Available online at www.sciencedirect.com

ScienceDirect

Journal of Non-Crystalline Solids 353 (2007) 4448–4452

JOURNAL OF NON-CRYSTALLINE SOLIDS

www.elsevier.com/locate/jnoncrysol

Dielectric and pyroelectric response of PVDF loaded with $BaTiO_3$ obtained by mechanosynthesis

J. Kułek, I. Szafraniak, B. Hilczer *, M. Połomska

Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179 Poznań, Poland

Abstract

Electroactive composites based on ferroelectric ceramic and polymer components are still of interest since their properties can be easily tailored to the requirements of smart structures, sensors and actuators. We studied the dielectric and pyroelectric response of poly(vinylidene fluoride) loaded with $BaTiO_3$ nanograins obtained by mechanically activated synthesis from BaO and TiO_2. The $BaTiO_3$ nanopowder was characterized by X-ray diffraction, transmission electron microscopy and NIR Raman scattering. The relaxation processes in the polymer matrix were found to determine the dielectric response of the composites but with higher permittivity values due to the presence of $BaTiO_3$. The activation energy of the segmental motion of the polymer matrix was found to increase with increasing contents of the filler. The dielectric response of the composites with volumetric fraction of $BaTiO_3$ equal to and greater than 0.24 was found to be dominated by a broad maximum at ~320 K, which we relate to the Curie point of the ferroelectric nanograins.

PACS: 77.84.Lf; 77.84.−s; 77.22.Gm; 77.70.+a; 77.80.Bh; 77.84.Dy

Keywords: Ceramics; Sensors; Dielectric properties, relaxation, electric modulus; Ferroelectric; TEM/STEM; Powders; Nanocomposites; Nanoparticles; Titanates; Polymers and organics; Long-range order; Short-range order

1. Introduction

Many-phase systems containing at least one phase with constituents of less than 100 nm in size are usually termed nanocomposites [1]. Electroactive nanocomposites of 0–3 type connectivity, consisting of polymer matrix loaded with nanograins of electroactive ceramics, have recently attracted a considerable interest due to enhanced sensing and controlling properties for application in smart structures, sensors and actuators. The properties of the composites can be tailored to various requirements by combining the excellent dielectric, piezoelectric and pyroelectric activity of the ceramic and the low permittivity and density of the polymer to obtain materials with low acoustic impedance and low dielectric permittivity and losses [2,3]. The temperature and frequency variation of the dielectric permittivity $\varepsilon^*(T,f)$ of the composites is essential for determination of the temperature and frequency operation range of electromechanical transducers and pyroelectric sensors because ε^* is involved in the Figures of Merits.

Poly(vinylidene fluoride) (PVDF) and its copolymers loaded with $BaTiO_3$ (BT) have been studied rather rarely [2,4–8] and the attention was directed mainly to establish the mixing rules of the dielectric, piezo- and pyroelectric activity of the composites. The dielectric permittivity was studied either as dependent on the frequency at room temperature or temperature variation of the permittivity was studied at 1 kHz only [5–7]. Recent studies of the dielectric response of $(BT)_x(PVDF)_{1-x}$ nanocomposites (with 20–30 nm BT nanograins obtained by nonisothermal decomposition of barium titanyl oxalate) have shown that though the response is determined by the relaxation processes in the PVDF matrix a contribution of the BT Curie point anomaly is apparent at ~320 K in composites with

---

* Corresponding author. Tel.: +48 61 8695140; fax: +48 61 8684524.
E-mail address: bhilczer@ifmpan.poznan.pl (B. Hilczer).

0022-3093/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2007.02.077

$x = 0.32$ [8]. Here we studied the dielectric response of 0–3 type nanocomposites made of BT nanograins, obtained by mechanosynthesis, embedded in PVDF matrix. The work was aimed at characterization of the dielectric and pyroelectric properties of the composites. Moreover, we were interested in determination of the Curie point of isolated ferroelectric nanograins. The problem of size-induced change of the phase transition is of great importance both from fundamental and application point of view. It is essential to know the temperature range of the stability of the ferroelectric phase in a volume with reduced spatial dimensions (in nanometer-size range) and the existence of a critical size for ferroelectric interaction since they may be a technological limitation for miniaturization.

