

## MAGNETIC SPECTRA ANALYSIS OF DIELECTRICS

J. Sláma<sup>1</sup>, V. Olah<sup>1</sup>, A. Grusková<sup>1</sup>, V. Jančárik<sup>1</sup>, I. Hudec<sup>2</sup>, R. Dosoudil<sup>1</sup>, P. Šíroky<sup>1</sup>, M. Šoka<sup>1</sup>

<sup>1</sup>Slovak University of Technology, Faculty of Electrical Engineering and Information Technology,  
Ilkovičova 3, 812 19 Bratislava, Slovak Republic

<sup>2</sup>Slovak University of Technology, Faculty of Chemical and Food Technology,  
Radlinského 9, 812 37 Bratislava, Slovak Republic

**Summary** Method of magnetic spectroscopy is used to analyze and to interpret the experimental data obtained by magnetic measurement of the complex permeability spectra of Mg ferrite and NiZn ferrite polymers. Ferrite polymers were prepared from various concentration of NiZn ferrite particles as a soft magnetic fillers dispersed in PVC polymer matrix. Effect of the filler content on the permeability spectra of NiZn ferrite polymers was examined and compared with presented sintered ferrite samples. The variations of permeability and relaxation frequency due to ferrite filler concentration in composite are presented and discussed from point of view the magnetization processes in samples.

### 1. INTRODUCTION

We are still finding the versatile material used over large frequency range, but without external bias field. The most important ones have been NiZn and Ni ferrites and substituted Li ferrites which are the best available soft magnetic materials for electronic application. One tool of develop a novel ferrites is to investigate selected cation substitution of Fe ions in ferromagnetic sublattices, the other tool is integration of ferrite particles to polymer matrix. In addition, the substituted ferrites and ferrite polymers are materials which the microwave engineer needs in the present time. The effect of change of selected substitution ions (Zn, Ti, Be, Cu) and the substitution rate on magnetic properties of Li ferrite, NiZn ferrite and Ni ferrite samples were studied and published [1,2,3]. Magnetization curves and related magnetic parameters have been measured by means of vibrating sample magneto meter. The size and shape of the ferrite powder particles have been examined by SEM. Polycrystalline ferrites were prepared by the standard ceramic method. The magnetic spectra of prepared ferrites were measured within frequency range of 1MHz – 2.2GHz using impedance spectroscopy. These magnetics have self bias properties, high squareness of hysteresis loop, high saturation, flux density and permeability, on the other hand low coercivity and losses. They allow integration and miniaturization up to nanocomposite films. The ionic and granular structures lead to a lower conductivity which permits the ferrites to be used easily up to high frequencies.

In presented paper the magnetic spectra analysis of selected ferrites and ferrite polymers were carry out in natural conditions, where internal magnetic field is determined by spontaneous magnetization and the anisotropies only. In addition, the spectra of sintered Mg and NiZn ferrites with prepared ferrite polymer composites are

compared from point of view the actual magnetization mechanism in presented samples.

### 2. EXAMPLE FREQUENCY SPECTROSCOPY OF FERRITE

The magnetic spectra of polycrystalline ferrites is associated with various mechanisms of magnetization. They are the domain wall displacement, the magnetization rotation and the gyromagnetic spin rotation. One can admit idea by finding two dispersion and absorption in a sample of Mg ferrite (Fig. 1) is in [4]. The first dispersion is attributed to the domain wall resonance, roughly at 20 MHz, and the second one at higher frequencies (~2 GHz), to the spin resonance in the natural effective anisotropy field. On the other hand, the first maximum, of  $\mu''(f)$  spectra i.e. absorption at 50 MHz is attributed mainly to d.w. relaxation. The second absorption range, at higher frequencies below 2 GHz, is due to the spin resonance. The complex permeability data  $\mu^*(f)$  are approximated by a complicated locus in complex plane, where the real part  $\mu'(f)$  of complex permeability is plotted against the imaginary part  $\mu''(f)$ , see Fig.2.

