Temperature dependence of the dielectric permittivity of BaTiO$_3$-CoFe$_2$O$_4$ceramic composites

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Abstract

Two-phase ceramic composites of cobalt ferrite dispersed in a barium titanate matrix were prepared and their dielectric permittivity was characterized. A rounding of their dielectric constant near the ferroelectric transition temperature of the BaTiO$_3$ phase was observed. A generalized brick-wall model, taking into account the BaTiO$_3$ contribution, fitted with the Landau-Devonshire theory, and the CoFe$_2$O$_4$ permittivity, experimentally determined, was used in order to obtain their effective dielectric constant. The effective model was applied to the discussion and fitting of the temperature dependence of the dielectric permittivity of the composites. The Landau-Devonshire coefficients for the BaTiO$_3$ phase were also obtained.

Running head: Dielectric permittivity of BaTiO$_3$-CoFe$_2$O$_4$ composites

Introduction

Magnetoelectric materials, which are simultaneously magnetic and ferroelectric have been attracting increasing scientific and technological interest due to their multifunctionality. In ferroelectric-ferrite composites, such as in the $BaTiO_3$-$CoFe_2O_4$ system, the stress mediated coupling between the piezoelectric and magnetostrictive components engenders a material presenting properties which are not available in the individual phases [1,2]. As a result, the dielectric properties of these composites depend on the phase morphology and composition, and are important to understand the polar behavior arising from the mixing. Here, two phase ceramic composites of cobalt ferrite ($CoFe_2O_4$ – magnetostrictive) dispersed in a barium titanate ($BaTiO_3$ – piezoelectric) matrix were prepared in order to characterize the temperature dependence of their dielectric permittivity, for different $CoFe_2O_4$ concentrations.

Cobalt ferrite ($CoFe_2O_4$) has a cubic inverse spinel structure [3] in which the octahedral B sites are occupied by eight Co^{2+} and eight Fe^{3+} cations, while the tetrahedral A sites are occupied by the remaining eight Fe^{3+}. The conduction and polarization mechanisms in the ferrite are due to electron hoping between Fe^{3+}/Fe^{2+} and Co^{3+}/Co^{2+} [2].

$BaTiO_3$ is a well studied ferroelectric perovskite and is a good candidate for high-performance lead-free piezoelectric applications [1,2]. At high temperatures $BaTiO_3$ is cubic, in which the large barium ions are surrounded by twelve nearest-neighbor oxygens and each titanium ion has six oxygen ions in octahedral coordination. The barium and oxygen ions together form a face centered cubic lattice, with titanium ions fitting in octahedral interstices. $BaTiO_3$ is known to undergo several phase transitions as a function of temperature. Starting from the high temperature, at ~122 ℃ $BaTiO_3$ transforms from a cubic to a tetragonal structure, which in turn changes to an orthorhombic phase at ~7 ℃ and finally to a rhombohedral phase

at ~ -80 °C. The room temperature tetragonal phase is ferroelectric and the high temperature cubic phase is paraelectric.

Experimental

The $(BaTiO_3)_{1-x} - (CoFe_2O_4)_x$ composites were prepared by mixing $CoFe_2O_4$ and $BaTiO_3$ powders with cobalt ferrite concentrations $x = 0\%$ ($BaTiO_3$), 30%, 50% and 100% ($CoFe_2O_4$). The $BaTiO_3$ powder had average grain size < 1 µm. The composites were then compressed into disks at 370 MPa and sintered at 1200°C during 1 hour. The cooling of the disks after the sintering process was done on the furnace. The end members, barium titanate and cobalt ferrite, were also prepared in this way. The structural studies were performed by X-ray diffraction (XRD) and were carried out with a Philips PW-1710 diffractometer using Cu Kα radiation. The dielectric permittivity and loss factor measurements were performed in the temperature range 25°C – 180°C, at frequencies 1 kHz and 10 kHz. A Waine Kerr 6440A precision component analyzer together with a dedicated computer and software were used in order to acquire the data. Shielded test leads were employed to connect the bridge to the samples to avoid parasitic impedances due to the connecting cables. The temperature measurements were performed at a rate of 1°C/min, with ±0.1 °C resolution, using a Polymer Labs PL706 PID controller and furnace.

