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Preparation of multiferroic composites of $BaTiO_3$–$Ni_{0.5}Zn_{0.5}Fe_2O_4$ ceramics

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Abstract

Magneto-electric coupling in ceramic composites formed by ferroelectric and ferromagnetic phases can be obtained via an adequate mechanical coupling between the individual piezoelectric and magnetostrictive phases (product property). In the present work, the possibility of forming diphase ferroelectric–ferromagnetic ceramics has been investigated. Composites of xBaTiO$_3$–$(1-x)$Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ with $x = 0.5$, 0.6 and 0.7 were prepared according two different procedures: (i) by direct mixing powders of perovskite $BaTiO_3$ and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ spinel prepared by solid state and (ii) by coprecipitating Fe^{III}–Ni^{II}–Zn^{II} nitric salts in a NaOH solution in which the $BaTiO_3$ powders were previously dispersed. Optimum processing parameters for good homogeneity, densification and for a reduction of the chemical reactions at the interfaces ferroelectric-ferrite were found. A temperature and composition-dependent magnetic order is present in all the composites, with a dilution effect of the magnetisation due to the presence of the non-ferromagnetic phase. A diffuse ferroelectric–paraelectric transition due to the $BaTiO_3$ phase was identified by the temperature-dependence of the permittivity and losses, showing that at room temperature the material preserves a ferroelectric order. The interfaces play important roles in the dielectric properties, causing space charge effects and Maxwell–Wagner relaxation, particularly at low frequencies and high temperatures. The combined ferroelectric and magnetic ordering will result in magneto-electric coupling in this material; further investigations are necessary.

Keywords: Composites; Electrical properties; Magnetical properties

1. Introduction

The multifunctional materials combining several properties in the same phase, showing new or enhanced properties, have in the last few years stimulated much scientific and technological interest. Among them, the magnetoelectric (ME) multiferroics, showing simultaneous magnetic and ferroelectric order became recently very interesting for their fundamental physics, and attractive for applications as sensors and transducers in radio-, opto- and microwave electronics and instrumentation.[1,2] Apart from the properties of the parent phases (ferro-, antiferro-, ferroelectricity and ferro-, antiferro-, ferri-magnetism), the ME effect adds a supplementary degree of freedom in designing materials for new applications, opening the possibility to manipulate the magnetic properties through electric fields and vice versa. These give additional potential for applications in spintronics, multiple state memory elements or novel memory devices which might use electric and/or magnetic fields for read/write operations.[2] Among them, it is worth mentioning the antiferromagnetic Cr_2O_3,[3] the boracite compounds $M_3B_7O_{13}X$ (where M is a divalent cation as Mg^{2+}, Cr^{2+}, etc. and X a monovalent anion: OH^-, F^-, Cl^-, etc.),[4] the antiferromagnetic-relaxor ferroelectrics as $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN)[5] and $Pb(Fe_{1/2}W_{1/3})O_3$ (PFW),[6] perovskites as rare-earth manganites, yttrium iron garnets, pseudo-ilmenites, $BaMeF_4$ (Me = Mn, Fe, etc.), Cr_2BeO_4 and inverted spinels,[7] $BiFeO_3$ and its solid solutions with $BaTiO_3$ or other ferroelectrics.[8–12] Although highly exciting for potential applications, the single-phase ME multiferroism is quite rare, due to the fact that it involves opposite requirements concerning

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the *d*-orbital occupancy, and is thus restricted to only a few systems.[13–15]

