Influence of SBN70 concentration in PVDF on dielectric and pyroelectric properties of nanocomposites

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Abstract. Strontium barium niobate Sr0.7Ba0.3Nb2O6 (SBN70) ceramic nanopowder was dispersed in a poly(vinylidene fluoride) (PVDF) matrix providing a composite with 0-3 connectivity. The SBN70-PVDF composites samples were obtained from ceramic and polymer powders by hot-pressing method. The SBN70 ceramic was prepared by a sol-gel method. The composite surface images were obtained by AFM tapping mode (NT-NDT Solver P47). The dielectric response of the composites was studied in the frequency range 100 Hz – 1 MHz and the temperature range 100 – 430 K. The dielectric properties of the composites display features originated from the PVDF polymer modified by those of SBN70 ceramics. The resulting pyroelectric currents were measured using a Keithley 6517 A electrometer and were used to calculate the pyroelectric coefficient \( p \). The \( p \) of poled composites increases from ~24 \( \mu \text{C/m}^2\cdot\text{K} \) in pure PVDF to ~40 \( \mu \text{C/m}^2\cdot\text{K} \) in the composites of \( \Phi = 0.2 \) at room temperature.

1. Introduction

Ceramic-polymer composites show unique properties for a wide range of applications in the field of microelectronics, biomedical engineering and other modern technologies. These materials (i.e., polymer loaded with ferroelectric ceramic powder) have aroused increased interest due to their unique opportunities blending polymeric properties like mechanical flexibility, formability and low dielectric permittivity with high electro-active properties characteristic for ferroelectric ceramics. They were developed to be an alternative material to ferroelectric ceramics and to ferroelectric polymers. The ceramic-polymer composites are arranged in a specific configuration called connectivity. In composites with 0-3 connectivity a three-dimensionally connected polymer phase is loaded with isolated ceramic particles. The dielectric permittivity \( \varepsilon' \) and dielectric losses \( \tan\delta \) of composites are involved in “figures of merit” (FOM₁ and FOM₂) of various physical quantities important for applications, therefore, the knowledge of dielectric response is essential for tuning their physical properties [1].

The ceramics type SrₓBa₁₋ₓNb₂O₆ (abbreviated as SBN, where 0.25 ≤ \( x \) ≤ 0.75) is a promising lead free ferroelectric material with tungsten bronze structure and it is a potential material for pyroelectric infrared detectors, piezoelectrics, electro-optics and photorefractive optics [2, 3]. It exhibits a ferroelectric phase with only one polar axis and a transition temperature depending on the Sr/Ba ratio. The SBN ceramics with \( x = 0.7 \) (SBN70), used to produce SBN70-PVDF composites, is characterized by the diffuse phase transition phenomena (i.e., they exhibit a broad Curie peak in the phase transition range) and is a well-known relaxor material [3, 4]. The SBN70 ceramics offer excellent piezo- and
pyroelectric properties, high dielectric permittivity ($\varepsilon' \sim 3000$ at 1 kHz) [3] and low dielectric losses, albeit with low mechanical flexibility. Pure PVDF is a semicrystalline polymer, it has a monomer unit ($\text{CH}_2\text{CF}_2$) and at least four crystallite modifications [5]. The two most important ones are the nonpolar $\alpha$ phase and the polar $\beta$ phase. PVDF film obtained from the melted material contains spherulites with nonpolar $\alpha$ phase. Mechanical stretching, annealing at high temperature or poled material in a high DC field is necessary to obtain the polar $\beta$ phase. Such material has a dipole moment of $7.0 \times 10^{-30}$ C·m perpendicular to the chain direction [6]. PVDF film (unpoled, radially oriented) offer low value of the dielectric permittivity ($\varepsilon' \sim 8-10$) [1], high dielectric losses, but also a high flexibility and mechanical strength.

In this work, we present the dielectric response of the SBN70 ceramics obtained by a sol-gel method, pure PVDF radially oriented and PVDF loaded with nanosize particles of SBN70 ceramic powder with the volume fraction of the ceramics $\Phi = 0.1$ and 0.2. The dielectric response was observed as a function of frequency and temperature. We investigated also the temperature dependence of pyroelectric coefficient with a selected DC electric field for composite samples. AFM tapping mode was used to perform SBN70-PVDF composite surface images.

