



Structure and magnetic properties of manganese–zinc-ferrites prepared by spray pyrolysis method



Dzmitry Kotsikau ^{a, *}, Maria Ivanovskaya ^b, Vladimir Pankov ^a, Yulia Fedotova ^c

^a Belarusian State University, 14 Leningradskaya, 220030 Minsk, Belarus

^b Research Institute for Physical-Chemical Problems of the Belarusian State University, 14 Leningradskaya, 220030 Minsk, Belarus

^c National Centre of Physics of Particles and High Energies, 18 Pervomajskaya str, 220088 Minsk, Belarus

ARTICLE INFO

Article history:

Received 19 June 2014

Received in revised form

7 November 2014

Accepted 26 November 2014

Available online 26 November 2014

Keywords:

Mn–Zn-ferrite

Spray pyrolysis

Structural characterization

Magnetic properties

Mössbauer spectroscopy

ABSTRACT

A spray pyrolysis of a water solution of iron, manganese and iron nitrates is applied to prepare $\text{Zn}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ single-phase ferrite with a spinel-type structure. The samples are characterized by means of differential scanning calorimetry, scanning and transmission electron microscopy, X-ray diffraction, infrared and ^{57}Fe Mössbauer spectroscopy. The mass magnetization σ and the magnetic susceptibility $1/\chi$ of the ferrites are measured as a function of temperature over the range of 78–728 K. The obtained sample contains nanoparticles with an average diameter $d \sim 7$ nm possessing $\text{Mn}_x\text{Zn}_y\text{Fe}_{3-(x+y)}\text{O}_4$ spinel-type structure with a uniform distribution of manganese and zinc atoms over the ferrite lattice. The Curie temperature is determined to be 375 ± 380 K.

© 2014 Elsevier Masson SAS. All rights reserved.

1. Introduction

Nanocrystalline ferrites are still the subject of tremendous interest due to their attractive fundamental electronic and magnetic properties as well as due their potential applications in electronics, microwave and computer technologies [1–19].

The advantageous feature of the spinel-type ferrites is that their properties could be easily tuned and controlled since they depend regularly on the variation of the compositions and the cation distribution in a material. The grain size distribution is also an important parameter affecting the functional characteristics of ferrites [1,8,12,14–16,20].

The studied ferrites can be considered as $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ solid solutions, which differ in a structural and a concentration inhomogeneities. To achieve the best magnetic characteristics, the preparation of a product consisting of a single spinel-type phase

with no traces of iron oxide or other ferrite phases like MnFe_2O_4 or ZnFe_2O_4 is required. The oxidation state of zinc, manganese and iron cations, and the positions they occupy in the spinel crystal lattice also influence the magnetic behavior of the Mn–Zn-ferrites. According to the Neel theory, a maximum magnetization value is reached when bivalent cations (Zn^{2+} , Mn^{2+}) occupy the tetrahedral positions of the spinel lattice, and trivalent cations (Fe^{3+}) are distributed over the octahedral sites [8,21].

In the technological cycle of the ferrite fabrication, $\text{Mn}^{2+} \rightarrow \text{Mn}^{3+}$ oxidation reaction might occur at high temperatures, which is likely accompanying by a reduction of Fe^{3+} ions to Fe^{2+} state and by a redistribution of the metal cations between the sublattices. Thus, a partial swap of the generated Fe^{2+} and Mn^{3+} ions between the tetrahedral and the octahedral lattice sites is possible. The described processes have an adverse effect on the magnetic features of the material. The oxidation of Mn^{2+} ions is known to proceed most rapidly at 900–1000 °C, while the optimal temperature to produce the Mn–Zn-ferrites lies over the temperature range of 1000–1200 °C. Specific cooling modes, including oxygen control in the furnace chamber, are typically applied to avoid Mn^{2+} oxidation and to produce ferrites with the proper functional features [17]. However, the only reliable way to prepare the ferrites in a form of powder and prevent Mn^{2+} oxidation is to reduce the synthesis temperature. Along with the conventional

Abbreviations: DSC, differential scanning calorimetry; DTG, differential thermal gravimetric analysis; IR, infrared; JCPDS PDF, joint committee on the powder diffraction spectra – powder diffraction file; RT, room temperature; SEM, scanning electron microscopy; TEM, transmission electron microscopy; TG, thermal gravimetric analysis; XRD, X-ray diffraction.

