

STUDY OF Sr AND Ba HEXAFERRITE PREPARED BY LOW TEMPERATURE AUTO-COMBUSTION METHOD

Vladimír Jančárik* — Anna Grusková* — Jozef Sláma* — Rastislav Dosoudil*

Abstract: Thermomagnetic analysis – temperature dependence of initial magnetic susceptibility $\chi(T)$ was used as main method of study of Ba and Sr ferrites. Mössbauer spectroscopy as well as temperature dependence of saturation polarization are also presented as supporting methods. Ferrite samples were prepared by various methods – ceramic, citrate precursor and low-temperature combustion. Magnetic properties as specific saturation and remanent magnetic polarization and coercivity were compared.

Keywords: magnetization characteristic, magnetic susceptibility, Curie temperature, Mössbauer spectrum, hexagonal ferrite

1 INTRODUCTION

Strontium (Sr) and barium (Ba) M-type hexaferrites ($\text{SrFe}_{12}\text{O}_{19}$) and ($\text{BaFe}_{12}\text{O}_{19}$) are extensively used as hard magnetic materials due to their relatively high coercivity. Hexaferrites have high anisotropy field ($H_a = 1.353 \text{ MA}\cdot\text{m}^{-1}$) compared to other hard magnetic materials. They are convenient for permanent magnets, high-density magnetic and magneto-optical recording with higher signal-to-noise ratio. Other possible application is for microwave circuits because of their high resistivity and permittivity at high frequency. Their preparation is relatively cheap, they exhibit corrosion resistance and good chemical stability [1]. Theoretical value of coercive field $jH_c = 533.169 \text{ kAm}^{-1}$ was estimated for Ba ferrite [2] and critical size of single-domain insulated spherical particles was predicted to $0.5 \mu\text{m}$ [3].

Ferrites with particle size around $1 \mu\text{m}$ can be produced by standard ceramic technology. Ba ferrites with average particle size approx. $0.1 \mu\text{m}$ can be obtained by heating treatment of chemically coprecipitated precursor. Such particles are near single-domain size. Therefore the coercivity can be considerably higher – typically $437 - 477 \text{ kAm}^{-1}$ than of those prepared by ceramic method. The particles are relatively free of defects and hence the possibility of the inverse nucleation centres formation is reduced. The coercivity $jH_c = 510 \text{ kAm}^{-1}$ near to theoretical limit has been reported when a chemical etching by HCl was performed [4]. It can be explained by considering that the acid preferentially reduces the surface defects and the edges of the grains. It reduces the surface demagnetising fields i.e. reduces nucleation of closing domains.

Hexagonal ferrites can be prepared by various processing techniques, especially by ceramic [3, 5], various wet methods [1, 2, 4] and [6-10] or mechanochemical processing [11]. Following preparation methods were used for samples analysed in this paper – ceramic method, citrate precursor method and low-temperature combustion synthesis. Three methods were used for evaluation of properties of the prepared ferrites – measurement of the temperature dependence of magnetic susceptibility, measurement of magnetization characteristics (hysteresis loops) using the vibration magnetometer and Mössbauer spectroscopy.

Measurement of the temperature dependence of magnetic susceptibility $\chi(T)$ was used as main method of analysis.

2 EXPERIMENTAL

2.1 Thermomagnetic analysis

Temperature dependence of magnetic susceptibility $\chi(T)$ is very sensitive to the phase composition of the ferrites. Beside other methods of analysis, it can give a useful information about the iron phase composition and magneto-crystalline structure of the ferrite sample. Such thermomagnetic analysis is usually more sensitive to find small amount of extraneous phases in the sample than the Mössbauer spectroscopy. Moreover, measurement of $\chi(T)$ dependence is cheaper than Mössbauer spectroscopy and it takes less time than recording the Mössbauer spectrum. However $\chi(T)$ dependence sometimes does not detect presence of some magnetic phases, for example in the case of hematite particles.

It is better to determine the Curie temperature from $\chi(T)$ dependence than from the temperature dependence of saturation polarization $J_S(T)$. The saturation polarization J_S is given by a difference of sublattices polarization with temperature dependence close to Brillouin function, while the susceptibility χ can be expressed by the formula

$$\chi = \frac{J_S^2}{A_{\text{eff}}} \approx \frac{J_S}{H_a}, \quad (1)$$

where J_S is saturation polarization, A_{eff} is effective energy of anisotropy and H_a is the anisotropy field. Because both $J_S(T)$ and $H_a(T)$ decrease with increasing temperature T , this competition may result in a maximum in the $\chi(T)$ dependence – the Hopkinson peak.

