Dynamic dielectric response of PLZT-P(VDF/TFE) nanocomposites

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Abstract. Dynamic dielectric relaxation of polymer P(VDF/TFE) (0.98/0.02) loaded with lead lanthanum zirconate titanate (Pb0.92La0.08)(Zr0.65Ti0.35)O3 (PLZT 8/65/35) ceramic nanopowders was studied in the frequency range from 100 Hz to 1 MHz and at temperatures from 100 K to 450 K. The PLZT nanopowders were prepared by the sol-gel method using: lead(II)acetate trihydrate, lanthanum acetate hydrate, zirconium(IV)propoxide and titanium(IV)propoxide. The crystallization process of PLZT powders was monitored by means of XRD analysis (Philips PW 3710) using Cu-Kα radiation in the range 20° ≤ 2θ ≤ 60°. The powders were analyzed before and after burning of the organic remains. The morphology observations of the powders were made using Hitachi S-4700 scanning electron microscope (SEM), and the grain size distributions were measured on a Zetasizer Nano ZS by the DLS method. The PLZT-P(VDF/TFE) composite samples of 0-3 connectivity were prepared from ceramic and polymer powders by the hot-pressing method. The volume fraction of the ceramics Φ amounted 0.1, 0.15 and 0.2. The dielectric response of the ceramics-polymer composite was found as a combination of the responses of pure polymer and the ceramics: (i) the addition of the PLZT ceramics increases the value of the dielectric permittivity ε', (ii) the composite shows the maximum of the permittivity coming from the PLZT ceramics, (iii) the dielectric absorption spectrum of the composites is dominated by the α-relaxation in pure polymer.

1. Introduction
Ceramic-polymer composite materials are perspective from the application point of view. In recent years, combination of ferroelectric ceramic filler and polymer matrix in form of flexible composites has been found to be a new way of obtaining the new materials with mechanical and electrical properties which can be evaluated on the basis of the properties of both components. Composites of 0-3 connectivity (a polymer phase three dimensionally connected with isolated ceramic particles) can be easily prepared in a form of flexible sheets and in a variety of shapes.

Lead lanthanum zirconate titanate (PLZT) are a family of oxide ceramics based on lanthanum doped solid solution of lead zirconate titanate system. These ceramics have attracted considerable attention in recent years because they offer a broad range of dielectric, electromechanical, and optical properties [1 - 4]. The nature and majority properties of PLZT are function of the La concentration,
and also the Zr/Ti ratio. At a Zr/Ti ratio of 65/35 mol. %, PLZT displays a very high electromechanical coupling coefficient, and stays ferroelectric up to a La content of about 10 at. % at the room temperature. The powder material of PLZT x/65/35 ceramics, used to produce PLZT-P(VDF/TFE) composites was containing 8 at. % La (x). (PLZT 8/65/35), is characterized by high dielectric permittivity (3400), high electromechanical coupling (0.65) [2], exhibiting rhombohedral symmetry and diffuse phase transitions [5]. Pure P(VDF/TFE)-(0.98/0.02) obtained by hot-pressing shows relaxation processes in the vicinity of glass transition (~ 303 K) [6, 7].

In the present work we report: (i) crystallization behavior of the PLZT 8/65/35 nanopowders; (ii) an experimental study on dynamic dielectric response of PLZT 8/65/35 ceramics, pure P(VDF/TFE)-(0.98/0.02) and PLZT-P(VDF/TFE) composites with the volume fraction of the ceramics \( \phi = 0.1, 0.15 \) and 0.2 measured as a function of frequency and temperature.

2. Experimental

Lead lanthanum zirconate titanate \((\text{Pb}_{0.92}\text{La}_{0.08})(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3\) (PLZT 8/65/35) nanopowders were prepared by the sol-gel method using: lead(II)acetate trihydrate, lanthanum acetate hydrate, zirconium(IV)propoxide and titanium(IV)propoxide. Powders obtained from dried gels were calcined at 873 K during 6 h to burn off organics remains. The powders morphology observations, were made using Hitachi S-4700 scanning electron microscope (SEM), and the grain size distributions were estimated by the DLS method using Zetasizer Nano ZS. Bulk ceramics was prepared from these powders by the hot pressing method at the controlled temperature, \( T_p = 1473 \text{ K} \), during 2 h, under pressure \( p = 20 \text{ MPa} \). X-ray analysis (Philips PW 3710 diffractometer, \( \Theta -2\Theta \) geometry, CuK\( \alpha \) radiation) was used to characterize the structure of the PLZT samples (the calcined powders and the hot pressed ceramics were studied). The composites were prepared from PLZT 8/65/35 powder which was carefully mixed with P(VDF/TFE) copolymer powder of VDF mol contents \( x = 0.98 \), delivered by Nitrogenous Concern (Tarnów, Poland). The PLZT-P(VDF/TFE) composite samples of 0-3 connectivity, were prepared from ceramic and polymer powders by hot-pressing method (3.2 MPa, 450 K, 10 min). The volume fraction of the ceramics \( \phi \) amounted 0.1, 0.15 and 0.2. The samples had the form of discs with a diameter of 11 mm and a thickness of 80 – 220 \( \mu \text{m} \). Gold electrodes were evaporated onto the sample surfaces using a BALTEC SCD 050 sputter coater.

The dielectric response was studied in the frequency range 100 Hz to 1 MHz using a computer aided HP 4284A LCR meter. The samples were mounted in the CF 1204 Oxford Instruments cryostat equipped with the ITC 4 temperature controller. The measurements were performed on unpoled samples during heating from 100 to 450 K at a rate of 1K/min.