* Corresponding author.

E-mail addresses: kotsikau@bsu.by (D. Kotsikau), ivanovskaya@bsu.by (M. Ivanovskaya), julia@hep.by (Y. Fedotova).

ceramic processing techniques [1,15] a number of modifications of the nanotechnology can be used to obtain nanocrystalline ferrites at comparatively low temperature, in particular, hydrothermal method [1,6,9,12], thermally stimulated dehydration of co-precipitated hydroxides of the corresponding metals [2–5,14,16] and spray pyrolysis of water solutions of metal nitrates [12,18,21–27].

As shown in [18], the spray pyrolysis method based on inorganic metal precursors allows preparing ferrites at temperature below 650 °C. An important point is that this technique provides highly homogeneous distribution of the components in the resulting product since the formation of its structure proceeds within microscopic droplets of the reacting mixture. The size of the resulting particles might be adjusted over a wide range (from 50 nm to 500 mkm) [100]. Non-agglomerated particles with a size down to 10 nm are achieved by applying soluble inert additives to the reaction mixture (NaCl, H₃BO₃ et al.). Furthermore, the inert components allow subsequent thermal treating the generated powder without a noticeable growth in the size [18].

The solution aerosol techniques take advantage of many of the available methods that have been developed for powder synthesis but then uniquely control the particle formation environment by compartmentalizing the solution into droplets. In this manner, the spray pyrolysis ensures a complete stoichiometry retention on the droplet scale, at least, and, thus, is particularly advantageous for mixed metal oxide synthesis. By controlling the type of a thermalysis reaction, a nature of the precursors (organic or inorganic salts, organic compounds, sols of oxides with preset morphology and phase composition), and a nature of a gaseous carrier, it is possible to synthesize oxide, non-oxide ceramic, metal [23], and complex composite particles [18,24].

The spray pyrolysis processes offer a number of opportunities for the synthesis of either hollow or porous particles that may be useful for thermal insulation or catalyst support applications [25]. Analogous to fiber formation by dry spinning, it has been demonstrated that concentration-discontinuous fibers can be produced by this method when using a two-fluid atomizer [26]. The pyrolysis is also well suited for producing thin films of the desired stoichiometry on large, non-planar surfaces [27]. A potential high production rate is another advantage of the chosen synthetic approach [24].

In this paper, we report a study of the structural features and the magnetic properties of Mn–Zn-ferrites prepared using a low-temperature spray pyrolysis of metal nitrates.

2. Materials and methods

A water solution of Zn (II), Mn (II) and Fe (III) nitrates taken in the stoichiometric proportion with a concentration corresponding to 0.25 mol/dm³ of Zn_{0.5}Mn_{0.5}Fe₂O₄ is used to synthesize the Mn–Zn-ferrite by the spray pyrolysis approach. The solution is transformed into an aerosol state with an ultrasonic atomizer and carried in the reaction zone with air or nitrogen (flow rate is 5 l/min). The reaction zone (a quartz tube with $l = 1.2$ m and $d = 42$ mm) is situated in a furnace heated to 650 °C. The produced powder are collected in an electrostatic precipitator heated to 200 °C to prevent the condensation of water vapors.

Thermal analysis (DSC, TG, DTG) of the mixed aqueous solution of Zn (II), Mn (II) and Fe (III) nitrates is carried out on a NETZSCH STA 449C instrument using an alumina crucible over temperature range of 30–1000 °C. The sample weight is 54.280 mg.

IR spectra are collected on a Thermo Nicolet AVATAR FTIR-330 spectrometer supplied with a diffuse reflectance accessory over a range of 400–4000 cm⁻¹.

