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1. Introduction

Ferroelectric (1-x)[Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)]-xPbTiO\(_3\) (PMN-PT) solid solutions are known for their exceptional electromechanical properties, sometimes one order of magnitude larger than classical PbZr\(_{1-x}\)Ti\(_x\)O\(_3\) (PZT) ceramics. Prepared with a suitable x composition, PMN-PT is technologically important for fabricating some of the most important solid state devices such as a piezoelectric transducer, actuator, FERAM, etc. PMN-PT ceramics, thin films or single crystal forms can be prepared with high piezoelectric coefficients, a high dielectric constant and a low dielectric loss. Some compositions of PMN-PT single crystals exhibit a very high piezoelectric coefficient (d\(_{33}\)) and electromechanical coupling coefficients (k\(_{33}\)) (d\(_{33}\) ~ 1240 pC/N and k\(_{33}\) ~ 0.923), a high dielectric constant (ε ~ 3100) with low dielectric loss (tanδ ~ 0.014) compared to those of polycrystalline ceramics (d\(_{33}\) ~ 690 pC/N and k\(_{33}\) ~ 0.73) (Park & Shrout, 1997; Viehland et al., 2001). Recently, researchers have also reported that PMN-PT single crystals have high remanent polarization (P\(_r\) ~ 35 μC/cm\(^2\)) at a low coercive field (E\(_c\) ~ 3.4 kV/cm), a high dielectric constant (ε ~ 2500), low loss tangent (tanδ ~ 0.031), the highest piezoelectric coefficient (d\(_{33}\) ~ 1500 pC/N) and a high electrochemical coupling coefficient (k\(_{33}\) ~ 0.82) for <112> grain-oriented PMN–PT ceramics (Sun et al., 2004). The piezoelectric coefficient determines the stress levels induced by a given electric field and thus is the parameter most frequently used to describe the performance of an actuator.

PMN-PT solid solutions present a perovskite ABO\(_3\) structure, where the A site is occupied by the Pb\(^{2+}\) ion, while the B site is randomly occupied by Mg\(^{2+}\), Nb\(^{5+}\) and Ti\(^{4+}\) ions. Different compositions of the PMN-PT present distinct physical properties. The complex perovskite Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) (x = 0) is a typical relaxor ferroelectric, characterized by a diffuse maximum of the dielectric constant associated with considerable frequency dispersion, that exhibits a non-polar paraelectric phase at high temperatures, similar in many aspects to normal ferroelectrics (Bokov & Ye, 2006). After cooling, a transformation occurs from the paraelectric phase to the ergodic relaxor state, characterized by the presence of polar nanoregions randomly distributed by the specimen, at the Burns temperature (T\(_B\)). This transformation is not accompanied by changes in the crystal structure on the macroscopic or mesoscopic scale and therefore cannot be considered a structural phase transition. In general, the state of a relaxor crystal at T < T\(_B\) is frequently considered a new phase different from the paraelectric phase, since the polar nanoregions substantially affect the behavior of...
the crystal properties. Cooling the crystal hundreds of degrees below $T_B$, the polar nanoregions become frozen in a nonergodic state at around the freezing temperature ($T_f$) which can be irreversibly transformed into a ferroelectric state below $T_f$. The substitution of Ti$^{4+}$ ions for the (Mg$_{1/3}$Nb$_{2/3}$)$^{4+}$ ions in the B site of PMN-PT results in a long-range breaking leading to complex domain structures (Ye & Dong, 2000). The fascinating relaxor effect tends to disappear with this substitution, and the so-called morphotropic phase boundary (MPB) emerges in the composition-temperature (x-T) phase diagram of the PMN-PT system located at $x \approx 0.35$ (Noblanc et al., 1996). In the past decade, intensive research work was undertaken on the scientific understanding of the MPB nature in ferroelectric solid solutions (Noheda, 2002). This interest was mainly motivated by understanding the mechanisms responsible for the high piezoelectric response of ceramic compositions around the MPB. Finally, at the other extreme of the x-T phase diagram ($x = 1$), the lead titanate PbTiO$_3$ shows a typical ferroelectric-paraelectric phase transition presenting a high Curie temperature ($T_C = 490 \, ^\circ C$).

One of the most common problems related to PMN–PT emerges during synthesis. Indeed, obtaining high-density ceramics is very difficult without rigorous control of several steps in the processing, which makes using these materials for practical applications difficult. In the processing of PMN-PT solid solutions, the formation of an undesirable pyrochlore phase has long been recognized as a major problem for widespread use of these materials in the technology. In the last few years, several attempts, including modifications of the columbite method and other solid state reaction routes by using ultrafine powders, have been made to develop a processing technique in which formation of the pyrochlore phase is suppressed. Based on these processes, high-density ceramics could be obtained, and consequently, some properties could be improved. The purpose of this chapter is to provide an overview of the current understanding of some issues of the PMN-PT ferroelectric system at compositions around the MPB, including processing, structure and dielectric properties.

