acta physica slovaca vol. 49 No. 5, 959 – 962 **October 1999**

INVESTIGATIONS OF PHASE COMPOSITION OF SUBSTITUTED Mn FERRITE

A. Grusková[1], V. Jančárik, J. Sláma
Faculty of Electrical Engineering and Information Technology, Ilkovičova 3, 812 19 Bratislava, Slovakia

Received 2 July 1999, in final form 27 July 1999, accepted 10 September 1999

The hematite samples with various content of impurities and its influence on final MnZn ferrite properties were studied. Final MnZn ferrite prepared from hematite with 0.04% SiO_2 impurity contains several ferrite phases. The composition was verified by the temperature dependence of magnetic susceptibility and the magnetization curve measurement. Presence of undesirable phases in hematite and MnZn was proved by the Mössbauer spectroscopy.

PACS: 75.30.C

1 Introduction

Iron containing raw material, hematite, is used for the production of various ferrite powders. The hematite as a raw material contains various impurities (for example SiO_2) as well as of maghemite in hematite depends on the technique of its preparation. Then the crystallochemical composition of the final product depends on the increased content of the impurities in hematite. The impurities appearance degrades the electromagnetic properties and the reproducibility of the final ferrite [1,2].

The measurement of the temperature dependence of initial magnetic susceptibility χ is the proper method for determination of the phase compositions an the Curie temperature. The measurements of the thermomagnetic curves were carried out by the bridge method. The samples were heated in air environment at the constant rate of 4°C min^{-1}. The susceptibility is given in arbitrary units and is related to the same amount of sample (1 mg) for the dependencies in all figures. The specific magnetic polarization J_s was investigated by the vibrating magnetometer at the external magnetic field $H_m = 300$ kA m^{-1}. For estimation of the phase composition changes in hematite and MnZn ferrite powder, the Mössbauer spectroscopy was used and the spectra were recorded at room temperature with the conventional Mössbauer spectrometer (the ^{57}Co source in Rh matrix).

[1]E-mail address: gruskova@iris.elf.stuba.sk

sample	% SiO_2	technological process
A	0	synthetic oxidation of iron
B	0.002-0.05	chemically and thermally treated
C	0.02	pyrolytic decomposition
D	>0.04	pyrolytic decomposition

Table 1. Method of the preparation of hematite.

2 Results and discussion

The samples of hematite with different content of the SiO_2 impurities were prepared by various methods and were marked as A,B,C, and D. The samples B,C,D were made by Ruthner's method (Tab.1).

Manganese-zinc ferrite was prepared by conventional ceramic procedure from α-Fe_2O_3, Mn_3O_4 and ZnO. The ferrite powder samples under investigation were made by PRAMET company (Czech Republic) and are commercially marked as H21 material. The temperature dependence of magnetic susceptibility $\chi(\theta)$ was used for the analysis of hematite samples. The samples were heated up to 750°C and cooled back to the room temperature. The thermomagnetic curves of the samples A and B are typical for the pure hematite (Fig.1). It was also proved by the Mössbauer spectroscopy, the spectrum was fitted by a single sextet with negative quadrupole splitting (QS=-0.2 mm s^{-1}) and magnetic hyperfine field $H_{\mathrm{ef}} = 51.5$ T. It corresponds to a pure hematite and was the same for both samples A,B, but also C (Fig. 2). The $\chi(\theta)$ dependence of sample C indicates an evident drop at the temperature 560°C (Fig. 1). This decreasing of χ probably corresponds to a little content of maghemite but the Mössbauer spectrum does not show it. Our experience show that behavior of the $\chi(\theta)$ dependence is capable of identifying very small content of maghemite in hematite.

