Journal of Thermal Analysis and Calorimetry, Vol. 84 (2006) 2, 391–394

THERMAL INVESTIGATIONS OF NICKEL–ZINC FERRITES FORMATION FROM MALATE COORDINATION COMPOUNDS

*Oana Carp**, *Luminita Patron, G. Pascu, Ioana Mindru and N. Stanica*

Institute of Physical Chemistry ‘I. G. Murgulescu’, Splaiul Independentei nr. 202, sector 6, Bucharest, Romania

Nickel–zinc ferrites have been synthesized via thermal decomposition of polynuclear coordination compounds containing as ligand the anion of malic acid, namely $(NH_4)[Fe_2Ni_xZn_{1-x}(C_4H_4O_5)(OH)_3]\cdot nH_2O$ (x=0.25, 0.5 and 0.75, n=3 and 5). A comparison between the thermal behaviour of the studied polynuclear coordination compounds is inferred. $Fe_2Ni_xZn_{1-x}O_4$ (x=0.25, 0.5 and 0.75) ferrites with mean particle sizes of 65–85 Å and free from other phases are formed after a heating treatment of only one hour at 500°C.

Keywords: *coordination compound precursor, nano nickel–zinc ferrite*

Introduction

Nickel–zinc ferrites are a well-known class of technologically important soft ferrites, due to their low magnetic coercivity, high resistivity values [1] and little eddy current loss in high-frequency operations (10–500 MHz) [2].

The synthesis of $Fe_2Ni_xZn_{1-x}O_4$ ferrites has to solve two major problems. The first is related to the presence of zinc. The volatilization of zinc at high temperatures changes the desired stoichiometry and also leads to Fe^{2+} formation, thereby increasing the electron hopping and reducing the resistivity. The second is connected with the presence of three different cations, which may determine a greater variety of intermediate phases.

The solid-state synthesis from individual oxides of these ferrites is associated with the formation of simple ferrites (Fe_2ZnO_4 and Fe_2NiO_4) as intermediates [3]. Starting from homogenous nickel–zinc–iron oxalates solid solution a homogenous ferrite may be obtained only above 750°C [4, 5]. At lower temperatures (400–750°C), areas rich in nickel and zinc are identified [4].

The spinel ferrite phases prepared hydrothermally from the coprecipitated hydroxide precursors contain either the individual ferrites or defect, non-stoichiometric oxides, dissimilar to their high-temperature analogous formed at ~1000°C [6, 7]. These cation deficient ferrimagnetic spinel phases may be considered as precursors of real stoichiometric ferrites, which are formed at ~850°C [7]. Recently, the literature reports a variant of this method where ferrites with particle sizes of 3–15 nm are obtained.

Although the temperature of obtaining a pure $Fe_2Ni_{0.5}Zn_{0.5}O_4$ ferrite by a variant of the combustion method is relatively high (1100°C), a mixed oxide with a surface area of 44.26 $m^2\ g^{-1}$ is obtained [8]. A citrate method [9], leads to NiZn ferrites with a resistivity of $\leq 10^8\Omega$, higher by at least two orders of magnitude than the reported one for ferrites prepared by conventional ceramic method [10, 11].

One of the unconventional routes to oxide materials is the use for synthetic gains coordination compounds (mono- and polynuclear). Thus, the exploitation of monocarboxylic, polycarboxylic and hydroxocarboxylic acid anions as ligands, leads to a wide variety of ordered molecular precursors, which decompose with evolving nontoxic compounds (H_2O and CO_2) at low temperature, leading to simple and mixed oxides.

The present article, which is part of a systematic study on mono- and polynuclear coordination compounds with malic anion as ligand [12–18], shows the possibility of nickel-zinc ferrites synthesis by the thermal decomposition of such compounds.

Experimental

Precursors preparation

As starting materials, $Fe(NO_3)_3\cdot 9H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, $Zn(CH_3COO)_2$ and malic acid of reagent grade (Merck), in a ratio 2Fe(III):1Me(II) (Ni_x^{2+} and Zn_{1-x}^{2+}):4malic acid are used. Metallic salts 2 mmol (0.808 g) of $Fe(NO_3)_3\cdot 9H_2O$ and 1 mmol M^{2+} (0.072/0.145/0.218 g of $Ni(NO_3)_2\cdot 6H_2O$ and 0.137/0.091/0.045 g $Zn(CH_3COO)_2$) are dissolved in a minimum amount of distilled water (50 mL). Separately 4 mmol of malic acid (0.536 g) are dissolved.

