Investigation of the dielectric relaxation processes in PbZr$_{0.65}$Ti$_{0.35}$O$_3$−BaFe$_{12}$O$_{19}$ multiferroic ceramic composites

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HIGHLIGHTS

- Dielectric relaxation was investigated in Pb(Zr$_{0.65}$Ti$_{0.35}$)O$_3$−xBaFe$_{12}$O$_{19}$ composites.
- Anomalous behavior was observed in the x dependence of the activation energy.
- The substitution of the Ti^{4+} ions by Fe^{3+} promotes the oxygen vacancies creation.
- The oxygen vacancies are responsible for the dielectric relaxation processes.

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ABSTRACT

The dielectric relaxation processes have been investigated in multiferroic ceramic composites based on the ferroelectric PbZr$_{0.65}$Ti$_{0.35}$O$_3$ (PZT) and ferrimagnetic BaFe$_{12}$O$_{19}$ (BaM) systems. The frequency dispersion of the complex dielectric permittivity was analyzed over wide frequency and temperature ranges, and the effect of BaM content is depicted. The activation energies for the relaxation processes were also obtained for all the studied compositions and the results suggest the oxygen vacancies-related hopping mechanism to be responsible for the observed behaviors in the studied composites. Furthermore, an anomalous behavior in the activation energy has been observed with the increase of the BaM concentration. The obtained results are discussed within the framework of current models reported in the literature for dielectric relaxation processes.

1. Introduction

Researches on multifunctional materials combining multiple physical properties have been attracting a significant interest of the scientific community during the last decade [1]. Special attention has been paid to multiferroic systems, which exhibit simultaneously two (or more) primary ferroic order parameters (electric, magnetic and elastic) [2]. Their multifunctional properties have led to increase the interest for the use of multiferroics in the manufacture of electronic devices for spintronics and communication fields [3]. However, till now only a limited number of multiferroic

materials that can offer enhanced properties have been synthesized. Indeed, in the last few years, most of the investigations have been conducted on the classical single-phase bismute ferrite (BiFeO$_3$) and rare-earth-based (R) manganites (RMnO$_3$) multiferroic compounds [4,5], where the ferroelectric and ferromagnetic components are intrinsically present.

On the other hand, with the advent of new electronic components applications, which demand a high miniaturization and a substantial increase of the speed data transmission, multi-phase systems, such as multiferroic composites, have been considered in the last few years as potential candidates [6]. In composites, the physical properties are controlled by the interaction between individual phase's primary physical properties (ferroelectric, ferromagnetic, ferroelastic), and such an interaction may result in enhanced responses, when compared with single-phase multiferroics [7]. The variation of the electric (or magnetic) properties

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under the application of a magnetic (or electric) field makes them greatly attractive for prospective applications. Most of the reported research so far has been focused on the investigation of the magneto-electric (ME) effect of such systems, produced from the interaction between the constitutive phases [8]. Among various multiferroic materials, ceramic composites based on barium titanate ($BaTiO_3$) as well as lead titanate zirconate ($PbZr_{1-y}Ti_yO_3$), combined with the magnetic phases of $CoFe_2O_4$ (CFO) and $NiFe_2O_4$ (NFO) [6,7,9], have attracted much attention due to their very attractive ME response. Quite recently, new evidences of enhanced ferroic characteristics, as well as magnetoeletric response, have been observed in $PbZr_{1-y}Ti_yO_3$–$BaFe_{12}O_{19}$ (PZT–BaM) ceramic composites [10]. The enhanced magnetoelectric (ME) effect has been in this case related to the strain caused by an applied external magnetic field, which induces a stress on the piezoelectric component (ferroelectric PZT) of the two-phase system. Subsequently, this stress induces an electric field that contributes to the orientation of the ferroelectric domains along the electric field, thereby increasing the polarization of the composite. Because revealing promissory for the manufacture of several electro-electronic devives with a wide-range of practical applications, in the present work we consider advancing the study of this composite system made up of ferroelectric PZT, with a composition near the morphotropic phase boundary (MPB, with Zr/Ti = 65/35 ratio) and, thus, enhanced piezoelectric properties [11], together with ferrimagnetic BaM, known to show enhanced magnetostrictive properties [12].