The $\chi(\theta)$ curve for sample D falls down at 560°C as well as for sample C. It corresponds to a change from maghemite to magnetite. During the heating, the maghemite easily changes to a magnetite and vice versa, γ-Fe_2O_3 can be obtained by an oxidation of Fe_3O_4 [3]. The peaks for all samples at 670°C show the presence of hematite particles. The sample C had the initial susceptibility only 0.25, on the other hand the value for the sample D was higher ($\chi = 1.45$). The presence of the maghemite component with the relative content 5.8% in the sample D was verified by a second sextet next to hematite sextet in the Mössbauer spectrum as shown in Fig. 2. (pattern D). Our experiments showed that the content of SiO_2 impurities is proportional to the volume of the maghemite component in the sample. The presence of the maghemite was also proved by the measurement of specific magnetic polarization J_s. The value of J_s was measured under applied external field $H_m = 300$kA m^{-1}. The saturated specific magnet polarization of the sample D (with the impurity of SiO_2) was 5.93 mT g^{-1} cm ^{3}. It was approximately five times higher than of the sample A (without impurities) where $J_s = 1.17$ mT g^{-1} cm^3. All measured data indicate the weak ferromagnetic character and although the hematite is canted antiferomagnetic, it is possible by an occurance of the small canting spins giving non-zero magnetic flux [4].

The samples of MnZn ferrite marked as 1MZF and 2MZF were made from various kinds

Fig. 1. Temperature dependence of the magnetic susceptibility for various kinds of hematite.

Fig. 2. Mössbauer spectra of the hematite samples A,B,C and D.

Fig. 3. Temperature dependence of the magnetic susceptibility of the MnZn ferrite samples 1MZF and 2MZF.

Fig. 4. Temperature dependence of the magnetic susceptibility of the MnZn ferrite sample H21.

of hematite. The sample 1MZF was prepared from the hematite B and has similar magnetic properties as other samples prepared from the hematite A or C respectively. Apparently different magnetic properties has sample 2MZF prepared from the hematite D. The temperature dependencies of magnetic susceptibility for both samples 1MZF and 2MZF are given in Fig. 3. to show these differences. The initial value of the susceptibility χ of the sample 1MZF was 75. The extreme fall of χ at the temperature 220^{o}C shows the stable phase composition with considerable transition to the paramagnetic state. The second small drop to $\chi = 0$ at the temperature 300^{o}C and local peak at the temperature approximately 400°C could be caused by the measurement conditions. Measurements were carried out on powders prepared by melting from the compact phase. During the measurement, powder samples were heated in the air environment. The sample 1MZF was powder prepared from the compact sample H21. For comparison, the $\chi(\theta)$ dependence of the compact sample H21 exhibits one strong drop at the temperature 220°C (Fig. 4). On the other hand, the $\chi(\theta)$ dependence of the sample 2MZF indicates the presence of several ferrite phases. The first decreasing of $\chi(\theta)$ at the temperature approximately 150°C could be caused by greater amount of Zn in the sublattice of one ferrite phase. The second considerable phase has parameters similar to the sample 1MZF. The third phase with a local maximum at 400°C reveals the presence of maghemite. The complex phase composition of the sample 2MZF could be caused by a higher presence of impurities coming from the raw material (hematite) used for the final product preparation [5]. The structural arrangement of the sample 1MZF and 2MZF was verified by Mössbauer spectra measurements and showed different relative content of Fe^{3+} in the particular subspectra.

3 Conclusion

The influence of basic raw material, hematite, and its purity on the phase arrangement of the final ferrite product was verified by the measurement of the thermomagnetic curves. The $\chi(\theta)$ temperature dependence of the sample C showed the presence of maghemite whereas the Mössbauer spectrum did not prove it. The $\chi(\theta)$ temperature dependence is probably more sensitive to a small amount of impurities in hematite than the Mössbauer spectroscopy. The ordered structural composition of the MnZn ferrite was reached when the impurity in hematite had very low contain (below 0.02%). The complex structural composition of the MnZn ferrite apparently arises when the content of the impurity (for example SiO_2, etc.) is higher then 0.04%. It causes worse magnetic parameters of the final ferrite product, such as power losses, permeability and so on.

Acknowledgements The work was supported by the National grant of Slovakia No. 1/4284/97. We also would like to thank to I. Tóth from the Faculty of Electrical Engineering and Information technology, Slovak University of Technology for the measurements of the Mössbauer spectra.

References

[1] A. Dias et al.: *J. Mag. Mag. Mat.* **172** (1997) L9
[2] T. Nakamura, Y. Okano: *J. Physique IV* **7 C1** (1997) 101
[3] L.J. Rabkin, S.A. Soskin, B.S. Epstejn: *Ferrites, Energy* (1968) 144
[4] C.B. deBoer, M.J. Dekkers: *Geophys. J. Int.* **133** (1998) 542
[5] S. Krupička: *J. Mag. Mag. Mat.* **19** (1980) 88