MAGNETIC POLYMER COMPOSITES WITH NANOPARTICLE MAGNETIC FILLER

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1. Introduction

In the last years an extensive attention has been paid to the study of nano-crystalline materials with regards to their properties as well as the advantages/disadvantages of diverse fabrication methods [1-3]. One of these methods - the glycine-nitrate process (GNP) takes benefit of using inexpensive raw materials; the preparation process is relatively simple and energy efficient. GNP is based on auto-combustion method of precursor comprising in metal nitrates and glycine followed by the sintering at temperatures which are lower than that of classic ceramic technique. Prepared ceramic products are characterised by fine particles with high homogeneity of size distribution. These nano-scale particles possess unique physical and chemical properties depending on the size of the grains consisting of nano-sized crystallites, surface area and various surface properties. Spinel ferrites are used for many years in various electronic devices and components thanks to their specialised magnetic properties as well as for the possibility of chemical composition targeted to prepare tailor-made materials for specific applications. Among the spinel ferrites, NiZn ferrites are commercially used in diverse electromagnetic devices operated at high frequencies and are attractive for their good microwave absorbing properties [3]. Incorporation of the ferrite powders into the polymer matrix brings about new composite materials that are characterised by good magnetic parameters as well as properties typical for pure polymers. The magnetic polymer composites with NiZn ferrite filler can be used as electromagnetic wave (EM-wave) absorbers in GHz frequency band. This paper is devoted to the study the influence of nano-sized ferrite particles prepared at various sintering temperatures on structural and magnetic parameters of ferrite samples as well as on magnetic and microwave-absorbing characteristics of the magnetic polymer composites with prepared ferrite powders used as the magnetic fillers.

2. Experimental details

Magnetic polymer composite samples with 50 vol.% concentration of magnetic filler were prepared by means of low-temperature hot-pressing process. The mixtures of ferrite filler and polyvinylchloride matrix (containing 50.0% of polyvinylchloride along with 48.5% of dioctyl phthalate, 1% of stearic acid and 0.5% of calcium stearate acting as surfactant, lubrication and stabilising agent) were thermally treated at 145°C and pressed into the ring shape by the pressing machine under the pressure of aproximelly 5 MPa. NiZn ferrite with chemical composition $Ni_{0.33}Zn_{0.67}Fe_2O_4$, prepared by GNP was used as the magnetic filler and the sintering was carried out at various temperatures T_s - 450°C, 650°C, 850°C and 1200°C for 6 hours in super khantal furnace [1, 2].

The crystalline structure of ferrite powders prepared at various temperatures was investigated by means of X-ray diffraction analysis using commercially available diffractometer equipped with X-ray tube with rotating Cu anode operating at 12 kW. The lattice parameters and the average crystallite sizes were determined by TOPAS 3.0 software. The size, shape and chemical composition of ferrite powder particles were examined by scanning electron microscope (SEM) with EDX semi-quantitative analysis. The magnetic properties, such as maximum (Φ_m) and remanent (Φ_r) magnetic flux were measured by means of vibrating sample magnetometer (VSM). The influence of ferrite filler sintered at various temperatures on the magnetic properties of prepared ring-shaped samples of composite with outer diameter of 8.0 mm, inner diameter of 3.5 mm and height of approximately 2 mm was studied using the measured frequency dependencies of real and imaginary parts of complex permeability $\mu(f) = \mu'(f) - j\mu''(f)$ by means of impedance spectroscopy carried out using commercially available vector analyzer in the frequency range of 10 MHz to 3 GHz.