Regarding multiferroics, in general, we however observe that no much attention has been paid to the investigation of the dielectric relaxation processes in such materials, in particular on PZT–BaM composites. There are reports suggesting that the dielectric response of multiferroics could be strongly dominated by conduction processes [13], which are intrinsic and due to large leakage currents and impurities [14,15]; but detailed investigation related to the origin of the conductive processes has been scarcely reported. In this paper, conventionally-sintered $PbZr_{0.65}Ti_{0.35}O_3$–$BaFe_{12}O_{19}$ (PZT–BaM) multiferroic ceramic composites are investigated in terms of dielectric relaxation, keeping in mind that the dielectric response of ferrite systems can be strongly dominated by conduction processes from their intrinsic semiconductor characteristics. The dielectric dispersion has been analyzed over wide temperature and frequency regions, and results are discussed in the framework of current models reported in the literature.

2. Experimental procedure

$PbZr_{0.65}Ti_{0.35}O_3$–$BaFe_{12}O_{19}$ (PZT–BaM) ceramic composites were obtained from the solid state reaction method, as previously reported [16]. Single ferroelectric (PZT) and ferromagnetic (BaM) phases were separately obtained starting from reactive oxides of high-purity grades, followed by calcination at 950 °C for 2.5 h, in the case of PZT, and 1000 °C for 3.5 h, in that of BaM. Next, the powders were mixed stoichimilacy taking into account the chemical formula $PZT_{(1-x)}BaM_x$ ($x = 0.03$, 0.04 and 0.05) and then calcined in air atmosphere at 800 °C for 2 h. After a milling process, the powders were uniaxially pressed into disc-shaped samples at 10 MPa, and then sintered in a closed alumina crucible at 1250 °C for 3 h. The ceramic samples were labeled as PZT, BaM003, BaM004 and BaM005 for $x = 0$, 0.03, 0.04 and 0.05, respectively. The structural properties were investigated by X-ray diffraction (XRD), using a Shimadzu XRD 6000 diffractometer with CuKα radiation. The diffraction data were collected from powdered ceramic samples in the 2θ range of 10°–130°, and analyzed by Rietveld refinement using the Fullprof Suite Package [17]. Scanning Electronic Microscopy (SEM) measurements were performed in order to

obtain the microstructural characteristics by using a JEOL JSM-840 microscope. Homogeneous and crack-free microstructures were observed, revealing average grain sizes around 3.17 μm, 3.04 μm and 2.73 μm for BaM003, BaM04 and BaM005, respectively. In order to obtain the electric properties, silver-paint electrodes were applied to the opposite faces of the ceramic samples and heat treated at 590 °C. The dielectric measurements were performed over a wide temperature range by using a HP4284A Precision LCR Meter, operating in the frequency range of 100 Hz–1 MHz.

3. Results and discussion

Fig. 1 shows the x-ray diffraction patterns for the studied compositions, obtained at room temperature. Results confirmed the coexistence of both rhombohedral (R3c) PZT and hexagonal ($P6_3/mmc$) BaM structures, for all the samples. In the identification process, Rietveld structural refinement revealed reliability factor values (χ^2) of about 2.3, 2.1 and 2.2 for the BaM003, BaM004 and BaM005 compositions, respectively. The obtained unit cell volumes (V_R) for the PZT phase of the studied composites revealed a slight decrease when compared to those values for the pure PZT phase [18]. It was also observed that V_R decreases with the increase of the BaM content (as shown in the inset of Fig. 1), indicating a straining (by compressive stress) of the PZT crystal lattice in the composites in presence of the BaM phase. Similar results have been reported for multiferroic composites based on $NiFe_2O_4$ (NFO) ferrite and $Pb_{0.93}La_{0.07}(Zr_{0.60}Ti_{0.40})O_3$ (PLZT) ferroelectric phases [19], showing a decrease of the PLZT tetragonality (c/a) with increasing ferrite. This indicates that NFO grains act as pinning centers for the ferroelectric phase.

