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Synthesis and Electrical Properties of PZT/$BaFe_{12}O_{19}$ Multiferroic Ceramics

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Abstract. Multiferroic ceramics, based on the ferroelectric and ferrimagnetic phases of the $Pb(Zr_{0.65}Ti_{0.35})O_3$ (PZT) and $BaFe_{12}O_{19}$ (BaM) systems, respectively, were obtained from the conventional ceramic method. The electrical properties have been investigated in a wide temperature and frequency range. The influence of the magnetic phase on the ferroelectric and dielectric properties of the ferroelectrics phases have been taken into account. The phase transition characteristics shown to be strongly affected by the amount of the BaM phase, while the dielectric properties revealed to be directly dominated by the presence of conductive effects related to the charge transport mechanisms associated to the magnetic phase.

Introduction

Research on materials exhibiting multiferroic properties has attracted the attention of the scientific community in the last decade because of its high potential to be used in the manufacture of electronic devices such as sensors, transducers and storage memories [1]. In particular, composite materials containing both ferroelectric and ferrimagnetic phases can be explored where new properties of great interest can be investigated. It has often been reported in the literature studying the phase transitions characteristics in ferroelectric ceramics modified with insertion of dopants or two ferroic phases interacting [2]. Compositional variations in this type of systems can often cause structural disorders as well as changes in the ferroelectric-paraelectric (FE-PE) phase transition properties, promoting the well-known diffuse phase transition (DPT) [3]. Another common, but not intrinsic, behavior in DPT materials is the frequency dependence of the dielectric permittivity (or relaxor characteristics) often related to structural defects, which cause dielectric relaxations [4]. Such relaxations due to defects can be attributed to vacancies on a specific site of the structure, space charges, or even impurities that are directly connected to the thermally activated conductive processes [4].

In particular, multiferroic materials have attracted a special attention with respect to their multifunctional physic properties, especially when there is coexistence between the electrical (ferroelectric) and magnetic (ferrimagnetic) properties [1,2]. It is known that the dielectric response of some of magnetic/ferrimagnetic systems is strongly dominated by conduction mechanisms because of its intrinsic semi-conductor character. So that, such conduction processes, intrinsic in the magnetic systems, could directly affect the dielectric properties of a multiferroic system where both ferroelectric and ferrimagnetic phases coexist. Thus, the character of the phase transition should be carefully analyzed. The objective of the present work is to investigate the electrical properties of a multiferroic ceramic system in a wide temperature and frequency range. The PZT/BaM ceramic samples have been synthetized by using the conventional ceramic method by mixing the $Pb(Zr_{0.65}Ti_{0.35})O_3$ (PZT) ferroelectric and $BaFe_{12}O_{19}$ (BaM) ferrimagnetic systems. The PZT ferroelectric ceramics have a perovskite structure and its composition (Zr/Ti=65/35) is relatively close (below) the Morphotropic Phase Boundary (MPB), where the PZT system displays excellent physical properties [5]. Other hand, the barium hexa-ferrite system (BaM) has hexagonal structure, with excellent piezo-magnetic and semiconductors properties [6]. Therefore, this work has been focused on the understanding of the physical properties as a result of the increase of the BaM on the PZT ferroelectric matrix. In particular, the character of the FE-PE phase transition has been investigated and the influence of conductive processes has been considered.

Experimental Procedure

PZT ferroelectric and BaM ferrimagnetic phases were separately obtained according to the conventional ceramic method from high purity powders. For the ferroelectric phase the starting reagents were milled for 8 h, and calcined at 950 °C for 2.5 h. On the other hand, for the ferrite phase the powders were milled for 8 h and calcined at 1000 °C for 3.5 h. After that, the ferroelectric-ferrimagnetic compounds were stoichiometrically obtained according to the relation $PZT_{(1-x)}BaM_x$, with x=0, 0.03, 0.04 and 0.05. The PZT-xBaM samples were ball milled for 2 h and calcined at 800 °C. The samples were uniaxially cool-pressed on a disc-shape and then sintered at 1250 °C. The structural properties were obtained from the x-ray diffraction (XRD) technique, using $CuK\alpha$ radiation. The ferroelectric properties (hysteresis loops) were performed at room temperature and 2 Hz by using modified Sawyer-Tower circuit. Frequency (100 kHz–1 MHz) and temperature (25–500 ^{o}C) dependences of the real (ε’) and imaginary (ε’’) components of the dielectric permittivity were carried out using an Agilent E4980A Precision LCR Meter coupled to a Carbolite MTF 12/38/250 Tube Furnace and an Eurotherm 3216P1 Temperature Controller, controlled by a PC computer. The samples were hereafter labeled as PZT 65/35 and BaM for the pure systems and BaM003, BaM004 and BaM005 for the x=0.03, 0.04 and 0.05 compositions, respectively.