Results and discussion

Figure 1 shows the X-ray diffraction spectra measured on the samples with cobalt ferrite concentration $x = 0\%$ (only barium titanate), 30%, 40% and 100% (only cobalt ferrite). The vertical lines mark the peak position of bulk tetragonal-$BaTiO_3$ and $CoFe_2O_4$ with the cubic

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spinel structure [4]. The composites spectra show that they are polycrystalline and composed by mixtures of tetragonal-BaTiO$_3$ and cubic-spinel-CoFe$_2$O$_4$. The lattice parameters of the cobalt ferrite and barium titanate phases of the composites, obtained from the X-ray diffraction peak positions, are $a_{CoFe_2O_4}$ = 8.400 Å, a_{BaTiO_3} = 4.004 Å and c_{BaTiO_3} = 4.028 Å for the sample with x = 30%, and $a_{CoFe_2O_4}$ = 8.386 Å, a_{BaTiO_3} = 4.001 Å and c_{BaTiO_3} = 4.024 Å for the sample with x = 50%. They are near the corresponding reference values for bulk tetragonal-BaTiO$_3$ and cubic-spinel-CoFe$_2$O$_4$: $a_{bulk,CoFe_2O_4}$ = 8.3919 Å, $a_{bulk,BaTiO_3}$ = 3.994 Å and $c_{bulk,BaTiO_3}$ = 4.038 Å [4].

Figure 2 shows the temperature dependence of the real part of dielectric permittivity (ε') of the pure barium titanate sample, measured at 10 kHz (fig. 2a), and pure cobalt ferrite sample, obtained at 1 kHz and 10 kHz frequencies (fig. 2b). The insets show the corresponding imaginary parts (ε''). The permittivity of BaTiO$_3$ measured at 1 kHz is similar, but above, to the one at 10 kHz. The somewhat lower permittivity values are due to the small average grain size in the BaTiO$_3$ samples (< 1 µm) [5]. A maximum, at a temperature near 130 °C, is observed in the ε' and ε'' of BaTiO$_3$, due to the ferroelectric-paraelectric phase transition. Also, the increase of its dielectric permittivity in the lower temperature region is due to the onset of the tetragonal-orthorhombic transition that occurs at around 7 °C. In CoFe$_2$O$_4$, the substantially higher imaginary part of its dielectric constant, particularly for temperatures above 100 °C and lower frequencies (1 kHz), is due to its higher DC conductivity.

Figure 3 shows the temperature dependence of the real part of dielectric permittivity measured on the composites with cobalt ferrite concentrations x = 30% and 50%. A rounding of real part of the dielectric constant (ε') near the ferroelectric transition temperature of the BaTiO$_3$ phase is observed. Also, an increase of ε' is observed at higher temperatures, for higher cobalt

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ferrite concentration, indicating an increase of the $CoFe_2O_4$ contribution to their permittivity with increasing $CoFe_2O_4$ content.

To fit the temperature dependence of the dielectric constant of the composites, the individual barium titanate and cobalt ferrite permitivities were first determined. The Landau-Devonshire model [6-8] was used to calculate the $BaTiO_3$ dielectric constant. In the Landau-Devonshire theory, the free energy of a crystal is expanded on even powers of its electric polarization (P) so that, assuming constant stress [6,7]:

$$F = F_0 + \beta(T - T_0)(P_x^2 + P_y^2 + P_z^2) - B(P_x^4 + P_y^4 + P_z^4) +$$
$$+ C(P_x^6 + P_y^6 + P_z^7) + D(P_y^2 P_z^2 + P_z^2 P_x^2 + P_x^2 P_y^2) - EP \tag{1}$$

where β, B and C are constants, F_0 is the free energy for zero polarization and E is the electric field. In the way the third coefficient (B) is defined it is positive, so that it describes a first order phase transition of $BaTiO_3$ where the saturation polarization has a discontinuous change at the transition temperature. From the minimization of the free energy the obtained equilibrium conditions are:

$$\frac{\partial F}{\partial P} = 0 \text{ and } \frac{\partial^2 F}{\partial^2 P} > 0 \tag{2}$$

They give the relation between the polarization and the electric field, from where it is possible to determine the macroscopic dielectric permittivity defined by:

$$\varepsilon = 1 + \frac{1}{\varepsilon_0} \frac{\partial P}{\partial E} \tag{3}$$

