

# PROPERTIES OF M-TYPE BARIUM FERRITE DOPED BY SELECTED IONS

Jozef Sláma<sup>\*</sup> — Anna Grusková<sup>\*\*</sup> — Mária Papánová<sup>\*\*</sup>  
Darina Kevická<sup>\*\*</sup> — Vladimír Jančárik<sup>\*</sup> — Rastislav Dosoudil<sup>\*</sup>  
Guillermo Mendoza-Suárez<sup>\*\*\*</sup> — Alvaro González-Angeles<sup>\*\*\*</sup>

The magnetic and structural properties of substituted Ba hexaferrite M-type samples with composition  $\text{BaFe}_{12-2x}(\text{Me}_1 - \text{Me}_2)_x\text{O}_{19}$ , where  $\text{Me}_1 = \text{Zn, Co, Ni}$ , and  $\text{Me}_2 = \text{Zr, Ti}$ , were compared. The powder samples with  $0.0 \leq x \leq 0.6$  were prepared by two processing routes. Different Fe/Ba ratio was used for mechanical alloying (Fe/Ba = 10.0) and for the citrate precursor method (Fe/Ba = 10.8). Magnetic properties were studied by both vibrating sample magnetometry and thermomagnetic analysis. The ferrite formation process was followed by Mossbauer spectroscopy.

**Key words:** substituted hexagonal ferrite, organometallic precursor, mechanical alloying, magnetic properties

## 1 INTRODUCTION

M-type barium hexaferrite  $\text{BaFe}_{12}\text{O}_{19}$  exhibits high-saturated magnetic polarisation  $J_s$ , strong uniaxial crystalline anisotropy and large coercivity  $H_c$ . For this reason, it is mainly utilized for the production of permanent magnets. Nevertheless, when substituting  $\text{Fe}^{3+}$  and/or  $\text{Ba}^{2+}$  ions by other metal cations or cation combinations, its great magnetocrystalline anisotropy can be diminished, which leads to its new properties for a variety of applications. Substituted barium hexaferrites are suitable for high-density perpendicular and magneto-optical recording [1], and microwave devices applications [2]. These electronical applications require a material with strict control of its properties such as magnetic parameters, homogeneity, particle size and shape, temperature dependence of the coercivity  $\Delta H_c/\Delta T$  and remanent polarization  $J_r$ .

Co-Ti mixture is one of the most studied that has demonstrated that  $H_c$  decreases (from  $\sim 360$  kA/m to  $\sim 80$  kA/m) with the increase in substitution level  $0 \leq x \leq 0.6$  without a significant reduction of magnetic polarisation [1]. Moreover, narrow switching field distribution (SFD) and excellent high-frequency response were found for this substitution [3, 4]. On the other hand, it is known, that  $\text{Ni}^{2+}$  ions reduce the temperature coefficient of coercivity ( $\Delta H_c/\Delta T$ ), which is an important parameter for the stability of the recorded data [5]. Likewise, it has been shown that  $\text{Zn}^{2+}$  ions have preference for  $4f_1$  tetrahedral sites and  $\text{Ti}^{4+}$  ions for  $4f_2$  and  $12k$  octahedral sites in BaM doped with Zn-Ti, besides, this hexaferrite possesses a positive temperature coefficient of coercivity [6]. Zn-Zr substituted barium hexaferrite nanoparticles exhibit an extraordinary high  $J_s$  at low substitutions (maximum at  $x = 0.4$ ), and a coercivity easily controllable (from

360 kA/m to 16 kA/m) [4]. Single-phase formation in Co-Zr system with the best properties was observed after calcination in a flux of NaCl at 900 °C for 4 h [7]. However, from economical point of view, Zr- salts are cheaper than those of Ti. In addition, these salts are easily soluble in water, being so even more suitable for liquid phase preparation [8].

