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Magnetic and ferroelectric domain structures in $BaTiO_3$–$(Ni_{0.5}Zn_{0.5})Fe_2O_4$ multiferroic ceramics

Catalin Harnagea [a], Liliana Mitoseriu [b,c,*], Vincenzo Buscaglia [d], Ilaria Pallecchi [e], Paolo Nanni [c]

[a] INRS-EMT, University Québec, 1650 Lionel-Boulet, Varennes, Que. J3X 1S2, Canada
[b] Department of Solid State & Theor. Physics, Al. I. Cuza University, Bv. Carol I, 11, Iasi 700506, Romania
[c] Department of Chemical & Process Eng., University Genoa, P-le Kennedy 1, Genoa I-16129, Italy
[d] Institute for Energetics & Interphases-CNR, Via de Marini 6, Genoa I-16149, Italy
[e] Physics Department & INFM, University of Genoa, Via Dodecaneso 33, Genoa I-16146, Italy

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Abstract

$BaTiO_3$–$(Ni_{0.5}Zn_{0.5})Fe_2O_4$ composites prepared by co-precipitation were investigated. The macroscopic magnetic properties derived from the magnetic phase (low coercivity, almost no M(H) hysteretic behavior and high permeability) are preserved in the composite. The dielectric properties are strongly influenced by interface phenomena (Maxwell-Wagner), due to the local electrical inhomogeneity. At low frequencies, the composites present thermally activated conductivity and relaxation, while at 1 MHz permittivity of around 500 and tan $\delta < 8\%$ is obtained at room temperature. The multiferroic character was demonstrated at nanoscale by the presence of the magnetic and ferroelectric domain structure in the same region. Imprint polarisation in the regions corresponding to the ferroelectric phase is found, as result of an internal electrical field created at the interfaces between the (Ni,Zn)-ferrite and $BaTiO_3$ regions.

Keywords: Composites; Electrical properties; Magnetic properties; $BaTiO_3$–(Ni,Zn) ferrite

1. Introduction

Composite materials have numerous applications exploiting their electromagnetic properties. Among them, the multiferroics are combining two ferroic properties in the same phase and a coupling among them. The outstanding recent interest in the magnetoelectric (ME) multiferroics is related to the potentiality to use the cross-correlation between the magnetic and electric properties in electronic devices.[1,2] The main results concerning the fundamental aspects and the new concepts in design, preparation, investigation and theoretical treatment of various ME structures in single-phase and composites, were presented in many recent reviews.[3–6] Fundamental requirements in the efficient design of novel materials are: (i) to correlate the nanostructural characteristics with the macroscopic functional properties and (ii) to predict the bulk behavior of a composite from knowledge of the intrinsic properties of its constituents. The ME coupling in composites is based on the concept of *product property*.[7] According to this principle, a suitable combination of two phases such as piezomagnetic or magnetostrictive and piezoelectric phases, can yield a desirable ME property. The challenge in preparing such materials is to find equilibrium ferroelectric and magnetic structures preserving both properties close to the room temperature. Sintered ME composites offer easy and cheap fabrication and the possibility to control the molar ratio of phases, grain size and densification. Ceramic composites of $xBaTiO_3$–$(1-x)Ni_{0.5}Zn_{0.5}Fe_2O_4$ (BT-NZF) were previously prepared both by mixing BT and NZF powders and by co-precipitation.[8] Dense and better homogeneous microstructures and good dielectric properties were found by the second approach. Once obtained the samples, it is important that each component preserves its ferroic character, in spite the presence of the other phase. The magnetic and ferroelectric domain structures besides the macroscopic dielectric and magnetic properties in a ceramic with composition $x = 0.70$, are reported here.

* Corresponding author at: Department of Solid State & Theor. Physics, Al. I. Cuza University, Bv. Carol I, 11, Iasi 700506, Romania. Tel.: +40 32 144760; fax: +40 32 213330.
E-mail address: lmtsr@uaic.ro (L. Mitoseriu).

