acta phys. slov. 35 (1985), No. 4—5

ANALYSIS OF FORMATION STAGES OF Li FERRITE PREPARED FROM SOLUTIONS[1]

A. GRUSKOVÁ[2], Bratislava

The preparation of Li ferrite powders starting from solutions of metallic salts of citric acid has been studied. Results of thermogravimetric studies and Mössbauer spectroscopy at various stages of decomposition are presented. It has been verified that the substitution of Zn into Li ferrite brings about the maximum saturation magnetization for $Zn = 0.3$ ($M_s = 3.42 . 10^5$ Am^{-1}).

АНАЛИЗ СТАДИЙ ОБРАЗОВАНИЯ Li-ФЕРРИТА ИЗ РАСТВОРА

В работе даются результаты изучения приготовления литиевых ферритовых порошков, образованных из раствора металлических солей лимонной кислоты. Приведены результаты термометрических исследований и мёссбауэровской спектроскопии для различных стадий расщепления. Обнаружено, что замещение цинка в литиевом феррите дает максимальное магнитное насыщение при $Zn = 0{,}3$ ($M_s = 3{,}42 . 10^5$ Am^{-1}).

I. INTRODUCTION

Ferrites with spinel structure, such as Ni-Zn, Co-Zn, Li-Zn ferrites, have been the subject of many studies because of their relatively easy preparation and low cost, making these materials suitable for various electromagnetic devices [1]. In recent years much attention of research workers has been given to the preparation of ferrite powders from solutions.

In general, various chemical methods, such as conventional coprecipitation, spray drying, freeze drying, liquid drying, pyrolysis of organic precursors, etc., allow to obtain a greater degree of chemical homogeneity and a control of stoichiometry in the powder. In most cases the starting materials are finely divided and allow the improvement of reactivity and sinterability in comparison with powders prepared by conventional processing. The aim of the present study is to better understand the mechanism of formation of the magnetic structure of ferrite powders formed from solutions [2].

Mixed-zinc ferrites with spinel structure $Zn_xLi_{0.5-0.5x}Fe_{2.5-0.5x}O_4$ have the saturation magnetization M_s increased by x up to $x = 0.3$ in agreement with Neél's two sublattice theories. Above $x = 0.4$ the value of M_s decreases, and at $x = 1$ there is $M_s = 0$ (pure zinc ferrite). A decrease of the saturation magnetization in a certain range of x can be explained by the magnetic dilution of the A sublattice with zinc, and therefore, by the weakening of the exchange interaction between the $Fe^{3+}_{(B)}$ and the $Fe^{3+}_{(A)}$ sublattice [3].

Table 1

Measured values of saturation magnetization M_s

Symbol	Formula	$M_s . 10^{-5}$ [A m^{-1}]
LF	$Li_{0.5}Fe_{2.5}O_4$	2.81
$LZ_{0.2}$	$Li_{0.4}Fe_{2.4}Zn_{0.2}O_4$	3.34
$LZ_{0.3}$	$Li_{0.35}Fe_{2.35}Zn_{0.30}O_4$	3.42
$LZ_{0.5}$	$Li_{0.25}Fe_{2.25}Zn_{0.50}O_4$	2.83
$LZ_{0.8}$	$Li_{0.1}Fe_{2.1}Zn_{0.8}O_4$	0.86
ZF	$Zn_{1.0}Fe_{2.0}O_4$	0.04