Fig. 2 shows the temperature dependence of the real (ε') and imaginary (ε'') components of the dielectric permittivity at two selected frequencies (500 Hz and 300 kHz), for the studied composites. The obtained values for the paraelectric–ferroelectric (PE–FE) phase transition temperature (T_C) are around 305 °C, 276 °C and 260 °C for BaM003, BaM004 and BaM005, respectively. (Results from pyroelectric current, not shown here, were also taken into account to access these values) As can be seen, the PE–FE phase transition temperature decreases with the increase of the BaM content, and no changes of T_C were observed with the increase
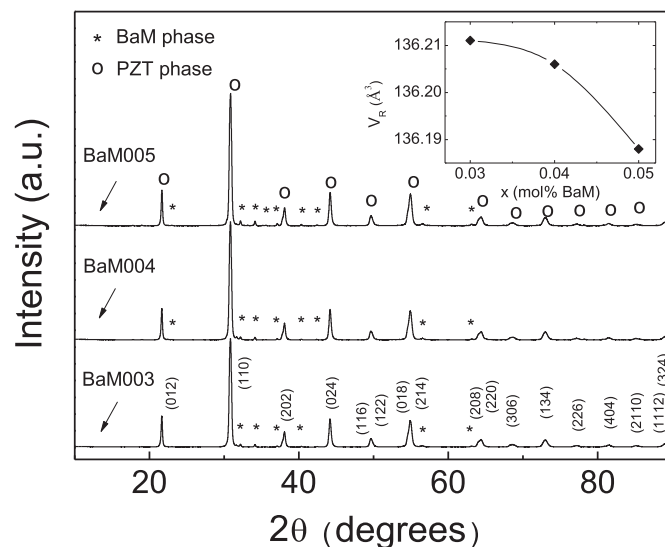

Fig. 1. Room temperature X-ray diffraction patterns for the studied multiferroic BaM003, BaM004 and BaM005 composites (powdered ceramic samples). The figure inset shows the composition (x) dependence of the unit cell volume, V_R.
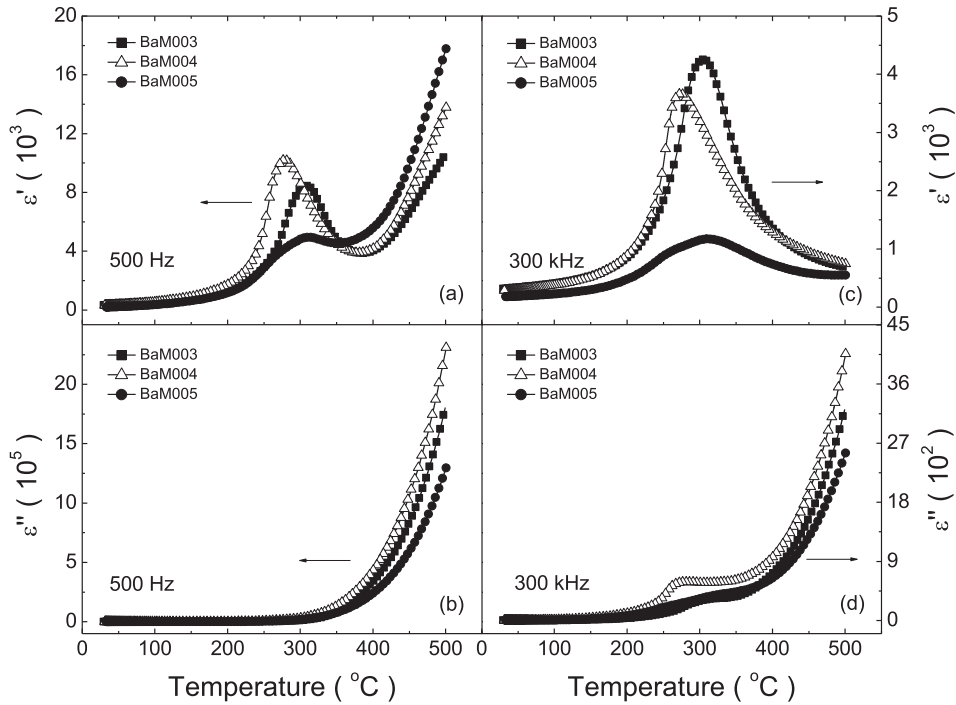
Fig. 2. Temperature dependence of the real (ε') and imaginary (ε'') components of the dielectric permittivity for the studied composites at two selected frequencies (500 Hz and 300 kHz).

