ELECTROMAGNETIC PROPERTIES OF SUBSTITUTED
Ba – FERRITES BY SELECTED CATIONS

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Summary   The powdered samples of barium hexaferrite $BaFe_{12-2x}(Me_1Me_2)_xO_{19}$ with x varying from 0.0 to 0.6 were prepared by citrate precursor method. The cation preference of mainly four-valence $Me_1 = (Zr, Ti, Sn)$ or La^{3+} ions and two-valence $Me_2 = (Co, Ni, Zn)$ ions and their combinations in substituted Ba ferrites were investigated by the thermomagnetic analysis, Mössbauer spectroscopy and measurement of the magnetic properties. Mössbauer studies reveal that Zr^{4+}, Sn^{4+} and less Co^{2+}, Zn^{2+} ions have a strong preference to occupy 2b position, this position has the greatest contribution to the magnetocrystalline anisotropy. The La^{3+}, Ti^{4+}, Ni^{2+} ions preferently enter $4f_2$ sites and Zn^{2+}, Co^{2+} ions also prefer to occupy $4f_1$ tetrahedral sites. 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 coercivity H_c was easily controllable by the substitutions level x.

1.   INTRODUCTION

The M - type hexaferrites $MFe_{12}O_{19}$ (M = Ba, Sr or Pb) are extensively used for a wide range of the technological applications. To achieve the values of the various magnetic properties necessary for particular applications, either new processing method have to used to change the morphology or the chemical composition has to be changed [1]. The hexagonal Ba ferrites have been extensively studied because of their large intrinsic uniaxial anisotropy and coercivity, which makes them widely used as permanent magnets [2], microwave devices and recording media [3]. Particular attention was paid to study of the magnetic characteristics of the ferrites, in which Fe^{3+} ions are substituted by various cations. The most studied substitution is Ti-Co [4, 5], Zr-Co [6, 7], Sn-Co [8], Ir-Co [2], Zr-Ni [9], Sn-Ni [10], Sn-Zn [11] and Ti-Sn [3].

The temperature dependence of the coercivity in the range between –196°C to 227°C is for substituted Ba ferrites substantially different as for nonsubstituted ferrite. Such difference can be caused by much steeper decrease of the magnetocrystalline anisotropy field and by the magnetization reversal mechanism to change from coherent to incoherent as temperature is varied [12].

It is known that the Ni^{2+} ion reduces the temperature coefficient of coercivity (dH_c/dT), which is an important parameter for the stability of the recorded data [9]. In Zn-Sn substituted Ba ferrites, Sn^{4+} ions decrease value dH_c/dT more than other ions [13]. Zirconium salts are cheaper and more soluble than titanium salts, therefore it is suitable for wet preparation [14].

These ferrites are known to have great potential properties as tapes for perpendicular magnetic recording and, hence, higher information storage capacity [15]. Those technological applications require materials with strict control of the microstructure (such as homogeneity, particle size and shape) that govern the extrinsic magnetic behaviour.

The magnetic properties of the substituted hexaferrites strongly depend on the electronic configuration of the substituing cations as well as on their site preference among the five different Fe^{3+} sublattices of hexagonal structure, namely, tetrahedral ($4f_1$), bipyramidal (2b), and three different octahedral (12k, $4f_2$ and 2a) [16]. On the other hand, it is known that more electronegative ions prefer octahedral coordination [14]. The electronegativity of selected ions La^{3+}, Zr^{4+}, Ti^{4+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Sn^{4+} is 1.10, 1.33, 1.54, 1.65, 1.88, 1.91, 1.96, respectively. According to the ligand field [16], ions with d^1, d^2, d^3 and d^4 orbitals prefer tetrahedral and ions with d^6, d^7, d^8 and d^9 orbitals occupy octahedral positions mainly. Ions with d^0, d^5 and d^{10} orbitals have no site preference. However, the tendency to occupy a particular site depends also on the ionic radii of the ions and their partner cations.

The influence of combinations of La^{3+}, Zr^{4+}, Ti^{4+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Sn^{4+} ions with different values of the ionic radii (summarized in Tab. 1) to the magnetic properties and magnetocrystalline structure of the barium hexaferrite was investigated.

