Synthesis, physical and microwave absorption properties of Barium ferrite - P(VDF-TrFE) nanocomposites

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Abstract. We present results concerning the synthesis, magnetic, dielectric and microwave absorption properties of BaFe$_{12}$O$_{19}$ / P(VDF-TrFE) nanocomposites. First, barium ferrite nanopowders were prepared by the hydrothermal synthesis method. Structural and morphological properties of the prepared powders were investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM), showing as result a good quality spherical plus platelet-like shaped nanoparticles. Afterwards, composite films with fuller nanoparticles of barium ferrite BaFe$_{12}$O$_{19}$ (BaFO, nominal 5-20 wt.%) dispersed within P(VDF-TrFE) acting as polymeric matrix have been prepared by solvent evaporation. Magnetic properties were examined by the vibrating sample magnetometry (VSM), and a direct comparison of results obtained for the composites respect to the pure nanopowder allow us to obtain the true nanofiller content value, different from the initially nominal one. Dielectric properties have been measured up to 2 MHz and show the typical behaviour of Maxwell-Wagner type interfacial polarization. From 10 kHz up, permittivity of the composites remains almost unchanged, with values that show a smooth increase as the %wt. of BaFe$_{12}$O$_{19}$ does. Finally, microwave absorption properties were analyzed by using ESR technique operating at X-band. All obtained results are discussed in terms of size and quantity of the composites BaFe$_{12}$O$_{19}$ filler nanoparticles.

1. Introduction
In the last years the fabrication of multifunctional composite materials by combining inorganic constituents with polymeric ones is receiving great attention and efforts [1]. A typical example of this is the inclusion of BaTiO$_3$ in silicon rubber to improve the properties of the dielectric elastomer for electromechanical actuators [2]. Polymers exhibit many advantages as easy processing and forming, thermomechanical stability, high dielectric breakdown strength and low cost. Dielectric and magnetic properties of polymers can be substantially altered by embedding suitable inclusions, and tuned by
controlling the amount and the type of the filler particle used [3,4]. More recently, mixtures of piezoelectric polymers with magnetic/magnetostrictive nanoparticles have been proposed to give as result potential magnetoelectric (ME) composites, being a clear example the particulate [poly(vinylidene fluoride)-trifluorethylene, (PVDF-TrFE), - ferrite] nanocomposites [5]. The barium ferrite (BaFe$_{12}$O$_{19}$) shows particular magnetic properties as high coercive force and hysteresis losses that make this ferrite to be widely used in milli- and microwave devices. It has very high magnetocrystalline anisotropy in the low-symmetry hexagonal magnetoplumbite crystal structure with hexagonal unit cell, and it usually appears shaped as thin hexagonal platelets with easy direction of magnetization along the c axis, which is perpendicular to the plates.

In a previous work [6] we presented a detailed study on the electric, dielectric and magnetic properties of purchased microsize BaFe$_{12}$O$_{19}$ (up to a 20% weight) - P(VDF-TrFE) composite films. Here we present new results concerning the behavior of the dielectric and magnetic properties of nanosize BaFe$_{12}$O$_{19}$ (up to a 10% weight) - P(VDF-TrFE) composite films, but being now the Barium ferrite nanoparticles synthesized at the laboratory by using a hydrothermal method. This study will extend also to microwave absorption properties of these nanocomposite films.

2. Experimental procedures

BaFe$_{12}$O$_{19}$ ferrite nanoparticles were synthesized following a hydrothermal route [7, 8]. For this purpose, stoichiometric quantities of the starting reagents sodium Hydroxide (NaOH), barium chloride (BaCl$_2$·2H$_2$O), ferrous chloride (FeCl$_2$·4H$_2$O), these three from Sigma Aldrich, and potassium nitrate (KNO$_3$), this last from Panreac, and deionized water were used in the synthesis reaction carried out in a Teflon autoclave without any agitation. The obtained powder was washed repeatedly using deionized water and alcohol, then dried at 240 °C for 10 h, and finally cooled down slowly to room temperature.

The structural characterization of the final product was done by using X-ray (Cu-Kα radiation, λ= 1.5418 Å) diffraction patterns analysis. Transmission Electron Microscopy (TEM) micrographs were obtained using a Philips CM200 microscope at an acceleration voltage of 200 kV. To measure particle size, ImageJ software was used.

The P(VDF-TrFE) copolymer in the form of powder was supplied by Piezotech. For the film shaped composites preparation, the desired amount of barium ferrite BaFe$_{12}$O$_{19}$ (BaFO, 5, 10 and 20 %wt.) was added to Triton surfactant and DMF solvent, and then placed in ultrasound bath for 3 h to facilitate the particles to be well dispersed in the solution and also to avoid aggregates. Then P(VDF-TrFE) powder was subsequently added. Further, the obtained mixture was placed in a Teflon mechanical stirrer with ultrasound bath for completing dissolution of the polymer. Later, the material was spread on a glass substract and introduced in an oven at 210 °C for 10 min, ensuring the total evaporation of the solvent as well as the melting of the polymer. Finally, the material crystalized at room temperature. In this way composite flexible films of about 85 μm thickness were obtained.