Starting from the room temperature, $\chi(T)$ decreases due to decreasing of saturation magnetization J_S (Fig. 1). At the critical temperature $T_k \sim 410 \text{ }^\circ\text{C}$ this decrease changes to a strong increase starting in a local minimum of $\chi(T)$ due to $J_S(T)/H_a(T)$ increasing, although both J_S and H_a still decrease.

*Slovak University of Technology, Faculty of Electrical Engineering and Information Technology, Ilkovičova~3, 812~19~Bratislava~1, Slovakia, E-mail: vladimir.jancarik@stuba.sk

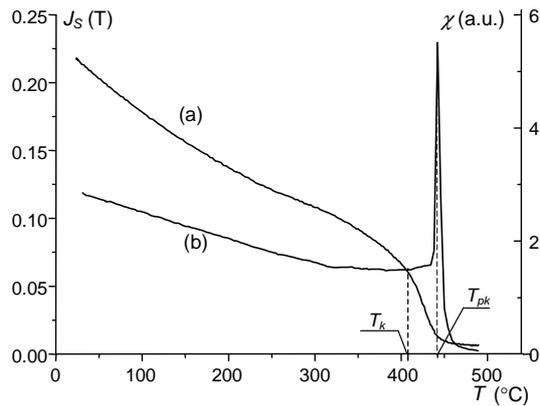


Fig. 1. Temperature dependences of saturation polarization $J_s(T)$ (a) and initial susceptibility $\chi(T)$ (b) of strontium ferrite.

All particles are magnetically stable (blocked) at temperature $T < T_k$. Probably at the temperature T_k the content of superparamagnetic particles increase in our case. The critical volume V_p of superparamagnetic particles at zero field H may be determined by a thermodynamic balance relationship

$$kT \approx J_s(T) H_a(T) V_p(T). \quad (2)$$

A mixture of both types of particles – stable and superparamagnetic – arise at the temperature $T > T_k$. Susceptibility increases when changing from the stable to the superparamagnetic state and the $\chi(T)$ dependence exhibits a sharp Hopkinson peak at the temperature $T_{pk} \sim 440$ °C. At this temperature, major part of particles is superparamagnetic and H_a approaches zero, so the height of the Hopkinson peak is several times larger than the value of $\chi(T)$ in the local minimum at T_k . At the Curie temperature $T_C \sim 450$ °C the susceptibility strongly decreases to zero because spontaneous magnetization vanishes ($J_s \rightarrow 0$) and the system becomes to be paramagnetic.

Several ways are commonly used for finding Curie temperature T_C from the $\chi(T)$ dependence:

- Temperature responding to the point of inflexion.
- Temperature responding to the cross-section of tangents to $\chi(T)$ dependence at point of inflexion with the temperature axis.
- Temperature responding to the Hopkinson's peak, if any.
- Temperature at which the susceptibility value is almost zero.

Automated system was used for measurement of temperature dependence $\chi(T)$ of the initial susceptibility [12]. Software was created for processing of the measured curves. Attention was focused on unambiguous algorithm of Curie temperature determination from point of inflexion mainly. It is important in order to make the results comparable between various samples.

The point of inflexion is found by a numerical procedure in case (a). Measured points of the $\chi(T)$ curve are fitted by natural cubic splines around the expected Curie temperature and the temperature at which

$$\frac{\partial^2 \chi(T)}{\partial T} = 0 \quad (3)$$

is found. Because this condition is usually valid at several points within the analysed region, the point it taken into account at which the slope is maximum

$$\left| \frac{\partial \chi(T)}{\partial T} \right| \rightarrow \max. \quad (4)$$

The results (a) and (b) are almost the same because the $\chi(T)$ dependence is usually steep near Curie temperature and the difference can be less than measurement uncertainty and inhomogeneity of sample temperature. However, Curie temperatures found by this way are comparable only if the shape of the analysed curves are of similar shape around the drop. When the ferrite sample contains more phases and several drops appear in the $\chi(T)$ dependence, point of inflexion for each drop brings adequate information about corresponding magnetic phases. The results obtained by the procedure (d) are usually too uncertain.

2.2 Methods of ferrite preparation

Two steps are necessary for preparation of hexagonal ferrite. In the first step, homogeneous mixture is prepared from the raw starting materials strontium - or barium - and iron-inorganic compounds by pre-sintering. In the second step, the calcinate is treated by heating to achieve ordered ferrite structure.