II. EXPERIMENTAL PROCEDURE

The composition of pure Li ferrite was prepared from a solution of $Fe(NO_3)_3 . 9\,H_2O$, $LiNO_3$ and citric acid in the ratio of 1 : 1 for each g-ion of metal ions to a g-mol of acid. The solution had been boiled to 80 °C to evaporate the water until a very viscous mass was obtained in a glass vessel supplied with a thermocouple and a stirrer. The viscous liquid was put into the evacuated even at 120 °C for 4 hours. The product obtained after this treatment was a coloured brittle glass-precursor. The decomposition stage consisted of the burning of citric acid in oxygen at approx. 410 °C. The decomposed precursor was pressed through a sieve. The granules were calcinated in the furnace at 450° and 550 °C for 4 hours in air. A 1 % solution of PVA was added into the calcinated powders as a binder. Then the powders were pressed at 10^8 Pa and fired at 1200 °C for 1 hour in air. The saturation magnetization was measured in dependence on Zn addition as shown in Table 1. Thermogravimetric (TGA) and differential thermal (DTA) analyses of the dried salts were obtained using standard techniques. The thermobalance (model OD-102, made in Hungary) was maintained at a temperature rise programmed up to 10 °C min^{-1}. The obtained thermograms are shown in Fig. 1 and 2. The Mössbauer spectra were measured by a conventional constant acceleration drive and a 512 channel analyser operating in the multiscaler mode. The

---

[1] Contribution presented at the 7th Conference on Magnetism, KOŠICE, June 5—8, 1984.

[2] Katedra teoretickej a experimentálnej elektrotechniky, Vazovova 5, 812 19 BRATISLAVA, Czechoslovakia.

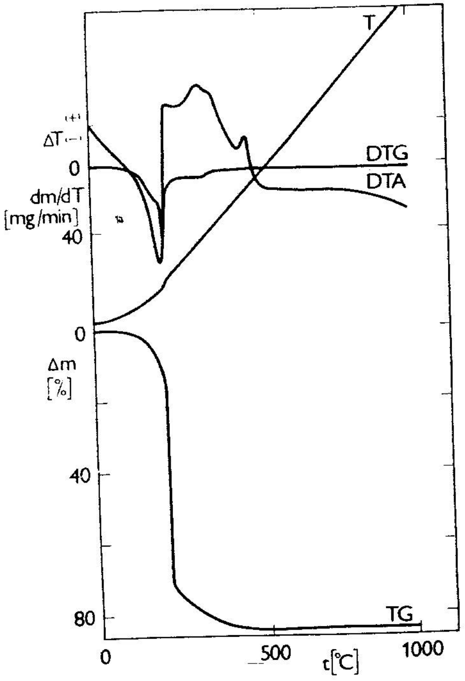

Fig. 1. The thermogram of specimen LF$_{(1)}$ withdrawn at a temperature of 120 °C.

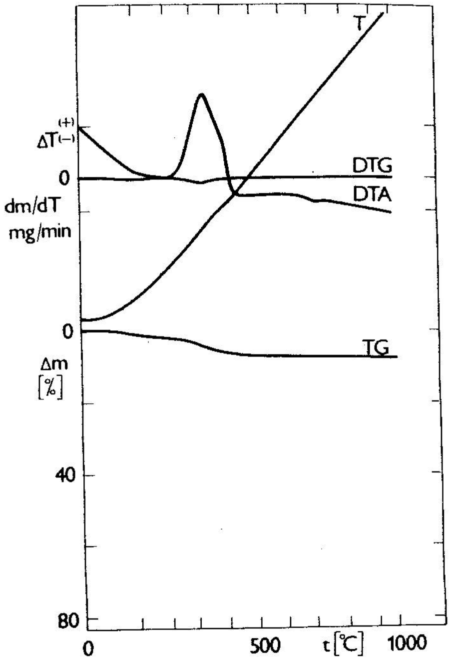

Fig. 2. The thermogram of specimen LF$_{(2)}$ withdrawn at a temperature of 410 °C.

source was ^{57}Co in a Rh matrix. Mössbauer spectra are represented in Figs. 3a, b, c, d and 4a, b, c.

