Journal of the University of Chemical Technology and Metallurgy, 47, 3, 2012, 263-268

SYNTHESIS AND CHARACTERIZATION OF Mg -Zn FERRITE/SiO_2 COMPOSITES WITH HIGH MAGNETIC LOSSES

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Received 05 May 2012
Accepted 12 June 2012

ABSTRACT

Composites based on Mg-Zn ferrites and SiO_2 were synthesized using a combination of the sol-gel and the citrate method. The samples were characterized by Fourier Transformed Infrared Spectroscopy (FT-IR), X-rays Diffraction (XRD) and Mössbauer spectroscopy. The initial magnetic permeability μ_i, the magnetic loss tg δ, the quality factor Q and the relative loss factor RLF were measured with a LCR meter at room temperature. The analyzed materials show high magnetic losses at 30 MHz.

Kaywords: *magneto-dielectric composites, superparamagnetic particles, sol-gel method, citrate method.*

INTRODUCTION

Magneto-dielectric materials with a nanosized magnetic phase and low magnetic losses are commonly studied for applying them in electronics [1 - 11]. The same can not be said for magneto-dielectrics with high magnetic losses. These materials are undesirable in electronics, but may find application in medicine due to the conversion of energy of radio frequency (RF) waves into heat. It was found that a human body absorbs RF in the range from 30 to 300 MHz [12]. Thus, applying RF waves of the this range on the human body can be used to heat previously coated with lossy magnetic material steel stents, with the aim of protecting them from the repeated formation of the atherosclerotic plaque.

In view of these facts, the study on the synthesis and the magnetic properties of Mg-Zn ferrite/SiO_2 composites as a potential magnetic material with high magnetic losses is of high interest.

EXPERIMENTAL

The starting materials were nitrate salts of Mg (II) and Zn (II); Fe (III) citrate; citric acid and TEOS (tetraethyl orthosilicate). The studied compositions contained 10 %, 20 %, 30 % and 50 % ferrite phase. The ferrite phase is with composition $Mg_{0.7}Zn_{0.3}Fe_2O_4$. According to the content of the ferrite phase the samples are labeled as K-10, K-20, K-30 and K-50. The quantity of the used TEOS corresponds to the SiO_2 in the selected compositions. The hydrolysis of TEOS was carried out with distilled water in ratio 1:1.5 at pH = 2, using nitric acid. A combination of the citrate and sol-gel method was applied for the synthesis of the Mg - Zn ferrite/ SiO_2 composites [4, 11]. For successful implementation of this technology for the synthesis of Mg-Zn ferrite/ SiO_2 composites it is necessary to combine both methods at a later stage for keeping the baseline level of pH in the preparation of the Mg-Zn citrate precursor [13] and achieve complete hydrolysis of TEOS in acidic conditions. With the aim to cover the ferrite phase with

insulating SiO_2 layers, granular gels were produced by sharp change of the pH of the Mg-Zn citrate precursor through adding it with hydrolyzed TEOS [14]. The citrate precursor was obtained by a technology described in previous works [13, 15]. All synthesized compositions were thermally treated at 650°C/ 3 h.

For the phase characterization of all synthesized materials FT-IR and X-ray diffraction analyses were applied. FT-IR spectra were collected for disk specimens with KBr using a Bruker Equinox 55 spectrometer in the range 4000 - 400 cm $^{-1}$. Powder X-ray diffraction spectra were collected within the range from 10° to 80° (2θ) with a constant step 0.04° (2θ) and counting time 1 s/step on a Bruker D8 Advance Diffractometer with Cu Kα radiation and SolX detector. The spectra were evaluated with the Diffracplus EVA package. The ferrite phase with composition $Mg_{0.7}Zn_{0.3}Fe_2O_4$ is present in all of the samples and therefore in order to avoid similar Mössbauer spectra, the Mössbauer spectrum was taken only for the powder specimen K-20. The transmission type spectrum was recorded with an electromechanical spectrometer Wissenschaftliche Elektronik GMBH, using a ^{57}Co/Cr source in a constant acceleration mode at room temperature. The velocity was calibrated by an α-Fe standard at room temperature. With a computer programme the experimentally obtained Mössbauer spectrum has been transformed into lines with Lorentzian shape. The parameters isomer shift (IS), quadruple splitting (QS), as well as the line width (FWHM) and the relative mass (G) of each component were determined as well.

Toroidal bodies have been prepared from all samples through bilateral and two-step pressing of preplasticized powders with polyvinyl alcohol (3 % solution). The applied pressure was 150 M Pa. All samples were sintered at 1250°C/2 h. The magnetic characteristics of the sintered samples were measured by a LCR meter.