A second class of ME materials consists of two-phase composites. The search for such systems was promoted by practical needs, due to the very low values of the magnetoelectric voltage coefficient found in single-phase materials (of the order of 1–20 mV/cm·Oe) and by the low temperature range for the ME effect, mostly at cryogenic temperatures.[16] The ME effect is realized in composites on the basis of the concept of product properties.[17] According to this principle, a suitable combination of two phases such as piezomagnetic and piezoelectric or magnetostrictive and piezoelectric phases, can yield a desirable ME property. The conceptual conditions for the ME effect in composites were pointed out by Boomgaard,[18] as the following: (i) the individual phases should be in chemical equilibrium, (ii) no mismatch between grains, (iii) high values for the magnetostriction coefficient of the piezomagnetic or magnetostrictive phase and of the piezoelectric coefficient of the ferroelectric phase, (iv) no leakage of the accumulated charges through the phases, enabling a deterministic strategy for poling. Following this principle, various ME bulk composites have been prepared, such as $Ni(Co,Mn)Fe_2O_4$–$BaTiO_3$, $CoFe_2O_4$–$BaTiO_3$, $NiFe_2O_4$–$BaTiO_3$, $LiFe_5O_8$–$BaTiO_3$, $CuFeCrO_4$–$BaPbTiO_3$, $CoFe_2O_4$–$Bi_4Ti_3O_{12}$, $NiFe_2O_4$–Pb(ZrTi)O_3, (Ni,Zn)Fe_2O_4–Pb(ZrTi)O_3, etc.[16–22] Giant values of the ME coefficients dE/dH of tens to hundreds of V/cm·Oe were obtained in bilayer and multilayer laminate composites of good piezoelectrics (as Pb(ZrTi)O_3 or $PbMg_{1/3}Nb_{2/3}$–$PbTiO_3$) with high magnetostrictive materials, such as terfenol-D.[16] Therefore, in these bulk composites, a large variety of dielectric and ME properties were reported for similar systems and even for the same compositions.[16–22] Thus, better control of the composition and microstructure and generally, a better understanding of their properties in relation to these parameters are still needed. In the present work, ceramic composites of xBaTiO$_3$–$(1-x)$Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ were prepared and investigated.

2. Sample preparation and experiment

Ceramic composites of xBaTiO$_3$–$(1-x)$Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ (BT–NZF) with $x = 0.5$, 0.6 and 0.7 were prepared according two different procedures: (i) by mixing BT powders and NZF powders and (ii) by coprecipitating Fe^{III}–Ni^{II}–Zn^{II} nitric salts in a NaOH solution in which the BT powders were previously dispersed.

(i) Mixed powders method: BT powders were prepared via solid state-reaction from $BaCO_3$ (99.9%, Solvay Bario Derivati) and TiO_2 (99%, Aldrich). The precursors were mixed for 48 h, freeze–dried, thermally treated at 1100 °C for 4 h and the resulting BT powders were milled and sieved at 50 μm. NZF powders were prepared by coprecipitation at room temperature[22] of stoichiometric amounts of $Zn(NO_3)_2·6H_2O$ (Aldrich), $Ni(NO_3)_2·6H_2O$ (Aldrich) and $Fe(NO_3)_3·9H_2O$ (Aldrich) solution with NaOH solution (molar ratio OH/NZF = 8). The resulting gel was washed several times with water, freeze–dried and calcined 1 h at 400 °C to promote the formation of the NZF phase. The powders of BT and NZF in the desired proportion ($x = 0.5$, 0.6 and 0.7 wt.%) were milled together, isostatically pressed at 2×10^8 Pa and then sintered at 1050–1150 °C for 1 h.

(ii) Coprecipitation method: BT powders, prepared according the procedure described above, were maintained in suspension in NaOH solution by sonication and vigorously stirred. The nitric cation solution was added quickly to the alkaline suspension using the same concentration, precursors and molar OH/NZF ratio described above. The resulting suspension was washed several times with water and trice with acetone. The powders were recovered by filtration, dried at 60 °C and calcined 1 h at 400 °C to promote formation of the NZF phase. The mixture was manually milled in an agate mortar, isostatically pressed at 2×10^8 Pa and sintered at 1050–1150 °C for 1 h.