III. RESULTS AND DISCUSSION

To obtain more information about the strongly exothermic pyrolysis reaction of precursors both TGA and DTA of the dried salts have been made. The thermogram of specimen LF$_{(1)}$ in Fig. 1 withdrawn at the temperature of 120 °C shows a weight loss up to 140 °C indicating the absence of adsorbed water. The total weight loss is 83 % and occurs below 350 °C. The DTA trace shows an endothermic peak at 130 °C which is apparently associated with the decomposition of nitrate probably by the reaction described in [4]:

$$6\,NO_3^- + C_6H_8O_7 \;\rightarrow\; 6\,OH^- + 6\,CO_2\uparrow + H_2O\uparrow + 6\,NO\uparrow\,. \qquad (1)$$

From 140 °C up to 380 °C a large exothermic peak, attributed to the decomposition of citric acid, occurs.

The thermogram of specimen LF$_{(2)}$ in Fig. 2, withdrawn at the temperature of 410 °C shows a weight loss of 7.5 % up to a temperature of 530 °C. The DTA trace shows an exothermic peak with a maximum at the temperature of 360 °C.

The corresponding spectra of Li ferrite are shown in Figs. 3a, b, c, d. The starting solution containing iron in the form of $Fe(NO_3)_3 . 9\,H_2O$ was measured by LNT (liquid nitrogene temperature) and the corresponding spectrum is in Fig. 3a. For

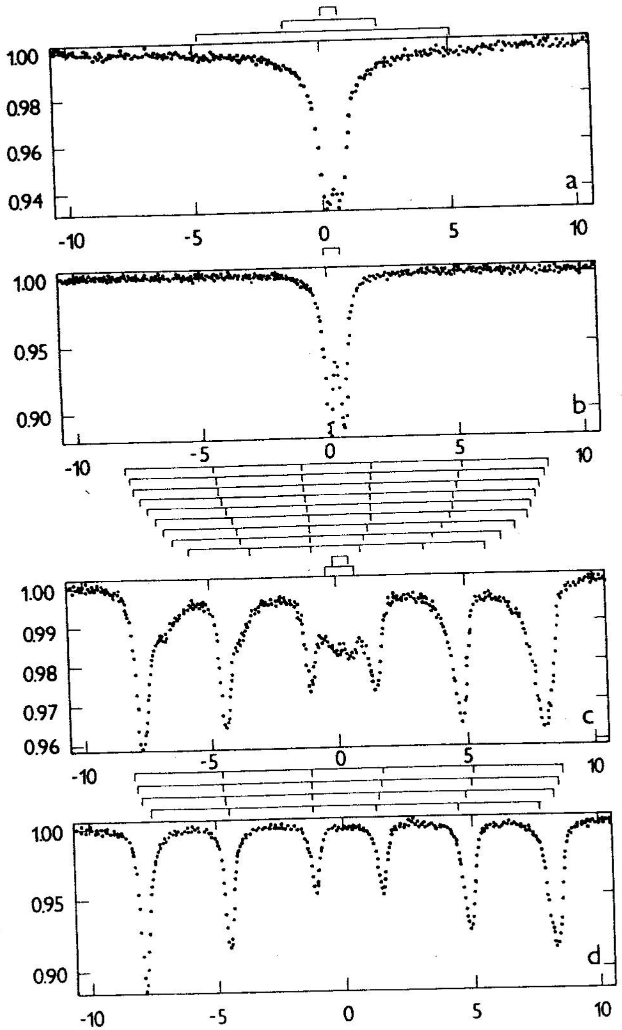

Fig. 3. Mössbauer spectra; the starting solution (a); the specimen LF$_{(1)}$ (b); the specimen LF$_{(2)}$ (c); the specimen LF$_{(2)}$ 1000 °C (d).

the specimen $LF_{(1)}$ Fig. 3b, the spectrum shows a quadrupole doublet corresponding to iron in anhydrate citrate. For the specimen $LF_{(2)}$ Fig. 3c, the spectrum is approximated by a superposition of nine six-line patterns and a quadrupole splitting. The specimen withdrawn at 1000 °C, Fig. 3d shows four six-line sets of Lorentzian curves. The Mössbauer spectra of the Li-Zn powders for specimens with $x = 0.3$, 0.5, 0.8 are shown in Figs. 4a, b, c. The specimens were withdrawn after calcination at 550 °C for 5.5 hours. Note that the spectrum for $x = 0.3$ exhibits broader six-line shapes as compared with pure Li ferrite. A quadrupole splitting and a paramagnetic doublet are coexisting with the magnetically ordered six-line pattern in the spectrum for $x = 0.5$. The spectrum for $x = 0.8$ shows only simple paramagnetic doublets.

