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Ferroelectric core/magnetic shell approach to control electric properties of composites

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Electrical properties of polymer-inorganic nanocomposites depend strongly on their structure, i.e. distribution of filler phase in a polymer matrix. This factor is especially important in the case of composites consisting of two phases with significantly different properties. To improve electric properties of such composites in this study ferroelectric core/magnetic shell approach is suggested. $BaTiO_3$ core was coated with a SiO_2–$CoFe_2O_4$ magnetic shell followed by incorporation of thus obtained core/shell particles into a polymer in the presence of external magnetic field to obtain composites featuring with a significantly increased dielectric permittivity. The developed composites may find various applications including embedded capacitors and other electronics devices, as well as sensors, electromagnetic radiation shields etc.

1. Introduction

Electrical properties of polymer-inorganic nanocomposites depend strongly on the composite structure, i.e. distribution of filler particles in polymer matrix. This factor is especially important in the case of composite consisting of two phases with significantly different properties. For example, high dielectric permittivity (high k) composites are made of polymer with k_1~10...30 and ferroelectric particles with k_2=1000...10000. In order to increase electric properties of such composites various methods to control the composite structure are used including filler surface modification, mixing process enhancement, etc. [1,2]. In this study a ferroelectric core/magnetic shell approach is suggested to improve the dielectric permittivity of such composites.

Multiferroics or ferroelectromagnets comprise a new intensively studied class of materials combining both magnetic and ferroelectric properties due to an effective interaction of the relating components (magnetoelectric effect). The coexistence of magnetic and electric subsystems and resulting magnetoelectric effect of material provide considerable improvements in design of drives, converters and data storage devices [3-5]. In [6] among the materials containing magnetic and ferroelectric phases the magnetoelectric effect was found to be determined by the structure of material, being the most prominent for the core-shell particle structure. Core-shell systems may be prepared using various methods including electrophoretic sedimentation, ion-exchange synthesis, modified sol-gel process, calcination and their combinations [3-7].

In [6] an external electric field applied to a composite was found to provide mechanical deformations in a ferroelectric material transferred to a magnetic shell resulting in the changes of magnetization state. Similarly, the application of external magnetic field leads to the change of polarization in a ferroelectric component. Thus, the considered effect may be used for the adjustment of properties of such materials. Moreover external magnetic field applied to polymer composite material during its formation should influence its structure and electric properties.

2. Experimental

In this paper composites with high dielectric permittivity were prepared from such components as barium titanate as a ferroelectric filler (featuring with one of the highest *k* values among inorganic materials) and cyan ester of polyvinyl alcohol (CEPVA) as a polymer binder with one of the highest permittivity values among the polymers [8].

Barium titanate HPBT-1B (Fuji Titanium, Japan) with dielectric permittivity k ≈ 4400 and average particle size 300-400 nm was modified by the formation on its surface of SiO_2 shell with $CoFe_2O_4$ nanoparticles inside. The magnetic shell was deposited by sol-gel method [8] from the mixture of barium titanate powder with silica sol doped with CoO and Fe_2O_3 in the ratio 1:1. Tetraethyl ortohosilicate (TEOS) ($Si(OEt)_4$), ethyl alcohol, nitric acid, the distilled water, cobalt (II) nitrate ($Co(NO_3)_2 \cdot 6H_2O$), iron (III) nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) were used as the precursors. The concentration of the components was selected to obtain samples with the shells containing 27%, 35% and 38,5%wt. $CoFe_2O_4$.

The modified filler comprised of barium titanate coated with a silica layer containing cobalt ferrite spinel nanoparticles was studied using D8-Advance Bruker diffractometer and Carl Zeiss NVision 40 scanning electron microscope (SEM). The characterization of magnetic properties of the synthesized materials involved the study of the hysteresis loop for thus modified filler by measuring the magnetization M as a function of the applied magnetic field intensity. The measurements technique was based on a nuclear magnetic resonance as described in [9]. First, the magnetic field intensity H_0 was measured without a sample. Then the studied powders were placed into the magnetic field and H_H and H values were measured by sensors. The corresponding magnetization plot is shown in the figure 3.