---

* Author for correspondence: carp@apia.ro

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Subsequently, the two solutions are mixed, tempted at ~60°C. At the cooled solution, methanol is added. The precipitation begins. For a complete precipitation the pH is adjusted to 5–6 with a NH_4OH 25%:methanol 1:1 solution. Afterward, the precipitates were filtered, washed with methanol and vacuum dried.

Characterization

IR spectra (400–4000 cm^{-1}) are recorded with a BIO-RAD FTIR 125 type spectrophotometer in KBr pellets. The crystalline phases in the calcinated powders are identified by XRD powder methods using a Seifert X-ray diffractometer (CuK_α radiation). SiO_2-α-quartz was used as internal standard. Diffraction peaks are fitted assuming Voight-function for the peak profile. A simplified least squares procedure (Savitsky–Golay) is applied in order to smooth the primary XRD collected data. The background is treated as a linear function. For the determination of the average crystallites size it has been used the Scherrer formula $D=0.91\lambda/(\beta\cos\theta)$, where D is the crystallite size, λ the wavelength (CuK_α), β the corrected half-width obtained using α-quartz as reference and the Warren formula, and θ the diffraction angle of [311] diffraction peaks [19].

The thermal measurements (TG, DTG, DSC) are performed using a Netzsch STA/PG/PC device in a dynamic synthetic air atmosphere, gas flow 15 $cm^3\ min^{-1}$ at a heating rate of 5 $K\ min^{-1}$. The magnetic properties (the magnetic susceptibility and the saturation magnetization) at room temperature are determined using a Faraday balance with Ni as calibrant.

Results and discussion

From the system Fe^{3+}–Ni^{2+}–Zn^{2+}–malic acid the following coordination compounds are isolated:

$(NH_4)[Fe_2Ni_{0.25}Zn_{0.75}(C_4H_4O_5)(OH)_3]\cdot 5H_2O$ (I)

$(NH_4)[Fe_2Ni_{0.5}Zn_{0.5}(C_4H_4O_5)(OH)_3]\cdot 3H_2O$ (II)

$(NH_4)[Fe_2Ni_{0.75}Zn_{0.25}(C_4H_4O_5)(OH)_3]\cdot 3H_2O$ (III)

The IR spectra of the synthesized compounds (Fig. 1) suggest that malic acid is coordinated to the metal ions through both its two COO^- and C–OH groups. This statement is supported by the split of the free acid carboxylic group band (~1730 cm^{-1}) into two strong bands characteristic for coordinated carboxylic group [20], ($\nu_{as(OCO)}$~1600 and $\nu_{s(OCO)}$~1380–1390 cm^{-1}) and by the shift towards lower frequencies (1120 → 1040–1100 cm^{-1}) of the band assigned to ν_{C-OH}.

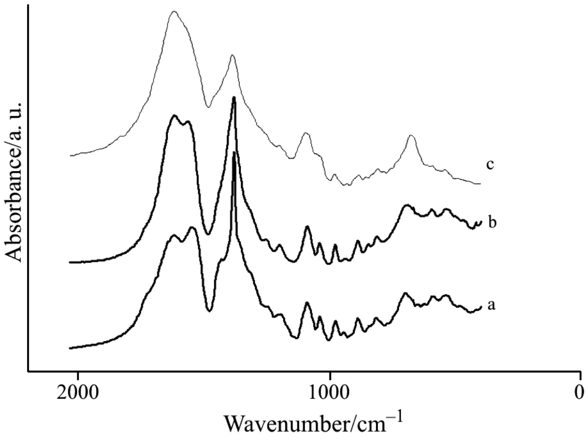

Fig. 1 IR spectra of the three coordination compounds;
a – $(NH_4)[Fe_2Ni_{0.25}Zn_{0.75}(C_4H_4O_5)(OH)_3]\cdot 5H_2O$,
b – $(NH_4)[Fe_2Ni_{0.5}Zn_{0.5}(C_4H_4O_5)(OH)_3]\cdot 3H_2O$,
c – $(NH_4)[Fe_2Ni_{0.75}Zn_{0.25}(C_4H_4O_5)(OH)_3]\cdot 3H_2O$

The three compounds underwent multistep decompositions in the temperature range 50–560°C (Fig. 2). The experimental mass loss recorded by TG measurements is 66.84/66.12/65.40% ((I)/(II)/(III) compounds) in comparison with the theoretical values of 67.23/65.69/65.85% when assumes the solid residual to be $Fe_2Ni_xZn_{1-x}O_4$ ($x=0.25$, 0.50 and 0.75).

