

HYBRID MULTIFERROIC COMPOSITE FILMS OF CoFe_2O_4 – BaTiO_3 NANOSTRUCTURES EMBEDDED IN POLYVINYLIDENE FLUORIDE

V. Corral-Flores, D. Bueno-Baqués, R. F. Ziolo

Research Center for Applied Chemistry, Enrique Reyna 140, Saltillo, Coah. 25253, Mexico.

Introduction

Multiferroic materials are functional materials that exhibit more than one ferroic order and can be single phase or composites [1]. Composites are more attractive from the technological point of view, since they present a response of around two orders of magnitude higher than single phases [2]. These materials have been widely studied as ceramic particulate bulk composites [3] and ceramic and ceramic-metal multilayers [4]. More recently, some attempts were made to synthesize multiferroic composites at the nanoscale as nanostructures grown over a substrate [5]. However, the clamping effect minimizes the mechanical coupling between the phases.

In order to avoid the clamping problems, we have synthesized multiferroic core-shell nanostructures to be used as building blocks for complex morphologies and different connectivities. In this work we present the preparation of multiferroic composites comprising such core-shell nanostructures embedded in polyvinylidene fluoride (PVDF), which, in the β phase, exhibits excellent piezoelectric properties.

Experimental

Cobalt ferrite – Barium titanate nanostructures were synthesized by sol-gel method. The details of the preparation were published elsewhere [6]. Compositions ranging from 20 to 60 wt.% of cobalt ferrite were prepared. Additionally, single phase samples of CoFe_2O_4 and BaTiO_3 were synthesized for comparison. A 15 wt.% PVDF (Kynar 761, Boedeker Plastics Inc.) solution was prepared in *N,N*-dimethylformamide (DMF, Sigma-Aldrich) by heating at 50°C and stirring. The solutions were cooled to room temperature and then the core-shell nanostructures were added at a weight ratio of 1:10 with respect to the polymer. Suspensions were stirred for one hour, sonicated for 2 hours and stirred again for at least two hours prior to film deposition. Films were spin-coated onto glass substrates and glass-ITO substrates at 4000 rpm. Immediately after deposition, samples were heat treated at 60°C for one hour to favor the crystallization of beta phase of the PVDF, as reported by M. C. Branciforti et al. [7]. The name of the samples was assigned by the content of cobalt ferrite in the core-shell nanostructures. Thus,

Co20-F stands for the sample containing core-shell nanostructures with ~20 wt.% of CoFe_2O_4 , and so on; while F means Film sample. One additional film was prepared without the ceramic component as a reference, called PVDF-F.

The morphology of the samples was studied by scanning electron microscopy (SEM, SM-510 Topcon). Infrared spectra were acquired by averaging 200 scans for each spectrum with a FTIR spectrophotometer (IR-Nexus 470) in reflectance mode (ATR Spectra-Tech Gemini Magna 60). Thermal analysis was conducted on a differential scanning calorimeter (DSC, TA Instruments Modulated DSC 2920). The heating rate was 5°C/min.

Results

Figure 1 shows a SEM image of the sample Co20-F. The spherulites have sizes of about 3-4 microns in diameter. The small white dots correspond to agglomerates of the ceramic nanostructures, with sizes of the order of 100 nm.

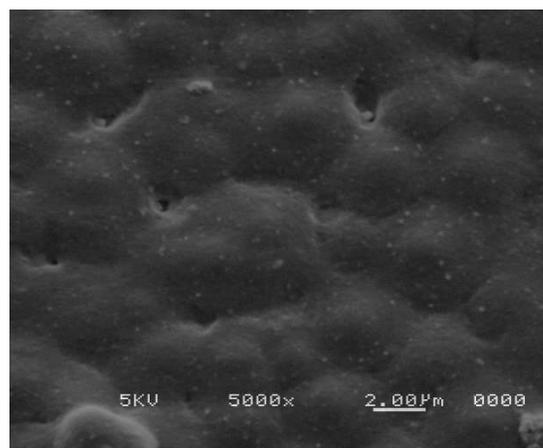


Fig. 1. SEM image of the sample Co20-F.

Fig. 2 shows the FTIR-ATR spectra of the as-received PVDF together with the sample PVDF-F. The FTIR absorption bands at 762, 795 and 974 cm^{-1} correspond to the alpha phase, the bands at 839 and 1276 cm^{-1} are assigned to the beta phase, while the gamma phase is identified at 1235 cm^{-1} [8]. The as-received polymer presented mainly α phase. Its counterpart in film form presented β and γ phases predominantly. The fraction of beta phase in each sample was estimated from the FTIR results using the equation proposed by Rinaldo et al. [9]:

$$F(\beta) = \frac{A_{\beta}}{1.26A_{\alpha} + A_{\beta}}$$

where A_{α} and A_{β} represent the intensity of the absorption bands of the α and β phases at 762 and 839 cm^{-1} . The fraction of beta phase in the as-received polymer was estimated as 0.12, while in the film it raised up to 1.

The spectra of the multiferroic composite films are presented in Fig. 3. As in the case of the PVDF film, all the spectra showed the presence of mainly β and γ phases, which indicates that the spin-coating technique, together with the heat treatment, is adequate for the crystallization of β phase.

