the coercivity  $H_c$ , while the value of saturation magnetic flux density  $J_{s-m}$  change is low, which is important for perpendicular data-recording media [6]. Such materials should exhibit high magnetic polarisation  $J_s$  and a relatively low coercivity  $H_c$ . Concerning microwave applications as absorbing media, the substitution by non-magnetic ions is known to reduce substantially the ferrimagnetic resonance of  $\text{BaFe}_{12}\text{O}_{19}$  ferrite.

### 2. EXPERIMENTAL

Coercivity and the temperature coefficient of coercivity was determined by vibrating magnetometer. The shape and the size of particles was studied using X-ray diffraction and SEM microscope [1, 3, 4]. The magneto-crystalline structure was observed by Mössbauer spectroscopy, the chemical purity and phase composition was

evaluated by the temperature dependences of the magnetic susceptibility [3, 4, 7].

It is a considerable problem to optimise the technological process to produce homogeneous and single-phase hexagonal ferrite system. It is necessary to determine the amounts of raw materials correctly to fix the initial ratio of Ba:Fe ions. Two ways were used for ferrite preparation – mechanical milling and citrate precursor method. It was found out that different ratios of raw materials amounts are necessary for these two preparation ways to achieve a single-phase hexagonal structure.

### 3. RESULTS AND DISCUSSION

Ferrite samples with various substitution levels  $x$  were prepared and tested. The temperature dependences of the initial magnetic susceptibility  $\chi(\vartheta)$  for Zn-Zr, Zn-Ti and Co-Ti substitutions prepared by citrate precursor method [7] (marked as Sk) are shown in Fig. 1, 2 and 3 respectively. The susceptibility is given in arbitrary units and it is related to the same weight of ferrite in all cases.

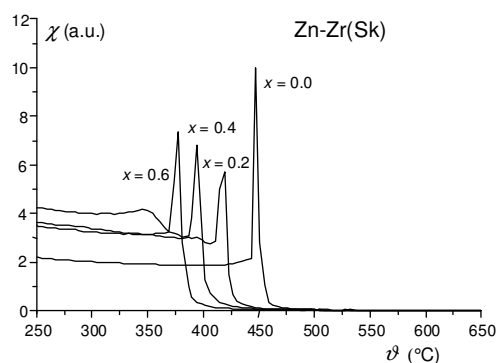


Fig. 1. The temperature dependence of the magnetic susceptibility for  $\text{Ba}(\text{ZnZr})_x\text{Fe}_{12-2x}\text{O}_{19}$ .

The  $\chi(\vartheta)$  dependences for pure ( $x = 0$ ) samples exhibit a sharp Hopkinson peak in the vicinity of the Curie temperature  $T_c$  for mono-phase M-hexaferrite. Single-phase dependence  $\chi(\vartheta)$  was found for all samples. However, Hopkinson peaks are broadened for ZnTi samples mainly with  $x$  increasing. It is attributed to a wide distribution of the particles shape.

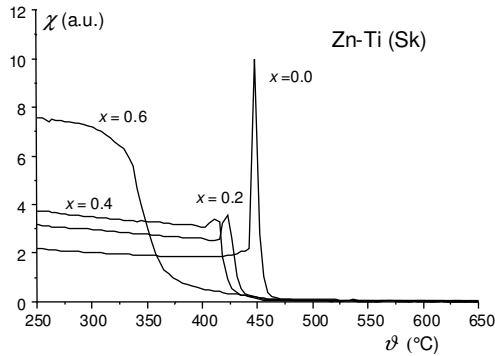


Fig. 2. The temperature dependence of the magnetic susceptibility for  $\text{Ba}(\text{ZnTi})_x\text{Fe}_{12-2x}\text{O}_{19}$ .

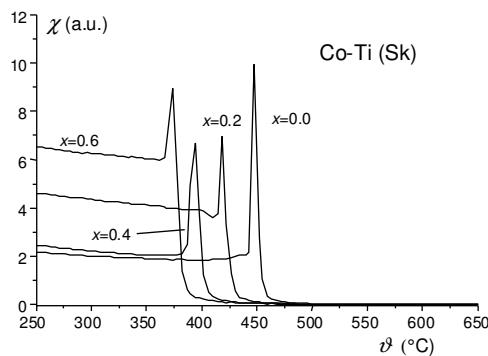


Fig. 3. The temperature dependence of the magnetic susceptibility for  $\text{Ba}(\text{CoTi})_x\text{Fe}_{12-2x}\text{O}_{19}$ .