2.   EXPERIMENTAL

High purity (99%) raw materials were used for preparation of polycrystalline powder samples of $BaFe_{12-2x}(Me_1Me_2)_xO_{19}$ compounds. The hexaferrite with $x = 0.0$ to 0.6 were prepared by citrate precursor method with an initial Ba/Fe ratio 10.8 according to the method described in [6]. Finally, the powdered samples were annealed at the temperature 1050°C for 2 hours.

The Mössbauer spectra were recorded using the constant accelaration source ^{57}Co in Rh matrix at the room temperature. The temperature dependences of the magnetic susceptibility $\chi(\vartheta)$ and the Curie temperature T_c were measured by the bridge method at constant rate 4 °C/min. The magnetic parameters were determined using the vibrating sample magnetometer with an external magnetic field of 540 kA/m.

3.   RESULTS AND DISCUSSION

The temperature dependences of the magnetic susceptibility $\chi(\vartheta)$ for Co-(Ti, Zr) are shown in Fig. 1, and for Ni-(Zr, Ti, Sn) substituted Ba hexaferrite in Fig. 2a, 2b and 2c. The initial susceptibility is given in arbitrary units and it is related to the same amount of the sample (1 mg) for all dependences. The results show that the value of χ increases with substitution at room temperature. For pure samples ($x = 0.0$), a sharp

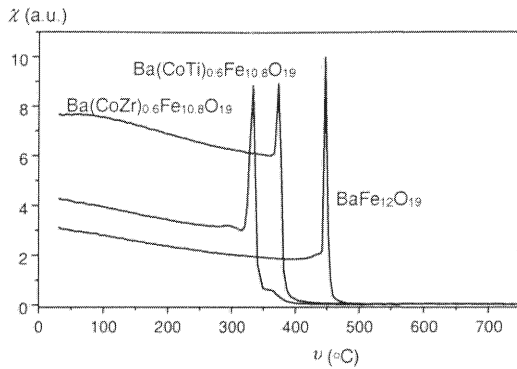Hopkinson peak near the Curie temperature indicated the single phase of the hexaferrite.

Fig. 1. The temperature dependences of the magnetic susceptibility for pure BaM and Ba(CoTi)$_{0.6}$Fe$_{10.8}$O$_{19}$ and Ba(CoZr)$_{0.6}$Fe$_{10.8}$O$_{19}$ substituted ferrite.

The dependences of Curie temperature for Co-Ti and Co-Zr substituted Ba ferrites (Fig. 1) were presented in [6]. The smaller decrease of the T_c in the case of the Co-Ti ions than Co-Zr ions can be caused by losses of the titanium at the dehydratation in ethanol during preparation procedure. The $\chi(\vartheta)$ dependences of Ni-Sn substituted BaM (Fig. 2a) show single-phase structure, but Hopkinson peaks are broadened and their peak value rise with x. This is attributed mainly to a distribution in the size and shape of the particles, whereas the $\chi(\vartheta)$ curves of the samples Ni-Ti and Ni-Zr (Fig. 2b, c) show a weak maximum, probably owing to the presence of disordering in the composition. The Curie temperatures T_c of all substitutions decreased with the substitution rate x (Fig. 3) The samples with La-Zn ions were prepared differently according to the composition Ba$_{1-x}$Fe$_{12-x}$(LaZn)$_x$O$_{19}$. The least slope of T_c for combination Zn^{2+}-La^{3+} ions may be caused by the reduction of Fe^{3+} ions by the formula $La^{3+} + Fe^{3+} \rightarrow La^{4+} + Fe^{2+}$, when a secondary phase can be produced (probably Fe$_3$O$_4$, confirmed by the reduction of the quadrupole splitting QS $\rightarrow$ 0, namely at $x = 0.6$).

The Mössbauer measurements at room temperature were described in [17] and are presented by the occupancy fractions (%). The occupancy fraction described in [18] determined the site preference of substituting ions in the Ba hexaferrites.

