Journal of Magnetism and Magnetic Materials 469 (2019) 398–404

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Research articles

Microwave composite structures on the base of nickel-zinc ferrite $Ni_{1-x}Zn_xFe_2O_4$ nanoparticles in the photopolymer matrix

M.A. Popov[a], O.P. Fedorchuk[b], S.O. Solopan[b,*], I.V. Zavislyak[a], A.G. Belous[b]

[a] Taras Shevchenko National University of Kyiv, Faculty of Radiophysics, Electronics and Computer Systems, Kyiv, Ukraine
[b] V.I. Vernadskii Institute of General and Inorganic Chemistry, Kyiv, Ukraine

ARTICLE INFO

Keywords:
Microwave materials
Composite structure
Ferromagnetic resonance
Nickel-zinc ferrites
Nanocrystalline thick film

ABSTRACT

The 3D printing compatible technology of “ferrite – nonmagnetic dielectric” composite structures preparation was proposed. Composite resonant elements for applications in the centimeter range of microwave frequencies comprising nonmagnetic dielectric $BaTi_4O_9$-ZnO and ferrite film made from spinel nickel-zinc ferrite $Ni_{1-x}Zn_xFe_2O_4$ ($x = 0$; 0.25; 0.5; 0.75; 1) magnetic nanoparticles in the photopolymer matrix were manufactured.

Microwave characteristics of the obtained composite resonators with different concentrations of ferrite nanoparticles in the film-forming suspension were investigated. It was shown, that magnetic field makes the influence on the transmission characteristics of composite resonators, namely the operating frequency, resonance linewidth and the resonant absorption level. The developed elements can be used to create the various microwave devices (solid-state oscillators, microwave filters and attenuators) with the magnetic field tunable parameters.

1. Introduction

Nowadays the composite elements for microwave technics, that combine properties of materials from which they were created and even demonstrate new properties, can be used in radiolocation, wireless and satellite systems equipment manufacturing, and thus are a subject of special interest.

The composite structures on the base of dielectric materials with semiconductor or ferroelectric constituents or microelectromechanical systems (MEMS) were developed for use in tunable varactors or diodes [1–4]. The usage of dielectric materials is stimulated by such their properties as low dielectric losses, small dimensions, thermal stability of characteristics and low sensitivity of parameters to the various external influences. Dielectrics are widely used in microwave technics for the solid state oscillators and antennas with stable characteristics [5–10]. The manufacturing of mentioned structures allowed to combine (to a certain extent) those highly sought-after properties of dielectric materials with the capability of whole structure parameters tuning by a voltage, current or temperature changes. Yet, microwave devices need to have a small switching times, which can be reached in the case of electric and/or magnetic fields tuning, but not with the thermal or mechanic control. In the same time, it is known, that ferrites have relatively low dielectric and magnetic losses, and their parameters (frequency, resonance absorption, resonance linewidth) strongly depend on applied external magnetic field [11] due to the emergence of the ferromagnetic resonance (FMR) phenomenon.

Therefore, in this work we present the composite structures consisting of dielectric nonmagnetic material and microwave ferromagnetic material (ferrite). In the works [11,12] the possibilities of, respectively, bulk ferrite sample and a thin monocrystalline ferrite plate characteristics tuning were already investigated. It was shown that in comparison to nonmagnetic dielectrics the pure bulk ferrite components are characterized by significant magnetic losses. Therefore the usage of magnetic constituent in the form of a film is, potentially, more efficient.

The most known among the currently used technologies of films obtaining are the liquid phase epitaxy (LPE) [13], pulsed laser deposition (PLD) [14], spin spray plating (SSP), chemical precipitation methods, sol-gel coating, etc. LPE method allows to create the best quality monocrystalline films, but is among the most expensive, requires a substrate with a defined structure and matched lattice parameters. PLD method allows to make a deposition of high-quality crystalline and quasicrystalline films (of a somewhat worse quality compared to LPE), but require usage of expensive vacuum equipment and thermal treatment at high temperatures after the deposition. Polycrystalline films are also obtained by SSP method, yet the

---

* Corresponding author.
E-mail address: solopan@ukr.net (S.O. Solopan).

https://doi.org/10.1016/j.jmmm.2018.09.006
Received 7 June 2018; Received in revised form 1 August 2018; Accepted 3 September 2018

disadvantage of SSP is films pollution due to chemical treatment. Chemical methods in most cases inferior in the terms of obtained films quality and require additional control over the morphology of resulting materials. Sol-gel coating method requires additional thermal treatment at high temperatures, etc.