2. Processing and synthesis of PMN-PT

A major problem concerning the scientific studies and applications of PMN and PMN-PT electroceramics is the difficulty in producing a single-phase material with a perovskite structure. The main obstacle in PMN-PT synthesis is forming a lead niobate-based pyrochlore phase, frequently formed in the initial stage of the reactions processes for different methods. The presence of such a pyrochlore phase in the PMN-PT system is commonly believed to significantly degrade their dielectric properties, and therefore, the resulting material is inadequate for technological applications or a systematic scientific study (Mergen & Lee, 1997; Swartz & Shrout, 1982; Shrout & Swartz, 1983). Thus, choosing the synthesis method is fundamental to prepare pyrochlore-free PMN-PT of good quality. In general, several complex problems in materials science, such as the correct determination of the structure of the PZT solid solution in the MPB, remain unsolved in part due to the difficulty comparing results obtained from different samples. Some differences observed in peak widths of the neutron diffraction pattern suggest that the precise structural arrangements in these materials depend on the method of preparation (Yokota et al., 2009). Compounds of the general formula $A_2B_2O_7$ (A and B metals) represent a family of phases isostructural to the mineral pyrochlore (NaCa)(NbTa)O$_6$F/(OH) (Subramanian, M.A. et al., 1983). Although $A_2B_2O_7$ compounds exhibit a wide variety of interesting physical properties, in high-performance ferroelectrics such as PMN-PT these compounds should be
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avoided due to their paraelectric characteristic (Kamba et al., 2007). The compound Pb$_{1.83}$Mg$_{0.29}$Nb$_{1.71}$O$_{6.39}$ (PMN) exhibits a pyrochlore structure (space group Fd3m), frequently growing in the perovskite PMN ceramics, where the dielectric constant was found to increase as the temperature decreased, presenting an anomalous peak near 20 K, attributed to relaxation phenomena (Shrout & Swartz, 1983).

Chemical methods used to obtain complex precursor powders are normally less expensive and enable better stoichiometric control of complex oxides. Among several chemical methods, the approaches for obtaining mixed-cation oxide powders may be frequently grouped into two categories: the sol-gel process that uses alkoxide compounds as starting precursors (Johnson, 1985) and the polymeric precursor method that uses chelating agents such as citric acid (Lessing, 1989). In the sol-gel process, the high surface area of the dried gels results in high reactivity that in turn permits low temperature processing or even the formation of nonequilibrium phases. This process can be categorized in polymerized alkoxides and colloidal sols. The main advantages in using the polymerized alkoxides are low temperature, densification and ease doping compared to the disadvantage of slow drying. However, colloidal sols present rapid drying and the low cost of the materials as advantages and doping difficulty as a disadvantage. In the popular polymeric precursor method, the synthesis of a cross-linked polymer resin provides some benefits such as homogeneous mixing of the cations and less tendency for segregation during calcinations. The main feature of the polymeric precursor method is that it allows a very homogeneous dispersion of the cations along the polymer. Thus, choosing a specific method to prepare mixed-cation oxide powders depends on several factors, including the kind of desired ceramic and the final objectives of each study.

Suppressing the pyrochlore phase is extremely difficult and depends on the synthesis method. To prepare pyrochlore-free PMN-PT ceramics or single crystals, several methods have been developed over the past three decades. The columbite process was known as a classical solid-state reaction method for synthesizing PMN (Swartz & Shrout, 1982). This method for solving the perovskite-pyrochlore reaction problem was proposed to bypass the formation of the intermediate pyrochlore phase reaction. By using the conventional mixed oxide technique and commercially starting materials, the following reaction sequences were proposed: MgO + Nb$_2$O$_5$ → MgNb$_2$O$_6$ and MgNb$_2$O$_6$ + 3PbO → 3(PMN). This procedure was adopted keeping in mind that the kinetics for liberating Nb$_2$O$_5$ from the MgNb$_2$O$_6$ columbite phase may be slow enough to prevent the pyrochlore phase from forming and that structure of the MgNb$_2$O$_6$ is a structure similar to the perovskite structure. At 900 °C, the reaction above is complete with small residuals of the pyrochlore phase. To remove this small amount of the pyrochlore phase, an MgO excess is introduced before the MgNb$_2$O$_6$ calcination step. Thus, powders with perovskite structure have been successfully synthesized with the two-step calcination technique described, where the columbite (MgNb$_2$O$_6$) phase is initially synthesized at 1000 °C and then reacts with PbO and TiO$_2$ at 900 °C to form the pyrochlore-free PMN-PT phase. The effects of the MgO excess on the microstructure and dielectric properties of PMN and PMN-PT ceramics prepared by the columbite revealed that excess MgO completely inhibits formation of the pyrochlore phase and increases the grain size without substantially changing the density (Swartz et al., 1984). A significant increase in the dielectric constant values for PMN and PMN-PT, with x = 0.1, was observed with the addition of excess MgO and the increase in grain size and sintering temperature, reaching 18000 and 31000 for PMN and PMN-PT, respectively. Combining these factors to improve the dielectric constant in PMN-PT ceramics with the columbite

