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$Ni_{0.5}Zn_{0.5}Fe_2O_4$ spinel nanoparticles obtained by complexation method using dimethylaminoethanol

C. I. COVALIU, G. GEORGESCU[a,*], J. NEAMTU[a], T. MALAERU[a], I. JITARU
University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science
[a]INCDIE ICPE – CA, Bucharest, Romania

$Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles were obtained by complexation method using the following system: $0.5Ni(NO_3)_2$ - $0.5Zn(NO_3)_2$ – $2Fe(NO_3)_3$ - DMAE (where DMAE is dimethylaminoethanol). The complex precursor has been characterized by FTIR and thermal analyses. The formation of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles was monitorized by thermal treatment of the complex precursor at 300 ^{0}C, 400 ^{0}C, 500 ^{0}C, 700 ^{0}C and 800 ^{0}C. The $Ni_{0.5}Zn_{0.5}Fe_2O_4$ spinel nanopowders have been investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM). The magnetic properties investigation revealed significant differences regarding the saturation magnetization values of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ samples obtained at different heating temperatures.

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1. Introduction

Magnetic nickel – zinc mixed ferrites are used for many years in electronic industry [1]. Nowadays these materials are intensively studied for improving their properties and nevertheless for finding new ways of applicability, especially at nanometric size as ultrafine powders.

The biomedical field is one of the most important applicability domain in which the magnetic nanoparticles may be applied [2]. The magnetic resonance imaging, hyperthermia and drug delivery are only few routes for diagnosis and cancer treatment which imply the using of an external magnetic field and the existence of the magnetic properties of oxide nanoparticles [3]. In particular, because the magnetic properties may be controlled by selecting their size, the magnetic oxide nanoparticles are being actively researched.

The capacity of some organic compounds (dioli, polioli, hidroxiacids, aminoalchohols, aminofenols etc.) of being versatile ligands for many metallic ions makes possible the isomorphic substitution of the cations in the structure of the heteropolynuclear complex compound; so it is possible the obtaining of mixed oxide systems by thermal decomposition using various combination ratios between the metallic ions.

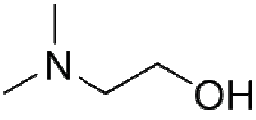

Fig. 1. Structural formula of DMAE.

In this paper is presented the preparation of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanopowders by complexation method starting from Fe^{3+}, Ni^{2+}, Zn^{2+} nitrates and DMAE (Fig.1.) as complexation agent. The influence of complex precursor heating temperature on the formation of the nickel – zinc mixed ferrites was studied.

2. Experimental part

Materials

Iron(III) nitrate ($Fe(NO_3)_3.9H_2O$), nickel nitrate $Ni(NO_3)_2{\cdot}6H_2O$, zinc nitrate $Zn(NO_3)_2{\cdot}$ $6H_2O$, dimethylaminoethanol (DMAE – $C_4H_{11}NO$) were supplied from Sigma Aldrich and used as received.

Methods

The Ni-Zn mixed ferrite nanoparticles were synthesized by complexation method from 0.5 mol L^{-1} aqueous solutions of corresponding nitrates. The dimethylaminoethanol (DMAE) was used as complexation agent. The molar ratio between Ni^{2+}: Zn^{2+}: Fe^{3+}: DMAE was 0.5:0.5:2:10. The reaction mixture was kept at 100 ^{0}C for 7h. The precipitate was separated by centrifugation, washed several times with water and dried at 100 ^{0}C for 2h. $Ni_{0.5}Zn_{0.5}Fe_2O_4$ crystalline powders were obtained by thermal decomposition of the complex precursor at 300 ^{0}C, 400 ^{0}C, 500 ^{0}C, 700 ^{0}C and 800 ^{0}C.

The complex precursor characterization was done using FTIR spectroscopy and thermal analysis. IR spectra (KBr pellets) were recorded on a BRUKER Tensor 27 spectrometer. Thermal analysis was done on Paulik-Paulik Erdey apparatus. The mixed ferrites samples were investigated by FTIR spectroscopy, XRD, SEM and magnetic measurements. X-ray diffraction analyses were performed on a Bruker AXS diffractometer type D8 ADVANCE with CuKα radiation. Scanning electron microscopy (SEM) images were obtained using a FESEM-FIB Germany. The magnetization measurements of the mixed oxide samples were determined as a function of magnetic field using a VSM Lake Shore 7300 magnetometer.