The aim of this work is to develop the manufacturing technology for composite structures, that consist of bulk nonmagnetic dielectric resonator of barium tetratitanate $BaTi_4O_9$-ZnO and thick nickel-zinc ferrite $Ni_{1-x}Zn_xFe_2O_4$ film with the spinel structure, which characteristics depend on applied external magnetic field; to investigate microwave properties of such structures; and to study out the prospects of this structures for the cheap electrically tuned frequency-selective microwave devices design. We concentrated our attention on the ferrites films composed from photopolymer and nickel-zinc ferrites nanoparticles $Ni_{1-x}Zn_xFe_2O_4$ ($x = 0$; 0.25; 0.5; 0.75; 1) with spinel structure synthesized by precipitation from aqueous solutions. Films were then obtained by modified tape-casting method, as described in details below.

2. Materials and methods

2.1. Synthesis of nickel-zinc ferrites nanoparticles ($Ni_{1-x}Zn_xFe_2O_4$, $x = 0$; 0.25; 0.5; 0.75; 1).

The powder precursors of the nickel-zinc $Ni_{1-x}Zn_xFe_2O_4$ with a spinel structure were obtained by the method of hydroxides sequential precipitation. For the synthesis the aqueous solutions of iron $Fe(NO_3)_3$, nickel $Ni(NO_3)_2$ and zinc nitrates $Zn(NO_3)_3$ were utilized, and the 1 M aqueous solution of sodium hydroxide was used as the precipitator. The precipitation of salts was carried out sequentially at different *pH* values, selected individually for each metal cations. At the first stage bidistilled water was poured in a reactor, the value of pH was brought to 4 ÷ 4.5, then the aqueous solution of salt $Fe(NO_3)_3$ and the precipitator (solution of NaOH) were being added as droplets with continuous stirring. After the precipitation the *pH* value of mother solution was brought to 7.0 ÷ 7.2, the solutions of salt $Zn(NO_3)_3$ and precipitator and being added sequentially as droplets with continuous stirring. After the previous precipitation the *pH* value of the mother solution was raised at the second time to 8.5 ÷ 8.7 and sequentially the droplets of salt $Ni(NO_3)_2$ and precipitator were being added.

The control of precipitator addition was carried out by the automatic titration block with a *pH*-meter, it allowed to obtain the precipitates under conditions of constant *pH* values. The *pH* value of mother solution was in the preset range and regulated by salt and alkali aqueous solutions. The speed of the precipitating solution supply was regulated by a peristaltic pump. Precipitation of 100 g of the final product was carried out for 4 h under intense stirring.

After the completion of all the components precipitation the resulting suspension was brought to a boil for 1 h. During the boiling the initial volume of suspension was being maintained constant, for this distilled water was being added and mixed for 5–10 min periodically.

A precipitate was filtered off from the mother solution and washed on a filter with bidistilled water. A washing had been performed until the concentration of sodium ions decreased to 0.1 mg/ml. The obtained product was dried with a drying cabinet in a cuvette at the temperature of 110–120 °C.

The resulting product was obtained after a calcination of precipitates in a muffle furnace with a block of automatic programed control in the atmosphere of air at the temperatures of 500 °C, 600 °C, 650 °C, 700 °C and 800 °C. As the research has shown, a single-phase product is formed already at 500 °C (773 K) (see the Section 4).

The dimensions and morphology of ferrites particles were defined with a transmission electron microscope JEM 1230 of the “Jeol” company. Dimensions of nanoparticles depend on the chemical composition of ferrite ($Ni_{1-x}Zn_xFe_2O_4$ with x = 0; 0.25; 0.5; 0.75; 1) and fluctuate in a range of 15–35 nm.

