Substituted Lithium Ferrite
Utilized as Magnetically Active Filler
for Composites with Acrylonitryle Butadiene Rubber Matrix

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Soft magnetic lithium ferrite ($Li_{0.525}Zn_{0.30}Ti_{0.35}Fe_{1.825}O_4$) with a small addition of Bi and Mn prepared by wet self-propagating combustion method was used as magnetically active filler in elastomeric composite materials with the content 17 to 45 vol%. XRD analysis confirmed single-phase cubic spinel structure of synthesized ferrite with average crystallite size of 38 nm. The magnetic characteristics specified from measured hysteresis loops and from the temperature dependences of magnetic susceptibility confirmed soft magnetic behavior of Li ferrite with good rectangularity. The effect of magnetic filler concentration on various magnetic and microwave absorption properties of magnetic polymer composites was investigated, and assessed from complex permeability measurements in the frequency range of 1 MHz to 6.5 GHz. Adding more filler increases the magnetic permeability while the resonance frequency decreases.

1. Introduction

Many electronic devices are designed to operate at extremely high frequencies. The use of various devices in gigahertz range may often result in malfunctioning due to electromagnetic (EM) interferences. Extensively used the iron oxides-ferrites belong to the class of appropriate shielding materials able to absorb such an EM pollution [1–3]. Other, e.g., lithium ferrites known as being magnetically soft, are widely accessible candidates for versatile applications in microwave frequency band due to their nearly rectangular hysteresis loops, relatively high the Curie temperature, high resistivity, low dielectric loss and cost. The substitution of lithium by properly chosen ions can further improve, and deliberately adjust, the magnetic behavior of final product via replacement and rearrangement of Li^+ and Fe^{3+} ions within tetrahedral and octahedral sublattices of an inverse spinel ferrite structure. The addition of Zn and Ti ions even in small amounts positively influences the magnetic characteristics of Li ferrites alongside with the conservation of single-phase spinel structure [4, 5]. The properties of ferrites can be tailored by appropriate fabrication process and related thermal treatment since the ferrite structure is very sensitive to synthesizing conditions. On the contrary to ceramic routes, the chemical preparation methods are more attractive because they allow to produce ferrite powder with almost equally sized nanoparticles. One of these methods, i.e., the combustion process based on thermal decomposition of organic precursor containing metallic ions, thanks to its simplicity, belongs to the best "wet" preparation techniques [6]. By incorporating ferrite materials into appropriate polymer matrix, the magnetic composites are prepared that are flexible, easily shapeable, lightweight, resistible to the corrosion and an aggressive chemical environment. Electromagnetic behavior of these materials can be easily managed and controlled with the type and the concentration of properly selected magnetic filler enabling to use the composites for various applications [7, 8]. The impact of substituted lithium ferrite used as magnetic filler at various concentrations on microwave absorption properties of the composites was studied via the frequency analysis of the complex permeability.

2. Sample preparation and tools used for analysis

Composite samples with magnetic ferrite filler concentration 17, 29 and 45 vol.% in natural Acrylonitrile-Butadiene rubber (NBR) acting as non-magnetic elastomeric matrix were prepared by two-step mixing process in laboratory kneading machine. The vulcanization was carried out at $160\,°C$ and a pressure of 15 MPa maintained by hydraulic pressing machine for an optimum curing time of 17, 14.5 and 13.5 min., respectively, as the filler concentration increased. The optimal value (i.e., the time needed to reach optimal crosslinking) was determined from the vulcanization curves measured by the rheometer with standardized procedure. Ring-shaped samples of an outer diameter 8 mm, an inner diameter 3.2 mm, and thickness 2 mm, were cut out from the composites to perform magnetic measurements.

