

INFLUENCE OF SUBSTITUTION ON BARIUM FERRITE PROPERTIES

Jančárik V. *, Papánová M. **, Kevická D. **, Dosoudil R. *, Grusková A. **, Tóth I. ***

*Department of Electromagnetic Theory, **Department of Electrotechnology, ***Department of Nuclear Physics and Technology, Slovak University of Technology, Faculty of Electrical Engineering and Information Technology, Ilkovičova 3, 812 19 Bratislava, Slovakia, e-mail: vlado@iris.elf.stuba.sk

Summary $\text{BaFe}_{12-2x}(\text{Ni,Zn})_x\text{Sn}_x\text{O}_{19}$ M - type compounds processed by citrate precursor method with substitution level $0.0 \leq x \leq 0.6$ were studied. Mössbauer spectroscopy and thermomagnetic analysis were used to investigate the magneto - crystalline structure of these hexaferrites. Coercive field intensity H_c , specific saturation magnetic polarisation J_{s-m} and remanent magnetic polarisation J_{s-r} of ferrite powder specimens were measured. A large change of the coercivity H_c from 330 kA/m ($x = 0.0$) to ~70 kA/m ($x = 0.6$) was reached as a function of the substitution x . These changes are caused by rearrangement of the Fe^{3+} ions within the crystalline lattice. Sn^{4+} ions replace Fe^{3+} ions on 2b and slightly 2a+4f₁ sites, while Ni^{2+} ions occupy 4f₂ and 12k sites and Zn^{2+} ions strongly prefer 4f₁ sites.

1. INTRODUCTION

The M - type substituted Ba hexaferrites are a promising media for high-density magnetic recording due to their better performance compared with other materials [1, 2]. In addition, substituted hexaferrites are suitable for using as high - frequency wave absorbers (1 – 50 GHz), where they compete with the spinel compounds [3].

The regular barium hexaferrite has the crystal structure of the mineral magnetoplumbite, Fig. 1. The dimension of the unit cell are $a = b = 0.588$ nm and $c = 2.32$ nm. The basic structure of the unit cell is built up by ten layers of oxygen ions, which are formed by a close packing of cubic or hexagonal stacked layers alternately. One O^{2-} ion is replaced by Ba in every fifth layer (Fig. 1). The crystal structure can be divided into several blocks. The S - block contains two oxygen layers forming a spinel structure, where the R - block is a three-layer block containing the layer with the Ba ion. The whole structure can be symbolically described RSR^+S^+ , where the R^+ and S^+ - blocks are built up by a rotation of 180° around the hexagonal c - axis. The Fe^{3+} ions occupy five different interstitial sites within the basic structure. Three sites named 12k, 2a and 4f₂ have an octahedral coordination, one site 4f₁ has a tetrahedral coordination and the 2b site has a five-fold (hexahedral) coordination. In addition, 4f₁ and 4f₂ spins are configured down, whereas contribution of the other three sites to the magnetic polarisation is positive. Therefore, each magnetic sublattice has a specific contribution to the total magnetic moment and to the crystalline anisotropy of BaM. The number in the expression of the different sites indicates the number of Fe^{3+} ions per unit cell. Non - substituted barium hexaferrite has a ferrimagnetic structure with a Curie temperature $T_c = 450^\circ\text{C}$ [4].

The way of the properties modification of the ferrite is to substitute the Ba^{2+} or Fe^{3+} cations to reduce the high magnetocrystalline anisotropy of M - type hexaferrite. This procedure yields decreasing of the coercivity H_c , while the saturation magnetisation J_{s-m} remains high. Suitable value of H_c for high-density magnetic recording media is 150 – 240 kA/m [5].

Recently, many workers focused their studies on Co-Sn [6], Ni-Sn [3, 7], Zn-Sn [8] and Ti-Sn [9]

substituted Ba ferrite particles prepared by attrition milling, citrate precursor, chemical co-precipitation and sol-gel methods. The Zn-Sn substituted BaM ferrite nanoparticles exhibit interesting magnetic properties; the magnetization J_{s-m} has a smooth maximum at low substitutions and the coercivity H_c changes strongly with substitutions [10].