Synthesized powders of $Ni_{1-x}Zn_xFe_2O_4$, where x = 0, 0.25, 0.5, 0.75, were investigated by the X-ray phase and full-time X-ray phase analysis methods with a diffractometer ДРОН-4 (CuKα radiation).

Table 1
Mass magnetization of synthesized nickel-zinc ferrites nanoparticles in permanent magnetic field $H = 5440$ Oe.

Ferrite	Mass magnetization at $H = 5440$ Oe, emu/g
$ZnFe_2O_4$	~0
$NiFe_2O_4$	28.9
$Ni_{0.25}Zn_{0.75}Fe_2O_4$	31.1
$Ni_{0.5}Zn_{0.5}Fe_2O_4$	46.8
$Ni_{0.75}Zn_{0.25}Fe_2O_4$	44.3

Measurements of the ferrites saturation magnetization values were made by the Faraday method, a ferrite with the highest value ($Ni_{0.5}Zn_{0.5}Fe_2O_4$, see Table 1) was used for a manufacturing of composite resonators.

2.2. Manufacturing of the composite structures “microwave dielectric – thick film of nickel-zinc ferrite $Ni_{1-x}Zn_xFe_2O_4$, $x = 0$; 0.25; 0.5; 0.75; 1”

For the ferrite films manufacturing the nickel-zinc ferrites $Ni_{1-x}Zn_xFe_2O_4$ nanoparticles were mixed with photopolymer (ultraviolet-cured glue Permabond UV630). Suspensions of ferrites powders with different concentrations of ferrites in polymer were being mixed with homogenizer *IKA T10 standard* during 5 min. Then the obtained suspensions were applied by the screen printing method on the dielectric resonators from zinc-doped barium tetratitanate ceramics. This ceramics is characterized in the microwave range by *Q*-factor value $Q \approx 5700$, dielectric constant $\varepsilon = 34$ and thermal stability (temperature coefficient of dielectric permittivity $TC\varepsilon \sim 10^{-6}\,K^{-1}$) [15]. After this the composites were covered with glass protecting plates.

According to the experience of our previous work [16,17] we decided to manufacture films with thicknesses of 100 μm. The heterostructure was placed in a permanent magnetic field between poles of an electromagnet to decrease crystallographic axes orientations scattering of ferrite particles, on the contrary to [16], where ferrite component of composite resonant structures were synthesized by sol-gel method without applying magnetic field. 15 min after switching on the field the polymerization process under the light of UV lamps was started. Composite resonators with ferrite films polymerized under 3 different conditions: 1) without the field, 2) field parallel to and 3) field perpendicular to resonator’s axis of symmetry with field strength being $H = 2900$ Oe. It had influence on quantitative indicators of their characteristics. Two UV lamps were used for films polymerization, time of polymerization was 1 h under the light of lamp with radiation wavelength $\lambda = 385$ nm and power 6 W in the magnetic field and 10 min under the light of lamp with $\lambda = 365$ nm and power 36 W after sample was removed from magnetic field.

3. Experimental procedure and theoretical background

3.1. 2.1. Measuring cell for the investigation of transmission characteristics of composite resonators “microwave dielectric – thick film of nickel-zinc ferrite ($Ni_{1-x}Zn_xFe_2O_4$, $x = 0$; 0.25; 0.5; 0.75; 1)”

Absorption spectra of manufactured composite nanoheterostructures “thick film of $Ni_{1-x}Zn_xFe_2O_4$ – high Q-factor dielectric resonator” were measured with *Agilent N5230A PNA–L Network Analyzer* and measuring cell, which was the section of X-band rectangular waveguide with the 23*10 mm^2 cross-section. The investigation of composite resonators properties was carried out in the centimeter wave band in a traveling wave mode, since in such way an effective excitation of both dielectric resonance in dielectric resonator (DR) and ferromagnetic resonance in ferrite were assured. Investigated structures were positioned on the glass substrate with a thickness of 0.2 mm inside