In this paper, the effect of several metal ion combinations (Zn, Co, Ni with Zr or Ti) on the magnetic properties and magnetocrystalline structure of the barium hexaferrite was investigated. The samples were synthesized by citrate precursor method and mechanical alloying. The estimation of the influence of doping concentration on structural parameters is shown.

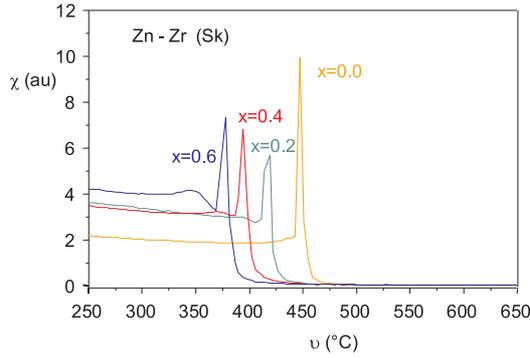
## 2 EXPERIMENTAL

Sample preparation route (1) — The preparation route, where the samples are labelled as (Mx), is as follows:  $\text{Fe}_2\text{O}_3$ ,  $\text{BaCO}_3$ , ZnO, NiO,  $\text{TiO}_2$  and  $\text{ZrO}_4$  purity ( $\sim 98\%$ ), were used as raw materials. The Fe/Ba ratio of 10 was chosen. Mechanical alloying was performed in a high-energy mill (Segvay Attritor) using a ball/powder ratio of 15. Milling was carried out for 45 h in air with an angular frequency of 400 rpm. A liquid medium (250 ml of benzene) was added to avoid agglomeration of powders at the bottom of the mill, and to assure active participation of powders in the milling process. After mechanical milling, the powders were annealed at 1050 °C for 1.5 h.

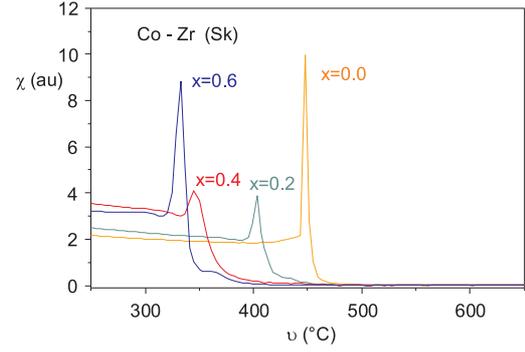
Sample preparation route (2) - samples labelled as (Sk), with high purity (99%)  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , and other reagents (*ie*  $\text{ZrOCl}_2$ , titanil acetylacetonate  $\text{TiO}(\text{acac})_2$ ,  $\text{Zn}(\text{CH}_3\text{COO})_2$ ,  $\text{Co}(\text{NO}_3)_2$  or  $\text{Ni}(\text{NO}_3)_2$ ) were used as the starting materials. In this

<sup>\*</sup> Slovak University of Technology, Faculty of Electrical Engineering and Information Technology, Department of Electromagnetic Theory, <sup>\*\*</sup> Department of Electrotechnology, Ilkovičova 3, 812 19 Bratislava 1, Slovakia, E-mail: maria.papanova@stuba.sk

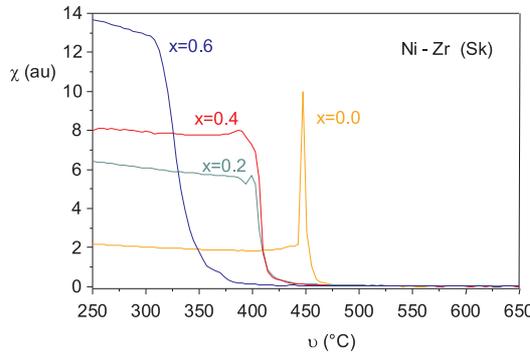
<sup>\*\*\*</sup> CINVESTAV-Salttillo-Mty Km. 13, Apdo. P.O.Box 663, 25900 Saltillo, Coah, Mexico,