For $T > T_C$, in the paraelectric region, the dielectric constant is isotropic $\varepsilon_a = \varepsilon_b = \varepsilon_c$ and the spontaneous polarization is zero, leading to a Curie-Weiss law for the dielectric permittivity:

$$\varepsilon = \frac{1}{2\beta(T - T_0)} \qquad (4)$$

In the ferroelectric region (T<T$_C$), BaTiO$_3$ is tetragonal and $\varepsilon_a = \varepsilon_b \neq \varepsilon_c$, $P_x = P_y = 0$, so that [8]:

$$\frac{1}{\varepsilon_a - 1} = 2\beta(T - T_0) + 2DP_z^2 \qquad (5)$$

$$\frac{1}{\varepsilon_c - 1} = 2\beta(T - T_0) - 12BP_z^2 + 30CP_z^4 \qquad (6)$$

$$2\beta(T - T_0) - 4BP_z^2 + 6P_z^4 = 0 \qquad (7)$$

Equation (7) gives the temperature dependence of the spontaneous polarization in the ferroelectric phase and was obtained from the equilibrium conditions of equations (2) assuming that the electric field is zero. The transition temperature (T$_C$) and the spontaneous polarization at T$_C$ (P$_{SC}$) are obtained by $T_C = T_0 + B^2 / 4\beta C$ and $P_{SC}^2 = B / 2C$ [8], respectively.

In a ceramic BaTiO$_3$ sample, with grain size of the order of 1μm, the grains can be considered to be single domain, but they can be oriented along the three different axes *a, b, c*. Then, for measurements with a small applied field perpendicular to the major surfaces, the dielectric constant value, in the ferroelectric tetragonal phase, depends on the relative ratio between the number of *c* domains and *a* domains (*a = b* for a tetragonal structure). Therefore the dielectric constant value depends of the ratio between *c* and *a* oriented grains. Thus, the samples are considered to be composed by two different *a* and *c* oriented grains and the Maxwell relation for the dispersion of spherical particles of dielectric constant ε_c in a matrix of dielectric constant ε_a is used [9]:

$$\varepsilon = \frac{v_a \varepsilon_a (\frac{2}{3} + \frac{\varepsilon_c}{3\varepsilon_a}) + v_c \varepsilon_c}{v_a (\frac{2}{3} + \frac{\varepsilon_c}{3\varepsilon_a}) + v_c} \qquad (8)$$

where v_a and v_c are the volume fractions ($v_a + v_c = 1$). Using equations (4)-(8), the dielectric permittivity of barium titanate was computationally fitted, using a Levenberg-Marquardt algorithm that iteratively varied the parameters until the weighted mean square difference between the experimental and calculated values was minimized. The six adjustable parameters were β, B, D, T_c, P_{SC} and v_c.

Figure 2a) shows the determined fitting curve of the dielectric constant of barium titanate. For the ferroelectric phase, below the transition temperature (T_C), the obtained values are $T_C = 134$ ºC, $\beta = 1.84 \times 10^{-6}$ C^{-1}, B = 4.98×10^{-3} Vm^{5}C^{-3}, D = 1.06×10^{-2} Vm^{5}C^{-3}, $P_{SC} = 12.3$ µC/cm^2 and $v_c = 0.3$, which are near the values reported for BaTiO$_3$ ceramics [7]. For the paraelectric phase the obtained transition temperature is the same as in the ferroelectric phase, $T_C = 134$ ºC, but β is higher $\beta = 4.28 \times 10^{-6}$ C^{-1}. These values were obtained for the measurement at 10kHz of figure 2, but they are similar to the ones determined from the 1 kHz curve.

With the determination of the dielectric permittivity of barium tiatanate, an effective model was used to determine the temperature dependence of the dielectric constant of the composites. Effective medium theories describe the dielectric behavior of a composite mixture in terms of the dielectric behavior of each phase. Using suitable mixing rules, the dielectric properties of the inhomogeneous system are approximated by the solution for an homogeneous medium with an effective dielectric permittivity. The best know examples of these theories are the Maxwell-Garnett and Bruggeman mixing rules [10-12].

The effective permittivity of granular dielectric ceramics with high permittivity can be represented by the brick-wall model, where the grains (bricks) are assumed to be of uniform shape and size and presenting boundaries with regions that are either perpendicular or parallel to the electric field [5,12]. Considering grains with bulk permittivity ε_1 and volume concentration x_1, and boundaries with permittivity ε_2 and volume concentration x_2, simple relations for the dielectric permittivity of ceramic are obtained. In the case where the boundaries have lower conductivity than the bulk grains the effective permittivity of the ceramic can be represented by an equivalent capacitor in series circuit with $\varepsilon_{ef}^{-1} = x_1\varepsilon_1^{-1} + gx_2\varepsilon_2^{-1}$. The parameter g represents the fraction of boundary that is perpendicular to the electric field ($0 \leq g \leq 1$), which is related to the geometry of the grains ($g = 2/6$ for cubic grains). If the grains have lower conductivity than their boundaries, then an equivalent capacitors in parallel circuit is used, g now takes into account the fraction of boundary that is parallel to the electric field and $\varepsilon_{ef} = x_1\varepsilon_1 + gx_2\varepsilon_2$.