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2. Experiment

The ceramic composites were prepared by co-precipitating Fe^{III}–Ni^{II}–Zn^{II} nitric salts in NaOH solutions in which the BT powders were previously dispersed. The powders were dried and calcined at 400 °C/1 h to form the NZF phase. The mixture was then milled, isostatically pressed at 2×10^8 Pa and sintered at (1050/1150)°C/1 h. The magnetic moments were measured in the range of (5/350)K using a superconducting quantum interferometric magnetometer SQUID (Quantum Design). The samples were cooled down to the measurement temperature in the absence of a magnetic field (zero-field cooling ZFC). The field was subsequently applied while heating (field heating FH) for the measurement of the temperature dependence on the magnetic moment. The dielectric measurements were performed with an impedance analyzer Solartron SI1260 for temperatures (30/210)°C with a heating/cooling rate of 0.5 °C/min in the frequency range ($1/10^6$)Hz. The ferroelectric and magnetic domain structures were investigated by using a Veeco/Digital Instruments Enviroscope AFM with a Nanoscope IIIa controller. Magnetic force microscopy (MFM) was employed for probing the local magnetic properties. The magnetic tips used were from Micromasch (NSC36 cantilevers, coated with Co/Cr), magnetized along the tip axis therefore detecting the field gradient normal to the surface. After performing the MFM measurements, the microscope mode was switched to contact and the same area of the sample was investigated for local ferroelectricity using piezoresponse force microscopy (PFM),[9] by using the same magnetic (and conductive) cantilevers. The measurements were performed using a computer-controlled lock-in amplifier (Signal Recovery Model 7265) connected to the AFM via a Signal Access Module. The ac testing voltage used had 0.5 V_{rms} at a frequency of 27.19 kHz and was applied to the tip, while the dc-bias was applied to the opposite face of the sample glued on a conductive holder with silver-paint. In the experiments presented here, white contrast stands for the downward direction of polarisation.

3. Results and discussions

The dielectric characteristics of the 0.70BT–0.30NZF composite are shown in Fig. 1a and b. Anomalies associated to the ferro-para phase transition of BT in the range of temperatures of (120, 180)°C are observed at f = 1 MHz. For this frequency, good dielectric properties are found at room temperature ($\varepsilon' \approx 500$, $\tan\delta < 8\%$). The increasing permittivity at high temperatures and lower frequency and the dispersion features of $\tan\delta$ (Fig. 1b) are probably due to thermally activated conductivity and relaxations attributed to interface (Maxwell-Wagner) mechanisms.[10,11] As analysed in detail in the review,[11] both intrinsic and extrinsic factors are responsible for the functional properties in multiferroic composites. In the case of dielectric data, the correlation between the apparent giant permittivity and conductivity giving rise to tangent loss above unity are well-known.[11,12] Due to these phenomena strongly affecting any electrical measurement of such samples, it is impossible to fully demonstrate if BT preserves its ferroelectricity in the composite, by using macroscopic electrical characterisation only. Practically, the electrical inhomogeneity at the BT-NZF interfaces and even at the BT grain boundaries (possible doped with Ni, Zn, Fe ions) create an extrinsic contribution that is driving the dielectric response of such sample. Oppositely, the magnetic properties are mainly determined by the NZF phase and only small differences derived from various percolation degrees were observed.[11,13] The M(H) hysteresis (Fig. 2a) prove the presence of the ordered magnetic structures causing a strong non-linear and almost non-hysteretic character and high magnetic permeability. As in the pure NZF, the spontaneous magnetization in the composites originates from the unbalanced antiparallel spins (ferrimagnetic character), giving rise to small values of the coercivity and saturation fields.[14] The evolution with temperature of the magnetic moment measured during a FC/ZFC sequence (Fig. 2b) shows a unique feature around (−243 °C, −223 °C), due to a magnetic transition from weak ferromagnetism to ferrimagnetism, as in the pure ferrite, and no other effects due to the presence of the BT phase. The