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method leads to a decrease at the Curie temperature ($T_c$) as the grain size increases. These facts clearly indicate that the processing method plays an important role in the investigation of the phenomenology of ferroelectric ceramics based on the dielectric properties, since variations such as the $T_c$ shift are attributed to the clamping of domains walls or internal stresses generated at the grain boundaries (Randall et al., 1998). This method was also used to prepare PMN-PT ceramics compositions around the MPB, with a dense microstructure, grain size around 2-3 µm and excellent electromechanical properties (Kelly et al., 1997). In addition to the columbite method, routes such as coprecipitation (Sekar & Halliyal, 1998), sol-gel (Yoon et al., 1995), modified sol-gel (Babooran et al., 2004), combustion synthesis (Cruz et al., 2002), semi-wet chemical route (Panda & Sahoo, 2005) and others have been proposed to prepare pyrochlore-free PMN powders, which can be also extended to PMN-PT synthesis. Alternatively, methods that require only one calcination step to produce single-phase perovskite PMN–PT and PMN powders were also proposed (Gu et al., 2003). In this case, the Nb$_2$O$_5$ powder is coated with Mg(OH)$_2$ in the first step, and in the second step, the Mg(OH)$_2$-coated Nb$_2$O$_5$ powder is mixed with PbO for calcinations. The pyrochlore-free perovskite powders obtained could be sintered to almost full density at 1150 °C. The main advantage of this method over the columbite method is the single calcination step.

Variants of the columbite method were proposed to optimize their electrophysical properties or to be used as alternative routes to obtain fine powders. Often, oxide precursor powders with specific characteristics, with controlled particle size as an example, are not available commercially. An alternative for each research laboratory is producing its own powder with the desired characteristic. Thus, variants of the processes already established have arisen. A variant is the polymerized complex method based on the Pechini-type reaction route (Pechini, 1967). The general idea of this approach is to distribute the metallic ions homogeneously throughout the polymeric resin, in which chelate is formed between dissolved ions and a hydroxycarboxylic acid (citric acid is the usual). Heating the resin in air causes a breakdown of the polymer, and subsequent calcinations at 500 to 900 °C are necessary to form the desired mixed oxides (Lessing, 1989). This alternative was also applied to produce MgNb$_2$O$_6$ powders, which were used as precursors to produce the PMN phase, obtained by the solid-state reaction between MgNb$_2$O$_6$ and PbO (Guarany, 2006; Guerra et al., 2009).

The polymerized based on the Pechini method combined with the columbite method was also applied to obtain good-quality PMN-PT ceramics at compositions around the MPB with a tendency to <111>-orientation (Áraújo et al., 2007). The texture tendency observed in these ceramics was attributed to shear rates introduced during the ceramic pressing when a fine powder was used. Similar <112> and <001> grain-oriented PMN-PT ceramics, at $x = 0.30$ and 0.32, respectively. The first one was prepared with a directional solidification method of the compressed powders prepared by the columbite method (Sun et al., 2004), and the second ceramic was produced with the templated grain growth method (Sabolsky et al., 2001). The latter method, responsible for synthesizing PMN-PT ceramics with good-quality texture, is a processing routine that uses a tabular (001)-oriented SrTiO$_3$ as a template (Kwon et al., 2005), at which the volume fraction of the oriented material increases as the thermal treatment continues at the expense of the finer grain matrix (Kwon et al., 2005). Despite the different methods proposed in the literature, studies of the phenomenology behind the MPB often have used ceramics prepared with the columbite classic method or some variation thereof. Table 1 summarizes the physical, dielectric and piezoelectric properties of PMN and PMN-PT ceramics for different compositions ($x$) around the MPB.
PMN ceramics

| References                  | K_{max} (at 1 kHz) | T_C (°C) | Comments                      |
|-----------------------------|--------------------|----------|-------------------------------|
| Swartz et al. (1984)        | 16200              | -10      | Columbite method              |
| Wang & Schulze (1990)       | 13700              | -10      | Modified columbite method     |
| Kong et al. (2001)          | 13979              | -        | High-energy ball milling      |
| Panda & Sahoo (2005)        | 10335              | -        | Semi-wet chemical route       |
| Paula et al. (2008)         | 19000              | -6       | Modified columbite method     |

PMN-PT ceramics

| x   | d_{33} (pC/N) | k_{33} | k_t | Comments                        |
|-----|--------------|-------|-----|---------------------------------|
| 0.30| ~1500        | 0.82  | 0.51| <112> Grain-oriented ceramics   |
| 0.32| ~1200        | 0.755 | -   | <001> Textured ceramics         |
| 0.30| 450          | -     | 0.41|                                 |
| 0.33| 640          | -     | 0.43| Random-oriented ceramics        |
| 0.35| 700          | -     | 0.44|                                |
| 0.30| 670          | -     | -   | Poled and unpoled ceramics      |
| 0.33| 690          | 0.73  | -   |                                |

Table 1. Summary of the maximum dielectric constant and Curie temperature (T_C) of PMN ceramics prepared from different methods, and piezoelectric properties of PMN-PT ceramics for different compositions (x) around the MPB.

The preparation method also has a strong influence on the microstructure and dielectric properties of ferroelectric ceramics. In general, chemical methods that produce fine powders are more favorable for producing PMN-PT ceramics with a dense microstructure and larger grain size, but the density and grain size both depend on the sintering temperature. For ceramics prepared with the columbite method, the density decreases as the sintering temperature increases while the grain size increases (Swartz et al., 1984; Kong et al., 2002). An increase in the dielectric constant as the sintering temperature increases has also been observed for different compositions of PMN-PT (Baek et al., 1997). Grain-size dependence of the dielectric constant of PMN-PT ceramics was observed in the ferroelectric and paraelectric region, and this observation indicates that it is not a domain or stress effect (Swartz et al., 1984).