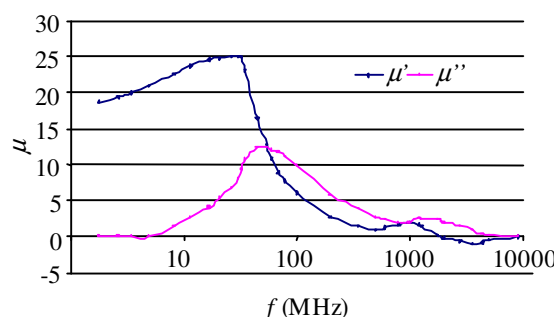


Fig. 1. Frequency spectra of real  $\mu'$  and imaginary  $\mu''$  components of permeability for  $\text{MgFe}_2\text{O}_4$  ferrite.

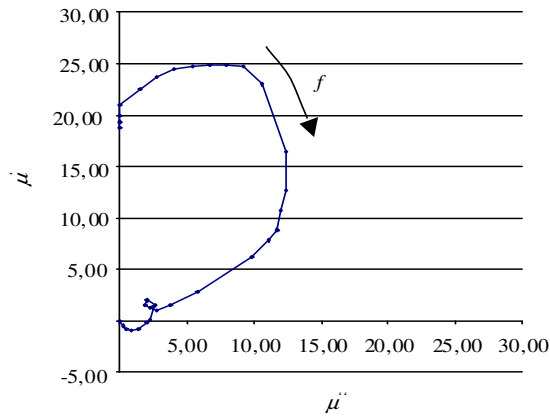


Fig. 2. Frequency spectra of complex permeability  $\mu^*$  of  $MgFe_2O_4$  ferrite,  $f=2MHz - 6GHz$ .

The first dispersion and absorption range of  $\mu^*(f)$  attributed to motion of domain wall in a ferrite is modeled similarly to the oscillation in the mechanical system. Hence, by analogy, the equation of domain wall motion can be derived. Based on that, and under certain simplifying assumptions, the permeability spectra for d.w. motion can be expressed by the formula

$$\mu_d^*(\omega) = 1 + \frac{\chi_d}{1 - (\omega/\omega_0)^2 + (j\omega/\omega_r)^\nu} \quad (1)$$

where  $\nu \in (0,1)$  is a dispersion parameter and  $\omega_0$  is angular frequency, when the walls are oscillating at resonance. The relaxation frequency  $\omega_r$  is reciprocal to the relaxation time  $\tau$ ,  $\omega_r = 1/\tau$ . This means that the alternating wall motion will lag behind the applied field, it is expressed as  $H = H_0 \exp(j\omega t)$ . There  $H_0$  and  $\omega$  are the amplitude and angular frequency of the field respectively. The  $\chi_d$  is initial susceptibility of d.w. motion. The first dispersion of  $\mu'(f)$  (Fig. 1) due to d.w. resonance oscillation is superimposed with the relaxation of d.w. and may be fitted by the real part of equation (1). Therefore the frequency value corresponding to maximum of absorption (losses) does not correspond to the zero of  $\mu'(f)$ . There is frequency ratio  $f_{off} \cong 0.4$ . It is seen from Fig. 2, that data of the permeability locus may be fitted by eq. (1) and they have a tendency to approach to circular arc indicating resonance behaviour starting at 2 MHz, and influenced by relaxation effects at lower frequency. In the high frequency region, one can assume that walls of grains are sequential pinned, having their own amplitude and relaxation frequency. Then next part of first locus imply the relaxation behaviour. In this frequency region, the permeability may be fitted by corrected eq. (1) to pure relaxation character as follow

$$\tilde{\mu}_d(\omega) = \frac{\chi_d}{1 + (j\omega/\omega_r)^\nu} \quad (2)$$

In frequency region higher than 0.5 GHz, the second resonance dispersion of permeability spectra