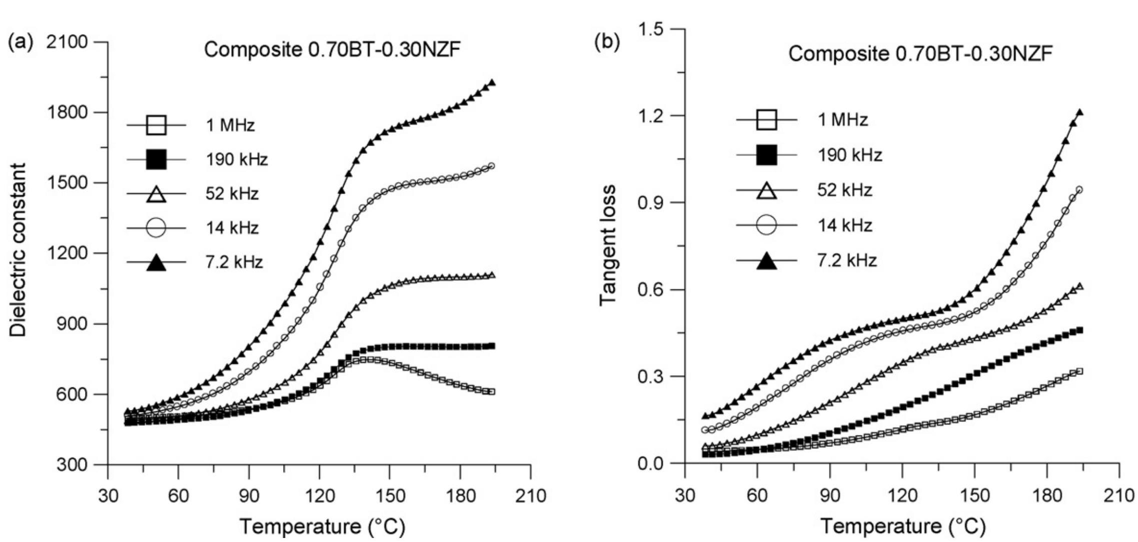

Fig. 1. (a) Dielectric properties of the composite $0.70BaTiO_3$–$0.30Ni_{0.5}Zn_{0.5}Fe_2O_4$ in the range 10^3–10^6Hz: (a) permittivity and (b) tangent loss. Note that thermally activated relaxations cause an apparent increasing of the permittivity and very high losses at low frequency.

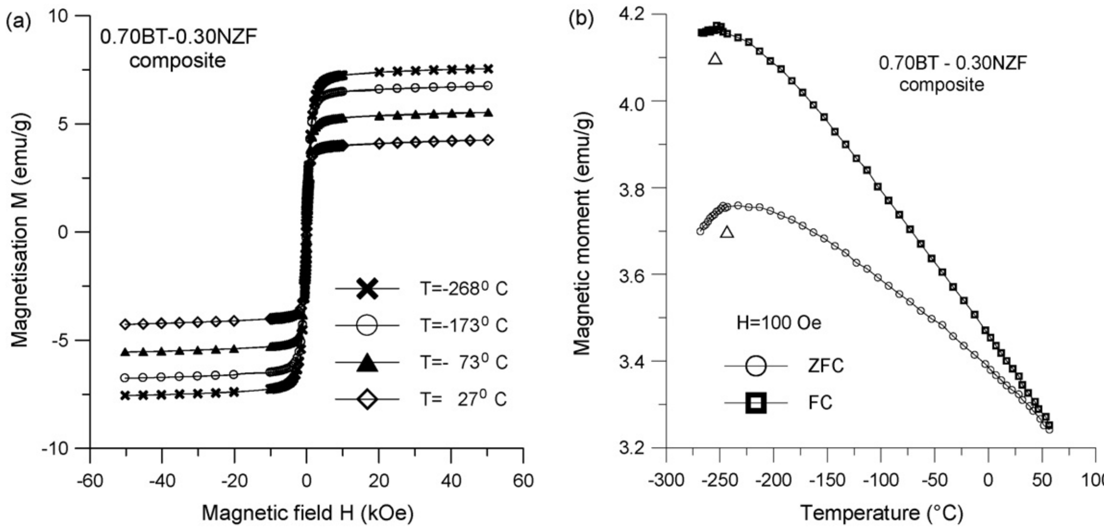

Fig. 2. Magnetic properties of the ceramic composite $0.70BaTiO_3$–$0.30Ni_{0.5}Zn_{0.5}Fe_2O_4$: (a) M(H) hysteresis loops at a few temperatures, showing ferimagnetic characteristics and (b) temperature dependence of the magnetic moment in field-cooling (FC) and zero-field cooling (ZFC) experiments, with an anomaly around (−243 °C, −223 °C), indicating a transition from weak ferromagnetic to ferrimagnetic properties.

ferrimagnetic character in the composite is thus, fully preserved at room temperature, as confirmed by the MFM experiments.