3. Results and discussion

FTIR spectroscopy

Fig. 2 shows the FTIR spectra of the DMAE, the complex precursor and nickel-zinc mixed ferrite powder. The complex precursor may be a heteronuclear complex compound containing DMAE as ligand, hydroxyl groups and/or water molecules as coordination or crystallization water and the following cations: Fe^{3+}, Ni^{2+}, Zn^{2+}.

The appearance of the band at 1610 cm^{-1} corresponding to δ_{HOH} in the complex precursor spectrum reveals the presence of hydroxyl or water molecules in its structure.

The shifting to smaller values of the frequencies assigned to $\nu_{C\text{-}O}$ from 1080 cm^{-1} in free DMAE to 1020 cm^{-1} in complex precursor spectrum may corresponds to a coordination of deprotonated alchohol groups. Also, the shifting and the splitting of the band assigned to $\nu_{C\text{-}N}$ from 1265 cm^{-1} in DMAE spectrum to 1280 cm^{-1} in precursor complex spectrum is a proof of the dimethylaminoethanol ligand coordination through N-alchil groups. Moreover, the presence of the 1385 cm^{-1} and 830 cm^{-1} bands is an evidence of the nitrate ions existence in the complex compound structure.

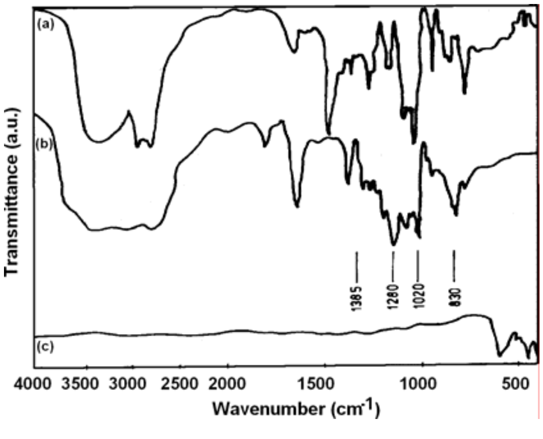

Fig. 2. The FTIR spectra of dimethylaminoethanol (DMAE) (a); complex precursor (b) and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ powder obtained at 700^0C (c).

The FTIR spectrum of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ferrite obtained by thermal decomposition of the complex precursor at 700 ^0C presents two bands (600 cm^{-1} and 440 cm^{-1}) characteristic to metal-oxygen bonds of the metallic ions lying in tetrahedral and in octahedral positions of ferrite [3]. The distribution of the metallic ions in crystalline lattice is: the non-magnetic ions Zn^{2+} are found in tetrahedral positions, the magnetic ions Ni^{2+} are placed in tetrahedral position and Fe^{3+} ions are located in octahedral positions forming the mixed ferrite $Zn^{2+}_{0.5}Fe_{0.5}^{3+}[Ni^{2+}_{0.5}Fe^{3+}_{1.5}]O^{2-}_4$ [4,5].

Thermal analysis

The temperature at which is formed the Ni-Zn mixed ferrite with spinelic structure was determine by thermal analysis of the complex precursor and X-ray diffraction of the final powder resulted by precursor heating. Fig.3 depicts the thermal analysis curves (TG, DTG şi DTA) of the complex precursor. The DTA curves show two endothermic peaks at 95 ^0C and 170 ^0C accompanied by a mass loss of 27% on TG curve assigned to water of hydration and a part of water of coordination.

As it was expected the decomposition reaction of the complex is exothermic. The exothermic effect placed at 270^0C is accompanied by a mass loss of 51% and could be attributed to coordination water and also to the organic ligand decomposition of the complex precursor, which burns in the presence of oxygen. At temperatures values higher than 280 ^0C is observed the total decomposition of the complex precursor.

