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STRUCTURE AND MAGNETIC PROPERTIES OF Mn–Zn-FERRITES

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Abstract Synthesis conditions, structure and magnetic properties of Mn-Zn-ferrites prepared by spray pyrolysis of solutions of manganese, zinc and iron nitrates have been considered. The applied technique provides low-temperature (650 °C) obtaining highly dispersed (7-8 nm) powder of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ ferrite with a narrow size distribution. Synthesis of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ at low temperature avoids $Mn^{II} \rightarrow Mn^{III}$ oxidation reaction that influences the ferrite properties. IR data collected from the ferrite samples obtained both in air and in N_2 ambient indicate their high structural and concentration homogeneity. Magnetic measurements confirm single-phase structure of the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ powders and give no evidence of the presence of individual iron oxide phases. Curie temperature (375-380 K) is consistent with the theoretically calculated value for $Mn_{1-x}Zn_xFe_2O_4$ (x = 0.5) (T_c = 365÷385 K). Parameters of Moessbauer spectra of the ferrites are typical of Fe^{III} state in oxide solid solutions with a considerable ionicity contribution in Fe-O bonds (δ = 0.33÷0.34 mm/s). Fe^{II} state was not revealed by Moessbauer spectroscopy that indicates the absence of $Fe^{III} \rightarrow Fe^{II}$ reduction accompanying the $Mn^{II} \rightarrow Mn^{III}$ oxidation process.

Introduction

The magnetic properties of Mn–Zn-ferrites are known to depend on their phase composition and other structural features. The studied ferrites are $Mn_{1-x}Zn_xFe_2O_4$ solid solutions differing in structural and concentration inhomogeneity. To achieve the best magnetic characteristics, the preparation of a product consisting of single spinel-type phase with no traces of iron oxide or other ferrite phases ($MnFe_2O_4$, $ZnFe_2O_4$) is required. The oxidation state of zinc, manganese and iron cations, and manner of their distribution over the spinel crystal lattice also influence the magnetic behavior of the Mn–Zn-ferrites. According to the Neel theory, maximum magnetization value is reached when bivalent cations (Zn^{2+}, Mn^{2+}) occupy tetrahedral positions of the spinel lattice, while trivalent cations (Fe^{3+}) – octahedral ones.

In the technological cycle of the ferrite fabrication, $Mn^{2+} \rightarrow Mn^{3+}$ oxidation reaction may occur at high temperature, which is likely accompanying by reduction of Fe^{3+} ions to Fe^{2+} state and also by redistribution of the metal cations between the sublattices. Namely, partial swap of the generated Fe^{2+} and Mn^{3+} ions between tetrahedral and octahedral lattice sites is possible. The described processes have an adverse effect on the magnetic features of the material. Oxidation of Mn^{2+} ions is known

to proceed most rapidly at 900–1000 °C, while the optimal temperature to produce Mn–Zn-ferrites lies in the temperature range 1000–1200 C. Specific cooling modes, including oxygen control in the furnace chamber, are typically applied to avoid Mn^{2+} oxidation and produce ferrites with the proper functional features. However, the only reliable way to produce ferrites in a form of powder, preventing Mn^{2+} oxidation, is to reduce the synthesis temperature. Instead of conventional ceramic processing techniques, a number of modifications of the nanotechnology can be used to obtain nanocrystalline ferrites at comparatively low temperature, in particular, i) thermally stimulated dehydration of co-precipitated hydroxides of the corresponding metals or ii) spray pyrolysis of their nitrates [1, 2].

As shown in [3], spray pyrolysis of metal nitrate solutions yields ferrites at temperature decreased down to 650 °C. An important point is that, this technique ensures highly homogeneous distribution of the components over the resultant product, since the formation of its structure proceeds within microscopic droplets of the reacting mixture.

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

Experimental procedure

To synthesize Mn–Zn-ferrite by spray pyrolysis, we used water solution of Zn (II), Mn (II) and Fe (III) nitrates with a concentration corresponding to 0.25 mole/dm^3 of $Zn_{0.5}Mn_{0.5}Fe_2O_4$. The solution was prepared by mixing the individual metal nitrate solutions in the required proportion. The ferrite samples were obtained in a tube furnace through which droplets of the liquid mixture, produced by ultrasonic atomizer, were entrained by a flow of air or nitrogen. The temperature of the hot face was 650 °C.