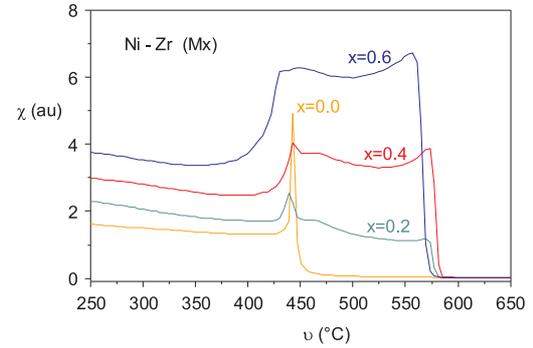
**Fig. 1.** The temperature dependences of the magnetic susceptibility for  $\text{Ba}(\text{ZnZr})_x\text{Fe}_{12-2x}\text{O}_{19}$  (Sk).



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



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



**Fig. 4.** The temperature dependences of the magnetic susceptibility for  $\text{Ba}(\text{NiZr})_x\text{Fe}_{12-2x}\text{O}_{19}$  (Mx).

case, a Fe/Ba ratio of 10.8 was optimal. An aqueous solution was prepared from dissolving  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  into deionized water, where the amount of the iron was gravimetrically determined. From this, iron hydroxide was precipitated by adding drop by drop a concentrated ammonia solution under constant stirring. A second solution was prepared by dissolving citric acid into deionized water along with the other reagents ( $\text{ZrOCl}_2$ ,  $\text{TiO}(\text{acac})_2$ ,  $\text{Zn}(\text{CH}_3\text{COO})_2$ ,  $\text{Co}(\text{NO}_3)_2$  or  $\text{Ni}(\text{NO}_3)_2$ ). 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 an excessive amount of alcohol during one hour. The finely divided precipitate was heated at  $80^\circ\text{C}$  with a soaking time of 30 min, and then filtered and dried in a vacuum oven. Afterwards, the amorphous citrate precursor was decomposed at  $360^\circ\text{C}$  for 5 hours. The samples were successively annealed at temperatures  $700^\circ\text{C}$  and  $1070^\circ\text{C}$  for 2 h in a muffle furnace.

The magnetic properties were measured on a vibrating sample magnetometer (VSM) with a maximum applied external magnetic field of 540 kA/m. The phase constitution was analyzed by Mössbauer spectroscopy using a conventional constant acceleration mode with a  $^{57}\text{Co}$  source in Rh matrix. The spectra were fitted using the NORMOS software package. The temperature dependences of the magnetic susceptibility  $\chi(\vartheta)$  were measured

by the bridge method while the samples were heated at a constant rate of  $4^\circ\text{C}/\text{min}$ .

### 3 RESULTS AND DISCUSSION

The temperature dependences of the magnetic susceptibility  $\chi$  versus temperature  $\vartheta$ , for selected substitutions  $x$  are shown in Figs. 1–4. The initial susceptibility is given in arbitrary units and is related to the same amount of sample for all cases. The  $\chi(\vartheta)$  dependences for pure  $x = 0.0$  (Mx and Sk) samples show, in the vicinity of the Curie temperature, a sharp Hopkinson peak for monophasic M-hexaferrite. For  $(\text{Me}_1\text{-Zr})$ , substituted (Sk) samples,  $\chi(\vartheta)$  up to  $x < 0.6$ , show single-phase curves (Figs. 1–3), however, the Hopkinson peaks are broadened. This is attributed mainly to a wide distribution in the shape of the particles and a spread in the composition. For Zn–Zr and Co–Zr substituted (Sk) samples,  $\chi(\vartheta)$  curves show a small maximum before the Hopkinson peak, probably owing to the disorders in the composition.

The results of curves for Ni-Zr (Mx) samples are not explicit in Fig. 4, due to both the presence of maxima below  $T_c$  of pure magnetoplumbite phase and a secondary magnetic phase with  $T_c$  of around  $560^\circ\text{C}$  which probably corresponds to a spinel phase. These results are very different from those found in Ni-Zr (Sk) samples, where the  $\chi(\vartheta)$  curves show almost a monophasic behaviour (Fig. 3).