The microstructures were characterized by scanning electron microscopy (SEM, LEO 1450VP, LEO Electron Microscopy Ltd., Cambridge, UK). Phase composition and crystal structure were investigated by X-ray diffraction (XRD, Co Kα radiation, Philips PW1710, Philips, Eindhoven, The Netherlands). Dielectric measurements in the frequency range 1–10^6 Hz were performed with an impedance analyzer Solartron SI1260 for temperatures 30–210 °C with a heating/cooling rate of 0.5 °C/min. The magnetic moments of ceramic samples were measured using a superconducting quantum interferometric device SQUID magnetometer (Quantum Design) in the range of temperatures 5–350 K. 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 of the magnetic moment.

3. Results and discussions

Fig. 1 shows the X-ray diffraction (XRD) patterns obtained for the sintered ceramics of xBaTiO$_3$–$(1-x)$Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ with various compositions: $x = 0.5$, 0.6, 0.70; the reference, the pattern of NZF spinel having $x = 0$ (JCPDS file nr. 96663) is also shown. Only the parent phases of the perovskite BT and spinel NZF in adequate proportions (corresponding to the indicated compositions) were found, confirming the successful preparation of di-phasic composites by both preparation procedures, with a limited chemical reaction at the interfaces.

In case of the simple mixing of BT and NZF powders (method (i)), poor densification and homogeneity of the sample with large aggregates of NZF octahedral crystals (grey) and large pores were found in some regions (visible in Fig. 2), in spite of good initial mixing of the two phases. Since an increase of the sintering temperature to achieve better densification would cause reactions at the interfaces, the coprecipitation method (ii) was adopted for improving the microstructures. Fig. 3 is a backscattered SEM image of the composite prepared by coprecipitation after calcining at 400 °C for 1 h. The white BT particles are well-dispersed in the grey NZF matrix and the formation of

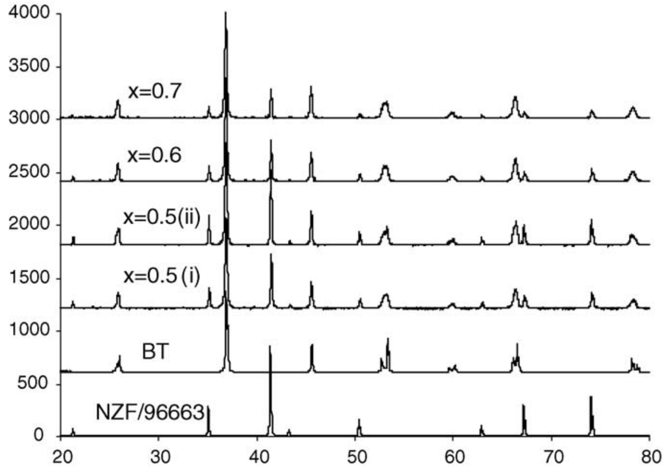

Fig. 1. X-ray diffraction patterns obtained for the sintered ceramic composites xBT–$(1-x)$NZF with $x=0$, 0.5, 0.6, 0.7 and 1. Only the parent phases of perovskite BT and spinel NZF in adequate proportions are present in the sintered composites.

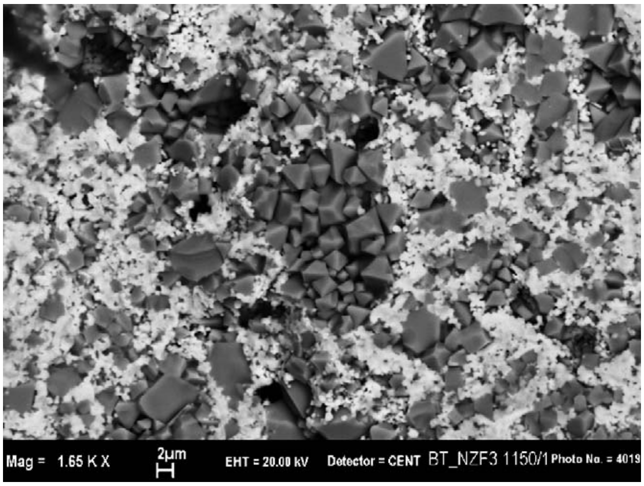

Fig. 2. Backscattered SEM image of a fracture surface of a 0.5BT–0.5NZF sintered body prepared by mixed powder method (white grains correspond to the BT phase, grey grains to the NZF spinel phase).