Thermal analysis (DSC, TG, DTG) of the mixed aqueous solution of Zn (II), Mn (II) and Fe (III) nitrates was carried out on a NETZSCH STA 449 C instrument

using alumina crucible in temperature range 30–1000 °C. The sample weight was 54.280 mg.

IR spectra were collected on a Thermo Nicolet AVATAR FTIR-330 spectrometer in diffuse reflection mode in the ν range 400–4000 cm^{-1}. A small amount of finely grinded powders was applied to a polished steel substrate.

X-ray diffraction (XRD) patterns were collected from the powders on a DRON-2.0 diffractometer with Ni-filtered CoK_α radiation ($\lambda = 0.178896$ nm) in the 2θ range 20–80°. Evaluation of the results was carried out by a standard procedure using JCPDS PDF data.

Morphology and grain size of the samples were estimated 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 were examined. The replicas were formed by the deposition of a thin layer of carbon onto powder samples in a vacuum evaporator. Then the replicas were removed by dissolving the ferrite powder in HCl solution. Etching length that enables to keep some ferrite powder on the carbon films was selected. Then the replicas were picked up onto TEM grids.

Room temperature ^{57}Fe Mössbauer spectroscopy was applied to reveal local structure and magnetic state of the ferrite samples. The spectra were recorded using MSMS2000 spectrometer in transmission geometry using ^{57}Co/Rh source (40 mCi). The fitting procedure was performed with the use of MOSMOD program assuming the distribution of hyperfine magnetic fields (H_{hf}) and electric quadrupole splittings (ΔE_Q). All isomer shifts (δ) were referenced to α-Fe.

Mass magnetization and magnetic susceptibility of the samples were measured as a function of temperature by Faraday's method in cooling and heating modes with an applying magnetic field $H = 0.86$ T in the range 78–728 K.

Results and Discussion

The results of thermal analysis of aqueous solution of Zn(II), Mn(II) and Fe(III) nitrates with the metal ratio corresponding to $Zn_{0.5}Mn_{0.5}Fe_2O_4$ composition are shown in Fig. 1.
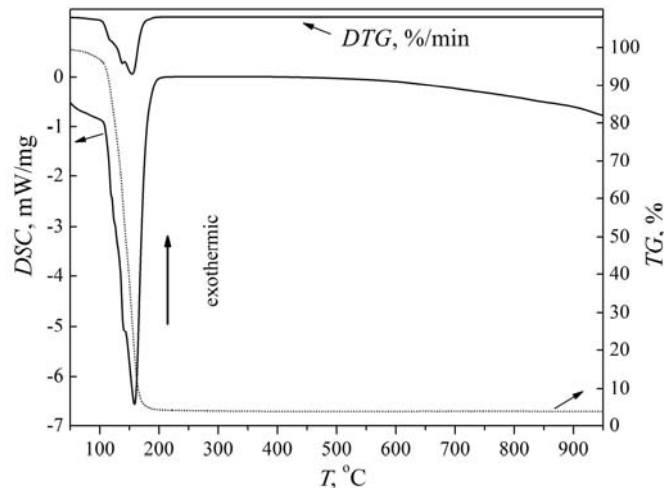

Fig. 1 DSC, TG and DTG curves recorded from a mixed aqueous solution of Zn(II), Mn(II) and Fe(III) nitrates with Zn:Mn:Fe = 0.5:0.5:2 molar ratio

As expected, the nitrates of the metals in question melt at 40–80 °C. Note, that in the beginning of heating, the formation of a colloidal solution may occur owing to the polycondensation of the nitrate aquacomplexes through bridge OH-groups. As a result, mixed polymerized precursors, $[(Fe^{2+}, Mn^{2+}, Zn^{2+}) (NO_x, OH, H_2O)]$, are formed. Their thermal treatment enables the preparation of highly homogeneous oxide product. It follows from the thermal analysis results that the removal of water and nitrate ions and the formation of metal oxide phases proceed simultaneously, and get completed at 200 C. No evidences of possible Mn^{2+} oxidation are present in the DSC–TG–DTG curves within temperature range 200–1000 °C. According to the IR spectroscopy results reported in [4], the removal of NO_x^- anion-radicals occurs most rapidly at 200–300°C and reaches completion at 500 °C under thermal decomposition of powder mixture of metal nitrates with the same composition as used in this paper.