is started. The explanation of this resonance is based on a Landau-Lifshitz idea, that crystalline anisotropy is equivalent to an effective static magnetic field  $H_{ef}$ , acting inside each crystallite, and that  $H_{ef}$  produces a Larmor precession of the appropriate electron spins. The resonance absorption occurs in any given crystallite if a small magnetic field, oscillating near the Larmor frequency, is applied to that crystallite along a direction differing from that of  $H_{ef}$ . For a polycrystal containing randomly oriented crystallites, Snoek found by means of an averaging calculation the angular resonance frequency due to domain rotations,  $\omega_{os}$ , given by formula

$$\omega_{os} = \gamma(M_s / \chi_{is})(2/3) \quad (3)$$

where  $\gamma$  is the magneto mechanical ratios,  $M_s$  is spontaneous magnetization and initial rotation susceptibility is

$$\chi_{is} = \mu_0 M_s^2 / 3K \quad (4)$$

The first anisotropy constant  $K$  plays here important role. For a number of applications in ferromagnetic resonance, the basic equation of motion of  $M$  with Gilbert term gives a good description of the loss mechanisms and it will therefore be used here. An unusual feature of resonance and relaxation is its sensitive dependence on shape of the specimen. This comes about because the magnetization and corresponding demagnetizing field are very large in a ferromagnetic. Kittel considered the ferromagnetic spin resonance in a damping free single domain ellipsoidal specimen. If a spherical sample is used and that the damping factor is not neglected, then for the high frequency permeability in the parallel direction to applied alternating field, can be expressed by the formula

$$\begin{aligned} \mu_s^*(\omega) &= 1 + \chi_s^*(\omega) = \\ &= 1 + \frac{\omega\omega_{os}\alpha + j\omega_{os}^2\chi_{is}}{2\omega\omega_{os}\alpha + j[\omega_{os}^2 - (1+\alpha)\omega^2]} \end{aligned} \quad (5)$$

where  $\alpha$  is damping parameter of motion of the magnetization. At high frequency (above 0.8 GHz) the data are consistent with part of circular arc locus in the first approximation, see Fig 2. In the highest frequencies the locus indicates practically resonance character with frequency  $f_{os} \cong 2$  GHz. The last part of locus can be fitted by eq. (5), and there the  $\mu'(f)$  corresponds to zero. This true resonance frequency can be estimated if real part of  $\chi_s^*(\omega)$  in eq. (5) will be given zero,  $\chi_s'(\omega) = 0$ . Thus the measure (true) resonance frequency  $\omega_{os}'$  is to be compared with the theoretical precession frequency and we obtain

$$\omega_{os}' = 2\pi f_{os}' = \frac{\omega_{os}}{(1+\alpha)^{1/2}} \quad (6)$$

### 3. FREQUENCY SPECTROSCOPY OF FERRITEPOLYMER

The ferrite composite materials were made by mixing the  $Ni_{0.36}Zn_{0.64}Fe_2O_4$  ferrite particles with appropriate amounts of PVC and pressing the mixture into toroidal form [5]. Several samples with various ferrite filler volume concentration  $\kappa_v$  (80, 60, 50, 30, 20 vol. %) were prepared and magnetic spectra were measured. Since the ferrite particle size and the filler content are important factors influencing permeability of the final composite, the average diameter of ferrite particles  $\langle D \rangle = 250 \mu m$  was used. Series of the samples was prepared to examine the effect of the ferrite content on the permeability spectra.

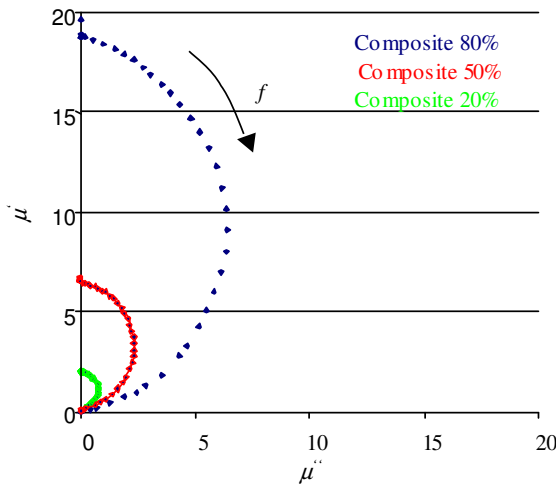


Fig. 3. Frequency spectra of complex permeability  $\mu^*$  for composite with  $\kappa_v=80, 50, 20$  vol. %,  $f=1MHz - 3GHz$ .

