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$BaTiO_3$–$(Ni_{0.5}Zn_{0.5})Fe_2O_4$ ceramic composites with ferroelectric and magnetic properties

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Abstract

Di-phase ceramic composites $0.50BaTiO_3$–$0.50Ni_{0.5}Zn_{0.5}Fe_2O_4$ with limited reaction at interfaces prepared by two methods: (i) mixing $BaTiO_3$ and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ powders and (ii) co-precipitation of Fe, Ni, Zn salts in solutions containing $BaTiO_3$ powders, are comparatively analysed. Homogeneous microstructures with higher density and better mixing of the two phases are obtained by the second method and consequently, better dielectric properties ($\tan\delta < 5\%$ and $\varepsilon_r \in 300$–800 for $f > 10^4$ Hz at room temperature) and higher magnetic moments. Some interface effects are playing important roles on the dielectric properties at low frequencies and high temperatures, mainly in the samples prepared following the method (i). Both the ferroelectric and magnetic phases preserve their basic properties in the bulk composite form and thus, these composites BT-NZF are good candidates as magnetoelectric materials.

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

1. Introduction

The magnetoelectric (ME) multiferroics possess two coupled order parameters (polarisation and magnetisation) in the same range of temperatures and display a ME effect consisting in the variation of a dielectric/ferroelectric property (polarisation, permittivity) under magnetic field changes and vice versa.[1,2] This property facilitates the magnetic–electric energy conversion and thus is attractive for applications as magnetic field probes, transducers, novel actuators, sensors, capacitive/inductive passive filters for telecommunications, etc. Due to their multifunctional properties, these systems attracted in the last years an outstanding interest.[3–5] Apart the single-phases, artificial ME structures are obtained by combining ferroelectric and magnetic systems via their piezoelectric/magnetostrictive characteristics, according to the principle of the "product property".[6] Following this idea, various ME bulk composites have been investigated, mainly ferroelectric–ferrite ceramics.[7–9] The successful preparation of the di-phase $xBaTiO_3$–$(1-x)Ni_{0.5}Zn_{0.5}Fe_2O_4$ ceramic composites with limited reaction at interfaces was recently reported.[10] In the present paper, new aspects concerning the magnetic and dielectric properties in relationship with the preparation method and microstructure for the samples with composition $x = 0.50$ are reported.

2. Sample preparation and experiment

Ceramic composites $xBaTiO_3$–$(1-x)Ni_{0.5}Zn_{0.5}Fe_2O_4$ (BT-NZF) were prepared following two different procedures[10]: (i) mixing the BT powders prepared by solid-state and NZF prepared by co-precipitation (particle size below 50 μm) in the desired proportion, milled, isostatically pressed and sintered; (ii) Co-precipitating Fe^{III}–Ni^{II}–Zn^{II} nitric salts in a NaOH solution, in which the BT powders were previously dispersed.

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The powders were dried and calcined at 400 °C for 1 h to promote the formation of NZF phase. The mixture was then milled, isostatically pressed and sintered. Both types of samples were pressed at 2×10^8 Pa and sintered at 1050–1150 °C for 1 h. Scanning electron microscoy (SEM, LEO 1450VP, LEO Electron Microscopy Ltd., Cambridge, UK) was used to characterise the microstructures and X-ray diffraction (XRD, Co Kα radiation, Philips PW1710, Philips, Eindhoven, The Netherlands) for determining the phase composition. Differential scanning calorimetry (DSC) measurements were performed on sintered samples of ∼100 mg in the range 0–300 °C with a heating/cooling rate of 10 °C/min. 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 the 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.

3. Results and discussions

The X-ray diffraction (XRD) patterns obtained for the sintered ceramics of $0.50BaTiO_3$–$0.50Ni_{0.5}Zn_{0.5}Fe_2O_4$ (Fig. 1) show that both the parent phases of perovskite BT and spinel NZF are present in the right proportion. Within the resolution limit of the XRD, almost no intermediate phases were detected; small traces of some other phases are visible at $2\theta \approx 40°$ for samples prepared by method (i) only. This confirms the successful preparation of the di-phase composite ceramics with a limited chemical reaction at the interfaces, by both procedures.