2. Experimental

Dielectric and pyroelectric response was studied for SBN70-PVDF composite samples of 0-3 connectivity and volume fraction of ceramics $\Phi$ from 0.0 to 0.2. The composites were prepared from ceramic and polymer powders by hot-pressing (450 K, 3.2 MPa during 10 minutes) and cooled to the room temperature under pressure at a rate of 10 K/min. Powders of SBN70 used for fabrication of SBN70-PVDF composites were prepared by a sol-gel route using strontium acetate ($\text{CH}_3\text{COO})_2\text{Sr}$, barium acetate ($\text{CH}_3\text{COO})_2\text{Ba}$ and niobium ethoxide ($\text{C}_2\text{H}_5\text{O})_5\text{Nb}$ as precursors. Powders obtained from dried gels were calcined at 870 K for 24 hours to burn off organics. Bulk ceramics was prepared from these powders by hot uniaxial pressing at 1470 K for 4 hours, under the pressure $p = 5$ MPa. The distribution of the ceramic grains on the surface of the PVDF matrix and the grain size were estimated by AFM tapping mode (NT-MDT Solver P47) in air at room temperature. The PVDF powder was delivered by Nitrogenous Concern (Tarnów, Poland). The samples had the form of discs with a diameter of 11 mm and a thickness of 50 – 100 μm. The samples were covered with gold electrodes on both surfaces.

Study of the dielectric properties of samples was carried out in the frequency range 100 Hz – 1 MHz using HP 4284A precision LCR meter. The measurements were performed on unpoled samples during heating from 100 to 430 K at a rate of 0.2 K/min. All the samples were aged for at least 72 h prior to measuring the dielectric and pyroelectric properties. The pyroelectric current response for each of the poled samples was measured by quasi-static method in the short-circuit regime. The samples were first cooled to the temperature of 100 K. Next they were heated to the temperature of 360 K and cooled to the temperature of 100 K in a DC electric field $E_p = 5$ MV/m. Heating and cooling was made at a rate of 0.2 K/min in the field applied. After poling, the electrodes were short-circuited for 0.5 h to eliminate surface charges at 100 K. Pyroelectric current was measured during heating of samples from 100 K to 360 K at a constant rate of $\beta = 3$ K/min using Keithley 6517 A electrometer coupled with a computer assisted cryogenic system. The pyroelectric coefficient is calculated from the formula $p = i_p/A\beta$, where $i_p$ is the measured pyroelectric current and $A$ is the area of the top electrode.

3. Results & discussion

SBN-PVDF composite surface image was obtained by AFM tapping mode. In the Figure 1 particles of ceramics are white and the polymer is dark. It is visible that value of ceramics grain size amounts < 200 nm. It is seen that the SBN particles are dispersed rather uniformly in the polymer matrix.
Dielectric permittivity $\varepsilon'$ and dielectric losses $\tan\delta$ were measured as a function of temperature and frequency. Figure 2 shows the $\varepsilon'$ behaviour for the pure PVDF (a) and the bulk ceramic SBN70 (b). For PVDF three dielectric anomalies are observed. A dispersive $\varepsilon'$ anomaly of the PVDF polymer (Figure 2a) in the temperature range 180 – 330 K is related to a freezing dipolar motion in the amorphous region. Dielectric behaviour in the range 330 – 380 K is ascribed to wide angle oscillations of dipoles attached to the chain, followed by their rotation with main chain co-operation appearing in the crystalline phase [1]. At ~420 K one observes a $\varepsilon'$ anomaly characteristic of the ferroelectric-paraelectric phase transition. The diffused dielectric anomaly obtained for the SBN70 ceramic sample (Figure 2b) in 250 K – 350 K temperature range as well as the characteristic dispersion of the permittivity points to the relaxor properties of the ceramics used to produce SBN70-PVDF composites [4].

In Figure 3 the temperature dependencies of dielectric permittivity $\varepsilon'$ and $\tan\delta$ of SBN70-PVDF composites with volume fraction of ceramic $\Phi = 0.1$ and 0.2 are presented. The values $\varepsilon'$ of the composites lay between the values for the PVDF and values for the SBN70 as expected (see Figure 2). The addition of the SBN70 ceramics increases the value $\varepsilon'$ of the composites in the whole temperature range, due to the high permittivity value of SBN70. The dielectric response of the composites is modified by the maxima originated from the PVDF polymer and the SBN70 ceramics.
The maxima of $\tan\delta$ in the temperature range 230 – 280 K are attributed to the $\alpha$-relaxation process, related to the glass transition in the polymer. In the temperature range 330 – 420 K the maxima of $\tan\delta$ are attributed to dielectric losses in the crystalline phase of the polymer. In the low temperature range described maxima of $\tan\delta$ increase and are shifting towards higher temperatures with increasing frequency, whereas in the high temperature the maxima decrease with increasing frequency. The addition of the ceramics to the polymer matrix decreases value of $\tan\delta$ in the composite.