The ceramic method is widely used for preparation of M - type hexaferrites. The drawback of the ceramic method is the necessity of the high-temperature annealing to build the hexagonal structure in the solid solution (in our case 1320 °C/2h). This processing yields large-size ferrite particles (approximately 10 μm) improper for our application.

Water solution of the raw strontium or barium and iron salts with organic solution is used for preparation of the ferrite by wet method. The homogeneity of the liquid solution is better than mechanically milled mixture in ceramic method, therefore the lower temperature is necessary to build the homogeneous ferrite powder with magnetoplumbite structure.

Two ways of ferrite preparation from gel was used in our case – cumulative annealing and low-temperature autocombustion.

The raw mixture containing strontium or barium and iron soluble in water nitrates and citric acid was dehydrated. Solvent was removed from citrate complex by pouring the solution into excessive amount of alcohol and then the amorphous citrate precursor was decomposed. The product was then cumulatively annealed, only the temperatures 700 °C and 1050 °C was enough to build the hexagonal structure. In our conditions, only small amount of the ferrite (tens of grams) was possible to prepare by this method. Therefore, low-temperature auto-combustion method was used for preparation of higher amount of hexaferrite (up to 1 kg). Glycine was used as organic component in the amorphous precursor. It burns at low temperature and no solid residues remain after the combustion process. Annealing at 750 °C was sufficient to reach or-

dered hexagonal structure in the ferrites prepared by this method.

3 RESULTS AND DISCUSSION

Temperature dependences of magnetic susceptibility $\chi(T)$ of Sr ferrite (SrF) and Ba ferrite (BaF) samples prepared by ceramic method are in Fig. 2.

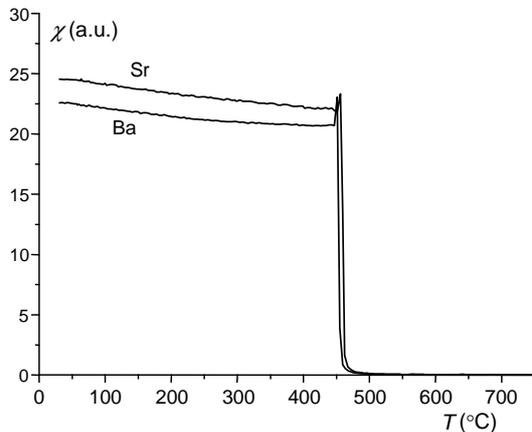


Fig. 2. Temperature dependences of $\chi(T)$ of Sr and Ba ferrite samples, prepared ceramic method, annealed at 1320°C/2h.

These dependences exhibit strong drop at temperature 450 °C with small indication of Hopkinson's peak. Curie point at the temperature 459 °C for Sr ferrite and 453 °C for Ba ferrite were determined. Particles of Ba and Sr ferrites prepared by the ceramic technology are large and multi-domain, which is caused by large annealing temperature (1320 °C/2h). It implies small coercive field H_C (below 100 kAm⁻¹) as shown in Tab. 1 and also higher value of the susceptibility χ at room temperature. $\chi(T)$ dependences of Sr and Ba ferrite samples prepared by citrate precursor method with the cumulatively annealing up to 1050°C/2h are in Fig. 3.

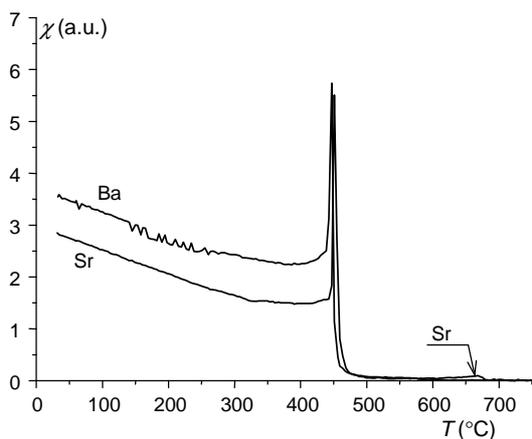


Fig. 3. Temperature dependences of $\chi(T)$ of Sr and Ba ferrite samples, prepared citrate precursor method, annealed at 1050°C/2h.

They correspond to the single-phase composition with local minimum and the expressive Hopkinson's peaks are at the temperature 457 °C (SrF) and 450 °C (BaF). Such behavior is due to occurrence of the ordered single-phase structure with

particles smaller than 1 μm. It is proved by relatively high value of H_C (Tab. 1).