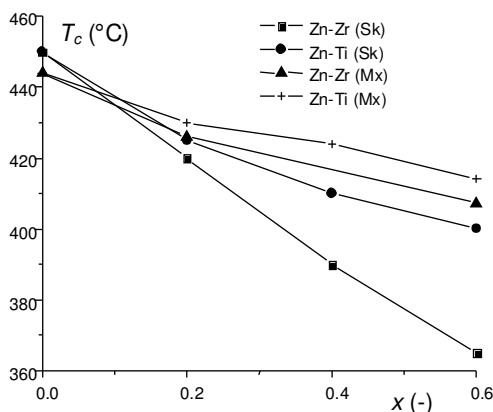


Fig. 4. Dependence of the Curie temperature on  $x$  of substituted  $\text{Ba}(\text{Zn-Ti or Zr})_x\text{Fe}_{12-2x}\text{O}_{19}$  ferrites.

The values of Curie temperature  $T_c$  were obtained by the Hopkinson's peak on  $\chi(\vartheta)$  curve. When the peak is too widely broadened or not present,  $T_c$  can be

determined from the point of inflexion of  $\chi(\vartheta)$  curve. The Curie temperature decreases with the substitution level  $x$  in all cases (Fig. 4) regardless on preparation method (Sk – citrate precursor method, Mx – mechanical milling). The highest  $T_c$  was found for Zn-Ti substitution prepared by mechanical milling. Ni-Ti and Ni-Zr substituted ferrites have similar  $T_c(x)$  dependence [8].

The specific magnetic polarisation  $J_{s-m}$  as a function of  $x$  is depicted in Fig. 5 for Zn-Zr and Zn-Ti substitutions. The values  $J_{s-m}$  are close to saturation state.  $J_{s-m}$  decreases with  $x$  for samples prepared by mechanical milling (Mx), while it increases for samples prepared by citrate precursor method (Sk). The reduction of  $J_{s-m}$  at higher substitution level  $x$  can be explained by assuming that the magnetic colinearity in basic cell will gradually break down after doping with non-magnetic cations.

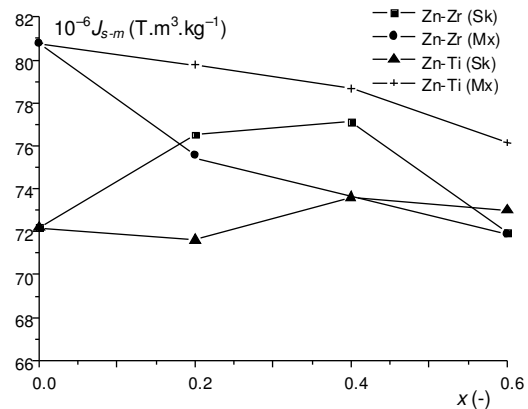


Fig. 5. The dependence of the specific magnetic polarisation  $J_{s-m}$  on  $x$  of  $\text{Ba}(\text{Zn-Ti or Zr})_x\text{Fe}_{12-2x}\text{O}_{19}$ .

The dependence of the coercivity  $H_c$  on  $x$  is in Fig. 6.  $H_c$  decreases with  $x$  in all cases. Such dependence as of Zn-Ti substitution prepared by mechanical milling [4] was found also for Co-Ti substituted samples prepared by citrate precursor method [9].

The magnetic properties of final product are strongly dependent on the conditions of synthesis.  $\text{Fe}^{3+}$  ions occur on five different sites in presented M-type hexaferrites: the octahedral  $4f_2$ ,  $2a$ ,  $12k$  and the tetrahedral  $4f_1$  and bipyramidal  $2b$  sites. Tetravalent ions prefer  $2b$  and slightly in  $4f_1$  sites where substitute  $\text{Fe}^{3+}$  ions. It is well known that the  $2b$  sublattice is the main contributor to the magneto-crystalline anisotropy and therefore coercivity. Such substitution results in decreasing of the coercivity.