Experimental data of complex permeability of ferritepolymer samples are plotted by three sets of the complex plane loci in Fig. 3 for ferrite particle contents  $\kappa_v=80, 50$  and  $20$  vol. %. The composites have simple frequency spectra  $\mu^*(f)$  showing only one dispersion due to relaxation process, contrary to the  $\mu^*(f)$  spectra of sintered NiZn ferrite.

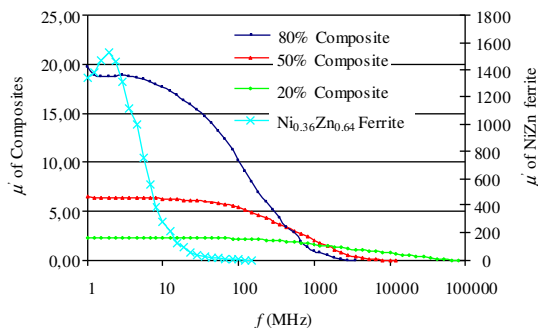


Fig. 4a. Frequency spectra of real  $\mu'$  component for composites, with  $\kappa_v=80, 50, 20$  vol. % of filler and of sintered NiZn ferrite.

$\mu'(f)$  curves for the corresponding ferritepolymers are presented in Fig. 4a, also spectrum of sintered

NiZn ferrite is plotted there for comparison. Corresponding magnetic absorption permeability  $\mu''(f)$  curves are depicted in Fig. 4b, for the same samples.

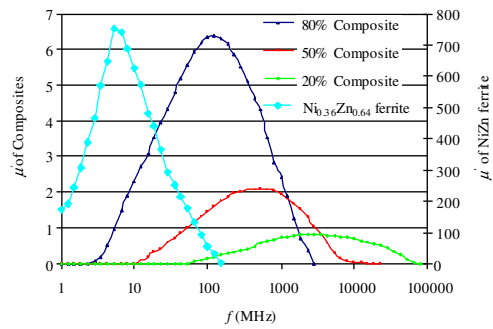


Fig. 4b. Frequency spectra of imaginary  $\mu''$  component for composites, with  $\kappa_v=80, 50, 20$  vol. % of filler and of sintered NiZn ferrite.

The real part  $\mu'(f)$  of complex permeability is characterized by dispersion characteristic in ferrite (Fig. 4a), which results from the contributions of the resonance-type of domain wall motion superimposed over the relaxation-type d.w. displacements through magnetization. This resonance may be explain by the existence of demagnetizing fields due to a worse grain axis continuity and to larger thickness of the grain boundaries. The magnetic dispersion  $\mu'(f)$  and absorption  $\mu''(f)$  curve (Fig. 4a,b) of NiZn ferrite can be fitted by real and imaginary part of eq. (1), respectively. In the ferritepolymer composites, the non-magnetic matrix cuts of intrinsic magnetic properties of particles as a result of changes the internal magnetic field in the composite. Therefore, compared with sintered ferrites, ferritepolymers are characterized by a different dispersion of permeability [6,7,8]. The surface of ferrite particle has irregular structure, both of a geometric and crystallographic nature, i.e. surface roughness, cracks, pores, impurities etc. The porosity parameter has been used to the study the behaviour of ferrites and ferritepolymer composites. The intragranular porosity plays the same role in both the sintered ferrites and the composites. It results in drastic decreasing of the initial permeability. The total porosity of NiZn ferrites was of intragranular porosity type, contrary to the intergranular porosity, which play a minor role in the magnetization mechanism. From this point of view, the situation with total porosity in ferritepolymer composites is different. Here the intergranular porosity plays higher role compared with sintered ferrites. The particle size and total porosity cause the demagnetizing field, which increase when filler concentration decreases. The demagnetizing field led to the pinning the domain walls in particles and hence, to the breaking of d.w. motion under an alternating external field. Thus the magnetization

rotation mechanism carries out rather than d.w. motion in studied NiZn ferritepolymers.