of the frequency from 500 Hz (Fig. 2a) up to 300 kHz (Fig. 2c). Moreover, the maximum values for the real and imaginary components of the dielectric permittivity (ε'_m and ε''_m, respectively) were in each of these cases found to locate at the same temperature,

indicating the occurrence of a 'normal' character of the PE–FE phase transition for the studied materials. In this study, as can be seen in Fig. 2b and d, a continuous increase in the imaginary component of the dielectric permittivity (ε'') was observed, even
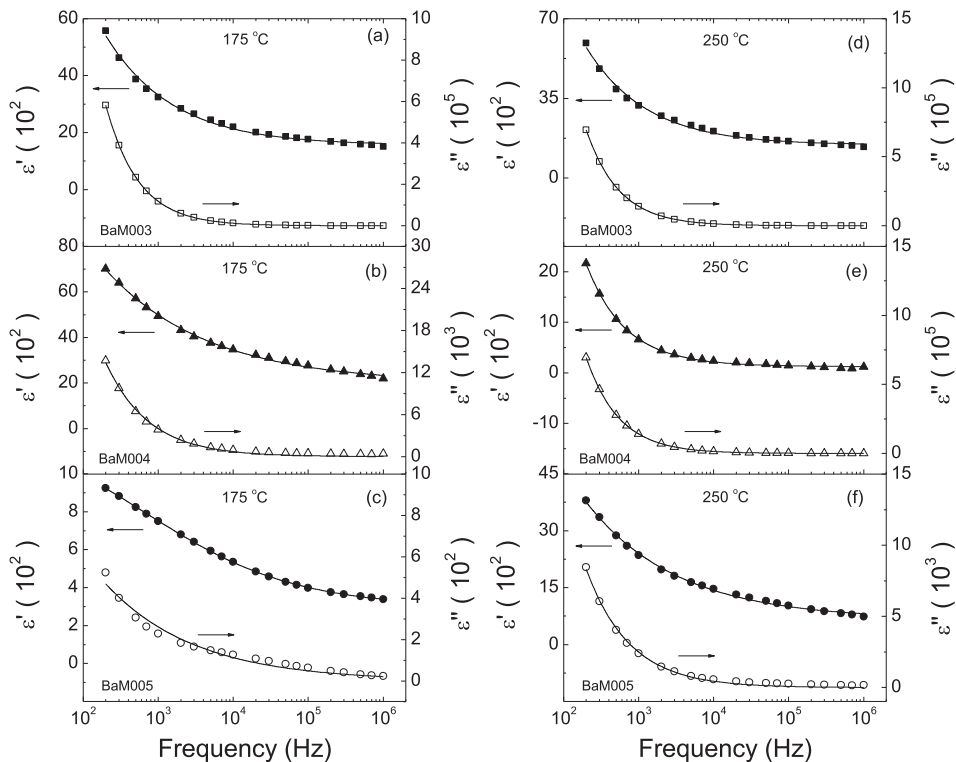

Fig. 3. Frequency dependence of the real (ε') and imaginary (ε'') components of the dielectric permittivity for the studied multiferroic composites at two selected temperatures: (a), (b) and (c) for 175 °C and (d), (e) and (f) for 250 °C. The solid lines represent the fitting of the experimental data (symbols) with Equation (1).

for temperatures above T_C. This behavior, also detected in Fig. 2a for the real component (ε'), can be related to conductive processes that are known to become prominent at low frequencies [20]. That is, in perovskite-type structure systems, relatively significant conductive processes and, hence, dielectric losses may be found with increasing temperature, and are ascribed by several authors to the hopping of oxygen vacancies, which may also induce space-charges polarization effects [21,22]. In ferroelectric materials based on lead zirconate titanate (PZT), in particular, intrinsic defects related with lead evaporation during sintering at high temperature are known to exist [21,23]. To compensate the charges unbalance promoted by lead volatilization, oxygen vacancies are commonly created, thus significantly modifying the physical properties of the studied ceramics [24,25]. In parallel, the defects originated by lead losses during sintering are also known to create a non-degenerate energy level, promoting the semiconductor characteristics of such ferroelectric ceramics for temperatures near the phase transition.

To access the influence of conduction processes and mechanisms in these composite materials, dielectric relaxation processes have been studied by looking at the behavior of the complex dielectric permittivity over wide frequency and temperature ranges. Fig. 3 illustrates the frequency dependence of the real (ε') and imaginary (ε'') components of the dielectric permittivity at two selected temperatures (175 °C and 250 °C) below the ferroelectric−paraelectric phase transition temperature. It is noticed that both properties (ε' and ε'') decrease as the frequency increases and remain almost constant in the highest frequency region (above 10^5 Hz). This behavior can be associated to space charge relaxation related to oxygen vacancies, which are commonly recognized as intrinsic defects [20]. At certain frequencies, such defects are no longer able to follow the electric field variations resulting in a relaxation-like behavior in the dielectric spectrum.