3. Structure of PMN-PT compositions at the MPB

The highest piezoelectric and electromechanical coupling coefficients of the PMN-PT (Park & Shrout, 1997) are found for compositions in the MPB at 0.27 < x < 0.37, between the tetragonal and rhombohedral regions of the x-T phase diagram (Noblanc et al., 1996). A typical example of the MPB between the tetragonal and rhombohedral perovskite phases can be found in the x-T phase diagram of the PZT system at around x ≈ 0.52 (Jaffe...
et al., 1971), where the highest piezoelectric coefficients are also observed. Since the 1970s, the MPB has been interpreted in terms of different models that attempt to explain the high piezoelectric response in the PZT system. The assumption that the morphotropic phase change is a first-order transition that defines a finite region where both tetragonal and rhombohedral phases coexists was one of the most discussed models (Arigur & Benguigui, 1975) until the mid-1990s (Mishra et al., 1996). The assumption of a metastable character for one of the two phases within the finite coexistence region (Isupov, 1975) and the propose of a true boundary explained with compositional fluctuations (Kakegawa & Mohri, 1977) were other models considered to understand the nature of the MPB in the PZT system. As often happens in science, complicated models reflect the degree of difficulty in understanding a problem, and new paradigms must be considered. These models began to decline when a study published in 1998 (Du et al., 1998), based on the phenomenological approach, revealed a great enhancement of piezoelectric coefficient $d_{33}$ of rhombohedral PZT compositions around the MPB oriented along the tetragonal polar direction (001). This result was unexpected since the expectative for the largest piezoelectric deformations was to occur along the polar direction, with (001) for the tetragonal phase and (111) for the rhombohedral phase. Although this result has been obtained with thin films, since due to the lack of single crystals of PZT preferential orientations of PZT thin films can be adequately obtained by choosing an appropriate substrate, deposition method or drying temperature (Chen & Chen, 1994), it can be considered a catalyst for changing our perception of piezoelectric materials.

The discovery of a stable monoclinic phase in the PZT system in 1999, at compositions in the MPB (Noheda et al., 1999, 2000, 2001), provides a new perspective for explaining the high piezoelectric response of PZT ceramics (Guo et al. 2000, Singh et al. 2008, Bellaiche et al. 2000), attributed before to the coexistence of tetragonal and rhombohedral phases. After the initial discovery of a monoclinic phase with space group $Cm$ ($MA$ type) on the PZT system, other new monoclinic phases with $Pm$ and $Cc$ space groups were also discovered (Singh & Pandey, 2001; Hatch et al., 2002; Ranjan et al., 2005). In addition, phenomenological and Raman scattering studies were performed on different PZT compositions around the MPB to confirm the presence of the monoclinic $Cm$ and $Cc$ phases (Souza et al., 2000; Souza et al., 2002). Consequently, a new x-T phase diagram of the PZT system was proposed (Pandey & Ragini, 2003), and more recently (Woodward et al., 2005; Pandey et al., 2008), a revised phase diagram was suggested including a region of monoclinic phases with $Cm$ and $Cc$ symmetries at compositions corresponding to the MPB. In addition to this context, more recent studies (Singh et al., 2007) suggest the presence of a monoclinic phase on the PZT system with the $Cm$ space group instead of the rhombohedral phase with the $R3m$ space group for Zr-rich compositions ($0.40 \leq x \leq 0.475$). Thus, the limits for the monoclinic phase existence in the x-T phase diagram of the PZT system are still open for discussion. Two years after the discovery of the monoclinic phase in the PZT system, a similar monoclinic phase with the space group $Pm$ was also observed in the PMN-PT system (Singh & Pandey, 2001). Other work followed these studies demonstrating the existence of another low-temperature monoclinic phase in the PMN-PT system, where the monoclinic phase with the $Cm$ space group transforms into the another monoclinic phase with the $Cc$ space group (Ranjan et al., 2002). This $Cm$-to-$Cc$ phase transition in PMN-PT could not be observed in the x-ray diffraction patterns because this transition leads to superlattice reflections, observed only in the electron and neutron diffraction patterns.
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Fig. 1. A) Modified x-T phase diagram of PMN-PT around the MPB, adapted from Noheda et al. (Noheda et al., 2002a), Noblanc et al. (Noblanc et al., 1996), Choi et al. (Choi et al., 1989) and Li et al. (Li et al., 2006). The MPB includes the phase coexistences $M_B + M_C (Cm + Pm)$, $M_C + T (Pm + P4mm)$ and $T + M_C (P4mm + Pm)$ based on Singh and Pandey’s results (Singh & Pandey, 2003). B) Direction of the polarization in the tetragonal phase, $M_C$ monoclinic phase, $M_B$ monoclinic phase and rohombohedral phase according to Vanderbilt and Cohen’s theory (Vanderbilt & Cohen, 2001).