The composites prepared by method (i) show poor homogeneity and densification, with big non-percolated aggregates of NZF octahedral crystals and large pores, in spite of a good initial mixing of the two phases. More homogeneous microstructures with good dispersion of BT and NZF grains and small pores were found in ceramics prepared by method (ii), when the formation of NZF hard aggregates is strongly inhibited (Fig. 2). In this case, the ferrite regions are percolated by small BT grains. Thus, the preparation method influences the degree of connectivity of the two phases and this can yield to different functional properties. The DSC responses of the composite in the range 50–200 °C show a broad feature with a maximum at 130 °C on heating and 127 °C on cooling, corresponding to the tetragonal-cubic phase transition of the BT phase (Fig. 3). The transition enthalpy seems to not be affected by the microstructural differences of the two types of samples.

The dielectric relaxation at room temperature for the frequencies 1–10^6 Hz is presented in Fig. 4(a and b). High

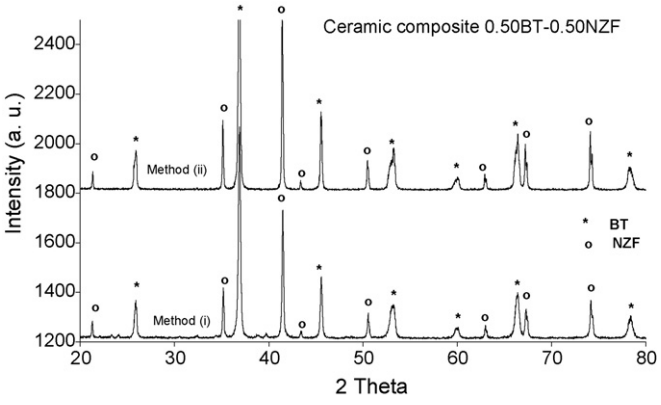

Fig. 1. X-ray diffraction patterns obtained for the $0.50BaTiO_3$–$0.50(Ni_{0.5}Zn_{0.5})Fe_2O_4$ sintered ceramic composites prepared by two methods: (i) mixed-powders and (ii) co-precipitation.

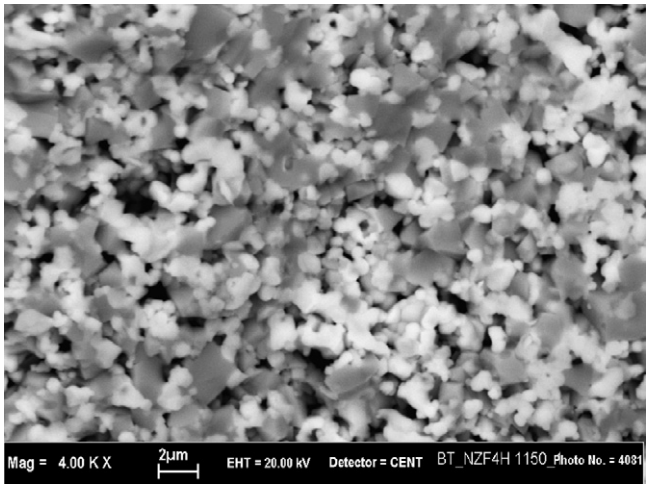

Fig. 2. Back scattered SEM image of a fractured surface of a $0.50BaTiO_3$–$0.50(Ni_{0.5}Zn_{0.5})Fe_2O_4$ sintered body prepared by co-precipitation.

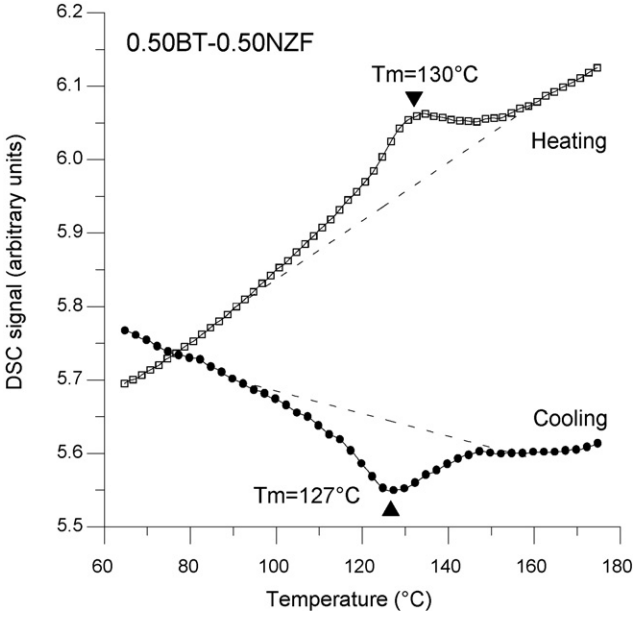

Fig. 3. DSC plots showing the tetragonal-cubic phase transition anomaly due to the $BaTiO_3$ phase.