The temperature coefficient of coercivity  $TKH_c = dH_c/dT$  is an important parameter for the stability of the recorded data [8]. The temperature coefficient was calculated from  $H_c$  measured at  $20^\circ\text{C}$  and  $120^\circ\text{C}$  by the formula

$$TKH_c = [H_c(120^\circ\text{C}) - H_c(20^\circ\text{C})]/100^\circ\text{C}. \quad (1)$$

The Zn-Ti doped BaM ferrite has a positive  $TKH_c$ . It is known, that  $Ni^{2+}$  ions reduce the  $TKH_c$ . The effect of several metal ion combinations Zn, Co, Ni with Zr or Ti on magnetic properties and magneto-crystalline structure of Ba hexaferrite were investigated from the point of view of  $TKH_c$ . We found that  $TKH_c = 0.01 \text{ kA/m}^\circ\text{C}$  was reached with Co-Zr substituted samples prepared by citrate precursor method at  $x = 0.6$ . These samples had values of  $TKH_c$ ,  $H_c$  and  $J_{s-m}$  optimal for magnetic recording [8]. They can be also important as a magnetic filler in polymer matrix. Such composite materials can be used as microwave absorbers.

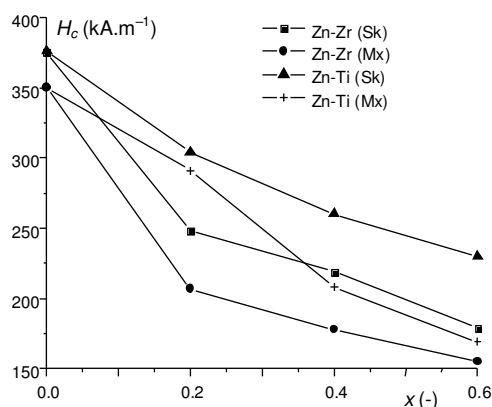


Fig. 6. The dependence of the coercivity  $H_c$  on  $x$  of  $Ba(Zn-Ti \text{ or } Zr)_xFe_{12-2x}O_{19}$

The research of hexaferrites was concentrated also on development of new M-type Ba ferrites substituted by ruthenium with other divalent cations (Ni, Zn, Sn). The results show that it is possible to obtain materials with suitable properties for high-density magnetic recording using low substitution of (Ni, Zn, Sn)-Ru mixtures [10, 11]. The combinations of (Ni, Zn, Sn)- $Sn^{4+}$  ions also seem to be convenient substituents to BaM systems [3]. From our results follows, that this system exhibits important decreasing of coercivity at low amount of substitution  $x = 0.3$ . For example, the  $Ni^{2+}$ - $Sn^{4+}$  substituted BaM system synthesised by citrate precursor method has  $H_c = 78 \text{ kA/m}$ ,  $J_{s-m} = 90.78 \times 10^{-6} \text{ T.m}^3.\text{kg}^{-1}$ ; the  $Sn^{2+}$ - $Sn^{4+}$  substituted and  $Sn^{2+}$ - $Ru^{4+}$  substituted BaM systems has  $H_c \sim 100 \text{ kA/m}$ ,  $J_{s-m} \sim 100 \times 10^{-6} \text{ T.m}^3.\text{kg}^{-1}$ . They could be used for perpendicular recording due to their excellent high-frequency response.

For example, narrow switch field distribution and excellent high-frequency response was found in Co-Ti [9] and other substituted BaM ferrites.

#### 4. CONCLUSION

The need of new magnetic materials explains the considerable interest on the study of hexagonal BaM ferrites. New applications require magnetics with control of chemical composition, homogeneity, particle size and shape.

The structural and magnetic properties of M-type Ba ferrites can be modified by the substitution with non-magnetic ions. Several combinations of substituent ions were tested and presented. Magnetocrystalline anisotropy and therefore the coercivity  $H_c$  decreases with the substitution level  $x$  while the magnetic polarisation  $J_{s-m}$  change is small. It is possible to use these materials for perpendicular magnetic recording and as magnetic fillers for composites.

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