Ferroelectric solid solutions exhibit high piezoelectric and electromechanical coupling coefficients and high dielectric permittivity at compositions in the MPB. But, what is the real importance of the monoclinic phases on the physical properties of these systems? Since the discovery of a monoclinic phase in PZT and PMN-PT solid solutions, several works have been published to understand the mechanisms responsible for the high piezoelectric response of these materials. The discovery of the monoclinic phases in these systems has catalyzed several exciting experimental (Guo et al., 2000; Bokov & Ye, 2004; Viehland et al., 2004) and theoretical developments (Fu & Cohen, 2000; Vanderbilt & Cohen, 2001). Interesting field-induced phase transitions were discovered in PMN-PT (Chen et al., 2002; Zhao et al., 2003), highlighting the important role of the intermediate monoclinic phase for the large electromechanical response of this material. Theoretical first principles calculations and phenomenological theory considerations have not only confirmed the existence of monoclinic phases in the MPB region but also revealed the dominant role of the rotational instabilities of the polarization vector across the MPB compositions (Fu & Cohen, 2000; Vanderbilt & Cohen, 2001). Further, phenomenological theory considerations have shown that the Devonshire free energy expansion up to the eighth-order term is needed to stabilize the monoclinic phases, indicating the highly anharmonic nature of these materials (Vanderbilt & Cohen, 2001). All these studies have also led to significant modifications of the x-T phase diagrams of these solid solutions (Noheda et al., 2002), including the phase diagram of the PMN-PT system, previously established by Noblanc et al. (Noblanc et al., 1996) and Choi et al. (Choi et al., 1989). Thus, based on these results, a new x-T phase diagram for PMN-PT near the MPB could be constructed, as shown in Fig. 1-(A) with the shaded area.

The monoclinic phase with the $Cm$ space group in the PMN-PT system was first proposed by Ye et al. (Ye et al., 2001) based on high-resolution synchrotron x-ray diffraction studies.
on single crystals for $x = 0.35$. Almost simultaneously, Singh and Pandey (Singh & Pandey, 2001) observed a new monoclinic phase with the space group $Pm$, instead of $Cm$, as Ye et al. proposed, in a study with Rietveld refinements of the x-ray diffraction data from sintered powders with different compositions in the MPB. These results showed that the intrinsic width of the MPB is an order of magnitude smaller than previously believed and that the structure changes abruptly around $x = 0.34-0.35$, from monoclinic ($Pm$) to tetragonal ($P4mm$). Subsequent studies revealed that the structure of the PMN-PT is rhombohedral ($R3m$) for $x < 0.27$, $M_B+M_C$ ($Cn+Cm$) phase coexistence for $0.27 < x < 0.30$, $M_C+T$ ($Pm+P4mm$) phase coexistence for $0.30 < x < 0.34$, $T+M_C$ ($P4mm+Pm$) phase coexistence for $0.34 < x < 0.39$ and tetragonal ($P4mm$) for $x > 0.39$ (Singh & Pandey, 2003; Singh et al., 2002; Li et al., 2006). A study of the molar fractions of different phases in the MPB by Singh and Pandey (Singh & Pandey, 2003) shows that for $M_B+M_C$ phase coexistence the amount of $M_B$ is majority (80-100%), the $M_C$ phase is dominant (70-100%) for $M_C+T$ phase coexistence, while for the $T+M_C$ phase coexistence region the amount of tetragonal one increases from 40% to 70% when $x$ increases from 0.35 to 0.39. Finally, for $x > 0.39$ the phase is purely tetragonal, as indicated in Fig. 1-A. The MPB region shown in Fig. 1-A was constructed based on room temperature dielectric measurements and Rietveld analysis of powder x-ray diffraction data obtained by Singh and Pandey (Singh & Pandey, 2003). Although these results were obtained for room temperature, the x-T phase diagram delineated in Fig. 1-A gives an idea of the complexity of the phase transitions involved in the MPB. Obviously, the structure of the PMN-PT system in the MPB as a function of temperature was much more complicated.

In the above paragraphs, the monoclinic phases $M_A$, $M_B$ and $M_C$ types observed in the PZT and PMN-PT systems were mentioned. The notation can be understood by considering the arguments of stability for the $Pm$ and $Cm$ phases described elsewhere (Vanderbilt & Cohen, 2001). The analysis of the phenomenology of the phase transitions in ferroelectrics is based on the order parameter $P$. In the space group $Pm3m$ cubic phase, $P_x=P_y=P_z=0$. If the polarization $P$ is constrained to a symmetry axis along (001) or (111), the resulting phase becomes tetragonal (space group $P4mm$) and rhombohedral (space group $R3m$), respectively.

A similar analysis can be applied to the $M_A$ (space group $Cm$), $M_B$ (space group $Cm$) and $M_C$ (space group $Pm$) monoclinic phases. For the $M_A$ phase, the magnitudes of the polarization to the pseudocubic cell are $P_x=P_y=P_z$ with $P_z>P_x$, for the $M_B$ phase $P_x=P_y>P_z$ with $P_z>P_x$ and for the $M_C$ phase $P_x=0$ and $P_y>P_z$ (Vanderbilt & Cohen, 2001). The directions of the polarization in the tetragonal, monoclinic ($M_B$ and $M_C$) and rhombohedral phases in the PMN-PT system are shown in Fig. 1-(B).