In the X-ray diffraction patterns of the samples synthesized both in air and in nitrogen, the reflections form spinel-type Mn–Zn-Fe_2O_4 ferrite phase was detected. The

reflections can be attributed to both $Mn_{0.4}Zn_{0.6}Fe_2O_4$ (JCPDS no. 74-2400) and $Mn_{0.6}Zn_{0.4}Fe_2O_4$ (JCPDS no. 74-2401) phases, which have close unit-cell parameters. The presence of other phases was not revealed in the samples by XDR analysis. Average grain size estimated by the broadening of the XRD reflections lies in the range 6–8 nm.

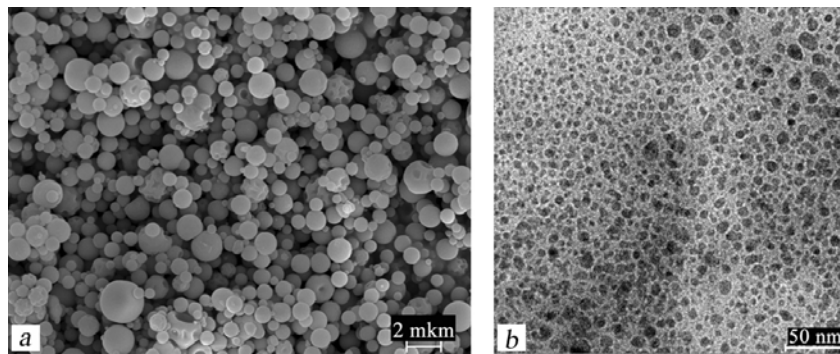According to SEM results given in Fig. 2a, the prepared samples consist of regularly shaped, spherical particles.

Fig. 2 SEM (*a*) and TEM (*b*) images of the Mn–Zn-ferrite obtained in nitrogen

The surface morphology of the spheres is typical of amorphous or glassy materials. The particle diameters range from 150 nm to 1.6 μm with a predominate size 650–800 nm. Spray pyrolysis in nitrogen atmosphere gives narrower distribution in particle size as compared to the samples synthesized in air. The observed particles are loose and polycrystalline. They consist of finer particles aggregated into bigger ones after the formation of the ferrite structure during the spray pyrolysis processing. As evidence, fine primary particles were distinguished in the TEM images of direct carbon replicas of the powder ferrite samples (Fig. 2b). The diameter of these particles corresponds to the average crystallite size determined by XRD.

It is known, that stretching vibrations ν_{Fe-O} and bending vibrations δ_{Fe-O-H} in iron oxides are strongly influenced by the symmetry of oxygen coordination and by force constant of Fe–O bond. In particular, the ν_{Fe-O} absorption bands in the IR spectra of spinel-type γ-Fe_2O_3 oxide, obtained by heating of γ-FeOOH at 300 °C, are centered at 420, 440, 551, 632 and 691 cm^{-1} (Fig. 3, spectrum 1).
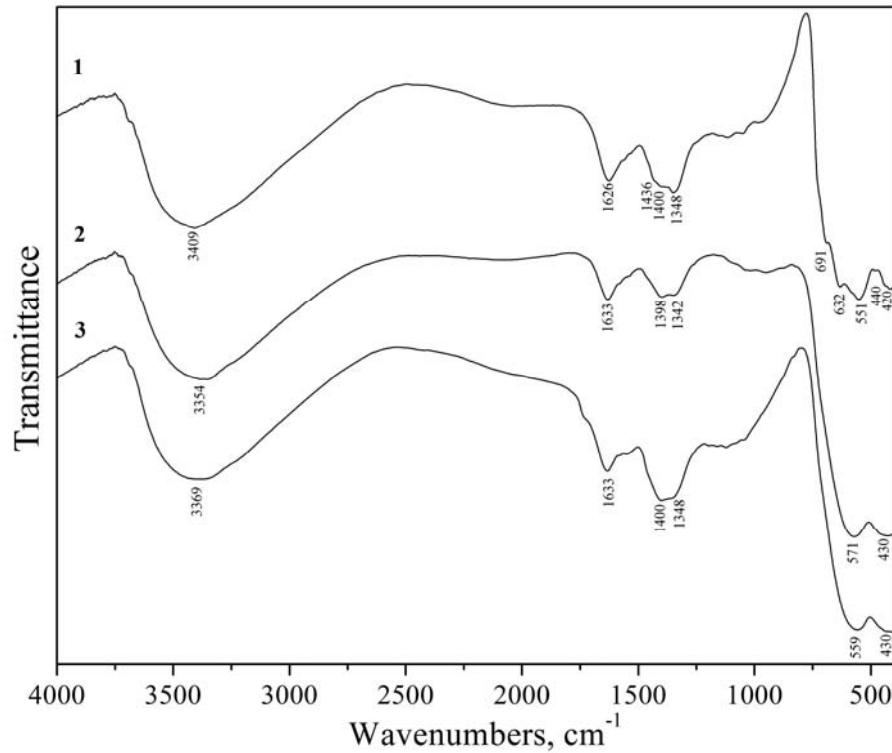
Fig. 3 IR spectra of γ-Fe_2O_3 (*1*) and Mn–Zn-ferrite obtained in nitrogen (*2*)