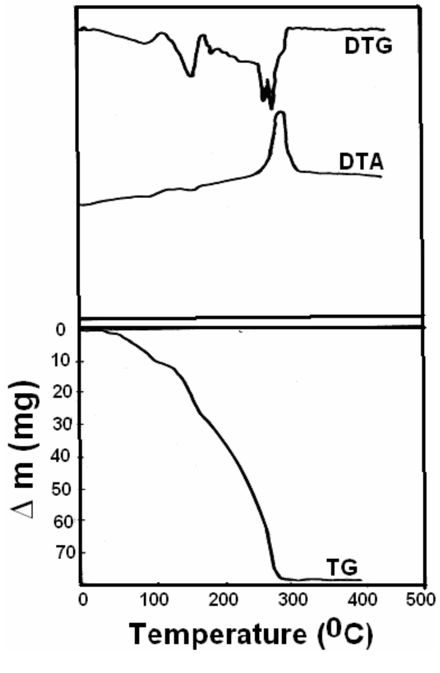

Fig. 3. The thermal analysis (TG, DTG, DTA) of the complex precursor.

X-ray diffraction analysis

The powders obtained by complex precursor calcination at different temperatures were structural characterized by X-ray diffraction (XRD).

Fig. 4 shows the XRD patterns of the powders obtained by complex precursor heating at 300 ^0C/1h 400

^{0}C/1h, 600 ^{0}C/1h, 700 ^{0}C/1h and 800 ^{0}C/1h. The XRD of the powder obtained by heating at 300^{0} C for one hour has an amorphous appearance without a precise prominence of the crystalline peaks. The heating of the complex precursor at 400 ^{0}C conducted to the formation of single phase $Ni_{0.5}Zn_{0.5}Fe_2O_4$ powder.

All the samples resulted from heating at temperatures equal or higher than 400 ^{0}C till 800 ^{0}C present spinelic structure with cubic symmetry and the cell parameter of 8.36(2) Å is similar with that reported in literature for the same compound [6].

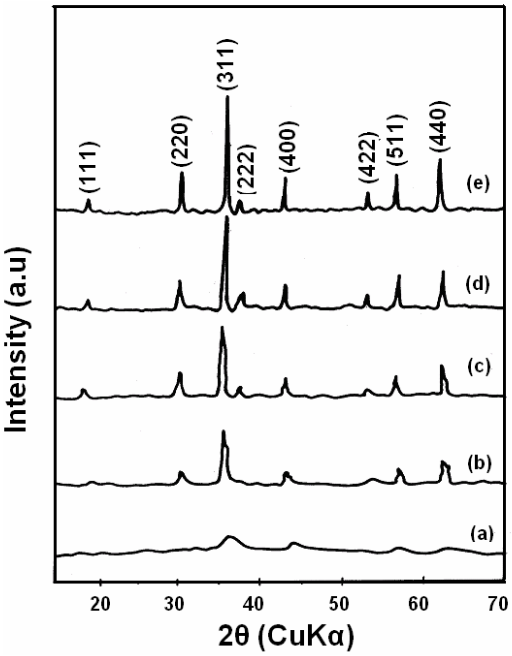

Fig. 4. The XRD patterns of powder samples obtained at different temperatures of complex precursor calcination: 300 ^{0}C for 1 h (a); 400 ^{0}C for 1h (b); 600 ^{0}C for 1 h (c); 700^{0}C for 1 h (d) and 800^{0}C for 1 h (e).

Table 1 lists the average crystallite sizes of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ powder obtained at different calcination temperatures of the complex precursor. As it was expected, the increase of the calcination temperature of the complex precursor conducted to an increase of the average crystallite size. The average crystallite sizes were calculated using Scherrer formula and the values are presented in Table 1.

Table 1. The mean crystallite sizes of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ powders obtained at different temperatures.

Temperature (^{0}C)	**400**	**600**	**700**	**800**
$(D)_{311}$ (nm)	12	18	26	35

SEM analysis

The morphology of the four $Ni_{0.5}Zn_{0.5}Fe_2O_4$ powders obtained at four different calcination temperatures was investigated by SEM. The SEM images reveal for all Ni-Zn mixed ferrite the existence of spherical agglomerates composed by small particles. The lowest particles and agglomerates sizes were found for $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanopowder obtained at 400 ^{0}C (Fig. 5a). As it was resulted from XRD investigation the increase of the calcination temperature of the complex precursor conducted to an increase of the average particles (and agglomerates) sizes of the Ni-Zn mixed oxide nanopowder (Figs. 5 b, 6 a, 6 b and Tabel 2).