To analyze the relaxation behaviors shown in Fig. 3, the experimental data (symbols) were fitted by using the semi-empirical complex Cole−Cole equation [26]:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{1 + (j\omega\tau)^{1-\alpha}} \qquad (1)$$

which presupposes development of relaxation processes with a distribution function of relaxation times. In this equation, ε_0 and ε_∞ represent the low (static) and high frequency dielectric permittivities, respectively, ω is the angular frequency ($\omega = 2\pi f$, where f is the measurement frequency), α the parameter related to the relaxation time distribution function, while τ stands for the mean relaxation time.

As can be seen in Fig. 3, a good agreement between the theoretical fitting (solid lines) and the experimental data (symbols) was observed for all the analyzed temperatures. The values obtained for the parameter α approached 0.4, i.e., actually different from unity, clearly meaning that a deviation from the ideal Debye-type relaxation process applies [26]. The mean relaxation time values were estimated and their temperature dependences are shown in Fig. 4. As discussed just below, the relaxation processes can be in this work described by considering an Arrhenius' law for the mean relaxation time, as given in Eq. (2):

$$\tau = \tau_0 e^{\frac{E_a}{k_B T}} \qquad (2)$$

where τ_0 is the pre-exponential factor, E_a is the activation energy for the relaxation process, k_B is the Boltzmann's constant and T is the absolute temperature.

The solid straight lines in Fig. 4 represent the fitting results to the relaxation time data, and a good agreement can be actually
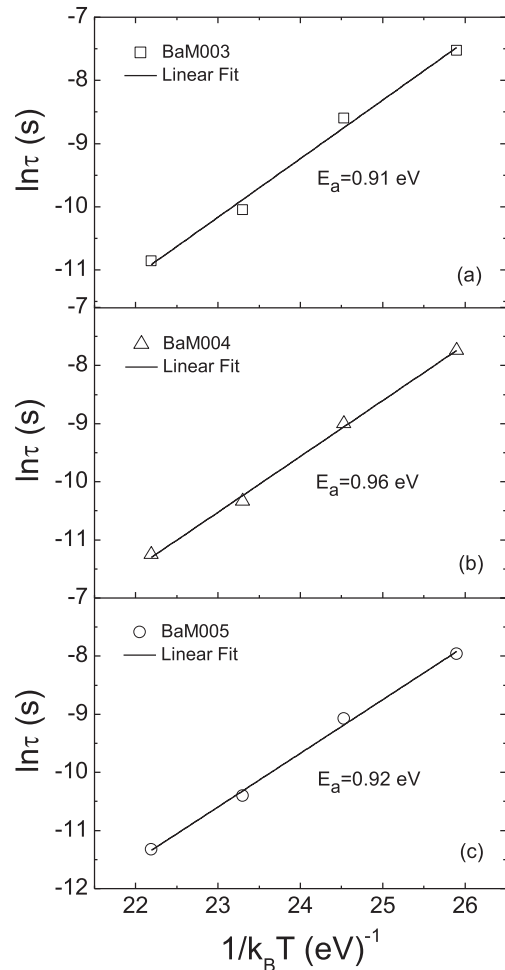

Fig. 4. Arrhenius plot for the mean relaxation time (τ) processed for the studied multiferroic composites at several temperatures below T_C. The solid lines represent the fitting of the experimental data (symbols) with Equation (2).

verified. The values estimated for the activation energy are 0.91 eV, 0.96 eV and 0.92 eV for BaM003, BaM004 and BaM005, respectively. The order of these E_a values (lying in proximity to 1 eV) indicates that, in these materials, the investigated dielectric relaxation phenomenon can be associated to conduction processes in which doubly ionized oxygen vacancies are the leading charge carriers [27,28]. This is in line with reports in the literature showing that, in perovskite-structured systems, oxygen vacancies are the typical mobile defects responsible for most of the direct current (DC) conductivity response measured in such materials [20,22,23].