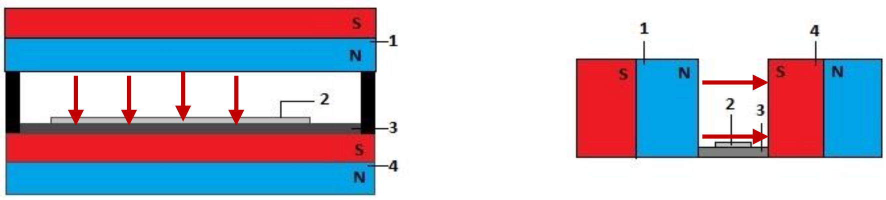


Fig. 1 Sample drying in a magnetic field: 1,4 – ferrite magnets with a constant magnetic induction B= 0.2-0.3 T; 2 – composite layer; 3 – substrate, arrows show direction of magnetic field

The dielectric composite films were prepared by incorporating the modified filler into CEPVA (Plastpolymer, Russia, k~19 [7]) 30% solutions in dimethylformamide followed by mixing and casting onto substrates using Dr. Blade. During drying of samples ferrite magnets were used to apply magnetic field in the direction perpendicular or parallel to substrate surface, figure 1. Using same compositions films were prepared without magnetic field application. Reference sample containing a non-modified filler were fabricated as well. The dried polymer composite layer' thickness was 200-300 μm as measured by micrometer.

To measure dielectric performances of composites glycerol-sodium electric contacts were deposited onto film surface. The dielectric loss tangent, conductivity and capacity of the composites were measured using E7-20 immitance meter at T=298 K and dielectric permittivity was calculated according to the determined capacity values.

3. Results and discussion

The X-ray diffraction curves of core/shell particles indicate the presence of $CoFe_2O_4$ phase, however the peaks relating to cobalt ferrite spinel are weak compared with $BaTiO_3$ peaks due to a low content of spinel phase in the samples and small spinel particle size (some 45 nm) comparing to barium titanate (diameter some 300 nm), figure 2.

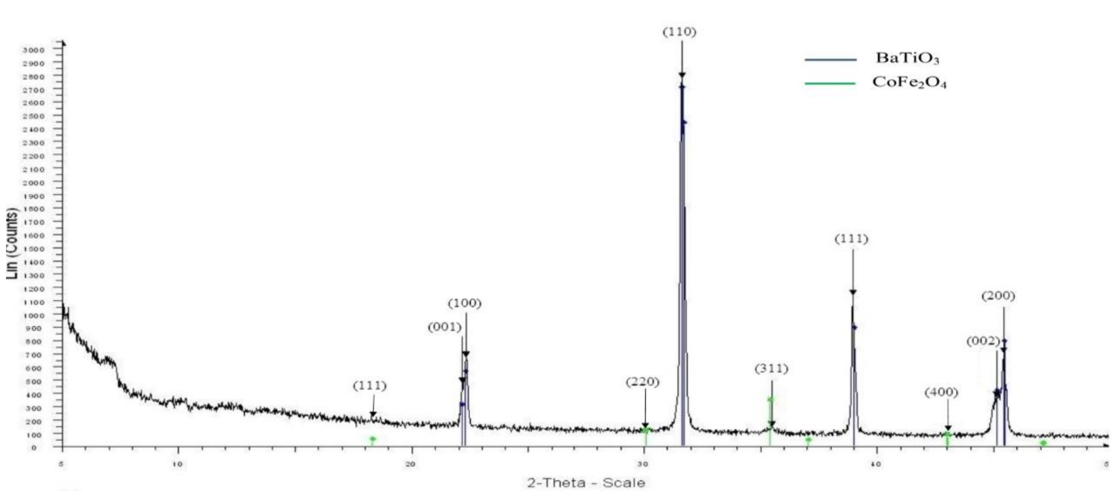


Fig. 2 The XRD pattern of $BaTiO_3/CoFe_2O_4$-SiO_2 particles

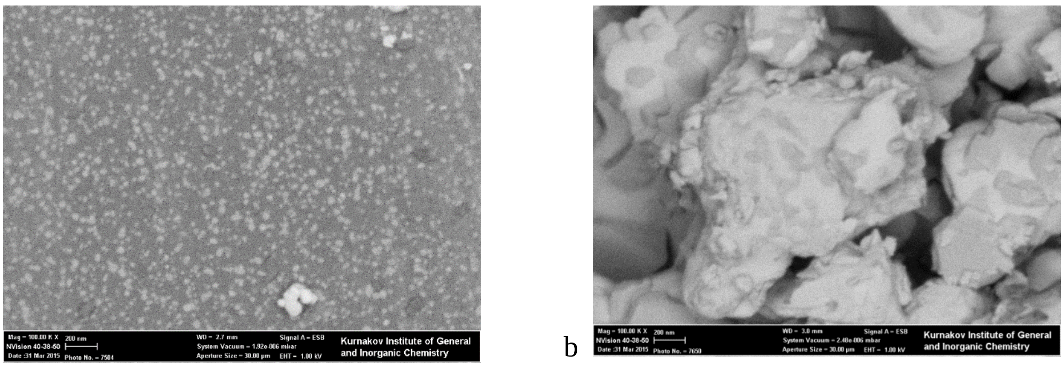
a  b

Fig. 3 Micrographs of ferrite-cobalt shell (a) and modified BaTiO3 particle (b)

The left image on the figure 3 shows distribution of $CoFe_2O_4$ nanoparticles within silica shell. According to SEM images, the performed sol-gel synthesis provided ferrite cobalt spinel particles of almost uniform in both size (about 45 nm) and distribution in SiO_2 matrix. Using this image and Altami Studio software $CoFe_2O_4$ particle size distribution was calculated. Average particle size found to be approximately 45 nm with narrow distribution between 35 and 55nm.