Table 2. The mean particles and agglomerates sizes of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ obtained at four different heating temperatures.

The heating temperatures(^{0}C)	**Mean particles size** (nm)	**Mean agglomerates size** (nm)
400	16	300
600	20	400
700	35	450
800	47	500

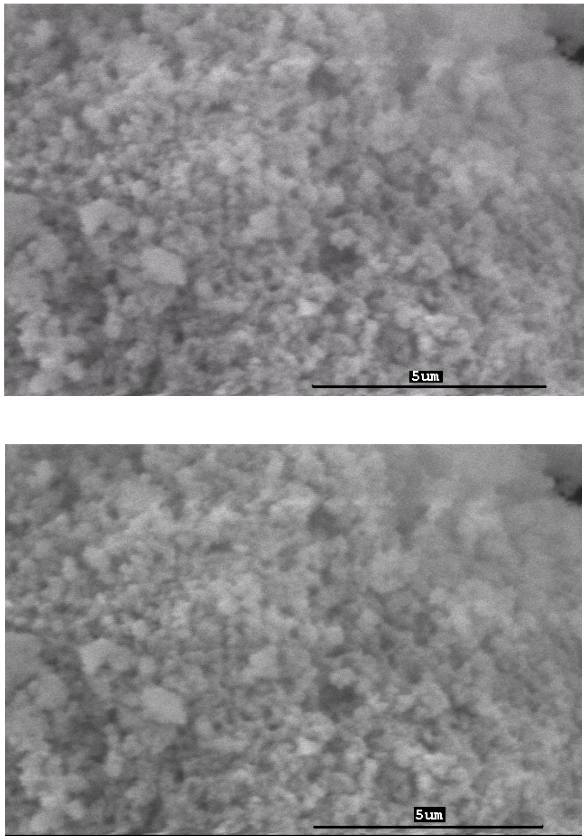

Fig. 5. The SEM images of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ obtained at 400^{0}C (a) and 600^{0}C (b).

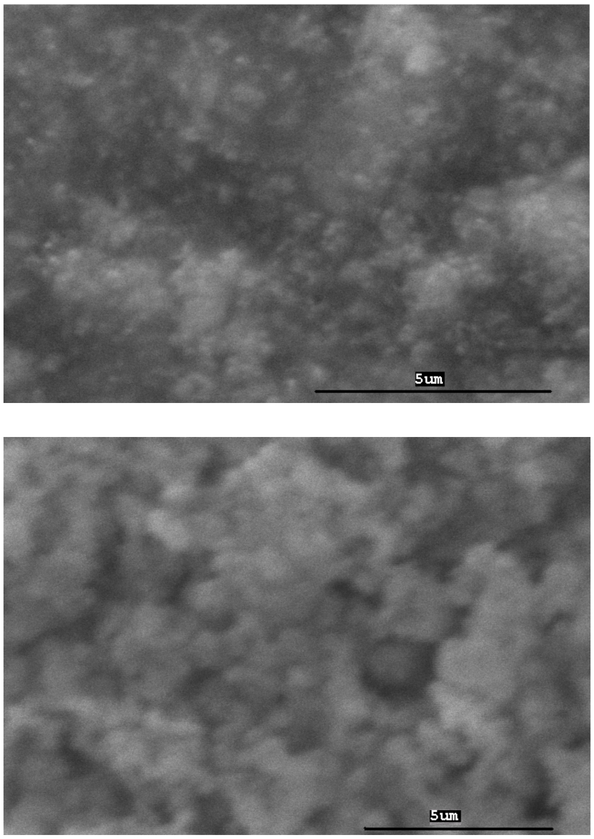

Fig. 6. The SEM images of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ obtained at 700^{0}C (a) and 800^{0}C (b).

Magnetic measurements investigation

The aim of the magnetic measurements investigation is to find the correlation between the characteristics of Ni-Zn mixed ferrite nanopowders (particle size and saturation magnetization) and the heating temperatures at which are formed the Ni-Zn mixed ferrites.