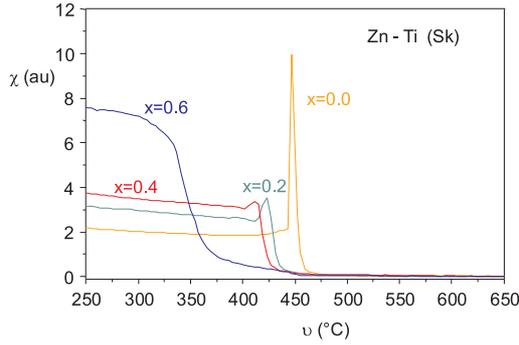


Fig. 5. The temperature dependences of the magnetic susceptibility for Ba(ZnTi)<sub>x</sub>Fe<sub>12-2x</sub>O<sub>19</sub> (Sk).

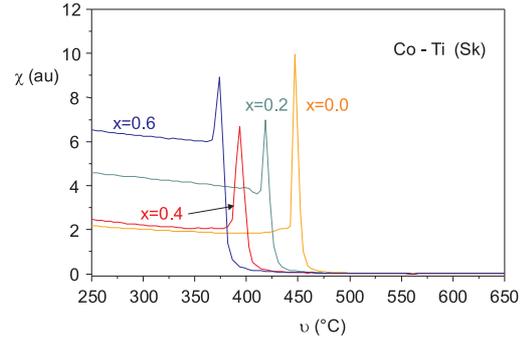


Fig. 6. The temperature dependences of the magnetic susceptibility for Ba(CoTi)<sub>x</sub>Fe<sub>12-2x</sub>O<sub>19</sub> (Sk).

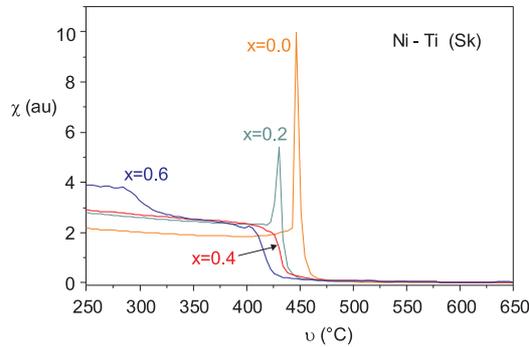


Fig. 7. The temperature dependences of the magnetic susceptibility for Ba(NiTi)<sub>x</sub>Fe<sub>12-2x</sub>O<sub>19</sub> (Sk).

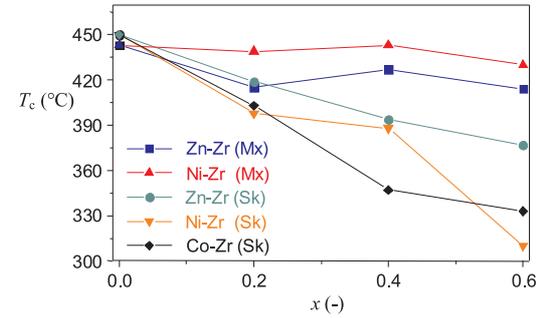


Fig. 8. Curie temperatures of substituted Ba(Me<sub>1</sub>-Zr)<sub>x</sub>Fe<sub>12-2x</sub>O<sub>19</sub> ferrites.

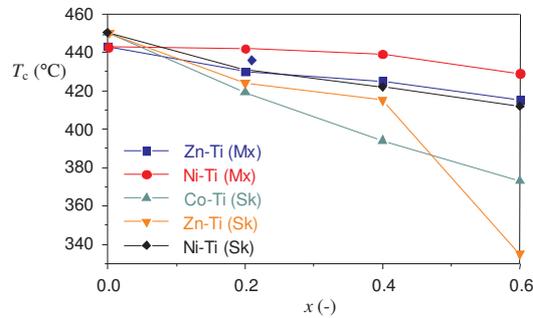


Fig. 9. Curie temperatures of substituted Ba(Me<sub>1</sub>-Ti)<sub>x</sub>Fe<sub>12-2x</sub>O<sub>19</sub> ferrite.