Figure 4 shows magnetization curve of fabricated core/shell particles. In spite of weak XRD peaks of spinel phase, magnetization curve is featured with a hysteresis loop typical for magnetically hard cobalt ferrite material. The magnetization saturation for the studied sample M_s approaching 1200

A/m is about one order of magnitude lower comparing to this value for pure $CoFe_2O_4$ powder since the studied material comprises a $BaTiO_3/CoFe_2O_4$-SiO_2 system.

During the composite synthesis the sample was affected by about 0.3 T magnetic field providing the magnetization close to the saturation level M_{sat} as shown in the figure 4. Therefore, the magnetic moments of all nanoparticles in the system are oriented in parallel to the magnetic induction vector and to each other. Dividing the magnetization saturation M_{sat} =1200A/m by $BaTiO_3$ particles $n = 10^{19} m^{-1}$, (estimated according to the weight ratios between the components at the composite synthesis) we can derive the magnetic moment of one particle as following:

$$P = \frac{M_{sat}}{n} = \frac{1200}{10^{19}} = 1{,}2 \cdot 10^{-16} \frac{A}{m^2} \tag{1}$$

Taking into account $BaTiO_3$ particle size R and using the equation:

$$F = \frac{3\mu_0 P^2}{4\pi^2 R^4} \tag{2}$$

the compressing and decompressing forces affecting the ferroelectric particle in the magnetic field are calculated as $F=2*10^{-12}$N and divided by the particle cross-section to yield the pressure p≈10Pa. Actual pressures may be much higher due to non-uniformity of force distribution. The distortion of $BaTiO_3$ crystal lattice caused by this pressure may account for the observed increase of dielectric permittivity for the samples synthesized under magnetic field. This effect may contribute to the observed increase in the permittivity of the composites due to the incorporation of a magnetic component even without the external magnetic field application.

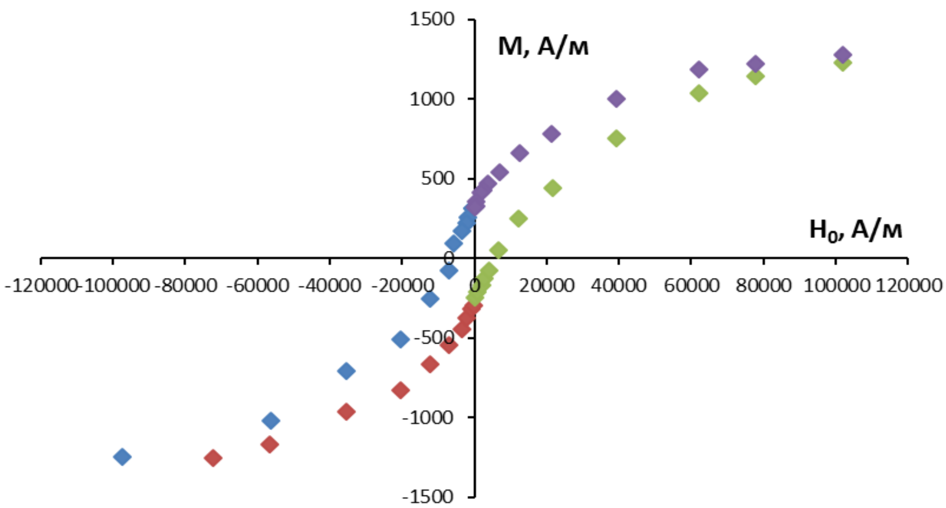


Fig. 4. Magnetization plot of $BaTiO_3$ particles encapsulated with a $CoFe_2O_4$ – SiO_2 shell

The dielectric permittivity measured at the frequency 1 kHz at various conditions of magnetic field application are summarized in the table I for the samples with various $CoFe_2O_4$ content in comparison with similar samples prepared without the external magnetic field and a sample synthesized from $BaTiO_3$ without SiO_2-$CoFe_2O_4$ coating.