Ferroelectric materials are conventionally obtained by solid-state reactions or wet-chemistry routes but the high-temperature calcination required in the processing results in coarsening and aggregation of the particles. In addition to this disadvantage the chemistry-based techniques are related to high production costs. A much less expensive procedure, a direct synthesis from respective oxides at room temperature via mechanically triggered chemical reaction, has been developed recently to obtain nanocrystalline electroceramic materials of perovskite structure [9–13]. In this paper we report the dielectric response of PVDF loaded with BT nanopowder obtained by sintering reaction of BaO and TiO_2 in a high-energy ball milling process.

2. Experimental

$BaTiO_3$–poly(vinylidene fluoride) nanocomposites of (0–3) type connectivity and volumetric fraction x of barium titanate were prepared by hot-pressing. $BaTiO_3$, was synthesized by mechanical activation from high purity BaO and TiO_2 (Aldrich). The milling was carried out in a SPEX 8000 Mixer Mill for 120 h at room temperature in the air atmosphere. The batch contained ∼6 g of the oxide powders and the ratio of the weight of the stainless steel balls to that of the oxides amounted to 2:1. The development of the synthesis was controlled by X-ray diffraction and we found it to be completed after 70 h milling. The BT powder was mixed carefully with poly(vinylidene fluoride) powder from Nitrogeneous Concern, Tarnów, Poland, and hot-pressed at 450 K and 600 MPa for 30 min. The $(BT)_x(PVDF)_{1-x}$ composite samples with $x \leqslant 0.32$, ∼100 μm thick and 11 mm in diameter, were slowly cooled down to room temperature, relaxed about 24 h and covered with gold sputtered electrodes. The PVDF samples, with the degree of crystallinity of about 50%, were prepared using the same procedure. The content of the ferroelectric phase of PVDF was controlled by the ratio of the IR band intensity at 530 cm^{-1} (CF_2 bending of the nonpolar form) and at 510 cm^{-1} (CF_2 bending of ferroelectric all-trans conformation). The spectra were obtained with Perkin Elmer FT IR 1725X and the ratio $I_{530}/I_{510} \approx 2$ indicated the majority contribution of the ferroelectric modification of PVDF.

The BT nanopowder was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and near infrared Raman spectroscopy. The powder diffraction with $Cu_{K\alpha 1}$ radiation was used to prove the perovskite structure of the BT powder after different milling times. Transmission electron microscope Philips CM-20 TEM operating at the accelerating voltage of 200 kV was used to study the powder morphology and the grain structure at room temperature. Raman scattering technique was applied to characterize the local dynamical symmetry in BT nanograins. NIR Raman spectra of BT nanopowder were recorded at room temperature in 180° geometry with Bruker IFS66 FRA106 spectrometer at the power of 100 mW of Nd:YAG laser ($\lambda = 1064$ nm). For comparison we recorded also the room temperature Raman spectra of barium titanate single crystal and conventional BT ceramic.

Dielectric response $\varepsilon^*(f, T)$ of the composites was measured in the frequency range 100 Hz $< f <$ 1 MHz with computer controlled HP-4284 A impedance analyzer at temperatures from 150 to 450 K. The samples were heated at a rate of 1 K/min.

Pyroelectric response of the samples, in form of a diaphragm fixed on its perimeter, was studied in the voltage mode at room temperature. The samples were illuminated by IR radiation (960 nm) from LED working at a power of 5 mW and modulated with a frequency f_m from 1 Hz to 1 kHz.

3. Results and discussion

3.1. Characterization of $BaTiO_3$ nanopowder

The process of mechanosynthesis was controlled by XRD and we found that after 70 h of milling the $BaTiO_3$ of perovskite structure was obtained. Longer milling times do not change the perovskite structure but result in a decrease of the mean grain size. High resolution transmission electron microscope (HRTEM) studies of the BT nanopowder revealed that the grains exhibit a quasispherical morphology and a core-shell structure. The core of the grains shows crystalline structure (Fig. 1), whereas the 1–2 nm thick shell is highly disordered.

The grain size distribution of the BT nanopowder obtained by 120 h high-energetic milling of BaO and TiO_2 is shown in Fig. 2. Some grains are agglomerated into clusters of mean size amounting to ∼100 nm.

As XRD yields the information on average and static symmetry we performed also Raman scattering studies of BT nanopowder to characterize the local dynamical symmetry. Fig. 3 shows Raman spectrum of BT nanopowder obtained after 120 h mechanosynthesis and the spectra of BT single crystal and ceramic samples.

The factor group analysis predicts $3A_1 + 4E + B_1$ Raman active modes for ferroelectric tetragonal BT and the long-range electrostatic forces split the A_1 and E modes into transverse (TO) and longitudinal (LO) components.