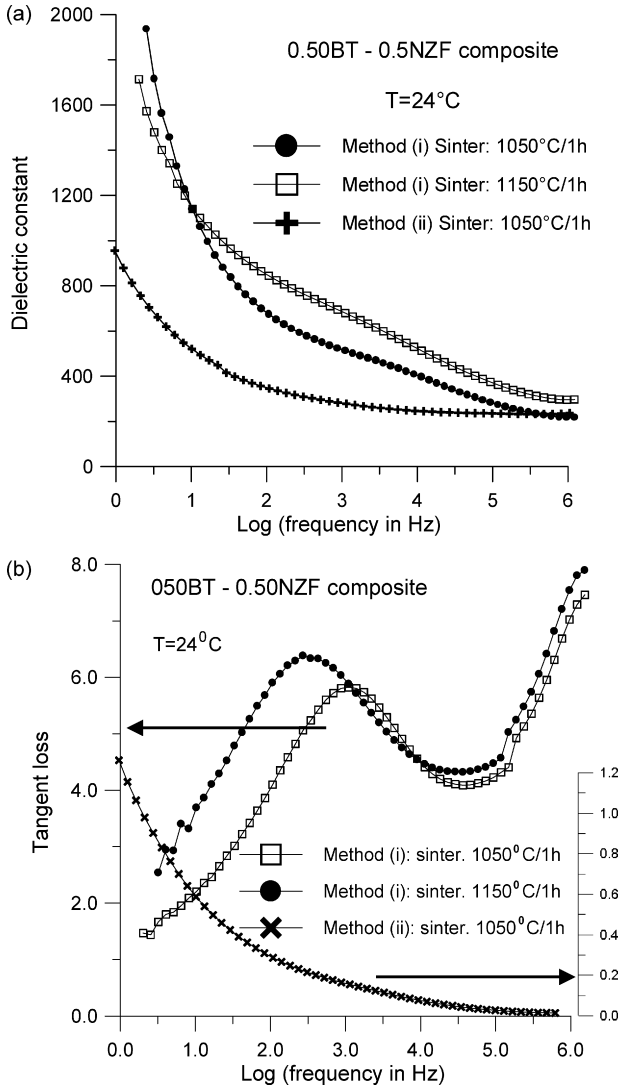

Fig. 4. Dielectric relaxation of the ceramic composite $0.50BaTiO_3$–$0.50(Ni_{0.5}Zn_{0.5})Fe_2O_4$ at room temperature: (a) permittivity data and (b) tangent loss data.

losses at low frequency and relaxation features in the range 10^2–10^3 Hz were obtained for different sintering temperatures by the method (i) and are most probably due to interfacial effects (Maxwell–Wagner) and poor homogeneity. The apparent high ε_r is due to high losses. An important improvement of the dielectric properties ($\tan\delta < 1$ even at low frequencies and $\tan\delta < 5\%$ for $f > 10^4$ Hz and $\varepsilon_r \in 300$–800) was obtained in the samples (ii) with the same compositions. These are good dielectric characteristics for such a system, in which the main problem is to reduce the conductivity at low frequency and high temperatures in order to have a high ME response.[6–9]

The magnetic hysteresis loops $M(H)$ at $T = 300$ K show the presence of the ordered magnetic structure derived from the unbalanced antiparallel spins as in the pure NZF material, causing a strong non-linear and almost non-hysteretic character and high magnetic permeability (Fig. 5). As a consequence of the "sum property"[6] and to interface effects, a reduction of the