Values of the relative area $S(i)$ (%) were obtained from the Mössbauer spectra, when $i = 1 - 4$, (4f$_2$, 2a+4f$_1$, 12k, 2b), which correspond to the number (N) of iron ions at the respective sites of Ba ferrite, $N(i)$ is the occupation number for the i - th site.

All particular values were calculated according to following formulae

$$N_{\text{Fe}}(i) = C_{\text{Fe}} \frac{S(i)}{\sum\limits_{i=1}^{5} S(i)} \qquad (1)$$

$$N_{(\text{Co,Ni,Zn})-\text{Zr}} = N(i) - N_{\text{Fe}}(i) \qquad (2)$$

$$F_{(\text{Co,Ni,Zn})-\text{Zr}} = \left[N_{(\text{Co,Ni})-\text{Zr}}(i) / N(i) \right] \times 100\% \qquad (3)$$
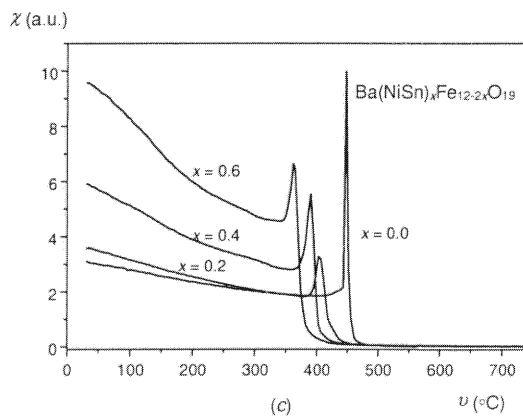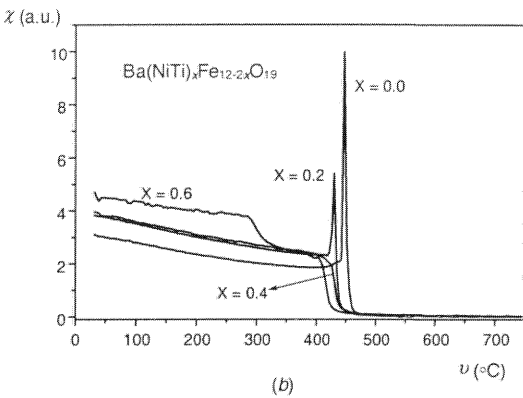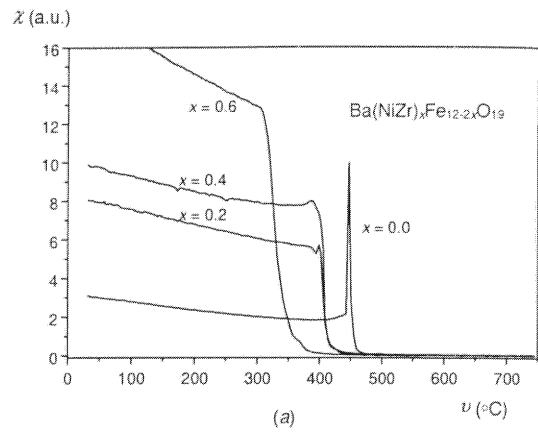

Fig. 2. The temperature dependences of the magnetic susceptibility for (Ni-Ti) (a), (Ni-Zr) (b), (Ni-Sn) (c) substituted BaNi$_x$(Ti, Zr, Sn)$_x$Fe$_{12-2x}$O$_{19}$ ferrites.
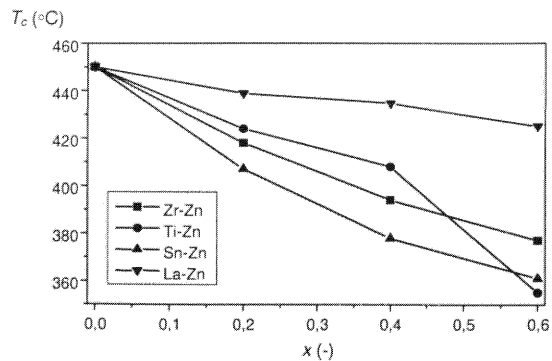

Fig. 3. The Curie temperature of substituted Ba ferrites.