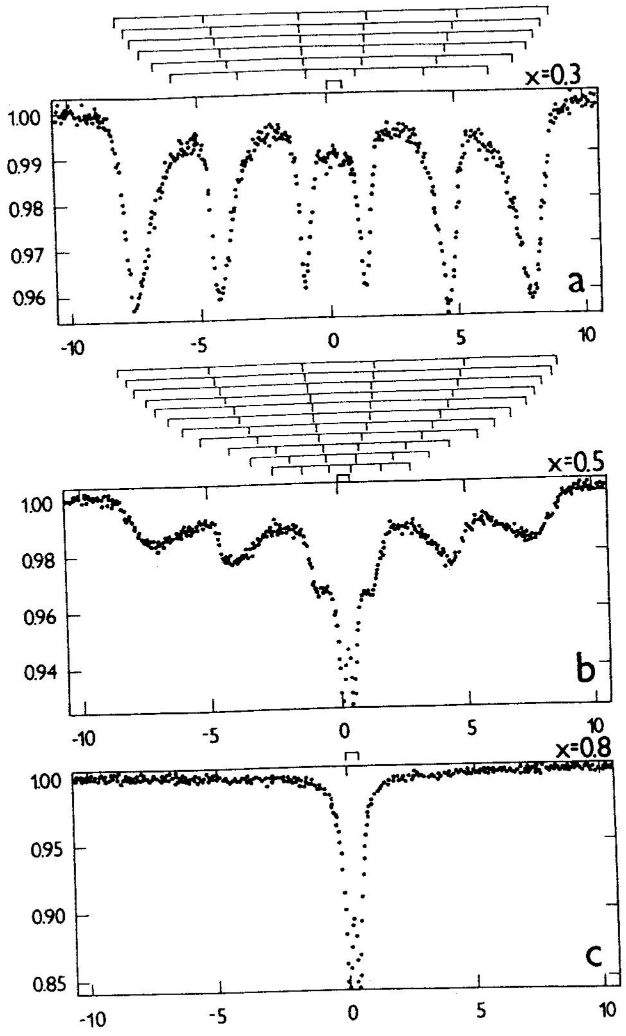

Fig. 4. Mössbauer spectra; specimen $LZ_{0.3}$ [3] after calcination at 550 °C for 5.5 h (a); specimen $LZ_{0.5}$ [3] (b); specimen $LZ_{0.8}$ [3] (c).

IV. CONCLUSION

Preparation of substituted Li ferrites from solutions of metallic salts of a polyfunctional organic acid has been studied. Special attention was paid to the decomposition behaviour of the amorphous citric precursor. The destruction process of the citric precursor and calcination were analysed by means of thermal analysis and the Mössbauer spectroscopy. Information about the magnetic structure of the wet prepared material derived from Mössbauer spectra makes it possible to choose a proper temperature for dehydration (130 °C) and decomposition (410 °C). It has been verified that the specimens with $x = 0.4$ have a decreased saturation magnetization as compared with the $x = 0.3$ sample and the specimen with $x = 0.8$ is paramagnetic.

REFERENCES

[1] Stuyts, A. L., De Lau, K. G.: Sintering 7 (1975), 147.
[2] Marcilly, C., Courty, P., Delmon, B.: J. Am. Cer. Soc. *53* (1970), 56.
[3] Rosenberg, M., Deppe, P., Dey, S., Janssen, U., Patton, C. E., Edmondson, C. A.: IEEE, Mag-*18* (1982), 1616.
[4] Courty, P., Ajot, H., Marcilly, C., Delmon, B.: Powder Technology 7 (1973), 21.

Received December 7th, 1984
Revised version received Jannuary 31st, 1985