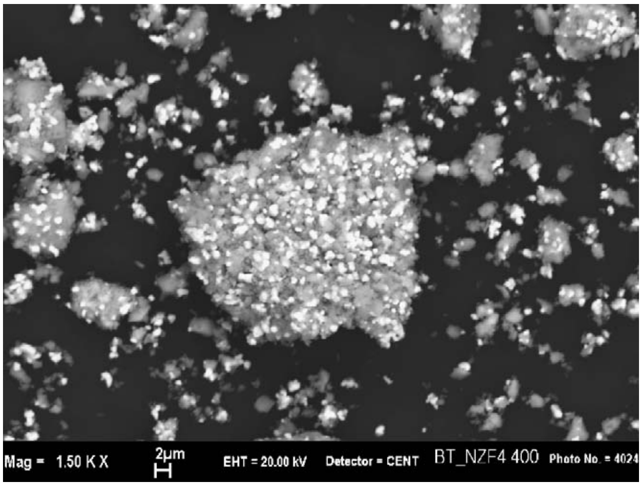

Fig. 3. SEM image (backscattered) of the BT–NZF powders after calcination at 400 °C/1 h (white grains: BT, grey matrix: spinel NZF).

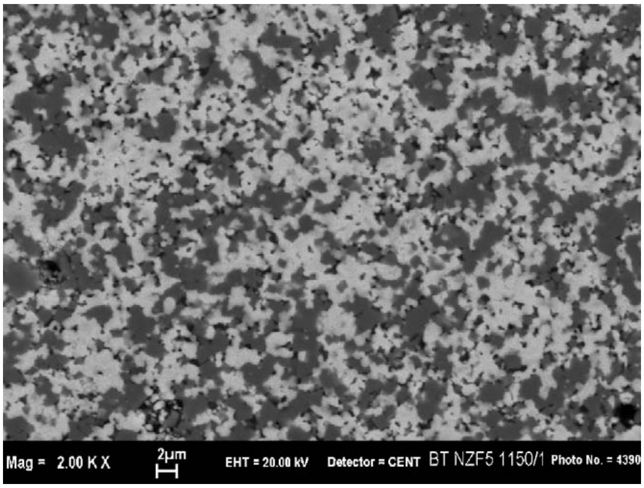

Fig. 4. Backscattered SEM image of a polished surface of a composite ceramic 0.6BT–0.4NZF prepared by coprecipitation (white grains correspond to the perovskite BT phase, grey grains to the NZF spinel phase).

hard NZF aggregates is strongly inhibited. The sintered bodies show a homogeneous microstructure (as presented for example in Fig. 4 for the composition with $x=0.6$) with comparable grain size of the perovskite and spinel phases and improved densification in comparison with the samples prepared according the method (i).

Once the pure diphasic composite is obtained, it is important to know if the intrinsic properties of the magnetic and ferroelectric phases are maintained, without major changes of the interaction mechanisms due to the foreign phase, particularly, the magnetic properties. If the presence of the BT phase does not cause intimate changes to the magnetic interactions, we expect in the magnetic properties to be diluted (proportional reduction of the magnetization M) with reducing amount of magnetic phase (by increasing x). The magnetic hysteresis loops $M(H)$ obtained for all the compositions show the presence of an ordered magnetic structure and clearly indicating this dilution effect (Fig. 5). It follows that the spontaneous magnetization of the composites originates from the unbalanced antiparallel spins, as in the pure NZF material, giving rise to small values of the coercivity and the saturation fields.[22,23] For the same composition, higher values of the magnetization, particularly at low temperatures (Fig. 6) were found in the ceramics prepared by the coprecipitation method, probably due to the better densification and lack of cracks controlling the effective magnetic permeability of the composites.