Three decomposition regions characterize the thermal decompositions of the three coordination compounds. The first one, (44.1–174.2/50.1–159.4/44.2–144.2°C, (I)/(II)/(III) compounds) is associated with an endothermic effect and assigned to dehydration and deamination (mass loss experimental/theoretical: 16.24/16.99, 12.49/12.08, 13.37/13.79% for (I)/(II)/(III) compounds).

The second decomposition region, (174.2–374.4/159.4–359.5/144.2–324.4°C, (I)/(II)/(III) compounds), represents the oxidative fragmentation of the malate ion via a malonate intermediate. A reaction mixture containing Ni, $NiCO_3$, iron oxides and hydroxides and zinc hydroxo-carbonate, probable hydrozincite $[Zn_5(CO_3)_2(OH_6)]$ is formed. The IR investigations of the reaction intermediates confirmed the presence of CO_3^{2-} group, (~1400 and ~670 cm^{-1}) and HO^- group (~3650, ~1730 and ~1100 cm^{-1}). A higher content of nickel in the coordination compound lowers the final temperature of this decomposition step. The experimental mass losses corresponding to the malonate intermediate formation are in good agreement with the theoretical ones (experimental 12.83/13.74/14.17% and theoretical 12.32/12.99/13.02% for (I)/(II)/(III) compounds). The presence of malonates as intermediates of malates decomposition is reported by earlier studies [13, 14, 16, 17].

The third decomposition region is dependent on the relative ratio of the two M^{2+} contained in precur-

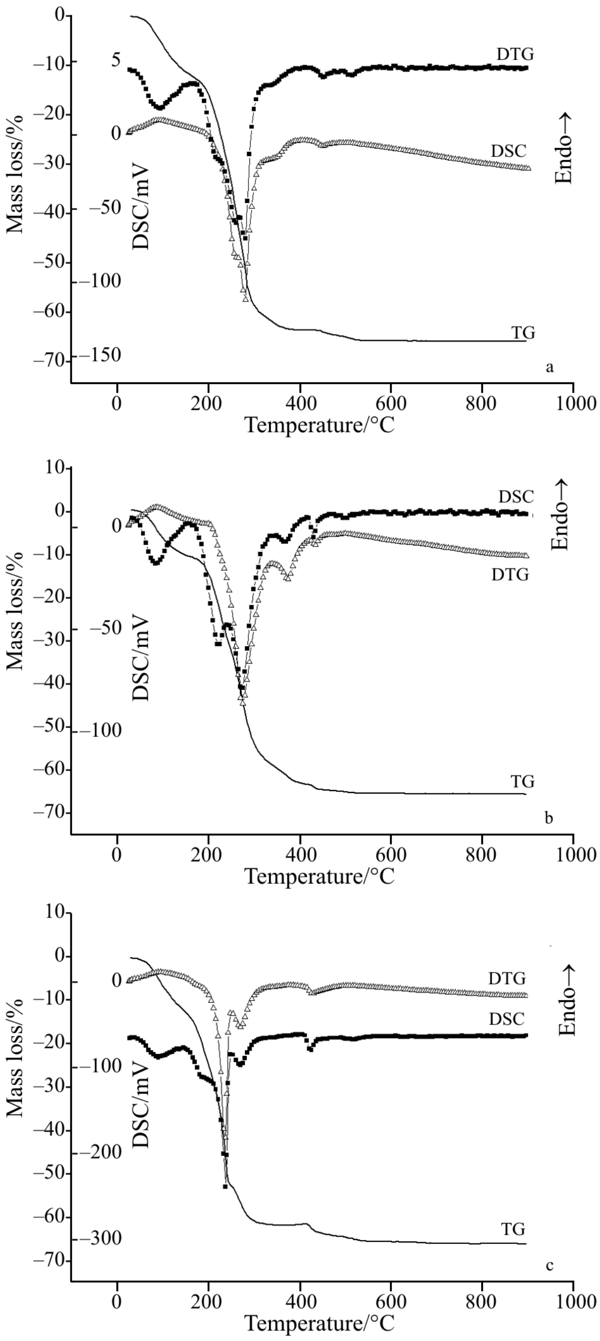

Fig. 2 TG curves registered at a heating rate of 5°C min^{-1} for the three coordination compounds:
a – $(NH_4)[Fe_2Ni_{0.25}Zn_{0.75}(C_4H_4O_5)(OH)_3]\cdot 5H_2O$,
b – $(NH_4)[Fe_2Ni_{0.5}Zn_{0.5}(C_4H_4O_5)(OH)_3]\cdot 3H_2O$,
c – $(NH_4)[Fe_2Ni_{0.75}Zn_{0.25}(C_4H_4O_5)(OH)_3]\cdot 3H_2O$