For a two-component composite with particles of arbitrarily shape and size, a generalization of the brick-wall model was determined [12]. The effective permittivity is calculated as a sum of two parts. One is the sum of the individual bulk permitivities, weighted by their volume fractions, related with the part of both phases that is percolated throughout the sample in the field direction. The other describes the isolated particles affected by depolarization fields and depends on the particle shape and its surroundings. In the particular case when one component is not percolated in the field direction, as in the case of diluted particles or grains inside their boundaries (brick-wall), the effective (complex) permittivity is obtained by [12]:

$$\varepsilon_{ef} = \left(1 - \frac{1-x}{1-gx}\right)\varepsilon_2 + \left(\frac{1-x}{1-gx}\right)\frac{\varepsilon_1\varepsilon_2}{(1-gx)\varepsilon_2 + gx\varepsilon_1} \quad (9)$$

where x is the volume concentration of the ε_2 phase and g ($0 \leq g \leq 1$) now represents a generalized depolarization factor characterizing the average particle geometry and surroundings.

Again, the dielectric constant of the composites was computationally fit using a Levenberg-Marquardt algorithm. Equation 9 was applied to the determination of the effective dielectric permittivity. Since the $CoFe_2O_4$ concentration is below (or equal) to 50%, the barium titanate phase was considered to be percolated and its dielectric constant was modeled using the previous Landau-Devonshire model. Since the imaginary part of the permittivity of barium titanate is much lower than the one of the cobalt ferrite, it was taken to be zero in the calculations. The cobalt ferrite phase was regarded as not being percolated in the field direction and its dielectric permittivity was considered to be the one determined for pure $CoFe_2O_4$ and shown in figure 2b). Besides the previous six fitting parameters for barium titanate, two additional parameters were included in the fitting program, the depolarization factor g and the volume concentration x.

During the fittings it was observed that the parameters describing the barium titanate phase didn't vary much from the ones already determined for pure $BaTiO_3$, in the composites concentration range studied ($x \leq 50\%$). As such, these parameters were kept constant during the fittings, on their values previously determined, and only g and x were varied.

Figure 3 shows the fitting curves to the dielectric permittivity of the composites, with cobalt ferrite concentrations of 30% (sample 1) and 50% (sample 2). For temperatures above ~120ºC the imaginary part of the dielectric permittivity of $CoFe_2O_4$ becomes significantly higher than the real part, due to the increasingly higher conductivity of the cobalt ferrite phase. Thus, it is expected that the model fitting becomes worse in this temperature region, as observed in figure 3. On the other hand, for temperatures below 120ºC the dielectric constant of the composites is

well described by the above model, as shown from the fitting to the permittivity curves of figure 3. The volume concentration x of the cobalt ferrite determined from the fitting is 27.0% for the sample 1 and 49.4% for sample 2, which are near from the expected 30% and 50% $CoFe_2O_4$ concentrations. The factor g is 0.26 for sample 1 and 0.40 for sample 2. These values are near from $g = 1/3$, that corresponds to coated spherical type particles presenting an outer layer with permittivity different from its bulk interior one. Also, since the coefficients of the Landau-Devonshire model were practically independent of the $CoFe_2O_4$ concentration, this indicates that the ferroelectric character of the barium titanate phase and, in particular, its ferroelectric-paraelectric phase transition was not much affected by the presence of the non-ferroelectric $CoFe_2O_4$ phase in the concentration range studied.

Conclusions

The temperature dependence of the dielectric permittivity of composites with cobalt ferrite dispersed in a barium titanate matrix was characterized and its effective dielectric constant was calculated and fitted using a generalized brick-wall model, that took into account the contributions from the $BaTiO_3$ and $CoFe_2O_4$ phases. The generalized depolarization factor characterizing the composites grains was determined. Also, the ferroelectric character of the barium titanate phase was observed not to be much affected by the mixing on the concentration range studied.