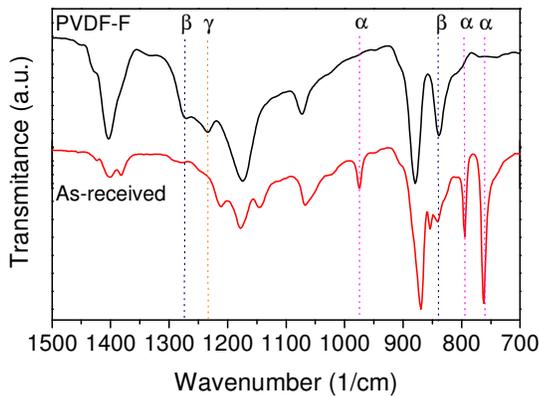


Fig. 2. FTIR-ATR spectra of the as-received and spin-coated PVDF.

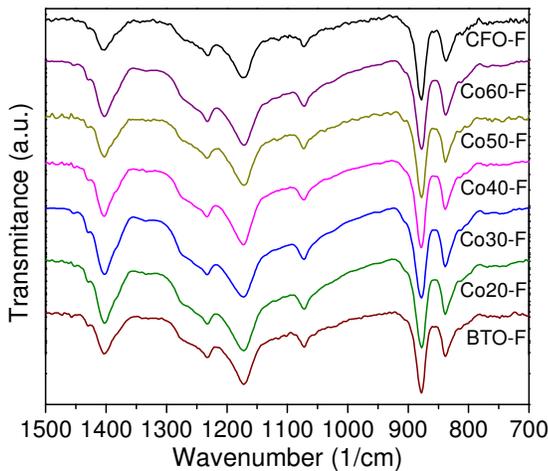


Fig. 3. FTIR-ATR spectra of the multiferroic composite films.

Fig. 4 shows the DSC results of the multiferroic composite films. The principal endothermic peak corresponds to the fusion of the polymer, while the secondary peak at higher temperature could be attributable to the presence of crystals of different sizes or two crystalline phases. Benz and Euler reported similar results for PVDF films, attributing the double endothermic peak solely to the crystal sizes [10].

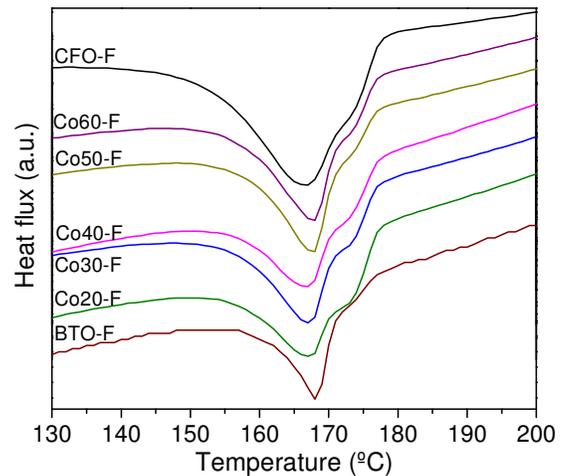


Fig. 4. DSC plots of the multiferroic composite films.

Conclusions

Hybrid multiferroic composite films were prepared from magnetostrictive-piezoelectric core-shell nanostructures embedded into PVDF and deposited by spin coating. The heat treatment at 60°C promoted the crystallization of β phase in the polymer, diminishing the amount of α phase such that the FTIR technique did not detect it. The secondary DSC peak suggested that two crystal sizes were present in the PVDF. The polar phase in the polymer is a key issue to enhance its piezoelectric properties and thus, improve the performance of the hybrid multiferroic composite as a whole.

References

- [1] W. Eerenstein, N. D. Mathur, J. F. Scott, *Nature* 442 (2006) 759-765
- [2] Jungho Ryu, Shashank Priya, Kenji Uchino, Hyoun-ee Kim, *J. Electroceramics* 8 (2002) 107-119
- [3] M.I. Bichurin, V.M. Petrov, Yu V. Kiliba, G. Srinivasan, *Phys. Rev. B* 66 (2002)
- [4] Jungho Ryu, Shashank Priya, Kenji Uchino, Hyoun-ee Kim, Dwight Viehland, *J. Korean Ceramic Soc.* 39 9 (2002) 813-817
- [5] Chaoyong Deng, Yi Zhang, Jing Ma, Yuanhua Lin, Ce-Wen Nan, *Acta Materialia* 56 (2008) 405-412
- [6] V. Corral-Flores, D. Bueno-Baqués, R. F. Ziolo, submitted to *Acta Materialia* (2009)
- [7] Marcia Cristina Branciforti, Vitor Sencadas, Senentxu Lanceros-Mendez, Rinaldo Gregorio, Jr., *J. Polym. Sci. B: Polym. Physics* 45 (2007) 2793-2801
- [8] Wu Aik Yee, Masaya Kotaki, Ye Lui, Xuehong Lu, *Polymer*, 48 (2007) 512-521
- [9] Gregorio Jr., Rinaldo; Cestari, Marcelo, *J. Polym. Sci. B: Pol. Phys.*, 32 5 (1994) 859-870
- [10] Marcel Benz, William B. Euler, *J. App. Pol. Sci.*, 89 (2003) 1093-1100