Results and Discussion

Fig. 1 shows the x-ray diffraction patterns of the investigated samples after the sintering process. As can be seen structural results revealed a pure perovskite, with rhombohedral R3m symmetry, and hexagonal (P63/mmc) structure, for the ferroelectric PZT and ferrimagnetic BaM systems, respectively. The obtained results are in agreement with the previously reported in the literature [5,6]. On the other hand, it can be also noted that the increase of the BaM content promotes the presence of the additional ferrite phases on the ferroelectric phases of the PZT system. However, a detailed inspection on Fig. 1, specifically for reflections around 31^{o}, reveals that there is a slight shift on the position of the peak toward lower angles, which might be an evidence of the formation of a solid solution with the addition of the ferrite phase on the ferroelectric phase. Indeed, small concentration of BaM phases could promote a structural change on the PZT ferroelectric phase, which can be associated to the insertion of Ba^{2+} ions on the A-site of perovskite structure giving place to the formation of a solid solution instead of an expected ceramic composite. According to the Bragg’s law, the inclusion of the Ba^{2+} ions on the perovskite structure lead to an increase of the crystalline planes and corresponding displacements of the peaks to lower angles [7].

The barium ion has equivalent valence to the lead ion, with an ionic radius of 1.35 Å, a slight higher that one for the Pb^{2+}, which exhibit ionic radius of 1.19 Å [8]. In this sense, taking into account the tolerance factor of the structure [5], the Ba^{2+} ion can occupy the generated Pb^{2+} vacancies at the A-site of the perovskite structure, which probably occurs during the sintering process [9].

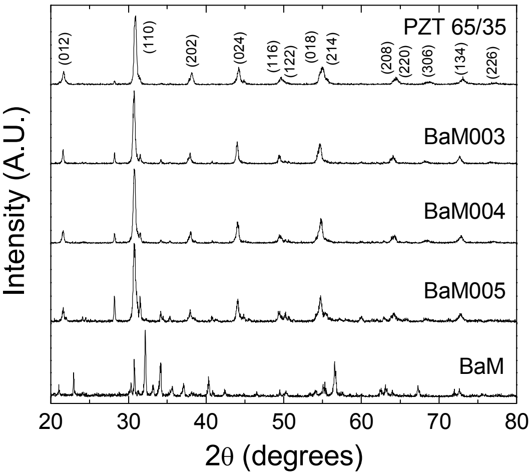

Fig. 1. XRd patterns of the PZT, BaM, BaM003, BaM004 and BaM005 sintered samples.

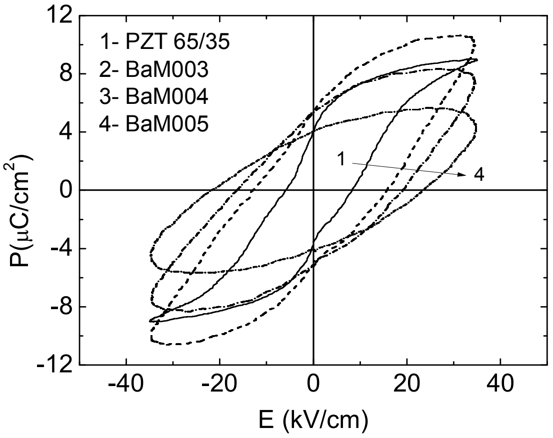

Fig. 2. Typical room temperature ferroelectric hysteresis loop of the studied ceramics, obtained at room temperature and 2 Hz.

Table 1. Ferroelectric parameters obtained from the hysteresis loops of the Fig. 2.

System	**Ferroelectric parameters**	
	P_R (μC/cm^2)	**E_C (kV/cm)**
PZT 65/35	4.90	8.3
BaM003	5.42	13.6
BaM004	5.36	17.5
BaM005	3.98	23.6

Fig. 2 shows the ferroelectric properties results from the electric field dependence of the electrical polarization (hysteresis loop) obtained at 2 Hz and room temperature, for all the studied compositions.