When comparing among the samples, nevertheless, it is observed that the activation energy increases as the BaM concentration raises from BaM003 to BaM004, and then decreases again for BaM005. It has been reported that the activation energy for perovskite-structured systems decreases with the increase of oxygen vacancies [20]. Thus, the results obtained in this study suggest that the inclusion of the ferrite phase (BaM) in the PZT matrix promotes the reduction of oxygen vacancies for compositions up to BaM004, whereas the defects increase again for the highest BaM compositions. Therefore, the increase of the activation energy for BaM004 can be explained by the fact that the Ba^{2+} ions from the ferrite system could be inserted in the A-site of the PZT perovskite structure, thus substituting the Pb^{2+} ions. The iso-valent substitution of Pb^{2+} by Ba^{2+} ions is expected to compensate the charge imbalance by reducing the oxygen vacancies created by the

volatility of lead during sintering at high temperature. Hence, a higher value of activation energy is found. This is in good agreement with previously reported results regarding the formation of a $(Pb_{1-y}Ba_y)Zr_{0.65}Ti_{0.35}O_3$ (PBZT)-containing PZT-BaFe$_{12}$O$_{19}$ composite system [16]. The decrease of E_a for BaM005 suggests that, for the highest BaM concentration, the Fe^{3+} ions should be substituting the Ti^{4+} and/or Zr^{4+} ions in the B-site of the PZT perovskite structure. Such a substitution is expected to promote the creation of a non-degenerated energy level, where the electronic distribution of the structure becomes unstable with an electron in excess [29]. Therefore, according to the following reaction, $Fe^{3+}_{B^{4+}} \rightarrow Fe'_B + (1/2)V_O$, oxygen vacancies ($V_O$) have to be created for charge imbalance compensation, which would be consistent with the decrease of activation energy value for the BaM005 composition. From another point of view that also applies, nevertheless, the trend in activation energy could as well be interpreted considering the structural results, from which it is expected that the lower the lattice volume, meaning a lower free volume for charge migration, the higher the activation energy [30]. For BaM005 (composite with about 21 vol. % of BaFe$_{12}$O$_{19}$), this trend is no longer valid because the main contribution to the conduction process comes from the ferrite phase, which is originally of semiconducting-like nature, and the percolation effect is in this case supposed to manifest and dominate [31].

The obtained results reveal that the physical properties of the studied PZT–xBaM multiferroic ceramic composites can be strongly affected by defect chemistry-modulated conductive processes that are frequency and temperature dependent. It is important to point out that additional conduction mechanisms, which are characteristics of the magnetic phase, could also coexist with the previously discussed conductive effects and overlap the dielectric relaxation processes observed in such composite systems. This is because ferrite-based compounds are known to be strongly conductive systems and their electrical properties can be toughly dominated by several conduction mechanisms, provided their intrinsic semiconductor character [32]. Concretely, the high conductivity in ferrites has been normally attributed to occurrence of a deviation from stoichiometry in the synthesized materials because of oxygen deficiency created, in most cases, during the sintering process [14,15]. This high-conductivity feature includes semiconductivity-like contribution because of presence of Fe^{+3} as well as Fe^{+2} ions (polaron mechanism) [33], the latter (Fe^{+2}) mostly arising as a result of charge compensation. Such an effect leads to the well-known super–exchange and double–exchange interactions of Fe^{3+}–O^{2-}–Fe^{3+} and Fe^{+3}–Fe^{+2} types, respectively, responsible for ferromagnetic and anti-ferromagnetic properties in these materials [32].

Therefore, further investigation of such overlapping conductive effects, which have not been identified from the Cole–Cole formalism, should be taken into account in these PZT–BaM composites. In this way, additional studies on the conduction mechanisms, which govern the relaxation processes in these materials, are in progress and the results will be reported in the near future. Such studies will consider the temperature regions not only below but also above the paraelectric-ferroelectric transition temperature (T_C).

4. Conclusions

The dielectric relaxation phenomenon in PZT–BaM multiferroic composites was in this work investigated. The empirical Cole–Cole equation was used to analyze the frequency dependences of the complex dielectric permittivity. The results strongly reveal that oxygen vacancies have an important contribution to the electrical response of these materials, thus being the main responsible factor for the dielectric relaxation processes observed in these materials toward the explored temperature region. The activation energy showed an anomalous behavior with the increase of the BaM concentration, characterized by an increase of E_a from the BaM003 to the BaM004 composition, and then a decrease for the BaM005 composition. The inclusion of Fe^{3+} ions in the B-site of the PZT perovskite structure is suggested as the main cause for the obtained result. The substitution of the B-site ions, with 4+ valence, by Fe^{3+} promotes the oxygen vacancies creation, thus leading to the decrease of the activation energy related to the relaxation process.

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