The observed phases and phase transition in barium titanate, BaTiO$_3$ and ferroelectrics in general were explained by Devonshire (Devonshire, Phil Mag 40, 1040 1949) in terms of the phenomenological Landau theory, based on a sixth-order expansion of the free energy in terms of order parameter $P$. However, the sixth-order Devonshire expansion fails to describe the existence of the monoclinic phase $M_A$ observed initially in the PZT system. A work published in 2000 (Souza et al., 2000) confirms that the Devonshire phenomenological theory is not adequate for predicting the observed monoclinic phase. Then, Vanderbilt and Cohen (Vanderbilt & Cohen, 2001) showed that the simplest extension of the Devonshire theory, including an eighth-order term in the ferroelectric order parameter, admits the monoclinic phases $M_A$, $M_B$ and $M_C$. An extension of the model to a twelfth-order term also predicts a triclinic ferroelectric phase.
3.1 Structural phase transition near the MPB: temperature-dependence

In addition to the complexity interpretation of the PMN-PT transformations for different compositions, the temperature dependence of the structural phase transitions in the MPB is another challenge. Several efforts have been made in the past few years to solve the phase transition problem for the PMN-PT system near the MPB, including structural studies conducted with high-resolution X-ray diffraction, spectroscopic studies (Araújo et al., 2008; Hlinka et al., 2006a) and dielectric analysis (Li et al., 2006; Hlinka et al., 2006b).

Spectroscopic techniques, such as Raman and infrared spectroscopy (IR), are useful tools for investigating phase transitions in polycrystalline materials and single crystals. Infrared spectroscopy can be used to study ferroelectric phase transitions since infrared vibrational frequencies, and consequently the interatomic forces, are affected by the onset of the ferroelectric state due to the temperature phase transitions. In the infrared spectra of the PMN-PT at composition x = 0.35, a broad band is observed from 472 cm$^{-1}$ to 870 cm$^{-1}$ (Araújo et al., 2008). This band is associated with $\nu_1$-(Nb-O), $\nu_1$-(Ti-O) and $\nu_1$-(Mg-O) stretching modes in the PMN-PT structure. The IR curve shape changes slightly when the temperature increases, and these discrete changes as a function of the temperature may be attributed to the phase transitions involved in this system, introduced by distortions in BO$_6$ octahedra.

Considering that an observed infrared spectrum for PMN-PT is a composition of the stretching modes in the BO$_6$ octahedron, each IR spectrum, recorded for different temperatures, can be fitted by considering three lorentzian functions:

$$I = \sum_i I_0 \frac{AW_i}{(\omega - \omega_f)^2 + W_i^2},$$

where $I_0$ is the constant, $\omega$ is the experimental frequency, $\omega_f$ is the fitting frequency, $A$ is the area under curve (associated with the number of the oscillators) and $W$ is the half width. The number of lorentzian functions used to fit each spectrum is assigned based on possible vibration modes in PMN-PT. The PMN-PT system presents a general ABO$_3$ perovskite structure and different phases depending on the PMN/PT ratio. The infrared vibrations for this perovskite family may be explained based on vibrations of the BO$_6$ octahedron (B = Mg, Nb and Ti), similarly to classical perovskites such as the BaTiO$_3$, SrTiO$_3$, PbTiO$_3$ and PbZrO$_3$ octahedron (Last, 1957; Spitzer et al., 1962; Perry et al., 1964). In these structures, the BO$_6$ octahedron presents four distinct vibration modes: $\nu_1$-stretching at higher-frequency and lower-frequency $\nu_2$-torsion, $\nu_3$-bending and $\nu_4$-cation-(BO$_3$) vibrations. These arguments justify the use of three lorentzian functions for analyzing $\nu_1$-stretching within the 400-1000 cm$^{-1}$, since the $\nu_2$, $\nu_3$ and $\nu_4$ vibrations are located in the far infrared region. The $\nu_1$-stretching vibration mode of the BO$_6$ octahedra in the perovskite structure is schematically illustrated in Fig. 2-A.

The shift for lower frequencies of $\nu_1$-stretching modes, as a function of increasing temperature (nonlinear behavior), can be explained by the inverse relationship between atomic separation and vibrational frequency if there is no structural phase transition in the observed temperature range. If we consider that the vibrational amplitude is proportional to the increasing temperature ($A \propto T$), then the nonlinear case described by the restoring force can be written as follows:

$$F(T) = -kT + \varepsilon(T),$$
where \( k \) is the corresponding force constant and \( \varepsilon(T) \) represents the departure from linearity. Expanding \( \varepsilon(T) \) as a power series in equation (2) and solving the differential equation with the successive approximations method, the wavenumber \( \nu(T) \) can be expressed as:

\[
\nu(T) = \sqrt{C_1 - C_2 T^2},
\]

in which \( C_1 \) and \( C_2 \) are constants. This equation describes the behavior of the \( \nu_1 \)-stretching modes as a function of increasing temperature.

The phase transitions for the PMN-PT system by using IR spectroscopy can be understood from the point of view of the group representation, considering the possible symmetries involving the BO\(_6\) octahedron. The cubic symmetry, point group \( O_h \), presents an \( F_{1u} \) species and a single triply degenerate band structure is expected, since three equivalent axes exist in the case of the cubic lattice. When the cubic phase transforms into the tetragonal phase, point group \( C_{4v} \), an \( E \) and \( A_1 \) species appear with the cubic triple degeneracy partially removed. Consequently, a double band structure is expected for the tetragonal phase.