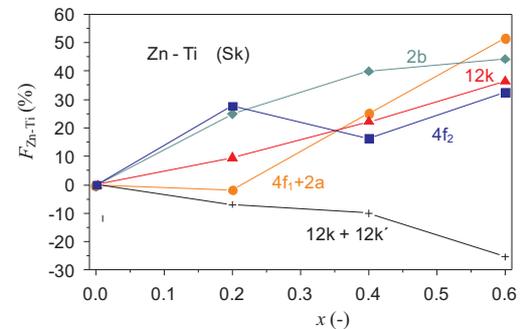


Fig. 10. Occupation fractions for Ba(ZnTi)<sub>x</sub>Fe<sub>12-2x</sub>O<sub>19</sub>, (Sk).

Figures 5, 6 and 7 show the  $\chi(\vartheta)$  dependences for substituted (Me<sub>1</sub>-Ti) (Sk) samples (where Me<sub>1</sub> = Zn, Co, Ni). One can observe single-phase curves for all (Me<sub>1</sub>-Ti) substituted samples except for Ni-Ti substitution  $x = 0.6$ . It could be observed that the Hopkinson peaks appeared for all Co-Ti substitutions.

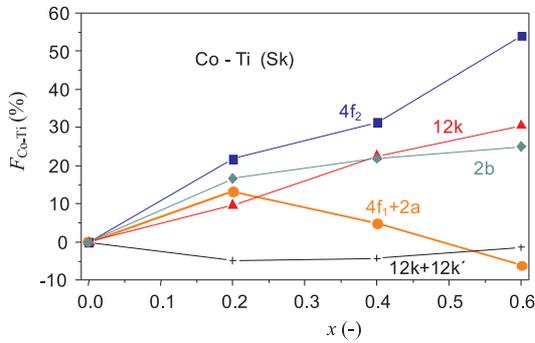
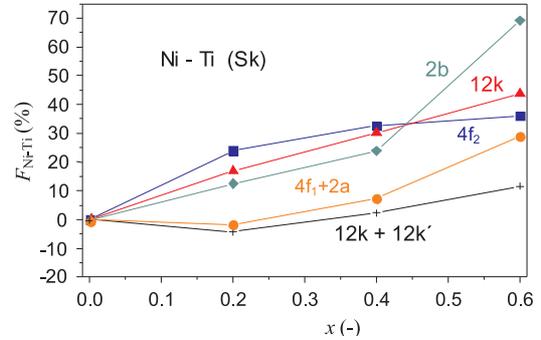
It is important to notice that  $\chi(\vartheta)$  curves measured for (Me<sub>1</sub>-Zr) substitutions had roughly similar behaviour like those for (Me<sub>1</sub>-Ti) substitutions (Sk) samples. One could also see a smaller decrease of  $T_c$  for Co-Ti mixtures than that for Co-Zr substitutions, probably caused by the deficiency in building in of titanium from the Co-Ti substituents in the hexagonal structure for (Sk) samples. This could be a result of the presence of dissolved tita-

nium ions in ethanol used for the ferrite preparation. The  $\chi(\vartheta)$  curves for Ni-Zr (Mx) samples presented multiphase system (Fig. 4) and the same behaviour have the Ni-Ti (Mx) samples. It confirms the  $T_c$  vs.  $x$  curves (Figs. 8 and 9), whose changes of  $T_c$  values with substitutions are negligible.