sors. A lower content of Ni^{2+} (compound (I)) is associated with a two-stepped thermal decomposition (399.4–479.4 and 479.43–544.3°C) assigned mainly to the thermal decomposition of the $NiCO_3$ and respective $[Zn_5(CO_3)_2(OH_6)]$ present in decomposition product. At an equal content of zinc and nickel, a single well-distinctive decomposition step assigned to $NiCO_3$ decomposition is identified (359.5–554.4°C). In the case of the coordination compound precursor of $Fe_2Ni_{0.75}Zn_{0.25}O_4$, a mass gain (354.4–414.4°C) followed by a mass loss (414.4–559.3°C) is identified. The mass gain (0.4%, corresponding to the addition of 0.086 oxygen moles), supports the assumption that the sample underwent an oxidizing reaction and may be explained as following: NiO formed during the decomposition promotes oxidation of carbon containing materials being concomitant reduced to Ni. Since the process is conducted in air, the metal undergoes a rapid reoxidation. A similar comportment at heating is registered for the nickel mononuclear coordination compound containing malate as anion ligand [15]. The registered subsequent mass loss may be attributed to the decomposition of the formed $NiCO_3$.

Nickel–zinc ferrites is identified as single product (Fig. 3) after a relative mild heating treatment (1 h–500°C) in comparatively with the literature data [7, 8, 21]. The mean crystallite particle sizes calculated with Sherrer formula using [311] diffraction peaks are 83/84/65 Å for $Fe_2Ni_{0.25}Zn_{0.75}O_4$/$Fe_2Ni_{0.75}Zn_{0.25}O_4$/$Fe_2Ni_{0.75}Zn_{0.25}O_4$ ferrites.

The saturation magnetization values of the obtained mixed oxides (Fig. 4) are 13.00, 17.79 and 25.50 emu g^{-1} for $Fe_2Ni_{0.25}Zn_{0.75}O_4$/$Fe_2Ni_{0.75}Zn_{0.25}O_4$/$Fe_2Ni_{0.75}Zn_{0.25}O_4$ ferrites respectively, lower than the literature reported ones for the corresponding bulk ferrites [22]. This reduction of the magnetization could be related to the nano-nature of the ferrite particles. It is known that the magnetic state of the ions in the particle surface area is different from the state in the bulk, and since the surface of so small particles is very large, the contribution of this ‘surface’ spins to the measured magnetic properties becomes substantial [23].

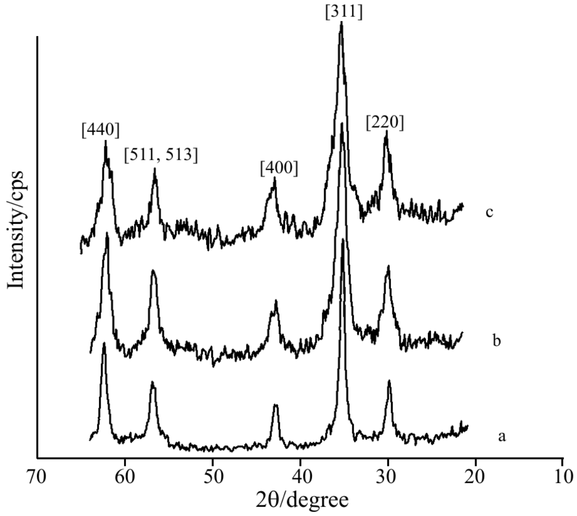

Fig. 3 X-ray diffraction patterns of the mixed oxides obtained after a heating treatment 1 h–500°C; a – $Fe_2Ni_{0.25}Zn_{0.75}O_4$, b – $Fe_2Ni_{0.75}Zn_{0.25}O_4$, c – $Fe_2Ni_{0.75}Zn_{0.25}O_4$