The obtained data show that the magnetic field effect during composite formation resulted in the significant change of the target performances. Comparing last three columns in the table I one can see that application of magnetic field perpendicular to the substrate surface during composite fabrication resulted in increase of its dielectric constant comparing to sample fabricated without application of magnets. It should be noted that during capacitance measurements electric field is applied in the same direction. At the same time application of magnetic field parallel to the substrate surface during composite fabrication have an opposite effect. Naturally these effects are due to structuring of ferroelectric particles along the force lines of magnetic field. Therefore increase in the content of magnetic phase in the shell provides rise of dielectric constant of composite fabricated applying magnetic field perpendicular to the substrate surface during drying. From the second column in the table I one can see that introduction of shell with low dielectric constant resulted in decrease of k of composites fabricated without application of magnetic field, except for the sample containing 18.4% vol. of $CoFe_2O_4$. This indicates that increase of dielectric constant may also be partly caused by distortion of $BaTiO_3$ crystal lattice due to pressure originated from magnetic forces.

Table I. Dielectric permittivity of CEPVA $BaTiO_3$/$CoFe_2O_4$–SiO_2 composites at 1 kHz

$CoFe_2O_4$ content (% vol.) in the dry composite	Without external magnetic field	Magnetic field applied perpendicular to the substrate surface	Magnetic field applied parallel to the substrate surface
No shell	142	-	-
14.2	112	143	86
18.4	174	278	-
20.3	104	460	-

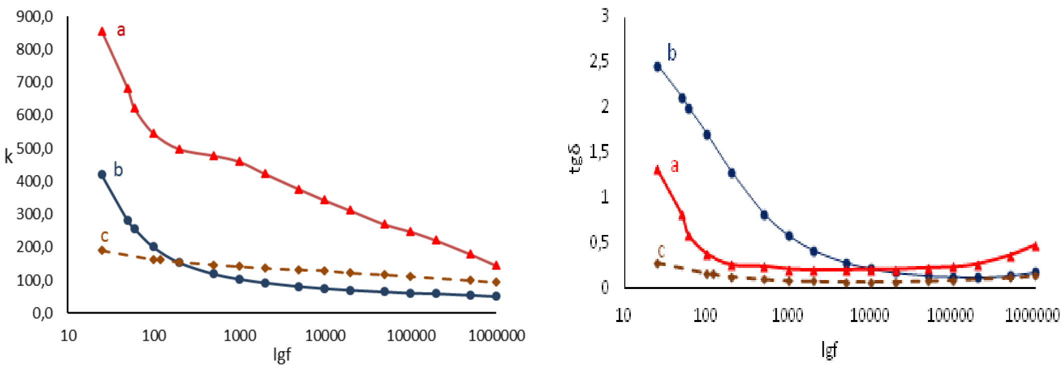


Fig. 5 Frequency dependence of dielectric permittivity for CEPVA-$BaTiO_3$ core/shell (20,3 vol.% of $CoFe_2O_4$) composites dried under the impact (a) and in the absence (b) of a magnetic field in comparison with the composite obtained using a non-modified commercial $BaTiO_3$ filler (c)

As a result, more than 3-fold increase in the permittivity (at 1 kHz) is achieved for the core/shell sample with $CoFe_2O_4$ content 20.3 %vol. subjected to the magnetic field perpendicular to the substrate surface during fabrication as compared to reference sample without shell. The frequency dependence (in the range from 25 Hz to 10 MHz) of dielectric permittivity for a sample with the highest k value is presented in the figure 5. The increase of frequency of electric field expectedly leads to the permittivity decrease for the samples fabricated in all the considered conditions. At the same time, for the samples with core/shell filler there is much more intense increase of k in the low frequency region due to increased interface (particle/shell, shell/polymer) and associated with Maxwell–Wagner effect (interfacial polarization) [10]. Dissipation factor in low frequency range also increases significantly while above 10 kHz it is comparable to samples with non-modified filler. It should be noted that samples fabricated in and without the presence of magnetic field have close values of conductivity, particularly $3.2*10^{-8}$ and $6.1 *10^{-8}$ S/cm for sample with 20.3% of $CoFe_2O_4$, but very different dielectric constant, thus this difference is not due to increased leakage current of studied samples.

4. Conclusion

The performed studies involved the synthesis and characterization of $BaTiO_3$ (core)/$CoFe_2O_4$-SiO_2 (shell) particles followed by their incorporation into CEPVA binder and drying of the resulting material in 0.2 – 0.3 T magnetic field in order to control composite's structure. The sol-gel formation of a shell featuring with magnetic properties onto $BaTiO_3$ filler surface is found to provide increase in the dielectric permittivity of the composites formed with the impact of magnetic field with the induction vector directed perpendicular to the dried composite sample surface. Generally, the presented approach to the modification of composite structure and functional properties is promising for obtaining of advanced materials.

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