These substitutions are no explicit, due to presence of maxima below  $T_c$  of pure Ba ferrite and second magnetic phases with  $T_c$  about 560 °C–580 °C. The values of ordering temperatures  $T_c$  were obtained from the maximum of the  $\chi(\vartheta)$  curve. The  $T_c$  of all substitutions for (Me<sub>1</sub>-Zr) systems decreased with the substitution rate (Fig. 8). The highest  $T_c$  values versus substitution  $x$  were obtained for Ni-Zr substituted (Mx) samples. In Fig. 9,

**Table 1.** Magnetic properties of substituted Ba ferrites.

$x$	(-)	$J_{s-m}$ ( $10^{-6}\text{Tm}^3\text{kg}^{-1}$ )	$J_{s-r}$ ( $10^{-6}\text{Tm}^3\text{kg}^{-1}$ )	$H_c$ (kA/m)		$J_{s-m}$ ( $10^{-6}\text{Tm}^3\text{kg}^{-1}$ )	$J_{s-r}$ ( $10^{-6}\text{Tm}^3\text{kg}^{-1}$ )	$H_c$ (kA/m)
Zn-Zr				Zn-Ti				
0.0	(Mx)	80.77	42.91	350	(Mx)	80.77	42.91	350
0.2	(Mx)	75.57	39.13	207	(Mx)	79.78	40.62	291
0.4	(Mx)	67.65	31.55	148	(Mx)	78.68	40.35	208
0.6	(Mx)	71.89	33.88	155	(Mx)	76.15	36.96	169
0.0	(Sk)	72.19	35.57	376	(Sk)	72.19	35.57	376
0.2	(Sk)	76.52	38.26	248	(Sk)	71.61	30.5	304
0.4	(Sk)	77.11	37.84	219	(Sk)	73.60	29.95	260
0.6	(Sk)	71.96	33.89	179	(Sk)	92.45	37.45	95
Ni-Zr				Ni-Ti				
0.0	(Mx)	80.77	42.91	350	(Mx)	80.77	42.91	350
0.2	(Mx)	75.06	38.47	215	(Mx)	75.79	39.96	246
0.4	(Mx)	72.46	35.37	152	(Mx)	73.28	36.75	208
0.6	(Mx)	69.95	31.77	127	(Mx)	71.97	33.50	175
0.0	(Sk)	72.19	35.57	376	(Sk)	72.19	35.57	376
0.2	(Sk)	82.63	42.76	254	(Sk)	75.24	39.01	320
0.4	(Sk)	85.94	42.28	207	(Sk)	72.31	37.49	254
0.6	(Sk)	79.99	38.24	190	(Sk)	62.59	29.84	221
Co-Zr				Co-Ti				
0.0	(Sk)	72.19	35.57	376	(Sk)	72.19	35.57	376
0.2	(Sk)	75.78	38.90	295	(Sk)	78.67	41.05	294
0.4	(Sk)	78.06	38.19	205	(Sk)	77.82	39.39	303
0.6	(Sk)	82.70	37.99	130	(Sk)	85.72	40.77	165

**Fig. 11.** Occupation fractions for  $\text{Ba}(\text{CoTi})_x\text{Fe}_{12-2x}\text{O}_{19}$ , (Sk).**Fig. 12.** Occupation fractions for  $\text{Ba}(\text{NiTi})_x\text{Fe}_{12-2x}\text{O}_{19}$ , (Sk).

one can see that  $T_c$  for all substitutions (Me<sub>1</sub>-Ti) system also decreased with the substitution rate.

The highest  $T_c$  values versus  $x$  were observed for Ni-Ti substituted (Mx) samples, since these ferrite systems are disordered and contain additional spinel phase with higher  $T_c$  than that of hexaferrite.

The magnetic properties of substituted BaM ferrites up to a substitution  $x = 0.6$  were measured according to the method explained in [9] and are summarized in Table 1. The values of  $J_{s-m}$  vs.  $x$  decreased for (Mx) samples whilst for (Sk) samples increased except for Zn-Zr, Ni-Zr at  $x = 0.6$  substitutions. The Ni-Ti substitution had a maximum at  $x = 0.2$  and then decreased. The reduction of  $J_{s-m}$  at higher substitution levels can be ex-

plained by assuming that the magnetic collinearity will gradually break down after doping with non-magnetic cations.