As can be seen, typical hysteresis loops were obtained for all the studied compositions, showing a remanent polarization (P_R) and coercive field (E_C) of 4.9 (μC/cm^2) and 8.3 (kV/cm), respectively, for the pure PZT system. It can be also noted that the remanent polarization increases for the BaM003 composition, and then decreases for higher compositions with the increase of the BaM content, while the coercive field showed an increase with the increase of the BaM content. Such observed effect can be an evidence of the decrease of the contribution of the ferroelectric phase in the samples with increase of the ferrite content. The obtained values of the ferroelectric parameters, remanent polarization (P_R) and coercive field (E_C), are shown in the table 1.

On the other hand, it can be observed that the shape of the hysteresis loops changes from a typical non-linear ferroelectric behavior, for pure PZT, to a circular one, with the increase of the ferrite (BaM) content on the PZT matrix. Such observed behavior can be associated to the existence of conductive processes on the samples [10], promoted from the inclusion of impurities as a result of the doping process of the PZT ferroelectric phase with a BaM ferrimagnetic phase, which lead to mask the remanent polarization values and, consequently, the real dipolar contribution. It is important to point out that it was not possible to obtain the ferroelectric hysteresis loop for the pure BaM sample because of the high conduction effects, which are characteristics of ferrites with semi-conductor properties [11].

Fig. 3 shows the temperature dependence of the real and imaginary component of the dielectric permittivity (ε' and ε'', respectively), obtained at several frequencies, for the pure PZT and the BaM003, BaM004 and BaM005 compositions. As can be seen, for the pure PZT sample the dielectric response results showed a well-defined peak of the real dielectric permittivity with a maximum value (ε_m) observed around 6600. On the other hand the temperature of the maximum dielectric permittivity was observed for a temperature of 357 °C, which is in agreement with the previously reported value for the ferroelectric-paraelectric transition temperature (Curie temperature, T_C) for this composition, according to the phase diagram for the PZT system [5]. It can be also noted a no frequency dispersion of the dielectric permittivity with the increase of the frequency for the pure PZT 65/35 sample, confirming the 'normal' character of the FE-PE phase transition for the PZT system [5]. On the other hand, the temperature of the maximum dielectric permittivity (T_m) showed a decrease with the increase of the ferrite content, which could be a clear evidence of the formation of a solid solution by doping the pure PZT 65/35 system with the ferrite (BaM) phase, as indeed previously observed on the Fig. 1 for the structural properties. The obtained values for T_m and ε_m are shown in the Table 2. Previously reported results for the $(Pb_{1-y}Ba_y)Zr_{0.65}Ti_{0.35}O_3$ (PBZT) system show that the addition of Ba^{2+} ion on the PZT structure decreases the FE-PE phase transition temperature [7], showing T_m values very close to those obtained in the present work. So that, the reduction of T_m, with the increase of the BaM content, could be related to the insertion of the Ba^{2+} ions, which occupy the A-site of the perovskite structure because of the lead vacancy promoted during the sintering process.