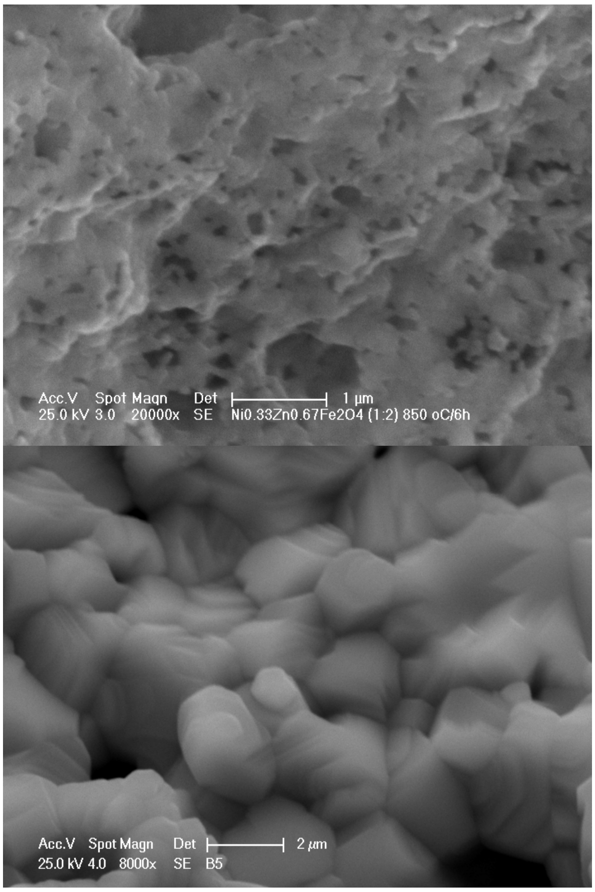
3. Results and discussion

X-ray diffraction analysis of NiZn ferrite samples prepared at various sintering temperatures indicates the single-phase cubic spinel structure without other crystalline phases. Increased sintering temperature caused growth of grains manifesting as an increase of the crystallite size *D* from 17.5 nm at temperature 450°C to 418 nm at 1200°C. The lattice parameter *a* varies only slightly with temperature from 0.841700 nm to 0.841399 nm (see Table 1).

Tab. 1. *The properties of prepared NiZn ferrite powders.*

T_s (°C)	D (nm)	a (nm)	Φ_r (nWb)	Φ_m (nWb)	f_r (MHz)
450	17.5	0.841700	12.9	54.7	1637
650	57.6	0.841560	21.9	67.8	956
850	157.0	0.841571	36.5	132.0	742
1200	418.0	0.841399	41.6	211.0	99

The morphology of ferrite powders prepared at temperatures 850°C and 1200°C for 6 hours was investigated by means of SEM and is shown in Fig.1. From SEM micrographs the presence of ferrite particles of polyhedral shape aggregating to clusters and thus the increase of particle size with increasing sintering temperature is visible. NiZn ferrite powder calcined at 850°C includes the clusters containing various nano-scale particles (see Fig.1a). On the other hand the particle size of ferrite powders thermally treated at 1200°C is above 2 μm and the particles are evidently crystallites (Fig.1b). Chemical composition $Ni_{0.33}Zn_{0.67}Fe_2O_4$ was monitored by means of EDX analysis that confirmed single-phase spinel structure of prepared samples (Fig.2).



a) 850°C *b) 1200°C*

Fig. 1: *SEM micrographs of NiZn ferrite powders prepared at various temperatures.*

Mass content of individual ions of NiZn ferrite sample calcined at 850°C is given in Table 2. The measured data fit to theoretical values of individual chemical elements very well.

Tab. 2. *The mass content of individual ions in NiZn ferrite.*

element	Ni	Zn	Fe	O
measured content (wt.%)	8.57	18.08	45.44	27.92
theoretical content (wt.%)	8.11	18.34	46.76	26.79

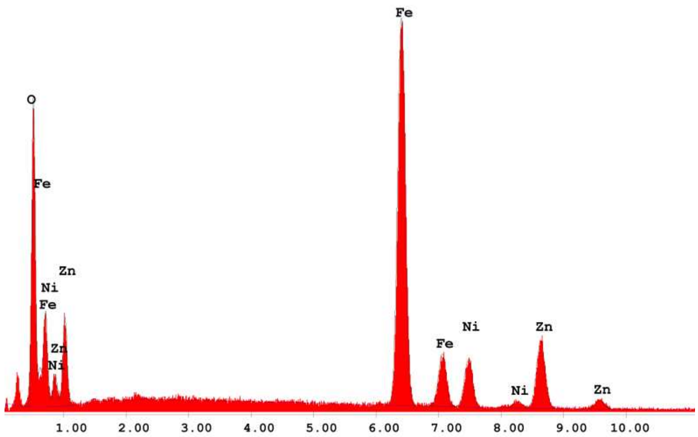
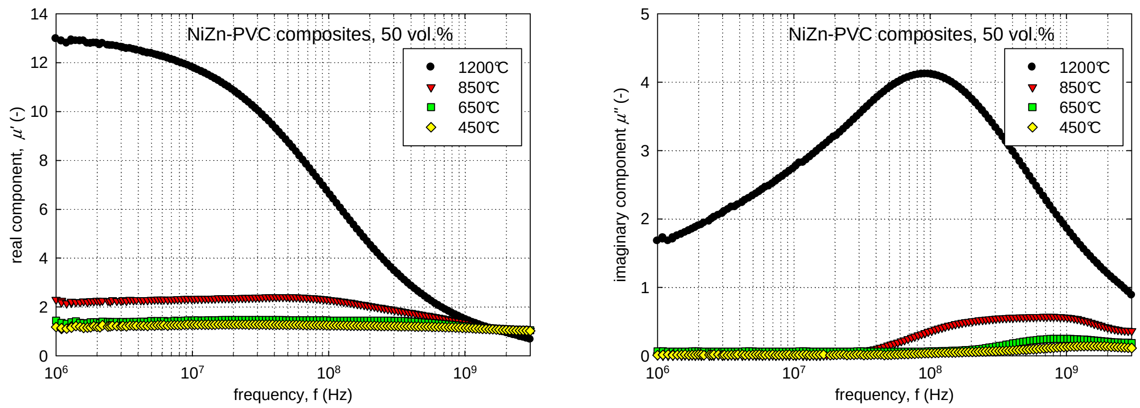