The relaxation of the dielectric data of 0.5BT–0.5NZF composite ceramic prepared by coprecipitation in the range of frequencies 10^{-1} to 10^{7} Hz are presented in Fig. 7. No relaxations of the permittivity and losses below 5% were found for frequencies $f > 10^{4}$ Hz. The evolution with temperature of the dielectric constant of the composites xBT–$(1-x)$NZF with $x=0.5, 0.6$ and 0.7 at $f=1$ kHz are shown in Fig. 8. Anomalies attributed to the ferroelectric–paraelectric phase transition of BT in the range of temperatures of 120–160°C, particularly for $x=0.6$ and $x=0.7$ can be observed. The phase transition was confirmed by DSC measurements, enabling this specific feature to be detected in

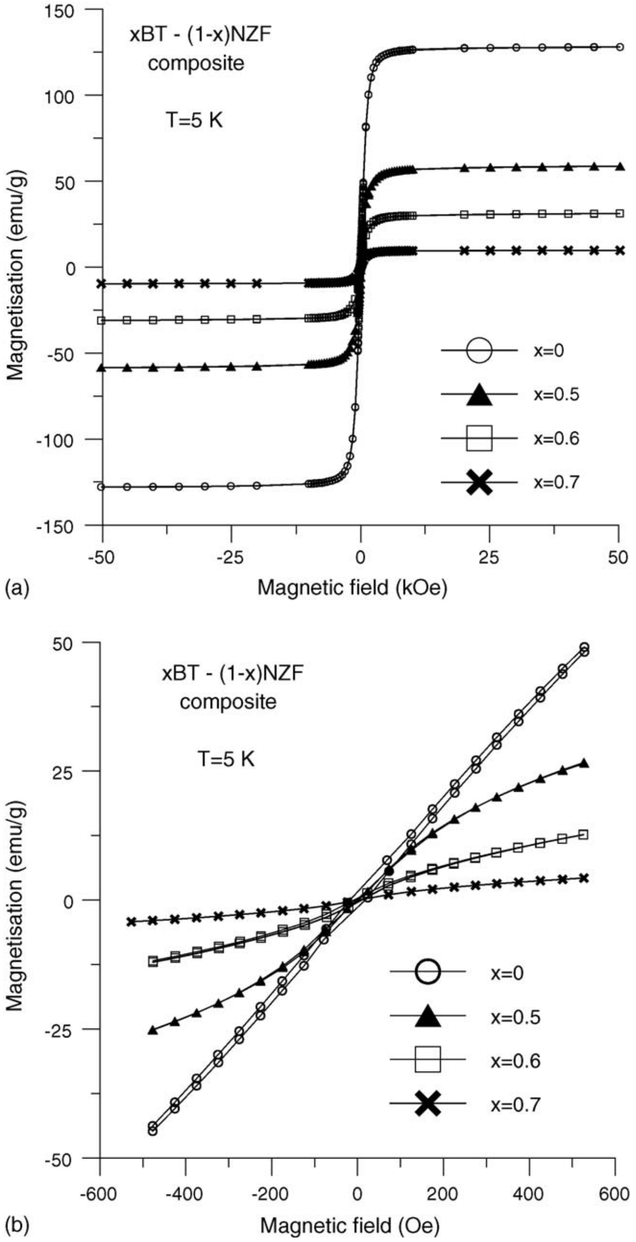

Fig. 5. Magnetic hysteresis loops *M*(*H*) obtained for the composites *x*BT–(1 − *x*)NZF with *x* = 0, 0.5, 0.6 and 0.7 prepared by coprecipitation at *T* = 5 K for: (a) high fields, (b) low fields.

all the compositions, as a result of the presence of the BT ferroelectric phase. The broad aspect of this phase transition is due to the local formation of solid solutions of BT particularly at the grain boundaries, leading to a slight increase of the local Curie temperature. It means that the ferroelectric character of BT and its ferro-para phase transition is preserved in all the composites, in spite of the presence of the NZF, non-ferroelectric phase.