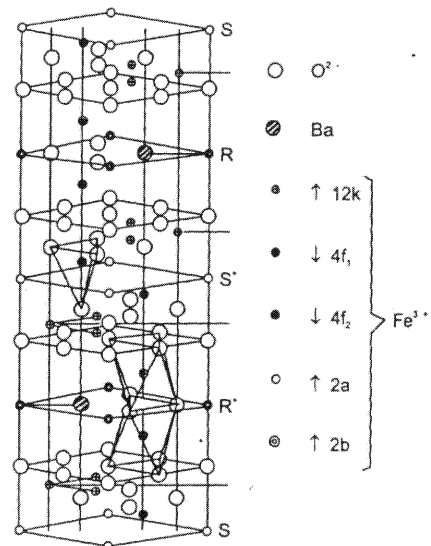


Fig. 1. Unit cell of barium hexaferrite based on two cells of $\text{BaFe}_{12}\text{O}_{19}$, and the spin orientation of the Fe^{3+} ions at different sites.

The aim of the presented work is the study of magneto-crystalline structure and magnetic properties of Ni-Sn and Zn-Sn substituted Ba ferrite particles. Mössbauer spectroscopy, thermomagnetic analysis and magnetic measurements were used for investigation.

2. EXPERIMENT

High-purity $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ or $\text{Ni}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, were used as raw materials. The Ba/Fe ratio of 10.8 was chosen. An aqueous solution was prepared by dissolving $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in deionised water, the amount of the iron was determined gravimetrically. From this, iron hydroxide was precipitated by adding a concentrated ammonia solution drop by drop under a constant stirring. A second solution was prepared by dissolving

citric acid in deionised water along with the other reagents ($\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$). Both solutions were mixed together and an additional small amount of ethylene glycol was added to obtain an amorphous phase after dehydration. The solvent was removed by introducing the solution in the excessive amount of the alcohol during one hour. The finely divided precipitate was heated at 80°C for 30 min, then it was filtered and dried in the vacuum oven. Next, the amorphous citrate precursor was decomposed at 360°C for 5 hours. Finally, the powdered samples were annealed at the temperature 1050°C for 2 hours.

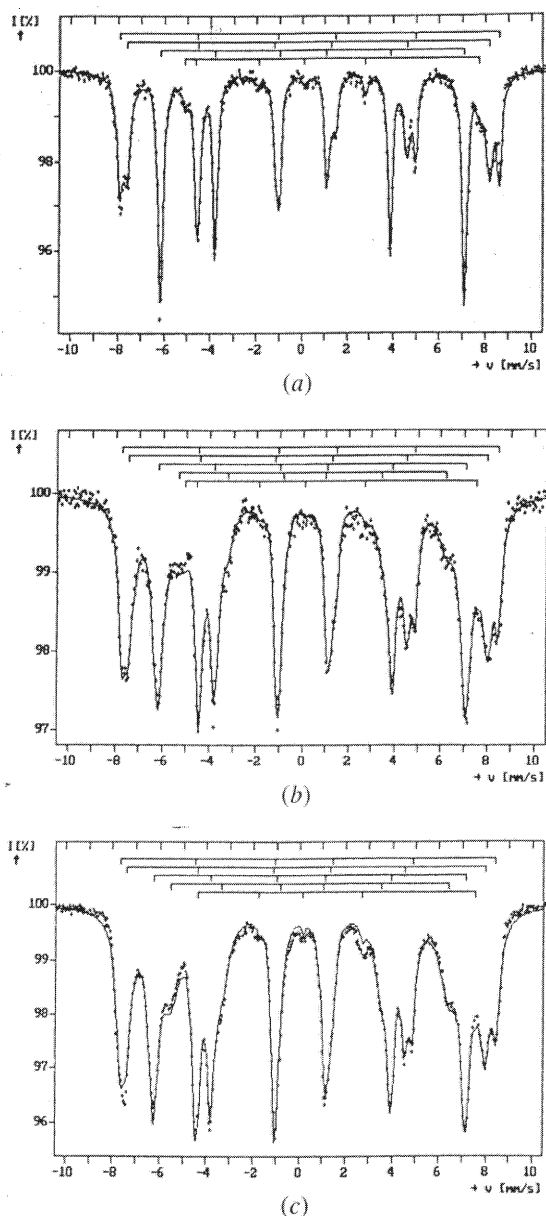


Fig. 2. The room temperature Mössbauer spectra of pure (a) and substituted $x = 0.4$ Ni - Sn (b) and Zn - Sn (c) BaM.