In the case of magnetization (spin) relaxation, we dealt with the special case of alternating field applied in a plane perpendicular to a projection of effective field corresponded with total magnetic anisotropy. Because of the precessional behaviour, a finite time is required for the magnetization to align itself with projection of  $H_{ef}$ , characterized by relaxation time  $\tau_s$ . This means that alternating magnetization will lag behind the applied field. Equation can be written for relaxation rotation of the magnetization

$$\tau_s \frac{dM}{dt} + M = \mu_0 \chi_{is} H(t) \quad (7)$$

Assuming a solution of this equation in the complex domain  $M(t) \hat{=} M \exp[j(\omega t - \phi)]$ , the permeability for relaxation-type of magnetization (spin) rotation mechanism is

$$\begin{aligned} \mu_{os}^* &= 1 + \frac{\chi_{is}}{1 + (j\omega\tau_s)^v} = \\ &= 1 + \frac{1 + (\omega\tau_s)^v \cos \frac{\pi}{2} v - j(\omega\tau_s)^v \sin \frac{\pi}{2} v}{1 + (\omega\tau_s)^{2v} + 2(\omega\tau_s)^v \cos \frac{\pi}{2} v} \chi_{is} \end{aligned} \quad (8)$$

where  $\chi_{is}$  is the initial susceptibility of rotation mechanism. In Fig. 3, the measured loci can be fitted by eq. (8) and they are parts of circular arcs or Cole-Cole flattened half-circle diagrams. The loci have higher values of  $\mu^*(f)$  for higher filler concentration  $\kappa_v$ . The magnetic dispersion  $\mu'(f)$  curves for ferritepolymers can be fitted by real part of eq. (8), in Fig. 4a. Corresponding magnetic absorption curves may be estimated by the imaginary component of eq. (8) for ferritepolymers, Fig. 4b. A decrease of filler content is accompanied by a decrease of  $\mu'(f)$  and  $\mu''(f)$  values with broader absorption maximum.

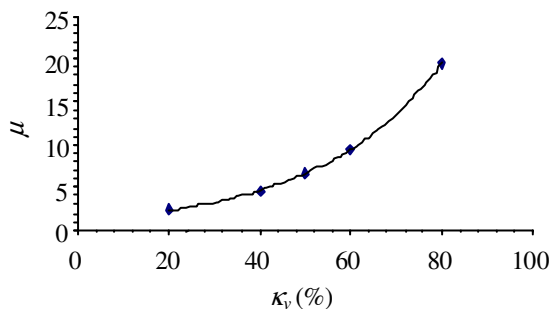


Fig. 5. Low frequency permeability dependence as a function of filler concentration  $\kappa_v$  in ferritepolymers.

Variation of the real part permeability  $\mu$  measured at low frequency ( $f \rightarrow 0$ ) is increasing with the ferrite volume concentration  $\kappa_v$ , Fig. 5. It can be explained by the decreasing the total anisotropy given by the magneto crystalline one, but mainly by magnetic interactions associated with

demagnetizing field decreasing. Thus  $\mu \hat{=} \mu_e$  can be estimated by Eq. (9) derived for two- component composite with ferrite filler in non magnetic matrix, and under certain simplifying assumptions for low frequency effective permeability of composite

$$\mu_e = 1 + \left\langle \frac{\chi_i (1 + \eta)^3 (1 + \sigma)}{1 + \eta \mu_i} \kappa_v^2 \right\rangle \quad (9)$$