The pyroelectric coefficient $p$ and figures of merit $FOM_I$ and $FOM_{II}$ of poled samples were studied. The pyroelectric current $i_p$ were measured during heating samples and values of $FOM_I = p/\varepsilon'$ (significant for sensor with high impedance amplifiers) and $FOM_{II} = p/(\varepsilon'\cdot\tan\delta)^{1/2}$ (important in the case when the noises of the sensor are mainly due to the pyroelectric element) are calculated. Figure 4 shows the dependence of pyroelectric coefficient on temperature for PVDF and composites with two volume fraction of ceramic.

Figure 3. Temperature dependencies of the dielectric permittivity $\varepsilon'$ and $\tan\delta$ for SBN70-PVDF composites with two volume fraction of ceramic

Figure 4. Dependence of pyroelectric coefficient on temperature for PVDF and SBN70-PVDF composites
fraction $\Phi$ of the ceramics: 0.1 and 0.2. The content of the SBN70 improves the pyroelectric properties of the investigated materials. The $p$ of composites increases from $\sim 24 \mu C/m^2\cdot K$ in pure polymer to $\sim 40 \mu C/m^2\cdot K$ in the composites of $\Phi = 0.2$ at room temperature. The thermal variations of $p$ (Figure 4) show anomalies corresponding to the dielectric behaviour mainly in the PVDF polymer. The calculated FOM$_I$ and FOM$_{II}$ of composites are higher in comparison with the PVDF polymer. The optimal of FOM$_I$ and FOM$_{II}$ equals to $3.5 \mu C/m^2\cdot K$ and $77.3 \mu C/m^2\cdot K$ for $\Phi = 0.1$, respectively. The increase of the $\Phi$ from 0.1 to 0.2 involved the reduction of the values of FOMs. We related this behaviour to the rapider increase of the value $\varepsilon'$ than of the pyroelectric coefficient with the increase of the volume fraction $\Phi$ of investigated composites.

4. Conclusions

The SBN70-PVDF 0-3 composites samples with SBN70 volume fraction $\Phi$ up to 0.2 were fabricated by hot-pressing method and their dielectric and pyroelectric response was studied. The distribution of the ceramic grains on the surface of the polymer matrix and the grain size estimation were also studied. The SBN70 ceramics is characterized by the diffuse phase transition phenomena in 250 K – 350 K temperature range. The results of the $\varepsilon'$ measurements for composites proved that the dielectric response of the ceramic-polymer composite is determined by the diffused dielectric anomaly coming from the ceramics and by relaxation processes in polymer. The addition of the ceramics to the polymer decreases dielectric losses in the SBN70-PVDF composite. Due to high permittivity value of the ceramics the $\varepsilon'$ of the composite increases with the volume fraction of the ceramics. The pyroelectric coefficient of the SBN70-PVDF is higher than that of the pure polymer. The results of the pyroelectric and dielectric measurements indicated that the value of the $\Phi = 0.1$ is the optimum which provides the highest values of the FOMs. The SBN70-PVDF composites can be recommended for pyroelectric applications.

References

[1] Hilczer B, Kulek J, Markiewicz E, Kosec M and Malič B 2002 J. of Non-Crystalline Solids 305 167
[2] Sakamoto W, Yogo T, Kikuta K and Hirano S, 1996 J Amer. Ceram. Soc. 79 2283
[3] Kim M.-S, Lee J.-H, Kim J.-J, Lee H Y, Cho S.-H 2002 J. of the Eur. Ceram. Soc. 22 2107
[4] Pawlaczyk C, Olszowy M, Markiewicz M, Nogas-Ćwikiel E, and Kulek J 2007 Phase Transitions 80 177
[5] Rollik D, Bauer S, and Gerhard-Multhaupt R 1999 J. of Appl. Phys. 85 (6) 3282
[6] Das-Gupta D K 2000 Smart Ferroelectric Ceramic/Polymer Composite Sensor, in Polymer Sensors and Actuators, Osada Y, De Rossi D E, eds., (Springer) 109-146.