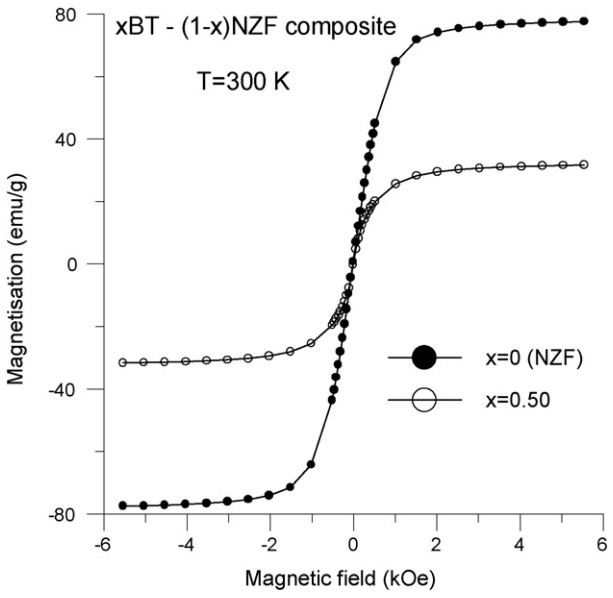

Fig. 5. Magnetic hysteresis loops at $T = 300$ K obtained for the pure $(Ni_{0.5}Zn_{0.5})Fe_2O_4$ ceramic and for the $0.50BaTiO_3$–$0.50(Ni_{0.5}Zn_{0.5})Fe_2O_4$ composite prepared by co-precipitation. (*Note:* 1 emu/g = 1 m^2A/kg.)

magnetic moment by comparison with the pure NZF ceramics takes place. Higher magnetisation is obtained in the ceramics prepared by method (ii) in the range 5–350 K (Fig. 6), due to the better densification and lack of cracks determining the effective permeability of the composites. As a consequence of better microstructures obtained by co-precipitation by comparison with the mixed-powders method, both dielectric and magnetic characteristics of the composite were seriously improved.

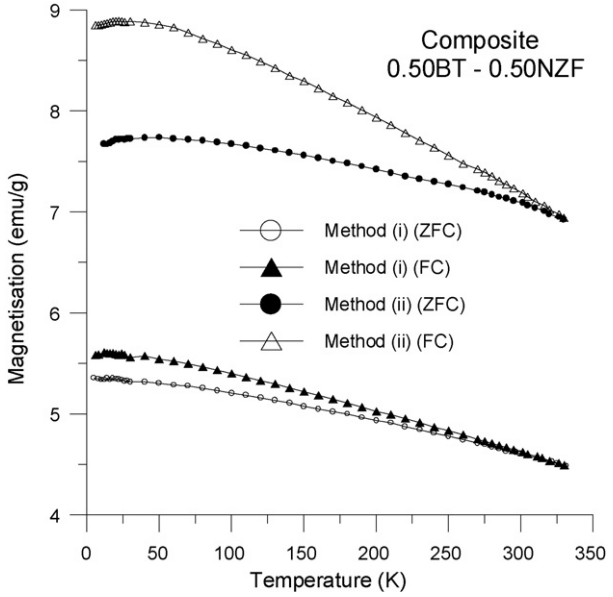

Fig. 6. The influence of the preparation procedure on the magnetic properties of the $0.50BaTiO_3$–$0.50(Ni_{0.5}Zn_{0.5})Fe_2O_4$ composites: magnetization–temperature dependencies at zero-field cooling (ZFC) and field cooling (FC) under $H = 100$ Oe.

4. Conclusions

The properties of 0.50BT–0.50NZF composite ceramics prepared by mixed powders and by co-precipitation are compared. By the last method, more homogeneous microstructure with higher density and similar grain sizes was produced, giving rise to better dielectric and magnetic properties. The ferro-para phase transition around 130 °C due to the BT component is preserved in the composites. Magnetic characteristics derived from the NZF parent phase were found, with a corresponding reduction of the magnetic moment. Interface effects play important roles determining the dielectric properties at low frequencies, mainly for the samples prepared by the mixing-powders method. Better dielectric properties with $\tan\delta < 5\%$ and $\varepsilon_r \in 300$–800 for $f > 10^4$ Hz were obtained in the composites prepared by co-precipitation. Since both the ferroelectric and magnetic phases preserve their basic properties in the bulk composite, the present BT-NZF ceramic are possible candidates for ME applications.

Acknowledgements

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