It is well known that the magnetic properties of the materials are strongly modified when the particles become very small (nanometric). This is due to the influence of thermal energy on the ordering of magnetic moments, named the superparamagnetic relaxation. Fig. 7 a and b shows the variation of the magnetization with the magnetic field (specific magnetization) for the Ni-Zn mixed ferrite obtained by precursor thermal decomposition at 400 ^{0}C and 800^{0}C. The saturation magnetization values (σ_s) decrease along with the decrease of the calcination temperatures at which are obtained the mixed ferrite nanopowders.

In our study, the magnetic properties of Ni-Zn mixed ferrite are determined by the average particles size in the following manner: the saturation magnetization σ_s increases from 28.80 emu/g to 58.30 emu/g, whereas the coercitivity (H_c) changes in 10-41 Oe range when the average particles size increases from 16 to 47 nm. The σ_s values obtained for $Ni_{0.5}Zn_{0.5}Fe_2O_4$ samples are much lower than those of the corresponding “bulk” materials. The saturation magnetization values of the samples obtained by calcination at 400 ^{0}C and 800 ^{0}C are about 1/4 and 3/4 from magnetization of NiZn-ferrites “bulk” material. This issue regarding the decrease of the saturation magnetization of the nanometric particles in comparison with the “bulk” correspondents was also observed by other researcher [7]. The sample obtained by heating at lower temperature (400 ^{0}C) consists mainly by mono-domain nanoparticles, while the other prepared ferrite samples are formed by multi-domain nanoparticles.

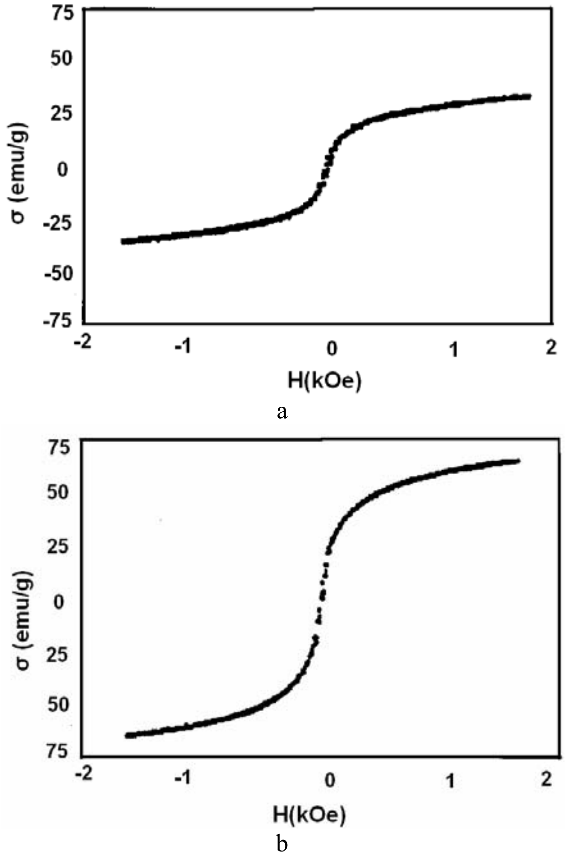

Fig. 7. The variation of magnetization with magnetic field of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ obtained by thermal decomposition of the complex precursor at 400^{0}C (a) and 800^{0}C (b).

The Ni-Zn ferrites with particle sizes less than approximately 20 nm are supposed to show superparamagnetic behaviour [8]. However, these are only the cases of Ni-Zn mixed ferrite obtained at 400 ^{0}C and 600 ^{0}C, while the other synthesized Ni-Zn mixed ferrite samples have non-superparamagnetic behavior ascribe to the obtaining of the Ni-Zn mixed ferrite at higher temperatures and probably to the agglomeration of the nanosized particles as it is obvious from the SEM images.

4. Conclusions

$Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles were successfully obtained as a result of calcination at 300 ^{0}C/1h 400 ^{0}C/1h, 600 ^{0}C/1h, 700 ^{0}C/1h and 800 ^{0}C/1h of a heteropolynuclear complex compound having dimethylaminoethanol ligand. Structural characterization by Fourier Transform Infrared Spectroscopy and X-ray diffraction proved the formation of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanopowders. The mean particle sizes and saturation magnetization values of Ni-Zn mixed ferrites increased as calcination temperature of the complex precursor increased. The magnetic properties investigation sustains the nanometric size of the prepared mixed ferrites.

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* Corresponding author: gabriela_georgescu@icpe-ca.ro