X-ray diffraction patterns are recorded from the powders on a DRON-2.0 diffractometer with a Ni-filtered CoK_α radiation

($\lambda = 0.178896$ nm) over 2θ range of 20–80°. The evaluation of the results and the identification of the ferrite structure are carried out by a standard procedure using JCPDS PDF data.

The morphology of the samples including the estimation of their grain size is analyzed by scanning electron microscopy (SEM) on a LEO 1402 instrument, and by transmission electron microscopy (TEM) on a LEO 903 microscope. In the TEM studies, direct carbon replicas of the surface are examined. The replicas are formed by the deposition of a thin layer of carbon onto the powder samples in a vacuum evaporator. Then the replicas are removed by dissolving the ferrite powder in HCl solution. The etching length that enables to keep some ferrite powder on the carbon films is selected. Then the replicas are picked up onto TEM grids.

Room temperature (RT) ⁵⁷Fe Mössbauer spectroscopy is applied to reveal the local structure and the magnetic state of the ferrite samples. The spectra are recorded on a MSMS2000 spectrometer in a transmission geometry using a ⁵⁷Co/Rh source (40 mCi). The spectra are fitted using MOSMOD program assuming the distribution of the hyperfine magnetic field (H_{hf}) and the electric quadrupole splitting (ΔE_Q). All the isomer shifts (δ) are referenced to α -Fe foil.

The mass magnetization σ and the magnetic susceptibility χ of the samples are measured as a function of temperature by Faraday's method in cooling and heating modes with an external magnetic field $B = 0.86$ T over the range of 78–728 K.

3. Results and discussion

The results of the thermal analysis of the aqueous solution of Zn(II), Mn(II) and Fe(III) nitrates with the metal ratio corresponding to Zn_{0.5}Mn_{0.5}Fe₂O₄ composition are shown in Fig. 1. As expected, the nitrates of the given metals melt down at 40–80 °C. Note, that at the earlier stages of the heating, the formation of a colloidal solution may occur owing to the polycondensation of nitrate aquacomplexes via OH-bridges. As a result, mixed polymerized precursors with a general formula [(Fe²⁺, Mn²⁺, Zn²⁺) (NO_x, OH, H₂O)] are formed. Their thermal treatment enables the preparation of a highly homogeneous oxide product. As follows from the results of the thermal analysis, the removal of water and nitrate ions and the formation of metal oxide phases proceed simultaneously below 200 °C. No evidences of a possible Mn²⁺ oxidation are present in the DSC–TG–DTG curves over the temperature range of 200–1000 °C. According to the IR spectroscopy results reported in

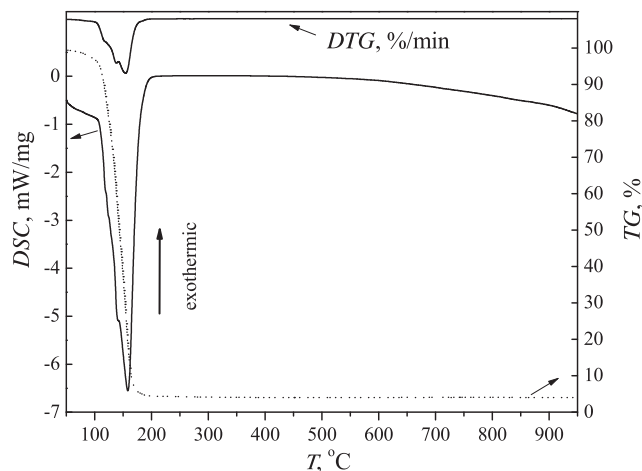


Fig. 1. The DSC, TG and DTG curves recorded from the mixed aqueous solution of Zn(II), Mn(II) and Fe(III) nitrates with Zn:Mn:Fe = 0.5:0.5:2 molar ratio.

Download English Version:

<https://daneshyari.com/en/article/1504334>

Download Persian Version:

<https://daneshyari.com/article/1504334>

[Daneshyari.com](https://daneshyari.com)