3. Results & discussions

The X-ray spectra were recorded for the powdered gel, the calcined powder (i.e., the powder devoid of the organic remains) and the powdered PLZT ceramics obtained by the hot pressing method. Figure 1 presents the thermal evolution of the crystal structure of PLZT 8/65/35 material. The X-ray pattern of the IR-dried powdered gel indicates presence of the diffraction lines originating from the organic remains. Their calcination \( (T = 873 \text{K}) \) leads to crystallisation of PLZT in the rhombohedral symmetry. The crystal structure was identified as rhombohedral with the space group \( R3m \) and the parameters of the unit cell \( a_h = 0.5745 \text{ nm} \) and \( c_h = 0.7060 \text{ nm} \) (the hexagonal setting was used for the indexing) [5].
The SEM micrograph (Figure 2) shows the calcined PLZT powders as agglomerates of submicron particles, typical for the other PLZT materials synthesized by the wet chemical route. Soft agglomerates were disintegrated to the nanoscale grains during sonification process, and after that the dynamic light scattering method (DLS) was used to estimate of the grains size distribution. The mean value of grain size amounts ~ 160 nm. Small particles of nanometer size have still tendency to create a large agglomerate size of the powders.

Figure 3 shows the temperature dependence of the dielectric permittivity $\varepsilon'$ obtained for the bulk ceramic sample. The dielectric spectrum of the PLZT ceramics shows dielectric anomaly in the temperature range from 370 K to 410 K. The temperatures of $\varepsilon'$ maximum are shifted towards higher temperature region on increasing frequency. Such a dispersive behaviour of the dielectric permittivity is typical for ferroelectric relaxors and our PLZT ceramics can be considered to be a ferroelectric relaxor.
The temperature dependencies of dielectric permittivity $\varepsilon'$ for the pure P(VDF/TFE) polymer as well as the PLZT-P(VDF/TFE) composites with the volume fraction of the ceramics $\Phi = 0.1$ and 0.2 are presented in Fig. 4.

The addition of the PLZT ceramics increases the value of the dielectric permittivity $\varepsilon'$ in the whole temperature range. It should be noticed that in the dielectric spectrum measured for the composites the maximum characteristic for the ceramics in the temperature range 350 – 400 K is also visible.
In Fig. 5 the temperature dependencies of the imaginary part \( \varepsilon'' \) of the dielectric permittivity for the pure P(VDF/TFE) polymer and the PLZT-P(VDF/TFE) composites are presented. The dynamic dielectric response of the pure polymer is dominated by the \( \alpha \)-relaxation process, related to the glass transition in temperature range 250 – 300 K. The response observed for the composites is also determined by \( \alpha \)-relaxation in P(VDF/TFE) polymer.

![Figure 5](image)

Figure 5. Temperature dependence of imaginary part \( \varepsilon'' \) of dielectric permittivity of pure polymer P(VDF/TFE) and PLZT-P(VDF/TFE) composites with volume fraction \( \phi = 0.0, 0.15 \) and 0.2 of ceramics measured at various frequencies

The analysis of the frequency dependence of dielectric absorption maxima allows to describe the \( \alpha \)-relaxation by the Vogel-Fulcher relationship:

\[
\tau^{VF}(T) = \tau_0^{VF} \exp \left[ \frac{B}{T - T_0} \right]
\]
Figure 6. Relaxation time $\tau_{VF}$ vs. reciprocal of the temperature ($1/T$) for pure P(VDF/TFE) polymer and the PLZT-P(VDF/TFE) composites

Fig. 6 displays the dependence of the $\alpha$-relaxation time $\tau_{VF}$ on the reciprocal of the temperature ($1/T$) for the pure polymer and the composites with the volume fraction $\Phi = 0.1, 0.15, 0.2$. The points relate to the experimental data and the curves are obtained from fitting to the Vogel-Fulcher equation. The parameters of the $\alpha$-process: pre-exponential factor $\tau_{0,VF}$, activation energy $B$ and the Vogel temperature $T_0$ resulting from fitting are given in the table 1. Because the values of the parameters are very similar, it can be stated that the addition of the PLZT ceramics to the P(VDF/TFE) polymer only slightly changes the dynamics of the glass transition in the polymer.

| parameter | volume fraction $\Phi$ |
|-----------|------------------------|
| $\tau_{0,VF}$ [s] | 0.0 | 0.10 | 0.15 | 0.20 |
| $B$ [K] | 5.44·10^{-11} | 3.15·10^{-11} | 5.19·10^{-11} | 6.94·10^{-11} |
| $T_0$ [K] | 756 | 824 | 731 | 750 |

Table 1.

4. Conclusions

By employing the hot-pressing method, PLZT-P(VDF/TFE) composite samples of 0-3 connectivity were obtained. The results of the dynamic dielectric permittivity measurements proved that the dynamic dielectric response of the ceramics-polymer composite is a combination of the responses of pure polymer and the ceramics. The dielectric properties of the composites can be matched to the expected requirements by means of the proper choice of the ceramic volume fraction. The value of the dielectric permittivity of the composites can be significantly increased due to high permittivity of the ceramics and can be to evaluate on the basis of the contents of the ceramics. The temperature dependence of the dielectric permittivity of the composite is determined by the dispersive maximum coming from the PLZT ceramics and the $\alpha$-relaxation peak, attributed to the segmental molecular motion in the polymer. The dielectric absorption spectra obtained for the composites point to only small decreasing the $\alpha$-relaxation peak with increase of volume fraction of the ceramics. The
compositions made from the PLZT ceramics and the P(VDF/TFE) polymer can be recommended for application as sensors and actuators.

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