and in air (*3*)

As shown in [5, 6], the formation of zinc or cobalt ferrites by introduction of Zn^{2+} and Co^{2+} ions into γ-Fe_2O_3 are accompanied by the shift of the main $\nu_{Fe–O}$ band towards greater frequencies. Similar changes we observe for our samples in Fig. 3 when compare individual γ-Fe_2O_3 oxide and the Mn–Zn-ferrite samples (420 $\rightarrow$ 430 cm^{-1}, 551 $\rightarrow$ 559 (571) cm^{-1}). The absence of the band assigned to γ-Fe_2O_3 phase (632, 691 cm^{-1}) in the spectra 2 and 3 confirms the formation of ferrite structure. Symmetric shape of the $\nu_{Fe–O}$ bands in the IR spectra of the ferrites testify for homogeneity of the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ spinel structure and uniformity of Zn^{2+} and Mn^{2+} distribution over the lattice.

IR absorption bands attributed to bending vibrations of OH groups directly connected to metal cations ($\delta_{M–O–H}$) are known to be very sensitive to a degree of the structural perfection of composite oxides [6]. Therefore, the region of IR spectra around the mentioned band can be used to evaluate the structural perfection of multicomponent spinel-type oxides. The characteristic bands of the Mn–Zn-ferrites are 832 cm^{-1} ($\delta_{Zn–O–H}$) and 946 cm^{-1} ($\delta_{Mn–O–H}$). The bands around 1030–1122 cm^{-1} attributed to $\delta_{Fe–O–H}$ are

also shifted against the corresponding γ-Fe_2O_3 bands thus reflecting the effect of Zn^{2+} and Mn^{2+} cations.

It follows from the reported IR results that the synthesized samples have Mn–Zn-Fe_2O_4 spinel-type structure with uniform distribution of manganese and zinc over the ferrite lattice.

Temperature-dependent magnetization $\sigma = f(T)$, squared magnetization $\sigma^2 = f(T)$ and magnetic susceptibility $1/\chi = f(T)$ curves for the ferrite sample obtained in nitrogen atmosphere are shown in Fig. 4.
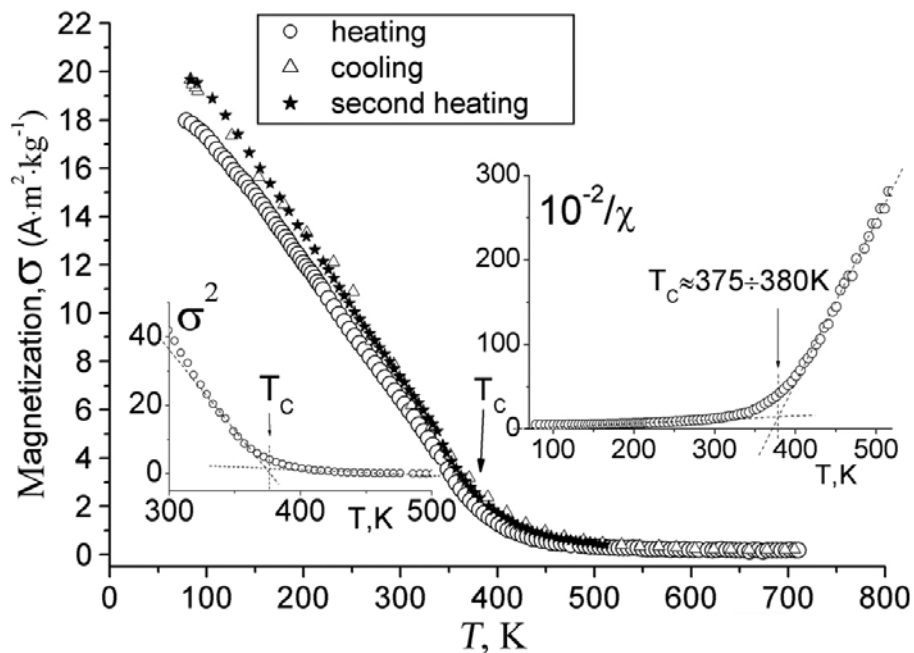