The Mössbauer spectra were recorded using the source ^{57}Co in Rh matrix with constant acceleration at the room temperature. The temperature dependences of the magnetic susceptibility $\chi(\vartheta)$ and the Curie

temperature T_c were measured using the bridge method in an alternating magnetic field of 360A/m and 920 Hz [11]. These dependences are very sensitive to phase composition of the specimen. They also give a good information about impurities and they detect majority of failings during ferrite preparation. The samples were heated up to 730°C at a constant rate of $4^\circ\text{C}/\text{min}$ during the $\chi(\vartheta)$ measurement. The Mössbauer spectra and the $\chi(\vartheta)$ dependences were used to determine the crystalline phases and the magnetic and chemical stability of the powdered samples. Measurement of the specific saturation magnetic polarisation J_{s-m} , remanence magnetic polarisation J_{s-r} and coercivity H_c was performed using the vibrating sample magnetometer with an external magnetic field of 540 kA/m .

3. RESULTS AND DISCUSSION

Four sextets corresponding to $4f_2$, $2a+4f_1$, $12k$ and $2b$ sites were found in the Mössbauer spectra of the pure Ba hexaferrite taken at room temperature (Fig. 2a). The spectra of substituted Ba ferrite (Fig. 2b, c) were fitted according to [12].

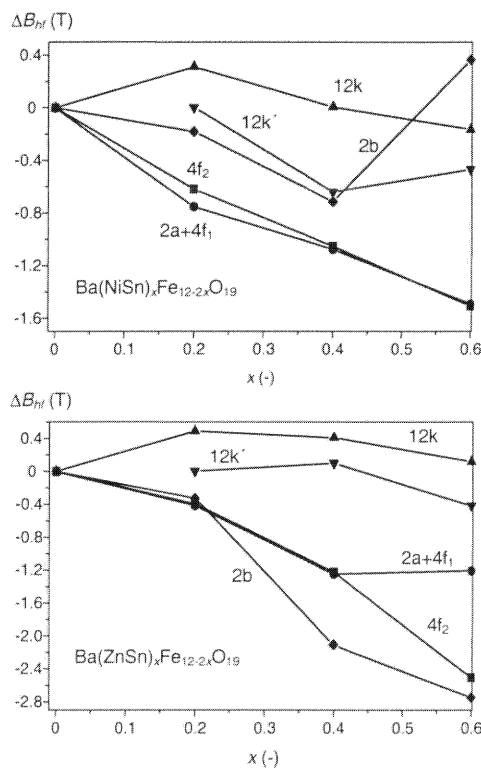


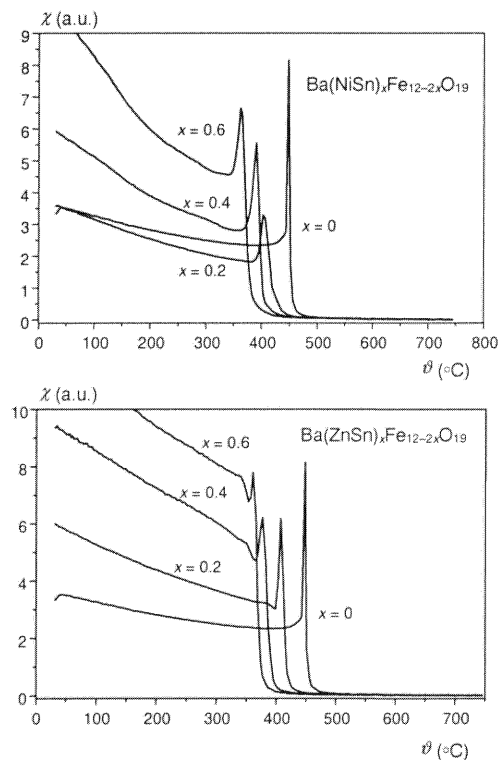
Fig. 3. ΔB_{Hf} vs. x of substituted Ba ferrites.