where

$N_{Fe}(i)$ - the occupation number of Fe ions in the i - th site,

C_{Fe} - the initial amount of Fe ions,

$S(i)$ - the relative area at the i - th site (%),

$N_{(Co,Ni,Zn)-Zr}(i)$ - the occupation number of (Co, Ni, Zn)-Zr ions in the i - th site (the difference between occupation number of Fe ions for pure $N(i)$ and substituted $N_{Fe}(i)$ ferrites in the i - th site),

$F_{(Co,Ni,Zn)-Zr}$ (%) - value describing the site preference of substituting ions in the substituted Ba hexaferrites in the i - th site.
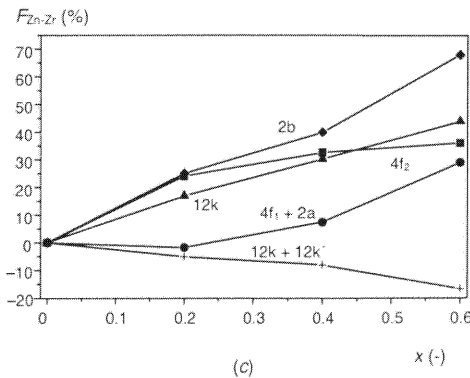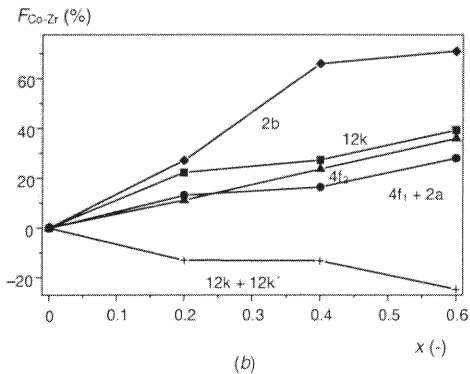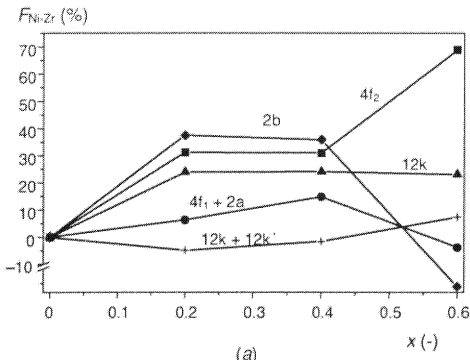

(a)

(b)

(c)

Fig. 4. The occupancy fractions for $BaZr_x(Ni, Co, Zn)_x Fe_{12-2x}O_{19}$ ferrites.

The calculated values for (Ni, Co, Zn)-Zr substituted samples are shown in Fig. 4a, b, c.

The occupancy fraction increased with substituting level for all non-equivalent positions of Fe^{3+} ions, except for 2b site of Ni-Zr samples at $x = 0.6$.

The same effect was found in [10] for samples prepared by a different preparation procedure. The results of ionic occupy preference for each position of magnetocrystalline structure for all substituted combination prepared samples are summarized in Tab. 1.

Tab. 1. The ionic preference for positions in the magnetocrystalline structure.

Ions	E	R (nm)	Preference for the Fe^{3+} positions			
			$4f_2$	$(4f_1 + 2a)$	12k	2b
La^{3+}	1.10	0.115	xxx	xx	xx	
Zr^{4+}	1.33	0.080		xx		xxx
Ti^{4+}	1.54	0.068	xxx		xx	x
Sn^{4+}	1.96	0.071		x		xxx
Zn^{2+}	1.65	0.074	xx	xxx	xx	xx
Co^{2+}	1.88	0.074	xx	xxx	xx	xx
Ni^{2+}	1.91	0.072	xxx		xx	

E – electronegativity
R – ionic radii (nm)
xxx – strong preference for site
 xx – medium preference for site
 x – slight preference for site