Finally, the \( E \) and \( A_1 \) transform into \( A' \) and \( A'' \) species when the symmetry changes from tetragonal to monoclinic. Thus, a double partially degenerate band structure is also expected for the monoclinic phase.

Under the above considerations, the monoclinic and tetragonal phase coexistence in PMN-PT must be interpreted as a superposing of two double partially degenerate band structures. Considering that these bands occur at very close frequencies, using three lorentzian functions is sufficient to fit each IR spectrum by using Equation (1). To illustrate this discussion, Fig. 2 shows the behavior of the \( \nu_1 \)-(Ti-O) mode as a function of temperature, obtained from the PMN-PT single crystal for composition \( x = 0.35 \) (Araújo et al., 2008). The singularities observed at around 230 K, 300 K and 422 K were interpreted as the result of structural phase transitions induced by the temperature increase while the curves in this figure represent the theoretical fitting of the experimental data by using Equation (3). The anomalous behavior observed for the \( \nu_1 \)-(Ti-O) mode between 230 K and 300 K, where \( \nu(T) \) increases rather than decreases, as predicted by Equation (3), suggests a possible explanation if the coexistence of the monoclinic and tetragonal phases is considered. Thus, based on the previous discussion and supported by the results in the literature (Noheda et al., 2002; Li et al., 2006), the occurrence of the following nondegeneracy \( M_c \) \( \rightarrow \) monoclinic \( (M_c) \) + tetragonal \( (T) \) \( \rightarrow \) tetragonal \( (T) \) \( \rightarrow \) cubic \( (C) \) phase transition can be assumed, as indicated in Fig. 2. The behavior of the \( \nu_1 \)-(Ti-O) mode as a function of temperature observed in Fig. 2 by itself does not allow assessment of the sequence of the above-proposed phase transition without considering the results in the literature obtained from other techniques. However, the linear increase in the \( \nu_1 \)-(Ti-O) mode between 230 K and 300 K is strong evidence in favor of the phase coexistence hypothesis within this temperature interval.

The stability of the monoclinic phase at low temperatures and the phase coexistence in the MPB of the PMN-PT system has also been frequently discussed in the literature. The phase coexistences in this system on zero-field cooling were considered in recent experimental works by using neutron diffraction, high-resolution X-ray diffraction and dielectric analysis (Singh & Pandey, 2006; Li et al., 2006). These studies have discussed the possibility of

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tetragonal-monoclinic (T-M\textsubscript{C}) and tetragonal-monoclinic (T-M\textsubscript{B}) phase coexistence in unpoled PMN-PT ceramics in a wide temperature range. From these studies, the metastable phase diagram for this system in the MPB (see Fig. 7 in Li et al., 2006) was constructed based on the arguments that the (T-M\textsubscript{B}) phase coexistence is a non-equilibrium state and is the result of a local stress field and clampdown and blocking effect. A more recent study on the heterophase structures and the domain state-interface in the PMN-PT system, including the intermediate monoclinic phases (M\textsubscript{B} or M\textsubscript{C}), provides insight into understanding the stress-relief conditions at the phase coexistence near the MPB (Topolov, 2009). A correlation between the domain structures and the unit-cell parameters of adjacent M\textsubscript{B} and M\textsubscript{C} phases in certain temperature ranges could be suggested as the possible origin of the different sequences of phase transitions in solid solutions near the MPB.

3.2 The origin of the morphotropic phase boundary
To explain the large piezoelectric and electromechanical coupling coefficients observed in ferroelectric systems that exhibit an MPB, a polarization rotation model was proposed (Fu & Cohen, 2000; Guo et al., 2000). A giant piezoelectric response has been observed for Pb(Zn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-PbTiO\textsubscript{3} (PZN-PT) and PMN-PT single crystals in the rhombohedral phase, which have a polarization along the \{111\} direction. The crystals respond mechanically with a remarkable increase in strain if a small electric field is applied along the (001) direction. However, when the magnitude of the electric field is increased, a very flat strain-versus-field slope is observed (Fu & Cohen, 2000; Park & Shrout, 1997). Thus, the giant piezoelectric response could be explained by the reorientation of the polar domains, which depends on the mesoscopic structure or ordering, or by the polarization rotation mechanism at the atomic level (Fu & Cohen, 2000). An intuitive explanation for this mechanism can be delineated based on fact that PbTiO\textsubscript{3} is a ferroelectric, which does not present a rhombohedral phase, with a large strain level of 6%. However, if there were a rhombohedral...
phase in PbTiO$_3$, a colossal mechanical strain would be induced by applying an electric field. The model was proposed based on first-principles calculations on the classical BaTiO$_3$ ferroelectric perovskite, by selecting different polarization directions and calculating their internal energies, provided explanations for the experimental observations (Park & Shrout, 1997; Park et al., 1999). Bellaiche et al. (Bellaiche et al., 2000) have succeeded in deriving the monoclinic phase of the PZT system at compositions around the MPB from first-principles calculations, showing that the predicted structural data were in good agreement with the measurements and consistent with the monoclinic phase as an intermediate phase between the tetragonal and rhombohedral phases.