RESULTS AND DISCUSSION

X-ray diffraction analysis

The X- ray diffraction patterns of the samples K-10, K-20, K-30 and K-50 are presented in Fig. 1. Crystallization occurs only in the sample K 50. Peaks correspond to a cubic spinel type lattice. The established spinel ferrite phase is a solid solution between $MgFe_2O_4$ (ASTM 36-0398) and $ZnFe_2O_4$ (ASTM 22-1012). A halo (the first diffraction peak, Fig. 1) was observed in the rest of the samples with a higher content of SiO_2. The reason for this is the amorphous structure of the resulting matrix of SiO_2. The intensity of the halo between sample K-10 and sample K-20 sharply decreases and that change suggests lowering of the amorphous SiO_2 due to its crystallization.

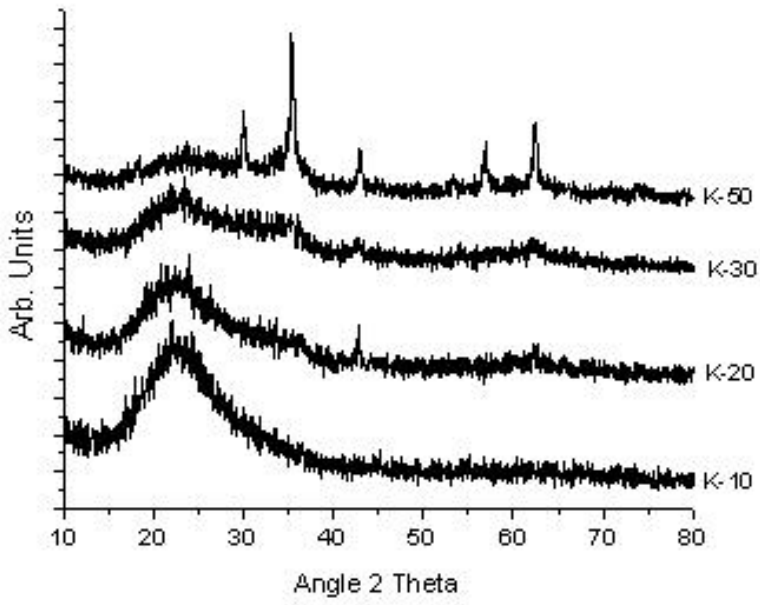

Fig. 1. XRD-patterns of samples K-10, K-20, K-30 and K-50 heat treated at 650 °C/3h.

Table 1. Mössbauer parameters.

Sample		IS, mm/s	QS, mm/s	FWHM, mm/s	G, %
K- 20	Dbl. 1	0.33	0.84	0.47	55
	Dbl. 2	0.31	1.41	0.56	45

IS - isomer shift; QS - quadruple splitting; FWHM - full with half maximum; G- relative mass.

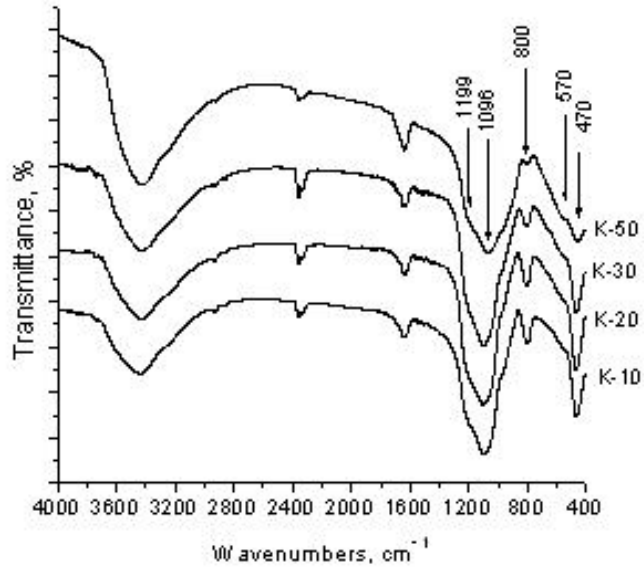

Fig. 2. FTIR-spectra of samples K-10, K-20, K-30 and K-50 heat treated at 650 °C/3h.

Table 2. Magnetic characteristics.

Composition	μ_i	tg δ=1/Q	Q	Frequency (MHz)	RLF (tg δ/ μ_i x10^{-6})
K- 10	4.56	0.0111	90	32.0	2434
K- 20	4.64	0.0111	90	32.8	2392
K- 30	4.91	0.0109	92	30.0	2220
K- 50	5.18	0.0106	94	29.0	2046

μ_i - initial magnetic permeability; Q - factor-quality factor; tg = 1/Q - magnetic loss; RLF - relative loss factor.