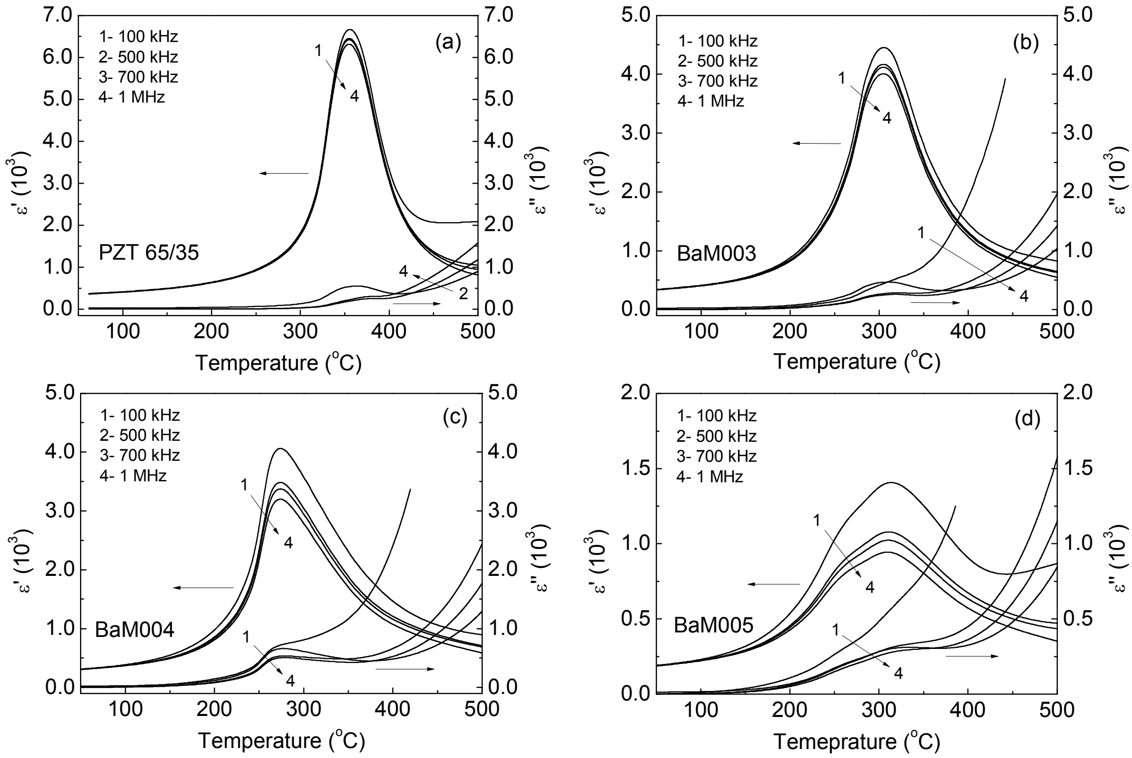

Fig. 3. Temperature dependence of the real and imaginary dielectric permittivity, at several frequencies, for the PZT 65/35, BaM003, BaM004 and BaM005 samples.

Table 2. Maximum real dielectric permittivity (ε_m) values and its corresponding temperature (T_m) as a function of the composition, at 100 kHz.

System	**Dielectric parameters**	
	T_m (°C)	ε_m
PZT 65/35	357	6669
BaM003	301	4457
BaM004	274	4065
BaM005	257	1077

However, the dielectric response obtained for the modified compositions revealed a frequency dependence of the dielectric permittivity (dielectric dispersion), mainly for temperatures near T_m, which seems to be intensified with the increase of the ferrite content. Such behavior can be associated to the conductive mechanisms related to the interfacial polarization effects characteristics of the ferrite phase [11], which change the configuration of the dielectric response from a ‘normal’ to a dispersive ferroelectric system. The contribution of the thermaly activated conductive processes becomes more evident for the high temperature regions, above T_m, characterized by an increase of the imaginary component of the dielectric permittivity for all the samples. As can be seen, the dielectric response for the BaM005 sample revealed two dielectric permittivity peaks for temperatures around 257 °C and 310 °C, which are related to the FE-PE phase transition and to the contribution of interfacial polarization effects related to the space charge carriers arising from ferrite phases. Thus, the obtained results for the dielectric properties show strong evidences of the formation of a solid solution with the increase of the ferrite content, with a solubility limit for the BaM005 composition.

Interestingly, another additional result observed on the Fig. 3 can be associated to the change of the characteristics of the FE-PE phase transition with the increase of the ferrite content. In fact, the dielectric response clearly reveals as the peak around the temperature of the maximum dielectric permittivity becomes broader as the ferrite content increase. Such a result evidences a change from a ‘normal’ FE-PE to a diffuse phase transition, with the increase of the ferrimagnetic phase. The obtained results can be associated to the fact that with the increase of the ferrite content a structural disorder of the ferroelectric phase can be reached, promoting a reduction of the long-range ferroelectric order for higher ferrite concentrations.

Summary

The structural and electrical properties of the PZT-xBaM multiferroic ceramics, obtained from the conventional ceramic method, have been investigated. The structural characteristics revealed the formation of both rhombohedral and hexagonal phases for the pure PZT ferroelectric and BaM ferrimagnetic systems, respectively. A strong influence of the ferrite phase on the structural properties of the studied ceramics, with the increase of the BaM content, was also observed. On the other hand, the dielectric response revealed a strong influence of the BaM content on the FE-PE phase transition characteristics. Indeed, a decrease of the maximum dielectric permittivity and its corresponding temperature was observed with the increase of the ferrite phase, with show clear evidences of the formation of a solid solution for the obtained multiferroic ceramics. On the other hand, the strong dielectric dispersion observed in a wide temperature range can be related to the conductive processes arising from interfacial polarization effects associated to the space charge carriers, characteristics of ferrite phases. A detailed study of such conductive mechanisms, which revealed to be thermally activated, is being taking into account by the present authors and results will be presented in further works.

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High-Performance Ceramics VII

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