The proposed polarization vector rotation for monoclinic phases in the PMN-PT system is schematically illustrated in Fig. 1-B. As the monoclinic phase represents the structural bridge between the tetragonal (space group $P4mm$) and rhombohedral (space group $R3m$) phases, the symmetry constrains the polarization vector to remain in the monoclinic plane, but is free to rotate within it (Noheda, 2002). The polarization vector of the $M_C$ phase can rotate along the $ac$ plane between the $(001)$ and $(101)$ directions, while the $M_B$ phase can rotate along the $bc$ plane between the $(101)$ and $(111)$ directions, configuring the polarization rotation model. The rotation of the polarization vector along these planes is responsible for the high values observed for the piezoelectric coefficients $d_{33}$ in the PZT and PMN-PT solid solutions, as calculated previously (Bellaiche et al., 2000; Fu & Cohen, 2000). Interesting reviews of advances in understanding the role of the monoclinic phases in structure and high piezoelectricity in lead oxide solid solutions can be found in several references (Noheda, 2002; Noheda & Cox, 2006). Although several authors have reported the existence of the $M_B$ phase for the PMN-PT system, this phase has not yet been effectively observed.

The revision of results and traditional notions acquired about ferroelectrics in the past few decades has led to new ideas and interpretations, demanding new experiments and models to explain the nature of the MPB (Kreisel et al., 2009; Khachaturyan, 2010). Some partial conclusions indicate that the MPB is considered more of a region than a boundary, characterized by two competing coexisting phases. However, some points still remain unclear to explain the giant electromechanical response of ferroelectric solid solutions near the MPB. The apparent violation of the Landau theory of the second-order phase transition, which does not permit a gradual rotation of the polarization vector under an applied electric field in the monoclinic phase, since the transition between different monoclinic phases is expected to occur, has resulted in alternative propositions to explain the phenomenology in the MPB (Khachaturyan, 2010). If the monoclinic phase is considered an adaptive phase, however, an adaptive state can be assumed in the MPB, and thus, gradual polarization rotation is now possible because of the easy rearrangement of nanodomains under the reduced polar anisotropy. The theory of an adaptive phase was developed to predict the ferroelectric transitions in solid solutions near the MPB and is based on stress-accommodating nanotwins domains (Jin et al., 2003; Bhattacharyya et al., 2008). The adaptive concepts have been extended to explain the origin of X-ray and neutron diffraction patterns of ferroelectric solid solutions systems near the MPB, but the existence of the monoclinic phase cannot be completely ruled out at low temperatures (Khachaturyan, 2010). These results demonstrate the necessity of additional experimental studies on traditional systems such as PZT and PMN-PT. The giant electromechanical response studied in PMN-PT single crystals was interpreted as a critical phenomenon such as in the electric-field-temperature-composition ($E$-$T$-$x$) phase diagram of PMN-PT a first-order paraelectric-
ferroelectric phase transition terminates in a line of critical points where the piezoelectric coefficient is the maximum (Kutnjak et al., 2006). In addition, the large piezoelectric response observed at PMN-PT relaxors could be also related to the competition between ordered states at nanoscale in the presence of disorder and to the fact that any weak stress or electric field strongly affects such competition (Dkhil et al., 2009). All this work has provided valuable contributions to understanding the phenomenology behind the MPB.

Exploring theoretical predictions and experimental results for the similar MPB in the pure lead titanate PbTiO$_3$, which appear under high hydrostatic pressure and cryogenics temperatures leading to tetragonal $\rightarrow$ monoclinic $\rightarrow$ rhombohedral phase transition, a more general idea of the morphotropic phase boundary could be introduced with perspectives of developing new high-performance electromechanical materials based on the chemical pressure idea (Ahart et al., 2008). In addition to these very attractive possibilities, observation of a low-symmetry monoclinic phase in the PbTiO$_3$ opened very recent discussions on the arguments that justify the origin of morphotropic phase boundaries in ferroelectrics (Ahart et al., 2008) and arguments against the validity of the rotation polarization model to describe the stability of the phases and the sequence of phase transformation in the MPB in pure PbTiO$_3$ (Frantti et al., 2008). This controversy is very interesting because the discussions illustrate how different ideas promote the advancement of science, showing the richnes behind the research in phase transitions of systems that exhibit the MPB and that this subject is still open to new contributions.

4. Conclusion

Most modern piezoelectric materials used for technological applications are solid solutions that display a transition region in their composition-temperature phase diagrams, known as the morphotropic phase boundary, where the structure changes abruptly and the electromechanical properties exhibit maximal values. Some composition of PMN-PT ceramics, which are simpler to prepare than single crystals, is frequently used for technological applications due to their very high piezoelectric coefficient and electromechanical coupling coefficients. A major problem concerning the application of these electroceramics is the difficulty in producing a pyrochlore-free perovskite structure. Therefore, to prepare high-quality pyrochlore-free PMN-PT ceramics, several methods have been developed over the past three decades. In addition to the technological interest, the scientific comprehension of the origin of the morphotropic phase boundary in these ferroelectric solid solutions was a great challenge in past decades. The discovery of a stable monoclinic phase in the PZT system provides a new perspective to explain the high piezoelectric response of ferroelectric ceramics. The subsequent experimental and theoretical studies provided valuable contributions to understanding the phenomenology behind the MPB and promoted a significant advancement in the area. However, recent new ideas about and interpretations of the structural phase transition in high-performance ferroelectric systems and the nature of the MPB demonstrated that this subject is still open for discussion.

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