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Substituted lithium ferrite filler was synthesized by auto-combustion process [9]. High purity starting reagents were used in the form of raw salts, namely Lithium Carbonate Li_2CO_3, Ferric Nitrate $Fe(NO_3)_3.9H_2O$, Zinc Acetate $Zn(CH_3COO)_2.2H_2O$, Titanylacetylacetonate $C_{10}H_{14}O_5Ti$, Bismuth Nitrate $Bi(NO_3)_3.5H_2O$, and Manganese Nitrate $Mn(NO_3)_2.4H_2O$. In order to lower the temperature of thermal treatment and improve the microstructure uniformity of ferrite particles, as well as to reduce dielectric loss and electrical conductivity, minimal amounts of Bi and Mn were added as the sintering aid [5, 7]. Water solution of Glycine NH_2CH_2COOH was used as the organic precursor enabling homogenous distribution of individual metallic ions. All the raw salts were solved in de-ionized water, except for the salts of Li^+ and Bi^{3+} solved in 4 M HNO_3 and further mixed with Glycine solution. Liquid Metal-Glycine mixture was homogenized and stabilized by mixing at $80\,°C$ in magnetic stirring apparatus. Next, the solution was evaporated until self-propagating auto-combustion reaction ignited. The reaction is accompanied with strong release of combustion gas, and production of highly voluminous and fluffy brown-gray powder. This powder was annealed in the furnace at $1050\,°C$ for 3.5 h. The temperature was slowly increasing $(100\,°C/1\,h)$ to achieve better formation of spinel structure. Further, the synthesized ferrite powder was crushed in agate ball-mill, and finally sieved to obtain particles sized bellow 40 μm. The structure, morphology and particle size of prepared ferrite powder was investigated by standard equipment, i.e., X-ray diffractometer (XRD) using CuK_α radiation ($\lambda = 1.5418$ Å), scanning electron microscope (SEM), and laser particle sizer. Important quasi-static magnetic characteristics (coercive field H_c, remanent flux density B_r, hysteresis loop area A_l, amplitude μ_a, and initial permeability μ_i) were derived from the series of magnetization curves measured on ring-shaped specimens by advanced computer-controlled BH-tracer. Sample excitation was provided by arbitrary waveform generator (16-bit output resolution) and high-power operational amplifier. Basic resolution of voltage signals measured by two identical digital multimeters at the sampling rate of 50 kHz was 4.5 digits. The Curie temperature T_C was found from the temperature dependencies of volume magnetic susceptibility χ, that were measured using impedance ac bridge with tailor-made heating system. The temperature was measured by Pt/PtRh thermocouple directly touching to the quartz-glass capsule filled with ferrite powder, applying 12-bit A/D conversion of amplified differential thermocouple signal linearized by lookup table (estimated error $\pm0.5\,°C$). Frequency dependencies of complex permeability $\mu(f) = \mu'(f) - i\mu''(f)$ were obtained by means of combined impedance/network analysis method using a network analyzer. The impedance analysis method was adopted in the frequency range from 1 MHz to 1 GHz. A ring sample was inserted into a coaxial short-circuit sample holder. Based on measured complex impedances, the complex permeability was evaluated with

$$\mu(f) = 1 + \frac{Z - Z_{\mathrm{air}}}{i\,h\mu_0 f\,\ln{(b/c)}},$$

where Z and Z_{air} are input complex impedances of the holder with and without sample, respectively. The permeability of free space is μ_0, h is the height of a sample, while b and c are the outer and inner sample diameters. Additionally, the network analysis method (utilizing 7 mm coaxial transmission line) was used in the range of 100 MHz–6.5 GHz, in which the permeability measurements of ring samples were given through reflection/transmission (or scattering) parameters [5]. Unless otherwise noted, all the instrumentation units are commercially available.

3. Results and discussion

The structure of prepared magnetic material analyzed by XRD confirmed single-phase cubic spinel structure typical for Li ferrites, with lattice parameter $a = 0.83752$ nm and average crystallite size $D = 38$ nm, see Fig. 1a. The morphology of ferrite filler obtained by SEM is presented in Fig. 1b. One can see there an agglomerate consisting of variably sized polyhedral particles. The measurement of particle size distribution confirmed sizes below 40 μm with average particle size $d_{50} = 22$ μm. Major hysteresis loop normalized to the maximum flux density $B(H)/B_{\mathrm{max}}$
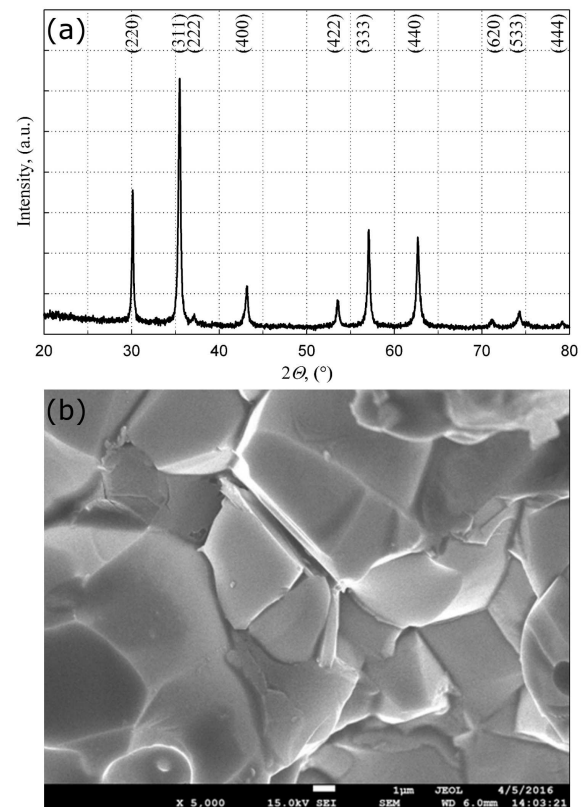