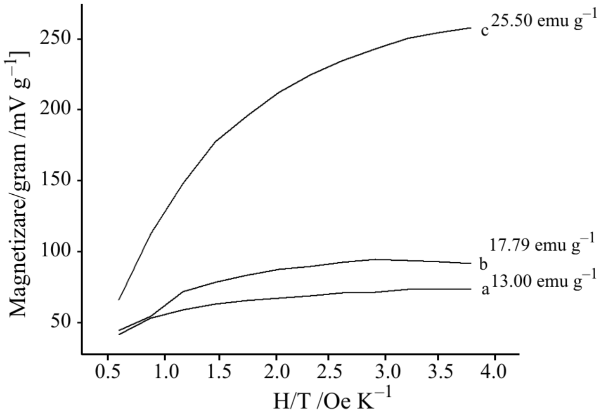

Fig. 4 Magnetic data of the mixed oxides obtained after a heating treatment 1 h–500°C; a – $Fe_2Ni_{0.25}Zn_{0.75}O_4$, b – $Fe_2Ni_{0.75}Zn_{0.25}O_4$, c – $Fe_2Ni_{0.75}Zn_{0.25}O_4$

Conclusions

Polynuclear coordination compounds containing malic acid anions as ligands represent suitable precursors for obtaining pure $Fe_2Ni_xZn_{1-x}O_4$ (x=0.25, 0.5 and 0.75) ferrites. The temperature is lower than the one reported by literature, leading to nanosized ferrites, with mean crystalline sizes of 65–85 Å. The lower obtained saturation magnetization could be related to the possible local canting of the magnetic moments due to the contribution of the surface spins.

Acknowledgements

The research was financially supported by Matnantech program.

References

1 P. S. Anil Kumar, J. J. Shrotri, S. D. Kulkarni, C. E. Deshpande and S. K. Date, Mater. Lett., 27 (1996) 293.
2 C. Y. Tsay, K. S. Liu and T. F. Lin, J. Magn. Mater., 209 (2000) 189.
3 V. Mitev, T. Peev and T. Dimova, Silikattechnik, 36 (1985) 104.
4 S. Fischer, H. Langbein, C. Michalk, K. Kneise and U. Heinecke, Cryst. Res. Technol., 26 (1991) 536.
5 H. Langbein and S. Fischer, Thermochim. Acta, 182 (1991) 39.
6 E. Wolska, W. Wolski, P. Piszora, M. Pietrusik, J. Šubrt, T. Grygar and M. Nejezchleba, Int. J. Inorg. Mater., 1 (1999) 187.
7 W. Wolski, E. Wolska and J. Kazmarek, Phys. Status Solidi, 139 (1995) 51.
8 A. C. F. M. Costa, E. Tortella, M. R.Morelli and R. H. G. A. Kiminami, J. Magn. Magn. Mater., 256 (2003) 174.
9 A. Verma, T. C. Goel, R. G. Mendiratta and R. G. Gupta, J. Magn. Magn. Mater., 192 (1999) 271.
10 J. Smit and H. P. J. Wijn, Ferrites Philips Technical Library, Edinhoven, The Netherlands 1990, pp. 234.
11 A. Goldman, Modern Ferrite Technology, Van Nostrand Reinholds, New York 1975, p. 71.
12 L. Patron, S. Plostinaru, A. Butucelea and P. Spacu, Rev. Roum. Chim., 36 (1991) 510.
13 T. V. Albu, I. Mindru, L. Patron and E. Segal, Thermochim. Acta, 340–341 (1999) 235.
14 L. Patron, O. Carp, I. Mindru and G. Grasa, J. Therm. Anal. Cal., 56 (1999) 597.
15 I. Mindru, L. Patron, O. Carp, G. Marinescu, M. Brezeanu and E. Segal, Rev. Roum. Chim., 45 (2000) 601.
16 L. Patron, O. Carp, I. Mindru, G. Marinescu and E. Segal, J. Therm. Anal. Cal., 72 (2003) 281.
17 O. Carp, L. Patron, I. Mindru, G. Marinescu, L. Diamandescu and A. Banuta, J. Therm. Anal. Cal., 74 (2003) 789.
18 O. Carp, L. Patron, A. Ianculescu, D. Crisan, N. Dragan and R. Olar, J. Therm. Anal. Cal., 72 (2003) 253.
19 H. P. Klug and L. E. Alexander, in X-Ray Diffraction Procedures, Wiley, New York 1954, p. 461.
20 K. Nakamoto, in Infrared and Raman Spectra of Inorganic and Coordination Compounds, Ed. 4, J. Wiley and Sons, 1986, p. 223.
21 X. Jiao, D. Chen and Y. Hu, Mater. Res. Bull., 37 (2002) 1583.
22 S. Cedighian, in ‘Ferrites’ (Romanian Edition), Ed. Technical, Bucharest 1966, p. 39.
23 J. Teillet, F. Bouree and R. Krishnan, J. Magn. Magn. Mater., 123 (1993) 93.

Received: January 27, 2005
Accepted: January 17, 2006

DOI: 10.1007/s10973-005-6920-4