Magnetic hysteresis loops at room temperature were measured using an in house vibrating sample magnetometer up to a maximum field of 1.8 T. Measurements of dielectric constant $\varepsilon$ and dielectric loss tangent $\tan \delta$ were performed with an automatic Keysight E4980A Precision LCR Meter, at frequencies ranging from 20 Hz to 2 MHz. Finally, microwave absorption properties were analyzed by using FMR technique operating at X-band (9.4 GHz).

3. Results and Discussion

3.1. Structure and morphology

From Rietveld analysis of measured X-ray diffraction patterns we infer the existence of two phases in our synthesized nanopowder, the desired BaFe$_{12}$O$_{19}$ (≈90% of the full content) and also Barium carbonate BaCO$_3$ (≈10% of the full content). From TEM pictures we see two different powder
morphologies: majority of spherical nanoparticles aggregates with particle diameters ranging about 30-80 nm, plus some hexagonal platelets with size from 100 to 500 nm.

Figure 1. Room temperature measured X-ray measured diffraction pattern of our synthesized barium ferrite nanopowder.

Figure 2. TEM pictures of the obtained BaFO powder showing spherical (left) and platelet-like morphologies (right).

3.2. Magnetic characterization
First, we have measured the hysteresis loop at room temperature of the pure Barium ferrite nanopowder, obtaining values of $M_s \approx 30$ emu/g at 1.8 T, $M_r/M_s \approx 0.32$ and coercitivity about $H_c \approx 800$ Oe.

Afterwards hysteresis loops were measured for the different composites. All loops exhibit similar shape with values of $M_r/M_s \approx 0.24-0.34$, and $H_c \approx 700-800$ Oe. As a first consequence of all these measurements, the direct comparison of the $M_s$ values obtained for all the composites respect to the pure nanopowder allowed us to deduce the true nanofiller content value and correct it from the initially nominal one. So, instead of the initially assumed 5, 10 and 20 %wt. contents, we have estimated true values of the BaFeO content within the polimeric matrix of 4.4, 8.1 and 12.5 %wt. content. These true values will be used in the following sections.
3.3. Dielectric behaviour

We have observed a quick decrease of the value of the dielectric constant as frequency increases, remaining almost constant for frequencies above 10 kHz. This behavior is explained assuming Maxwell–Wagner type interfacial polarization, in agreement with the Koop’s phenomenological theory [9, 10]: the dielectric constant of a composite with heterogeneous structure of ferrite grains embedded in a polymeric matrix can be imagined as consisting of conducting grains separated by highly resistive grain boundaries. Thus, the voltage applied to the sample drops mainly across the Barium ferrite nanoparticle surfaces and space charge polarization is built up at those boundaries.

Figure 4. Permittivity and loss tangent against frequency for the 5%wt. nominal content composite (left), and values measured at 10 kHz for all the different BaFO content films (right).

From 10 kHz up, permittivity of the composites remains almost unchanged. These measured values show a smooth increasing behaviour as the BaFO filler content increases in the composites that tell us about this nanofiller acting as a reinforcement within the composite.
3.4. Microwave absorbing behaviour
All room-temperature recorded spectra exhibit the same essential features, showing complex behavior with rather large line widths (ΔH_{pp} ≈ 1.8 kOe) as usually happens with barium ferrite samples [11]. Microwave absorption is maximum around 3 kOe in all studied composites, a field value that is in good agreement with our previous observation of a majority of spherical shaped nanoparticles in our synthesized powder [12].

![EPR spectra (at 9.4 GHz) obtained for the different composites.](image)

The measured value of H_{res} (field of maximum absorption, when dP/dH=0) smoothly decreases (from 3.01 to 2.95 kOe when changing from true 4.4%wt to 12.5%wt) with the increase of magnetic filler content, a fact that one can expect when interactions increase inside these composites as Barium ferrite content also does.

In all cases significant absorption near zero-field has been observed, absorption that increases proportionally to the ferrite content in the nanocomposite. This zero field signal is not surprising and arises from the non neglectable electrical conductivity of the BaFO ferrite.

4. Conclusions
We have synthesized BaFe_{12}O_{19} ferrite nanoparticles by using the hydrothermal route. As probed by TEM microscopy, we have obtained a nanopowder with majority of spjerical particles with diameters ranging from 30 to 80 nm, plus some bigger platelets.

When these Barium ferrite nanoparticles are embedded within a P(VDF-TrFE) polymeric matrix, we obtain film-shaped composites in which the dielectric behavior smoothly improves as the filler content increases. Very similar behavior has been observed for microwave absorption characteristics when EPR curves are measured. Thus, we can conclude that the BaFe_{12}O_{19} ferrite nanoparticles act as a reinforcement within the polymeric matrix, making so these nanoparticles promising candidates for the development of new multifunctional composites.
Acknowledgements

J. Gutiérrez wants to thank financial support from the Basque Government Industry Department under Project Actimat, (ELKARTEK Program). A.M. Gutiérrez Muto wants to thank the BCMaterials Center for an expertising stay. Technical and human support for magnetic measurements provided by SGIker (UPV/EHU, MICINN, GV/EJ, ESF) is gratefully acknowledged.

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