Fig. 1. XRD pattern (a), and (b) morphology of $Li_{0.525}Zn_{0.30}Ti_{0.35}Fe_{1.825}O_4$ ferrite filler obtained by SEM.
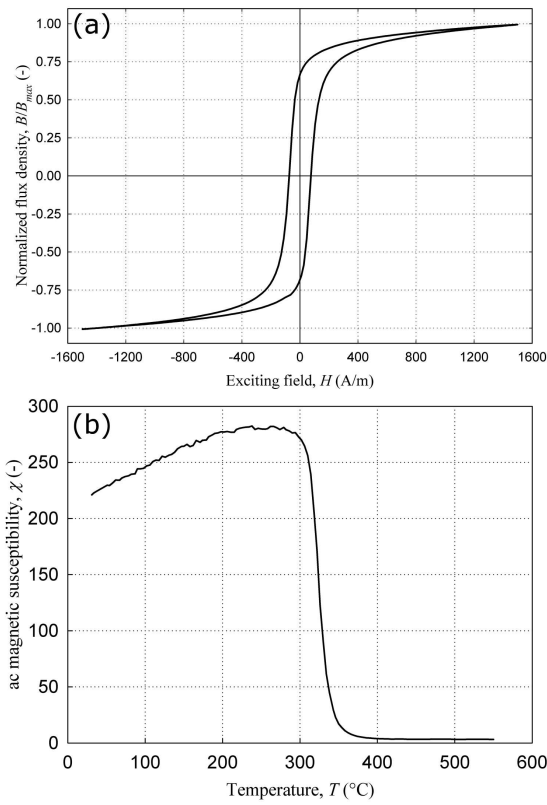
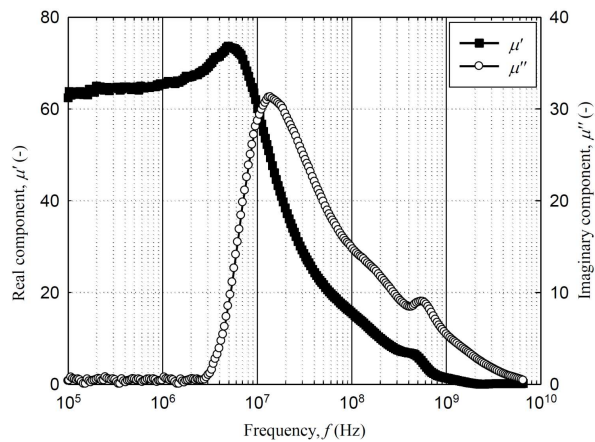Fig. 2. Hysteresis loop (a), and (b) temperature dependence of susceptibility $\chi(T)$ of Li ferrite filler.

Fig. 3. The frequency dependencies of the complex permeability of $Li_{0.525}Zn_{0.30}Ti_{0.35}Fe_{1.825}O_4$ ferrite filler.
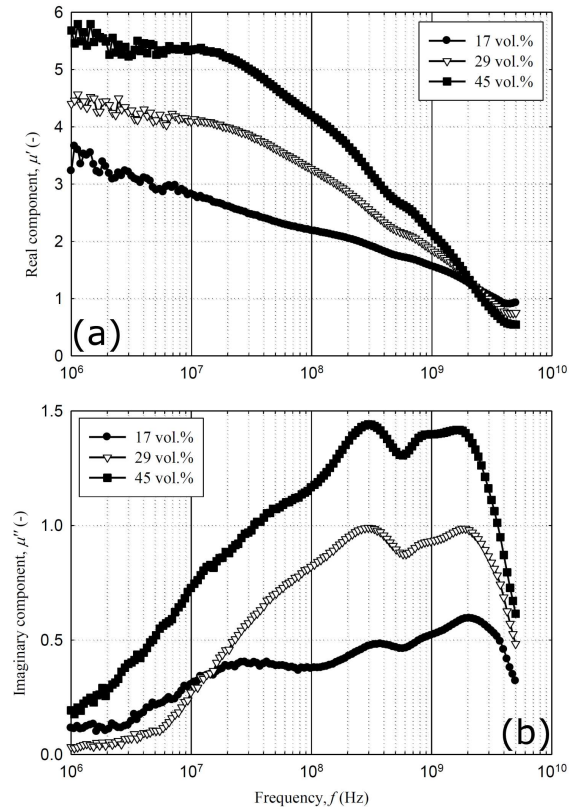

Fig. 4. The frequency dependencies of the real component $\mu'(f)$ (a), and (b) imaginary component $\mu''(f)$ of the complex permeability of Li ferrite filler/NBR composites.