The  $H_c$  vs  $x$  behaviour decreases in all substitution rates for both (Mx) and (Sk) samples. The occupation fractions  $F$  (%) were calculated from the relative areas  $S$  (%) and for pure BaM sample we can estimate it as a superposition of four subspectra ( $4f_2$ ,  $4f_1 + 2a$ ,  $12k$  and  $2b$ ). The occupation fractions for  $\text{Ba}(\text{NiTi})_x\text{Fe}_{12-2x}\text{O}_{19}$ , (Sk) samples (Fig. 12.) were calculated.

For substituted Ba ferrites,  $12k$  positions splits into ( $12k$  and  $12k'$ ), from which  $12k'$  has the smallest hyperfine field  $\sim 36\text{ T}$ . The values of relative area  $S$  (%) correspond to the number of iron ions ( $N$ ) at respec-

tive sites. The occupation fractions of substituted ions  $(F)_{sub}$  for  $BaFe_{12-2x}(Me_1-Ti)_xO_{19}$  samples on the five sites (Figs. 10–12) were estimated according to the formula:  $F_{sub}(i) = [N_{sub}(i)/N(i)]x100\%$  [4]. From the figures, it can be seen that the sites were more substituted for  $2b$ ,  $4f_2$  and  $12k$  for all types of samples.

#### 4 CONCLUSIONS

The magnetic properties  $J_{s-m}$ ,  $J_{s-r}$ , and  $H_c$  for samples (Mx) of  $(Me_1-Me_2)$  prepared by mechanical alloying decreased in all concentration rates. Whereas the  $J_{s-m}$  of  $(Me_1-Me_2)$  samples (Sk) prepared by citrate precursor method increased except to Zn–Zr and Ni–Zr substitutions at  $x = 0.6$ . The substitutions Ni–Ti show a maximum at  $x = 0.2$ .  $H_c$  decreases in all substitution levels for (Sk) samples. The  $\chi(\vartheta)$  curves showed, that (Sk) samples were monophasic in all cases, whilst (Mx) samples with substitutions Ni–Ti and Ni–Zr showed secondary phases. The values of Curie temperature,  $T_c$  decrease faster for (Sk) samples with substitution  $x$  than for (Mx) samples. The lower diminution in the  $T_c$  was due to the presence of the secondary magnetic phase observed in Ni–Zr and Ni–Ti substituted (Mx) samples.

Mössbauer studies show that the preference occupy of the metal ions combinations were as follows:

(Sk) samples:

$Co^{2+} - (4f_1 + 2a)$ ,  $2b$ ,  $4f_2$  and  $12k$

$Ni^{2+} - 4f_2$  and  $12k$        $Zn^{2+} - 4f_1$ ,  $2b$ ,  $4f_2$  and  $12k$

$Ti^{4+} - 4f_2$  and  $12k$        $Zr^{4+} - 2b$  and  $4f_1$

(Mx) samples:

$Zn^{2+} - 4f_1$        $Ni^{2+} - 4f_2$  and  $12k$

$Ti^{4+} - 12k$  and  $4f_2$        $Zr^{4+} - 2b$  and  $4f_1$

The optimal values of  $H_c$  and  $J_{s-m}$ , suitable for magnetic recording media were reached for Co–Zr substitution of (Sk) samples at  $x = 0.6$ . Prospectively, these materials can be important as well as fillers in microwave absorbers of the ferrite — polymer composites.

#### Acknowledgement

The work has been supported by VEGA under projects No. G-1/0163/03 and 1/0142/03. Authors wish to acknowledge CONACyT – Mexico under project J28283U for the support. We also thank Ing. I. Tóth from FEI STU for the measurements on the Mössbauer spectrometer.