$\chi(T)$ dependences of Sr hexaferrite samples prepared by the combustion synthesis are in Fig. 4. Immediately after the first step a mixture of the iron oxides arose, containing the maghemitized magnetite mainly (a). After the annealing at 750 °C/3h, uniform particles with hexagonal structure appear, as indicated by excessive Hopkinson's peak at temperature 455 °C (b). Composition of this annealed sample was verified by Mössbauer spectrum (Fig. 5). It was resolved as superposition of subspectra (4f₂, 2a, 4f₁, 12k and 2b) [13]. The relative areas S(%) of all subspectra (14.1 %, 9.9 %, 21.4 %, 48.3 % and 6.3 %) show the ordered magnetic structure of Sr ferrite.

In the case of small ferrite particles with the size below 1 μm they can be assumed as non-interacting uniaxial, single-domain and disordered. According to the Stoner-Wohlfarth theory, the intrinsic coercivity H_C resulting from coherent rotation of magnetization can be then estimated for by the formula

$$H_C = C \cdot \left[\frac{2K_1}{J_s} - N \cdot J_s \right], \quad (5)$$

where K_1 and N are the first anisotropy constant and demagnetization factor of particles, C is dimensionless constant of material. In such case, the value of coercivity is high and susceptibility is low as proved by the measurements.

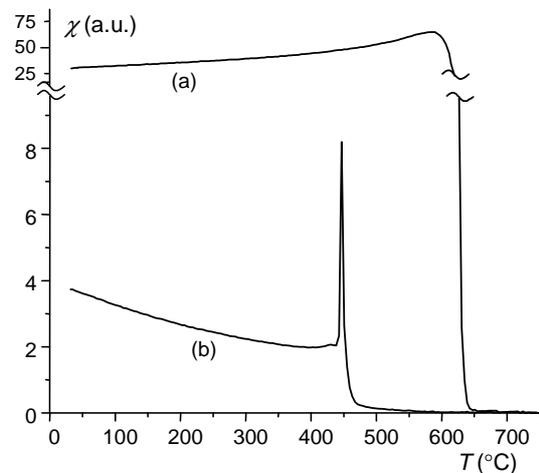


Fig. 4. Temperature dependences of $\chi(T)$ of Sr ferrite prepared by combustion synthesis without annealing (a), annealed at 750°C/3h (b).

The values of specific saturation and remanent magnetic polarization (J_{s-m} and J_{s-r}) and of coercivity H_C of SrF and BaF prepared by ceramic method (1), citrate precursor (2) and combustion synthesis (3) are in Tab. 1. They were measured by vibrating magnetometer [14]. The maximum values of J_{s-m} and J_{s-r} are for SrF and BaF (2) and maximum value of H_C is for SrF (3). The grain size of samples (1) was approx. 10 μm, samples (2) and (3) below 1 μm.

Coercive field H_C of samples prepared by citrate precursor method was by 33 % (SrF) and 11 % (BaF) less than of heat-treated chemically co-precipitated ferrites

(particle size 0.1 μm), [2]. However, H_C of the Sr ferrite prepared by low-temperature combustion synthesis and then annealed was less by 8.9 %. Such value is less by 25 % only than the theoretical value.

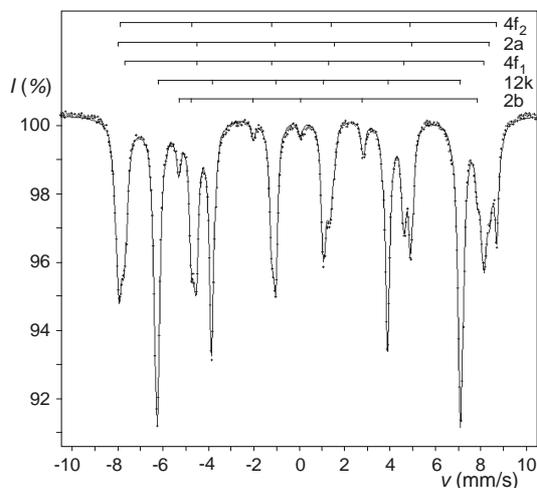


Fig. 5. Mössbauer spectrum for Sr ferrite sample prepared combustion synthesis, annealed at 750°C/3h.

Table 1. Magnetic properties of Sr and Ba ferrites prepared various methods.