Where  $\langle \rangle$  denotes a statistical mean value;  $\eta$  is demagnetizing and  $\sigma$  is area structural parameter.  $\mu_i$  and  $\chi_i$  are the filler intrinsic permeability and susceptibility. The parameter  $\sigma$  is a ratio of polymer area to filler area in elementary cell of composite and  $\eta$  is ratio  $d/D$ , where  $d$  is gap dimension between neighbouring particles within the direction of applied ac field. For selected constant  $\langle D \rangle$  of filler particles, the demagnetizing parameter  $\eta$  and then  $\kappa_v$  plays majority role in eq. (9).  $\tau < 1$  and  $\eta \ll 1$  for higher filler concentration. The value of  $\eta$  decreases with increasing of  $\kappa_v$ . Thus eq. (9) is monitoring fact, that the increase of filler concentration is connected with decreasing of  $\eta$ , i.e. with decreasing of demagnetizing interactions between particles.

Decreasing of filler content leads to a shift of relaxation frequency  $f_r$  - maximum of imaginary part  $\mu''(f)$  is moved to higher frequencies. Measured dependence of  $f_r$  on filler concentration  $\kappa_v$  is depicted in Fig. 6. The relaxation frequency  $f_r$  is roughly inversely proportional to  $\kappa_v$ . The relaxation frequency  $\omega_{rs} = 1/\tau_s$  due to domain rotation can be

$$f_{rs} = -\frac{\gamma \alpha M_s}{2\pi \chi_{is}} = \frac{1}{2\pi} \frac{\gamma \alpha M_s}{\mu - 1} \quad (10)$$

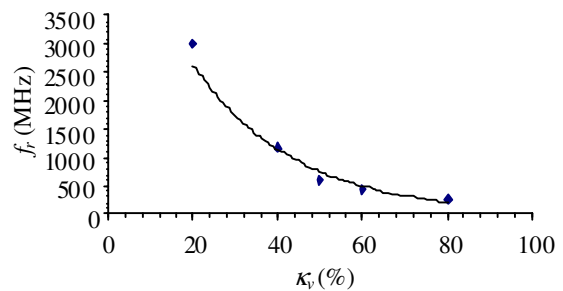


Fig. 6. Relaxation frequency  $f_r$  dependence as a function of filler concentration  $\kappa_v$  in ferritepolymers.

Dependence of relaxation frequency  $f_r$  on reciprocal of permeability  $1/\mu$  is depicted in Fig. 7, there is roughly linear dependence. This dependence can be fitted by eq. (10) and it can serve as proof as indication of the natural rotating magnetization in ferritepolymers.

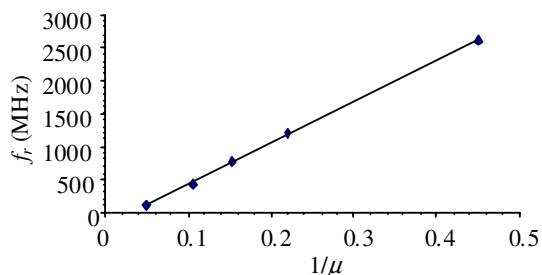


Fig. 7. Relaxation frequency  $f_r$  dependence as a function of inverse value of permeability  $1/\mu$ .

#### 4. CONCLUSION

The magnetic resonance or relaxation spectroscopy was showed as a powerful technique for the study of magnetization mechanism and dispersion or absorption of permeability in investigated magnetic dielectrics. The ferrite polymer manifest itself as magnetic media with the reduction of low frequency permeability, but on the other hand, having acceptable value of permeability in higher frequency region compared with NiZn sintered Mg ferrite. It has also very low losses in the high frequency region. Compared with sintered NiZn and Mg ferrites, the NiZn ferritepolymer composites is perspective for application in a range high frequency. From theoretical point of view in the Mg ferrite one can attribute the first dispersion and absorption to domain wall motion resonance and relaxation. On the other hand, the magnetization rotation mechanism can be attributed

to ferritepolymer magnetization for all filler concentrations. This opinion is due to that, the character of relaxation frequency dependence versus inverse value of permeability has linear behaviour and can serves as a proof of the indication of the natural rotating magnetization in ferritepolymers.

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