The magnetic properties J_{s-m}, J_{s-r} and H_c of (Ni, Co, Zn)-(Zr, Ti, Sn) substitution combined BaM ferrites up to $x = 0.6$ are in Tab. 2. The value of H_c vs. x decreases for all substitutions, while the saturation magnetization J_{s-m} slighty increases. The expressive fall of the coercivity H_c was observed for Sn-Zn and Sn-Ni substituted BaM down to $H_c = 65$ kA/m at $x = 0.6$. The temperature coefficient of the coercivity dH_c/dT was defined as $dH_c/dT = [H_c(120°C) - H_c(20°C)]/100°C$, and the coercivity was measured at 120°C and 20°C, respectively. The dependences of dH_c/dT are in Fig. 5.
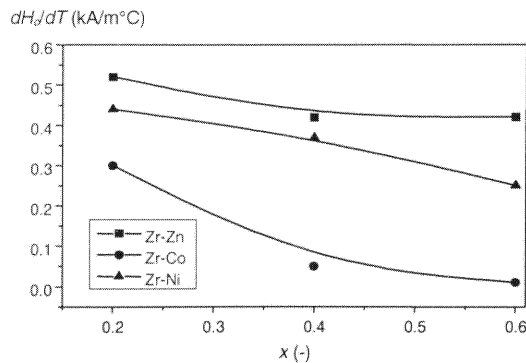

Fig. 5. The temperature dependences of dH_c/dT for $BaZr_x(Zn, Co, Ni)_xFe_{12-2x}O_{19}$ ferrites.

Tab. 2. Magnetic properties of substituted Ba ferrite.

	Zr-Co				Zr-Ni			Zr-Zn		
	0.0	0.2	0.4	0.6	0.2	0.4	0.6	0.2	0.4	0.6
J_{s-m} $(10^{-6}Tm^3\,kg^{-1})$	72.19	75.78	78.06	82.70	82.63	85.94	79.99	76.52	77.11	71.96
J_{s-r} $(10^{-6}Tm^3\,kg^{-1})$	35.57	38.90	37.19	37.99	42.76	42.28	38.24	38.26	37.84	33.89
H_c (kA/m)	376	295	205	130	254	207	190	248	219	179
	Ti-Co				Ti-Ni			Ti-Zn		
	0.0	0.2	0.4	0.6	0.2	0.4	0.6	0.2	0.4	0.6
J_{s-m} $(10^{-6}Tm^3\,kg^{-1})$	72.19	78.67	77.82	85.72	75.24	72.31	62.59	71.61	73.60	92.45
J_{s-r} $(10^{-6}Tm^3\,kg^{-1})$	35.57	41.05	39.39	40.77	39.01	37.49	29.84	30.50	29.95	37.45
H_c (kA/m)	376	294	303	165	320	254	221	304	260	95
	Sn-Zn				Sn-Ni					
	0.0	0.2	0.4	0.6	0.2	0.4	0.6			
J_{s-m} $(10^{-6}Tm^3\,kg^{-1})$	72.19	90.89	87.80	90.78	84.00	90.85	88.31			
J_{s-r} $(10^{-6}Tm^3\,kg^{-1})$	35.57	44.71	38.51	32.34	39.30	30.75	28.2			
H_c (kA/m)	376	200	120	78	189	80	65			

4. CONCLUSION

Magnetic properties and magnetocrystalline structure of $BaFe_{12-2x}(Me_1Me_2)_xO_{19}$, $Me_1 = (Zr, Ti, Sn)$ or La^{3+} ions and $Me_2 = (Co, Ni, Zn)$ ions synthesized by precursor method were investigated. Mössbauer studies show, that preference occupancy of various metal ion combinations were found. Zr^{4+}, Sn^{4+}, less Co^{2+}, Zn^{2+} ions strongly prefer 2b and then $(4f_1+2a)$ sites. The La^{3+}, Ti^{4+} and Ni^{2+} ions prefer to enter the $4f_1$ sites and slightly 12k sites. The Zn^{2+} ions also strongly prefer $4f_1$ sites.

It is possible to control the value of H_c by the substitution, which is interesting from the point of view for perpendicular magnetic recording.

The highest influence on H_c have Sn^{4+} ions from 4-valence and Zn^{2+} ions from 2-valence group. The highest change of H_c was achieved with Sn^{4+}- Ni^{2+} couple as with a combination of these groups.

Acknowledgement

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