Sample	J_{s-m} ($\text{mT}\cdot\text{cm}^3\cdot\text{g}^{-1}$)	J_{s-r} ($\text{mT}\cdot\text{cm}^3\cdot\text{g}^{-1}$)	H_c ($\text{kA}\cdot\text{m}^{-1}$)	Particle size (μm)
SrF (1) 1320°C/2h	75.09	35.76	95	~ 10
BaF (1) 1320°C/2h	73.32	31.88	89	~ 10
SrF (2) 1050°C/2h	91.87	56.61	296	< 1
BaF (2) 1050°C/2h	89.86	52.05	391	< 1
SrF (3) no anneal.	67.73	24.01	30	—
SrF (3) 750°C/3h	71.98	42.85	401	< 1

note: $H_m = 755 \text{ kA}\cdot\text{m}^{-1}$; (1) ceramic method, (2) citrate precursor, (3) combustion synthesis

4 CONCLUSIONS

Temperature dependence of magnetic susceptibility was used as a method of hexagonal ferrites properties evaluation. It can bring good information about the magnetic phase composition. Because susceptibility is dependent on magnetization process of the particles, it is influenced by ferrite particles shape, size and anisotropy.

Annealing 750 °C/3h was enough to achieve ordered hexagonal structure of Sr and Ba ferrite samples prepared by the low-temperature combustion synthesis.

High coercivity and excessive Hopkinson peak appear with monodomain particles of size below 1 μm .

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-1/3096/06 and G-1/3189/06, respectively. We also thank to V. Žvak from the TAUCHEM Ltd. company as well as M. Ušáková for the effort with preparation of ferrite samples and I. Tóth for measurement of Mössbauer spectra.

REFERENCES

- [1] HUANG, J. – ZHUANG, H. – LI, W.: Mater. Res. Bull. 38 (2003), pp. 149.
- [2] HANEDA, K. – MIYAKAWA, Ch. – KOJIMA, H.: J. Am. Ceram. Soc. 57, 8 (1974), pp. 354.
- [3] RATHENAU, G. W. – SMIT, J. – STUIJTS, A. L.: Z. Phys. 133 (1952), pp. 250.
- [4] ROOS, W. – HAAK, H. – VOIGT, C. – HEMPEL, K. A.: J. de Phys. 38, 4 (1977), pp. C1-35.
- [5] HUANOSTA-TERA, A. et al.: Scripta Mater. 42 (2000), 603.
- [6] ALAMOLHODA, S. – SEYYED EBRAHIMI, S. A. – BADIEI, A.: J. Magn. Magn. Mater. 303 (2006), pp. 69.
- [7] WANG, C. S. et al.: J. Magn. Magn. Mater. 183 (1998), pp. 241.
- [8] CORRAL, J. C. et al.: J. Magn. Magn. Mater. 242-245 (2002), pp. 430.
- [9] TURILLI, G. et al.: IEEE Trans. on Magn. 24 (1988), pp. 2865.
- [10] GRUSKOVÁ, A. – SLÁMA, J. – DOSOUDIL, R. – KEVICKÁ, D. – JANČÁRIK, V. – LIPKA, J.: Czech. J. Phys. 52, 2 (2002), pp. 135.
- [11] GONZÁLEZ-ANGELES, A. et al.: J. Magn. Magn. Mater. 270 (2004), pp. 77.
- [12] JANČÁRIK, V. – UŠÁK, E.: Jour. El. Eng., 50, 8/S (1999), pp. 66
- [13] LIPKA, J. – MIGLIERINI, M.: Jour. El. Eng., 45, 8/S (1994), pp. 12.
- [14] DOSOUDIL, R.: Jour. El. Eng. 53, 10/S (2002), pp. 139.

Received 15 December 2006

Vladimír Jančárik (Doc, Ing, PhD), born in Bratislava, Czechoslovakia, in 1965, graduated from the Faculty of Electrical Engineering, Slovak University of Technology, Bratislava, in 1988 from solid state physics and received the PhD degree in Electromagnetic Theory at the same university, in 1996. Since 1988 he has been with the Department of Electromagnetic Theory, from 2001 as Associate Professor for electromagnetic theory. He teaches electric circuits and electronic devices theory. In research he is involved in measurement of magnetic properties of materials and design of sensor systems based on magnetic field.

Anna Grusková (Doc, Ing, PhD), born in Spišská Belá, Czechoslovakia, 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, Faculty of Electrical Engineering and Information Technology. Her research activities are mainly soft and hard ferrites, and ferrite-polymer composite materials.

Jozef Sláma (Prof, Ing, CSc) for biography see page 150 of this issue.

Rastislav Dosoudil (Ing, PhD) for biography see page 146 of this issue.