The intensity of each sextet is directly proportional to the number of iron ions in that site. The substitution of a part of Fe^{3+} by Zn^{2+} , Ni^{2+} and Sn^{4+} ions lead to changes in the exchange interactions between the magnetic sublattices and to the appearance of new positions of the iron ions. Therefore, the $12k$ sites can split into two non-equivalent subpatterns $12k$ and $12k'$ with increasing x . The relative area of $12k'$ increases at the expense of the disturbed $12k$ sites.

Tab. 1 The magnetic properties of $\text{BaFe}_{12-2x}(\text{Ni,Zn})_x\text{Sn}_x\text{O}_{19}$.

x (-)	J_{s-m} ($10^{-6}\text{Tm}^3\text{kg}^{-1}$)	J_{s-r} ($10^{-6}\text{Tm}^3\text{kg}^{-1}$)	H_c (kA/m)
$\text{BaFe}_{12-2x}(\text{NiSn})_x\text{O}_{19}$			
0.0	73.6	39.1	330
0.2	84.0	39.3	189
0.4	90.9	30.8	80
0.6	88.3	28.2	65
$\text{BaFe}_{12-2x}(\text{ZnSn})_x\text{O}_{19}$			
0.0	73.6	39.1	330
0.2	90.9	44.7	200
0.4	87.8	38.5	120
0.6	90.8	32.3	78

The Ni^{2+} ions would shift to octahedral 12k and $4f_2$ sites, Sn^{4+} ions to bipyramidal 2b and spinel block $2a+4f_1$ sites, whereas Zn^{2+} enter $4f_1$ sites. In all ferrites containing Ni^{2+} ions, Ni^{2+} is found to occupy octahedral site, since it has large site preference energy for symmetric octahedral site, which is 20 kcal/mol higher compared to site preference energy for tetrahedral site [13]. As it can be seen in Fig. 3a, b, a negative ΔB_{hf} slope from $x=0.0$ to 0.6 beside 12k position was observed. These changes of slope can be related to the variation in the lattice volume and grain growth [14].

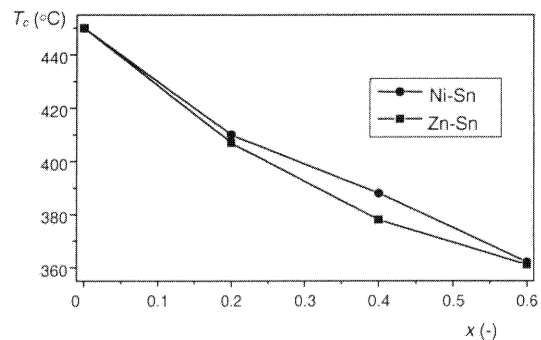
Fig. 4. Temperature dependences of magnetic susceptibility for $\text{BaFe}_{12-2x}(\text{Ni,Zn})_x\text{Sn}_x\text{O}_{19}$.

The measurement of the temperature dependence of the magnetic susceptibility $\chi(\vartheta)$ of pure Ba ferrite ($x=0.0$) shows, in the vicinity of the Curie temperature, a sharp Hopkinson peak for single phase M-hexaferrite. The $\chi(\vartheta)$ dependences show a single-phase structure for both kinds of the specimen (Ni-Sn, Zn-Sn) up to $x=0.6$,

but Hopkinson peaks are broadened and peak values fall with increasing x , Fig. 4. The initial susceptibility χ is given in arbitrary units and it is related to the same amount of the sample for all cases. Initial susceptibility χ increased with Ni, Zn, Sn substitutions at the room temperature. The Curie temperature T_c was determined from the Hopkinson's effect (Fig. 4) and it decreases with increasing of the substitution level x .

The dependences of the Curie temperature on the substitution level x are in Fig. 5. The values of T_c are slightly higher for Ni-Sn Substitution.

The contribution of noncollinear spins in the magnetic structure increases due to the replacement of Fe^{3+} ions by either nonmagnetic Zn^{2+} , Sn^{4+} or less magnetic Ni^{2+} ions. This effect causes a partial disappearance of the superexchange interactions between Fe^{3+} ions via O^{2-} ions.