At nanoscale, the magnetic field gradient contrast along the *z*-direction (Fig. 3a) shows the presence of magnetic domains extending over several adjacent grains. According to the contrast formation mechanism,[15] black regions in the image reflect areas where the field gradient is attractive. While the extraction of the true magnetic domain orientation is impossible due to the complexity of the problem, it is possible to deduce (as it has been done recently for epitaxial thin film heterostructures of ferrimagnetic and ferroelectric components[16]) that isolated regions of the same contrast (like those encircled) represent magnetic domains with magnetization oriented normal to the sample plane. Taking into account that the magnetic tip has been magnetized prior to measurements with the magnetization vector pointing out of the sample surface, these black or white isolated regions show magnetization pointing out or into the sample, respectively. In contrast, for those regions showing black/white contrast in close proximity it is generally not possible to deduce the orientation of the magnetization.

The PFM image acquired from the same area (Fig. 3b) proves that indeed the BT component preserves its ferroelectric nature in the composite sample. Grey contrast in the image represents regions where there is no piezoelectric response, and therefore corresponds to the NZF component. A careful comparison with the MFM image shows that above these grey regions the magnetic field gradient is high (the overlapping being possible due to the long range character of the magnetic interaction). As revealed in the PFM image, most ferroelectric regions exhibit downward polarization (into the sample). This imprint is probably a surface effect due to an internal electric field induced at the interfaces between the BT and NFZ phases. This supposition seems to be related to the conclusions of the dielectric study showing strong interface phenomena. The relative low value of the piezoelec-

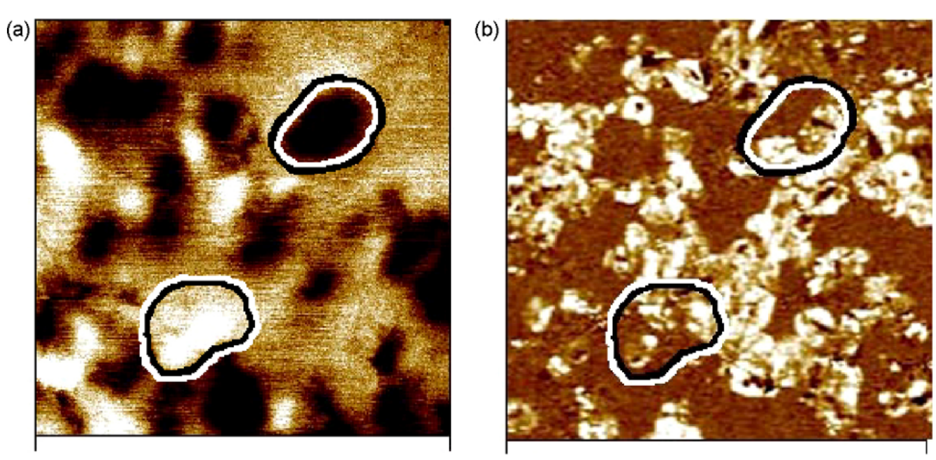

Fig. 3. AFM investigations of the same area of the $0.70BaTiO_3$–$0.30Ni_{0.5}Zn_{0.5}Fe_2O_4$ ceramic composite: (a) MFM contrast and (b) PFM image.

tric coefficient (10 pm/V compared to 90 pm/V in bulk BT) is caused by the low tetragonal distortion of BT in this composite (*c*/*a* = 1.006), as result of the small grain size, combined with the non-ideal contact between the tip and sample due to the mentioned interface effects.

4. Conclusions

The magnetic properties of the $0.70BaTiO_3$–$0.30Ni_{0.5}Zn_{0.5}Fe_2O_4$ ceramic composites are resulting as a *sum property* from the ferrite's characteristics, while the dielectric data are mainly determined by the interface phenomena rather than by intrinsic properties of the BT compound. The multiferroic nature of the ceramic composites is demonstrated by the presence in the same area of both magnetic and ferroelectric domain structures as resulting from the combined MFM/PFM study. To achieve good values of the ME coefficients, a deep understanding of the nature and control of the interface-driven electrical properties are further necessary.

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