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Figure captions

Figure 1: X-ray diffraction spectra measured on the $(BaTiO_3)_{1-x}$-$(CoFe_2O_4)_x$ composites with concentrations x = 0%, 30%, 50%, 100%. The vertical lines indicate the reference peak positions of the bulk tetragonal-$BaTiO_3$ and $CoFe_2O_4$ with the cubic spinnel structure.

Figure 2: Temperature dependence of the real parts of the complex dielectric permittivities of the pure a) barium titanate, measured at 10 kHz, and b) cobalt ferrite samples, measured at 1 kHz and 10 kHz. The insets show the corresponding imaginary parts. In a) the fitting curve was obtained from the Landau-Devonshire model.

Figure 3: Temperature dependence of the real parts of the complex dielectric permittivities of the composites with cobalt ferrite concentrations of a) x = 30% and b) x = 50%, along with the corresponding fitting curves.

Figure 1
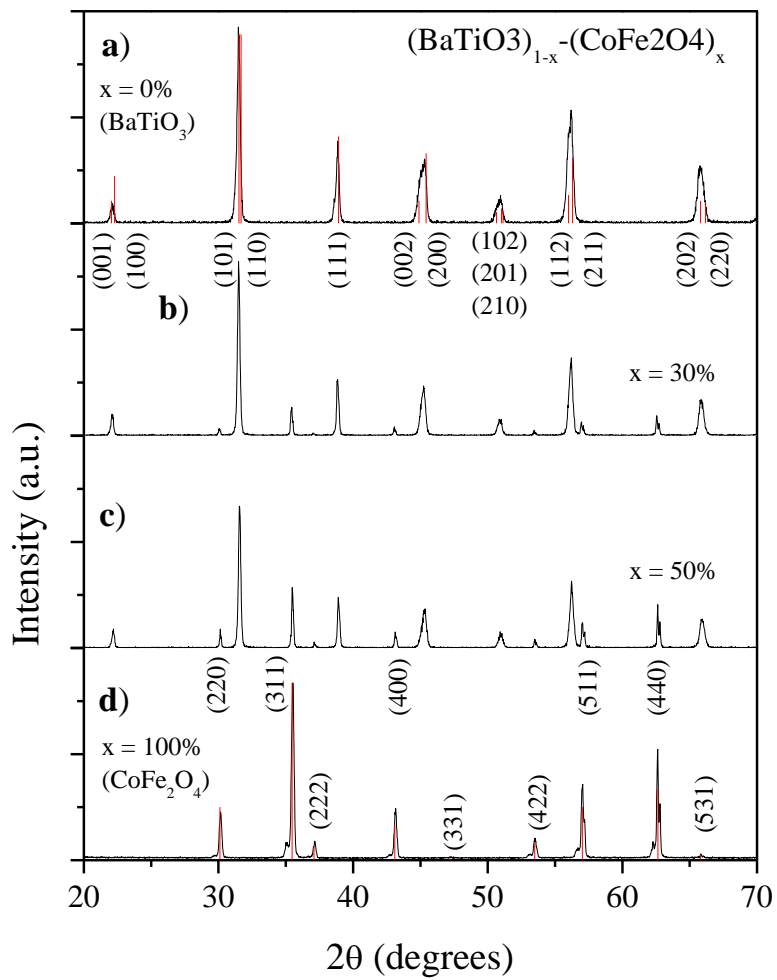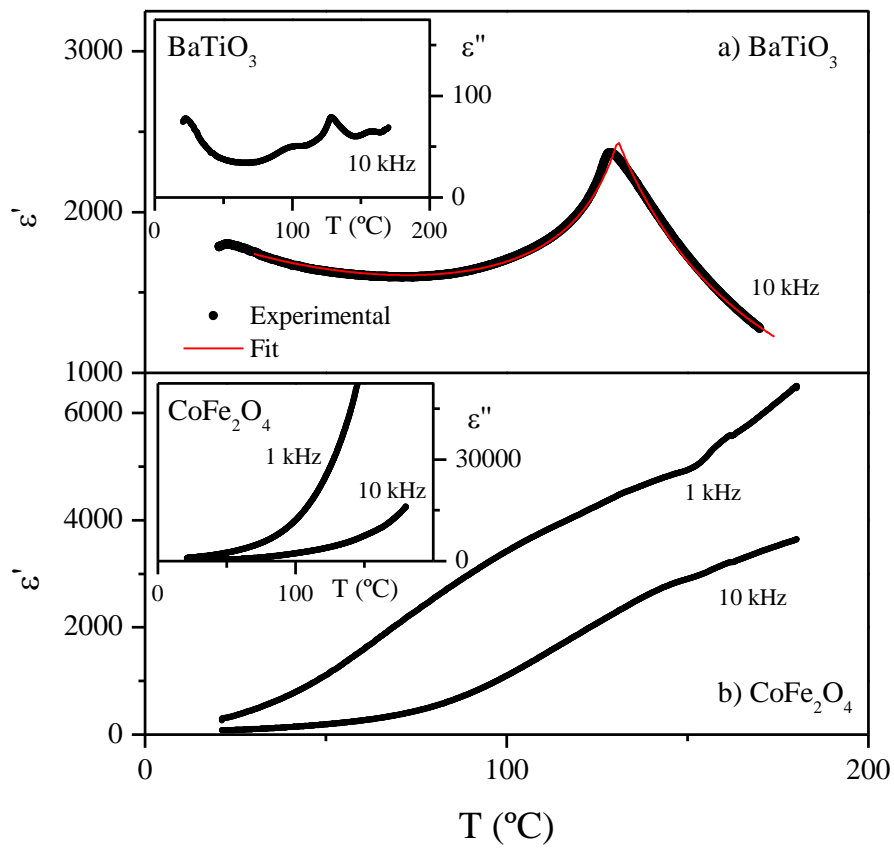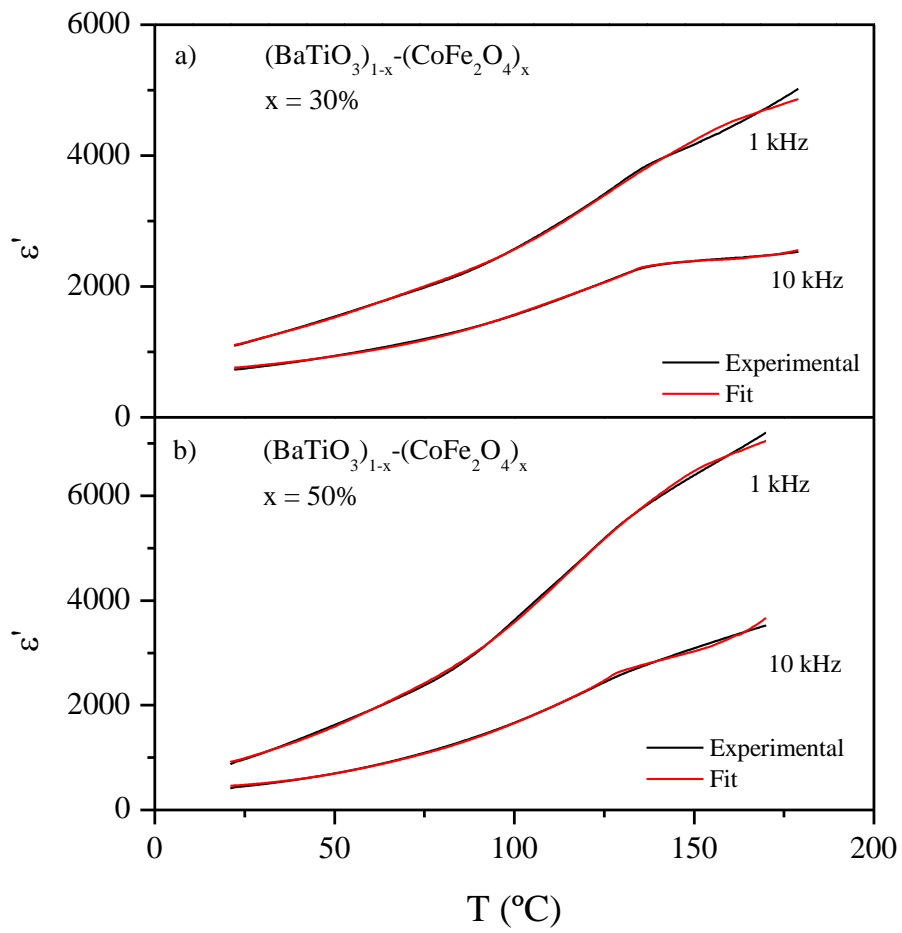
Figure 2

a) $(BaTiO_3)_{1-x}$-$(CoFe_2O_4)_x$
x = 30%

1 kHz

10 kHz

Experimental
Fit

b) $(BaTiO_3)_{1-x}$-$(CoFe_2O_4)_x$
x = 50%

1 kHz

10 kHz

Experimental
Fit

ε'

T (°C)

Figure 3