Fig. 5. The Curie temperature for $\text{BaFe}_{12-2x}(\text{Ni,Zn})_x\text{Sn}_x\text{O}_{19}$.

The behaviour of the magnetic properties (Ni,Zn)-Sn substituted BaM ferrites are summarised in Table 1. The magnetic properties directly depend on the electronic configuration, electronegativity and ionic radii of the dopand cations and on their preference to occupy different Fe^{3+} sublattices of the magnetoplumbite structure [3]. Both the coercivity H_c and the specific remanence magnetic polarisation J_{s-r} (except the substitution $x=0.2$) decreased with the substitution level x . J_{s-m} slightly increased up to $x=0.4$ for both substitutions. H_c decreased from 330 kA/m down to approximately 70 kA/m, which represents 75% drop. The decrease of H_c is related to the reduction of the magneto-crystalline anisotropy field H_a , which is

attributed to the preference of the Sn^{4+} ions for the 2b sites. Vincent et al. [15] show that the uniaxial magnetic anisotropy for Zn-Ir mixtures becomes planar at lower substitutions ($x \sim 0.4$).

4. CONCLUSIONS

Ni-Sn and Zn-Sn substituted Ba hexaferrites were synthesized by citrate precursor method changing the substitution level x . The coercivity H_c could be easily controlled without a significant reduction of J_{s-m} . The Sn^{4+} ions substituted Fe^{3+} ions mainly on the bipyramidal 2b and slightly on tetrahedral $4f_1$ sites, while the Ni^{2+} ions preferred octahedral $4f_2$ and $2a+4f_1$ sites at low and high substitutions respectively. Zn^{2+} ions strongly preferred the $4f_1$ sites. The drop of ΔB_{hf} is caused by the substitution of non-equivalent Fe^{3+} positions. The 12k site splits into two sublattices 12k and 12k' with the substitution of different ions. This may be the results of changes of the neighbours of the Fe^{3+} ions on 12k site, when substitutions take place at hexagonal blocks.

J_{s-m} reached maximum at $x = 0.4$ probably due to the substitutions Sn^{4+} into $4f_1$ and less magnetic ions Ni^{2+} on $4f_2$ sites. Zn-Sn substitution effectively decreased particles size and coercivity H_c , while the value J_{s-m} remains constant.

Acknowledgement

The authors thank to VEGA Scientific Agency of Ministry of Education of the Slovak Republic, for the support given to carry out this work under the projects No. G - 1/0142/03 and G - 1/0163/03 respectively. We also thank to Dr. J. Šubrt from Czech Academy of Sciences for partial measurements of the specimens and Prof. J. Lipka from Department of Nuclear physics and technology for Mössbauer spectroscopy.

REFERENCES

- [1] Yang Z. et al., Mat. Sc. and Eng. B, 90, 1-2 (2002) 142.
- [2] Wei F. et al., Jour. Magn. Magn. Mat. 191 (1999) 249.
- [3] González -Angeles A. et al., Jour. Magn. Magn. Mat. 270 (2004) 77.
- [4] Wartewig P., et al. , Jour. Magn. Magn. Mat. 192 (1999) 83.
- [5] Mendoza - Suárez G. et al., Mat. Res. Bul. 36 (2001) 2597.
- [6] Han D. H. et al., Jour. Magn. Magn. Mat. 137 (1994) 191.
- [7] Grusková A. et al., Proc. SMM'03, conf., Düsseldorf, in press (2004)
- [8] Ong C. K. et al., Jour. Magn. Magn. Mat. 213 (2000) 413.
- [9] Mendoza - Suárez G. et al., Mat. Phys. B 339 (2003) 110.
- [10] Li Z. W. et al., Phys. Rev. B 62 No 10 (2000) 6530.
- [11] Jančárik V. et al., Jour. El. Eng. 50 (1999), 63.
- [12] Lipka J. et al., Jour. El. Eng. 45 (1994) 12.
- [13] Rane M. V. et al., Jour. Magn. Magn. Mat. 192 (1999) 288.
- [14] Rane M. V. et al., Jour. Magn. Magn. Mat. 195 (1999) L256.
- [15] Vincent H. et al., Jour. Magn. Magn. Mat. 101 (1991) 170.