($B_{max} = 0.1883$ T) measured at exciting field amplitude $H_{max} = 1500$ A/m, shown in Fig. 2a, is typical for lithium ferrites, i.e., nearly rectangular with low coercive field. Important magnetic parameters of substituted Li ferrite found from magnetization curves are $H_c = 74.61$ A/m, $B_r = 127.4$ mT, $A_l = 62.41$ J/m^3, and $\mu_i = 107$. The Curie temperature $T_C = 324\,^\circ$C was found from the temperature dependence of volume magnetic susceptibility $\chi(T)$, see Fig. 2b.

The results of complex permeability measurements on the $Li_{0.525}Zn_{0.30}Ti_{0.35}Fe_{1.825}O_4$ ferrite (prepared by wet process) as a function of frequency are shown in Fig. 3. Within the measured frequency range, the permeability is of a dispersive character. One can see that at first the real part μ' of permeability is nearly constant, starting at the value of 62.45. Only a slow rise is observed with increasing frequency value. Absolute peak (value 73.69) at 4.94 MHz and a secondary local maximum (6.15) at 488.75 MHz is reached, followed by drop to zero. The imaginary part μ'' of permeability exhibits two maxima: the first equals 31.29 at $f_{c1} = 13.77$ MHz, and the second is 9.02 at $f_{c2} = 539.94$ MHz. The measured frequency dispersion of permeability is of a resonance type, attributed to two elementary types of resonance phenomena, i.e., the domain wall resonance, and magnetic moment rotation resonance (natural ferromagnetic resonance) [5]. The first originates from the oscillations of domain walls at minor critical (or resonance) frequency f_{c1}, while the other one is attributed to the precessions of magnetic moments in domains at major critical (or resonance) frequency f_{c2}. The critical frequency characterizes the limit above which the use of studied material in electronic applications is restricted. On the other hand, when the ferrite is assumed for use as electromagnetic wave absorber,

the magnetic loss (represented by μ'' term) related to the absorption ability in the frequency interval concerned should be as high as possible. Figure 4 envisages the measured variations of complex permeability for prepared composite materials with $Li_{0.525}Zn_{0.30}Ti_{0.35}Fe_{1.825}O_4$ ferrite being the magnetically active filler and natural Acrylonitrile-Butadiene Rubber acting as non-magnetic matrix. In contrast to the sintered ferrite, observed frequency dispersion of permeability appears to be rather relaxation than the resonance type. Lower values of permeability may be attributed to the nature of composite in which so-called magnetic dilution takes place. Ferrite particles are dispersed in a polymeric medium. As a result, demagnetizing field H_d is formed, generated by the "magnetic poles" of isolated ferrite particles surrounded by NBR matrix material [10]. Decreasing the magnetic filler content in composite material μ' (at $f = 1$ MHz) also dropped from about 5.4 for the composite with 45 vol.% of filler content, to around 3.2 for the composite with 17 vol.% of filler. The real component μ' decreased, and the critical frequencies changed towards higher values (compared to ferrite filler itself). It is a consequence of an emergence of demagnetizing field H_d ($f_{c1} = 297.4$ MHz for 45% and 29% filling, and 374.6 MHz for 17% filling, $f_{c2} = 1.612$ GHz for 45%, 1.806 GHz for 29%, and 2.050 GHz for 17% filling, respectively).

4. Conclusion

Dynamic magnetic properties of LiZnTi ferrite composites in natural acrylonitrile-butadiene rubber matrix represented in this paper by the frequency dependencies of the complex permeability and corresponding parameters (e.g., critical frequencies and local maxima, etc.) were studied. An interesting information resulting from the experiments is that the second maximum of the imaginary component corresponding to the major critical frequency f_{c2} becomes more dominant with less filler concentration. Hence, a natural ferromagnetic resonance of increasingly isolated ferrite particles moves towards higher frequencies, and becomes slightly more important over a domain wall resonance. The parameters of interest in general exhibit monotonic, nearly linear behavior depending on the filler concentration, thus allowing easy control and tailoring of resultant properties of the composites.

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