The apparent increase of the dielectric constant at higher temperatures is due to activation of conductivity mechanisms at these temperatures causing high dielectric losses (tan $\delta > 1$). This is common behaviour found by numerous authors in similar systems and is the main problem to be solved to achieve good poling and high ME response.[12,18,20,24,25] The problem is attributed to space charge effects, Maxwell–Wagner relaxation at the interface of the ferroelectric–magnetic phases or even to other defect mechanisms, particularly those activated at low frequencies and high temperatures.[24] For the same preparation strategy and even for the best microstructures obtained in this study, the increasing ferroelectric phase content (BT) does not automatically lead to a reduction of losses (Fig. 8). It follows that a further complete study of the conduction mechanisms for each composition, correlated with optimum processing parameters is necessary, in order to understand the dielectric properties and the mechanisms of losses in this system. Since both the parent phases keep their

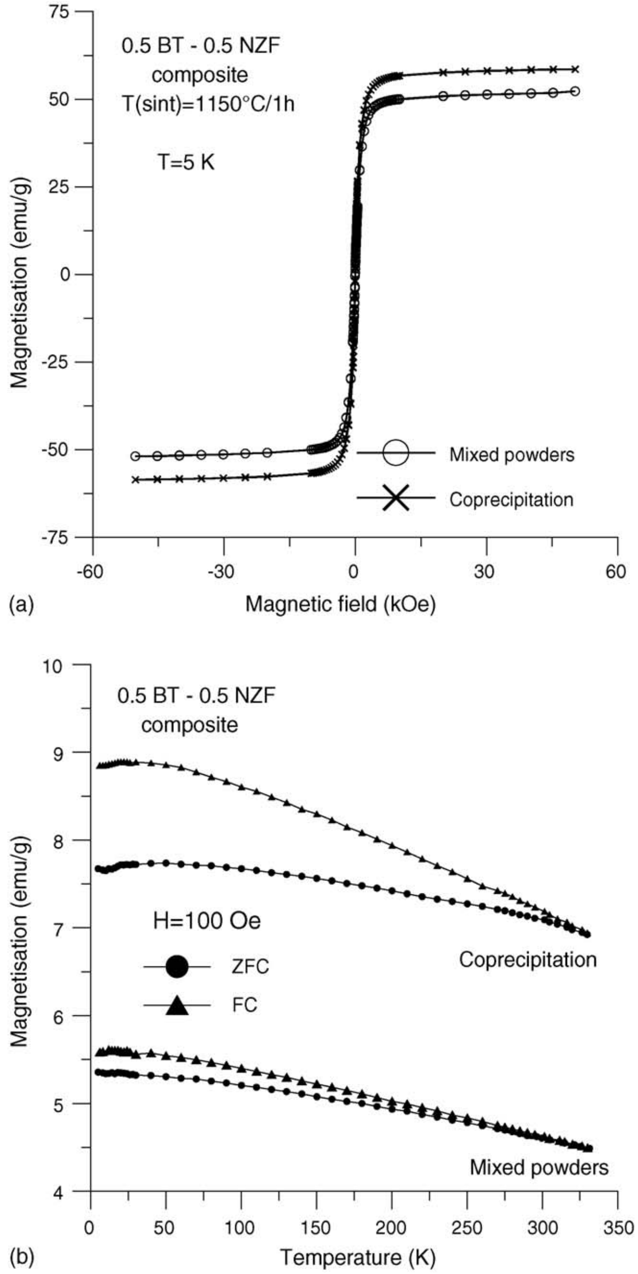

Fig. 6. Influence of the preparation procedure on the magnetic properties for the composites 0.5BT–0.5NZF obtained by mixed powders and coprecipitation methods: (a) Magnetization-field *M*(*H*) hysteresis loops at *T* = 5 K, (b) Magnetization-temperature *M*(*T*) dependences at zero-field cooling (ZFC) and field cooling (FC) at *H* = 100 Oe.