#### REFERENCES

- [1] BATLLE, X.—OBRADORS, X.—RODRIGUEY-CARVAJAL, J. *et al*: J. Appl. Phys. **70** No. 3 (1991), 1614.
- [2] KREISEL, J.—VINCENT, H.—TASSET, F. *et al*: J. Mag. Mat. **213** (2000), 262.
- [3] ZHOU, Z. X.—MORRISH, A. H.—LI, Z. W. *et al*: IEEE Trans. on Magn. **27** (1991), 4654.
- [4] LI, Z. W.—ONG, C. K.—YANG, Z. *et al*: Phys. Rev. B **62** No. 10 (2000), 6530.
- [5] RANE, M. V.—BAHADUR, D.—KULKARNI, S. D.: J. Mag. Mat. **195** (1999), 256.

- [6] WARTEWING, P.—KRAUSE, M. K.—ESQUINAZU, P. *et al*: J. Mag. Mat. **192** (1999), 83.
- [7] CHIN, T. S.—HSU, S. L.—DENG, M. C.: J. Mag. Mat. **120** (1993), 64.
- [8] RANE, V. M.—BAHADUR, D.—MANUAL, S. K. *et al*: J. Mag. Mat. **153** (1996), L1.
- [9] DOSOUDIL, R.: J. Elec. Eng. **53** No. 10/s (2002), 135.

Received 3 June 2004

**Jozef Sláma** (Prof, Ing, PhD) — graduated from the Faculty of Electrical Engineering, Slovak Technical University, Bratislava, in Solid state Physics branch, 1963 and received the PhD degree in Theory of Electromagnetism in 1969. At present, he is a Professor at the Department of Electromagnetic Theory, Faculty of Electrical Engineering and Information Technology (FEEIT). His research activities are mainly experimental physics of magnetism, research of ferromagnetic domains, magnetization processes, losses and the permeability phenomena.

**Anna Grusková** (Doc, Ing, PhD) — graduated from Faculty of Chemical Technology, Slovak Technical University, Bratislava in Electrochemistry Branch in 1966 and received the PhD degree in Electrochemistry in 1986. At present, she is an Associate Professor at the Department of Electrotechnology FEEIT. Her research activities are mainly soft and hard ferrites, and ferrite-polymer composite materials.

**Mária Papánová** (Ing) — graduated from FEEIT, Slovak University of Technology, Bratislava in 2001, at Department of Electrotechnology. At present, she is a PhD student at the Department of Electrotechnology FEEIT.

**Darina Kevická** (RNDr) — graduated from the Faculty of Natural Sciences, Comenius University, Bratislava in Analytical Chemistry Branch, in 1983. At present, she is a PhD student at the Department of Electrotechnology FEEIT.

**Vladimír Jančárik** (Doc, Ing, CSc) — graduated from Faculty of Electrical Engineering, Slovak Technical University, Bratislava in Solid State Physics branch, 1988 and received the CSc (PhD) degree in Theory of Electromagnetic Field Theory in 1996. At present, he is an Associate Professor at the Department of Electromagnetic Theory FEEIT. His research activities are mainly ferromagnetic domains, losses and the permeability phenomena.

**Rastislav Dosoudil** (Ing, PhD) — graduated from FEEIT, Slovak University of Technology, in Bratislava, in Material Engineering branch, 1993 (technology of electronic equipments) and received the PhD degree in Theory of Electromagnetism in 2000. At present, he is an Assistant Professor at the Department of Electromagnetic Theory. His research activities are mainly ferrite-polymer composite materials, complex permeability phenomena and magnetic measurements.

**Guillermo Mendoza-Suárez** — received a Bachelors degree in Physics from UMSNH-Mexico in 1990 and PhD from the Department of Materials Engineering at University of Sheffield, UK. Currently is with Research Scientist at Cinvestav-Salttillo, Mexico. His research activities are mainly concerned with magnetic ceramics and nanocomposite structures.

**Alvaro GonzálezAngeles** — currently PhD student at Cinvestav-Salttillo, Mexico. His research activities are mainly concerned with magnetic ceramics and nanocomposite structures.