FT-IR spectroscopy

Fig. 2 presents IR spectra of samples K-10, K-20, K-30 and K-50 after thermal treatment at 650°C/3h. The spectra of all studied samples contain bands at 1199, 1096, 800, 570 and 470 cm^{-1}. The positions of the first two bands are related with the asymmetric vibrations of the Si-O-Si bond. The band at 800 cm^{-1} was assigned to the symmetric vibrations of the same chemical bond. The bands at 570 and 470 cm^{-1} are typical for the out-of-plane deformation vibrations of the Si-O bond [16]. The presence of the spinel phase was not detected because its characteristic bands around 600 and 400 cm^{-1}

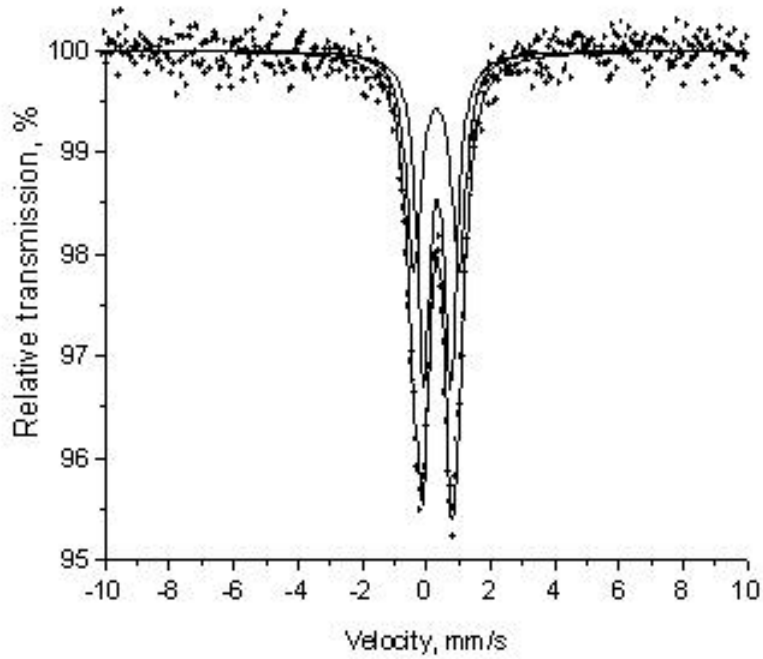

Fig. 3. Mössbauer spectrum of sample K-20 at room temperature.

were completely masked by the vibrations of the Si-O bond.

In the IR spectra of the amorphous SiO_2, the band belonging to the Si-O-Si bond is present at 1080 cm^{-1}, while, in the crystal SiO_2 this band splits and appears at 1100 cm^{-1} and 1250 cm^{-1} [17]. The shift of the position of the Si-O-Si band to the higher wave numbers could be considered as a beginning of the formation of four- and six-member rings of [SiO_4] [17], i.e. occurrence of a polymer network, characteristic of crystal SiO_2. In the studied samples a shift has been observed from 1076 cm^{-1} up to 1096 cm^{-1}. Along with the recorded change of the band positions, a broad intense shoulder which appears at 1199 cm^{-1} suggests also the crystallization of the SiO_2 matrix.

Mössbauer spectroscopy

The Mössbauer spectrum of the sample with a composition K-20, registered at room temperature, is typical for particles with extremely small dimensions, which manifest superparamagnetic behavior (Fig. 3). Parameters obtained by processing the spectrum (Table 1) indicate the presence of a spinel phase and Fe (III) ions [13, 18, 19]. The higher quadrupole splitting of K-20 compared to that of $Mg_{0.7}Zn_{0.3}Fe_2O_4$ (Dbl.1 0.84; Dbl.2 1.41(Table 1) vs. Dbl.1 0.545; Dbl.2 0.752 [13]) suggests decreasing crystallinity [20].

Magnetic characteristics

The values of some magnetic characteristics for all samples are presented in Table 2. The initial magnetic permeability μ_i, varies from 3.54 to 5.18 when the ferrite phase amount increases from 10 to 50 %. For all samples the highest Q-factor was measured between 29 and 32.8 MHz (Table 2). The magnetic losses depend on the composition and they are more pronounced when the quantity of the nanosized ferrite-phase decreases while that one of the dielectric phase increases. The substantial magnetic losses from 2046 to 2434 X 10^{-6} (RLF – Table 2) can be explained with fast relaxation of the magnetization vector of the superparamagnetic nanoparticles [21, 22].

CONCLUSIONS

The Mg-Zn ferrite / SiO_2 composites have been synthesized with a combination of the sol-gel and the

citrate method. The combination of both methods supports the crystallization of SiO_2 at low temperatures (650 °C). The magnetic parameters of the bulk Mg-Zn ferrite / SiO_2 composites determine them as materials with substantial magnetic losses in the range from 29 to 32 MHz when the ferrite phase varies from 50 to 10 %. The highest magnetic losses were obtained for the composition with 10 % ferrite phase. The synthesized Mg-Zn ferrite/composites were characterized as magnetic materials with significant losses close to the 30 MHz; a radio-frequency which allows moderate, steady and deep penetretion in the human body [23].

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