Fig. 4 Temperature dependences of magnetization, squared magnetization, and magnetic susceptibility measured from the Mn–Zn-ferrite obtained in nitrogen

The Curie temperature T_C was determined to be 375÷380 K. These values are consistent with the T_C range theoretically calculated for $Mn_{0.5}Zn_{0.5}Fe_2O_4$ ferrite under variation of Fe^{3+} distribution over the crystal lattice (365÷385 K). Individual iron oxide phases, γ-Fe_2O_3 ($T_C = 865$ K) and α-Fe_2O_3 ($T_N = 965$ K), were not revealed in the synthesized samples from the magnetic measurements. The shape of the $\sigma = f(T)$ curves and the σ values, which lie in the range 100÷300 K, are expected for nanosized ferrites with an equal Mn:Zn ratio.

Room temperature Mössbauer spectra of the ferrite samples synthesized by spray pyrolysis both in nitrogen and in air flow represent quadrupole doublets indicating paramagnetic state of iron. Note that paramagnetic state is typical of nanosized Mn–Zn-ferrites below their Curie point. Similar parameters of the spectra of the ferrites obtained in nitrogen and in air suggest that $Mn^{2+} \rightarrow Mn^{3+}$ and $Fe^{3+} \rightarrow Fe^{2+}$ reactions did not take place under the applied synthesis conditions. Fe^{2+} state was not revealed by Mössbauer spectroscopy in the sample prepared in nitrogen atmosphere. Isomer shift values measured for the samples ($\delta = 0.33 \div 0.34$ mm/s) are characteristic of Fe^{3+} ions in oxide solid solutions, including Mn–Zn-ferrites, and points to a significant ionicity contribution into Fe^{3+}–O covalent bond [7]. The observed broadening of the Mössbauer peaks is caused by the combination of poor crystallinity of the ferrite phase and nanosized scale of the particles.

The measured electric quadrupole splitting values ΔE_Q ($0.42 \div 0.53$ mm/s) lies between the values characteristic of individual $MnFe_2O_4$ (0.54 mm/s) and $ZnFe_2O_4$ (0.32 mm/s) ferrites that confirms the formation of the expected $Zn_{0.5}Mn_{0.5}Fe_2O_4$ composition. The quadrupole splitting observed in the Mössbauer spectra is due to the distorted symmetry of oxygen coordination around Fe^{3+} ions located in the octahedral sites. The distortion is a result of filling tetrahedral sites of spinel lattice by Zn^{2+} and Mn^{2+} ions, which have diameters greater than Fe^{3+}. Local distortion of oxygen coordination can also be evoked by Mn^{3+} ions occurred in the ferrite structure; however, this fact did not find confirmation since the decrease of neither T_C nor σ values were not observed for the studied ferrites.

Conclusion

Single-phase $Zn_{0.5}Mn_{0.5}Fe_2O_4$ ferrite with spinel-type structure was synthesized by spray pyrolysis of a water solution of Fe(III), Mn(II) and Fe(III) nitrates at 650 °C. The ferrite sample consists of primary particles with a size $d \sim 7$ nm, which are aggregated into spherical particles with $d = 0.15-1.6$ μm. The presence of single nanosized ferrite phase in the sample was confirmed by magnetic measurements.

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