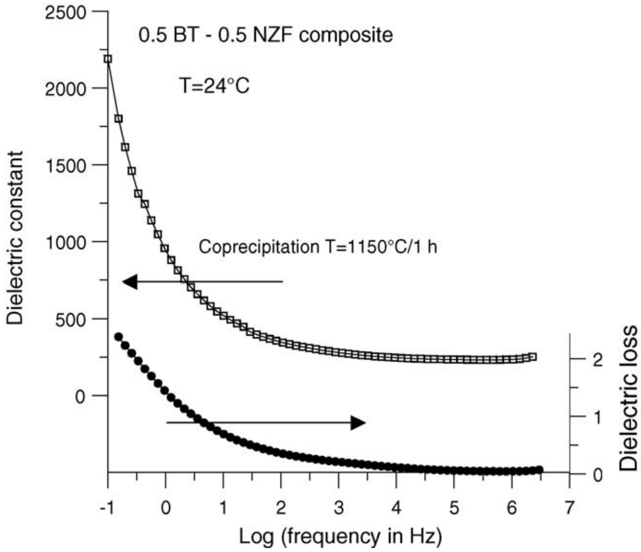

Fig. 7. Dielectric relaxation at room temperature for the composite 0.5BT–0.5NZF prepared by coprecipitation. Dielectric losses below 10% are obtained at frequencies $f > 10^3$ Hz.

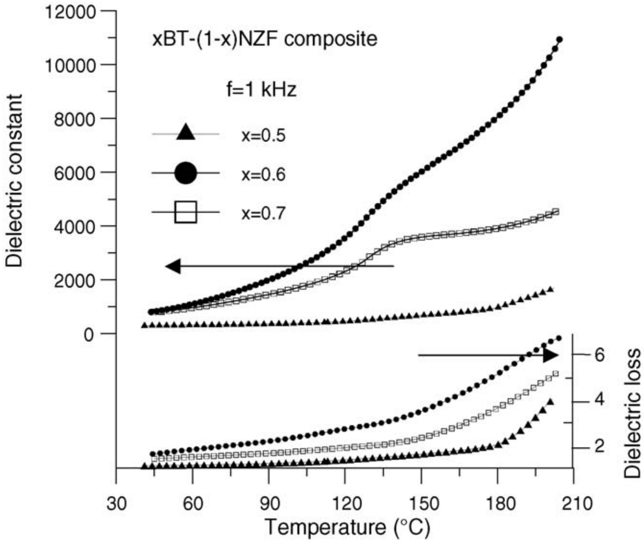

Fig. 8. Dielectric properties of the ceramic composites xBT–$(1-x)$NZF with $x = 0.5$, 0.6 and 0.7 at $f = 1$ kHz. An anomaly associated with the BT transition are observed in the temperatures range 120–160 °C.

ferroic properties (ferroelectric and magnetic order), the present composites are good candidates for good ME materials at room temperature.

4. Conclusions

Composite ceramics of BT–NZF with limited reaction between the two phases were prepared both by mixed powders and by coprecipitation methods. By the latter method, samples with higher density, more homogeneous microstructures and similar grain sizes were obtained, giving rise to better dielectric and magnetic properties. A dilution of the magnetic phase with reducing NZF content was found, showing that no other major changes in the magnetic properties were induced by the presence of the nonmagnetic phase (BT). The ferroelectric character of the BT phase and its ferro-para phase transition does not appear to be affected by the presence of the nonferroelectric phase (NZF). Therefore, interface effects play important roles in modifying the dielectric properties, causing space charge effects and Maxwell–Wagner relaxation, particularly at low frequencies and high temperatures. Further investigations are necessary to understand and control the nature and the role of the grain boundaries and interfaces on the dielectric properties. By further reducing the losses, the ceramic composites $BaTiO_3$–$Ni_{0.5}Zn_{0.5}Fe_2O_4$ will be good candidates for ME applications, due to the fact that both the ferroelectric and magnetic phases preserve their basic properties in the bulk composite form.

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L.M. would like to dedicate this study to the memory of her professor Constantin Papusoi from the University Al. I. Cuza Iasi, Romania. Many years ago, he had the idea of combining the ferroelectric and ferromagnetic order in one material in the view of multifunctionality.

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