Fig. 2: *EDX analysis of NiZn ferrite powder prepared at 850°C.*

The magnetic properties of ferrite powders (Curie tempeature T_C, remanent magnetic flux Φ_r and maximum flux Φ_m) thermally treated at various temperatures are given in Table 1.

NiZn ferrite fillers noticeably influence the magnetic properties of magnetic polymer composites. Fig.3 illustrates the real (a) and imaginary (b) parts of complex permeability vs. frequency curves $\mu(f) = \mu'(f) - j\mu''(f)$ for fabricated composite materials with NiZn ferrite filler and PVC polymer matrix and with fixed filler concentration of 50 vol.% (the parameter of curves is the sintering temperature of ferrite filler). Increased maximum and remanent magnetic flux (Tab.1) as well as μ' at 1 MHz (Fig.3a) with sintering temperature (up to 1200°C) was attributed to increased grain size (or crystallite size) as observed in SEM micrograph shown in Fig. 1 and in Tab. 1. The decrease of μ' with frequency f (Fig.3a) and simultaneously the growth of μ'' (Fig.3b) with the frequency of applied ac electromagnetic field is associated with the presence of various types of magnetising mechanisms, namely the domain wall motion and magnetic polarisation vector (or spin momentum) rotation in the magnetic domains [5, 6]. At lower frequencies (below about 100 MHz), the influence of domain wall motion dominates over the rotational processes especially in composite samples with higher average crystallite size (157 and 417 nm) related to higher sintering temperatures (850°C and 1200°C). The permeability of composite samples with lower crystallite size (17.5 and 57.6 nm) and lower sintering temperatures (450°C and 650°C) is mainly related to the contribution of rotational processes, since the critical diameter at which the particles of a given chemical composition of NiZn ferrite filler become single domains (≈40 nm, [3]) is lower than the grain size of sintered samples (Fig.3). The permeability is in general directly proportional to the saturation magnetisation (and thus also to maximum magnetic flux) and the average grain size, but indirectly proportional to the first magnetocrystalline anisotropy constant. As a result, μ is improved by higher sintering temperature resulting in higher crystallite sizes. On the other hand, the composite structure which comprises the NiZn ferrite filler particles embedded in PVC polymeric matrix shifted the resonance frequency (Fig. 3b) towards higher frequency band as the sintering temperature of filler decreased.



a) $\mu'(f)$ *b) $\mu''(f)$*

Fig. 3: *Frequency dependences of real (a) and imaginary (b) parts of complex permeability $\mu(f) = \mu'(f) - j\mu''(f)$ of NiZn-PVC composite samples.*

4. Conclusions

The effect of nano-sized NiZn ferrite fillers prepared by GNP with various sintering temperatures on the structural and magnetic characteristics of ferrite samples as well as the magnetic and microwave-absorbing parameters of the magnetic polymer composites with ferrite fillers was studied. Higher temperature during GNP caused the increase of grain (or crystallite) size and the improvement of magnetic properties of NiZn ferrite powders. On the other hand, as the sintering temperature decreased, the resonance frequency f_r of magnetic polymer composites with ferrite filler shifted towards higher frequency, maximum value f_r = 1637 MHz was achieved for composite sample with 50 vol.% of ferrite sintered at 450°C.

These composites show potential as the materials for using as EM-wave absorbers in GHz frequency region.

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