

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

5,000

Open access books available

125,000

International authors and editors

140M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Recent Advances in Processing, Structural and Dielectric Properties of PMN-PT Ferroelectric Ceramics at Compositions Around the MPB

Eudes Borges Araújo

*Universidade Estadual Paulista, Departamento de Física e Química Ilha Solteira, SP
Brazil*

1. Introduction

Ferroelectric $(1-x)[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]-x\text{PbTiO}_3$ (PMN-PT) solid solutions are known for their exceptional electromechanical properties, sometimes one order of magnitude larger than classical $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (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}) ($d_{33} \sim 1240$ pC/N and $k_{33} \sim 0.923$), a high dielectric constant ($\epsilon \sim 3100$) with low dielectric loss ($\tan\delta \sim 0.014$) compared to those of polycrystalline ceramics ($d_{33} \sim 690$ pC/N and $k_{33} \sim 0.73$) (Park & Shrout, 1997; Viehland et al., 2001). Recently, researchers have also reported that PMN-PT single crystals have high remanent polarization ($P_r \sim 35$ $\mu\text{C}/\text{cm}^2$) at a low coercive field ($E_c \sim 3.4$ kV/cm), a high dielectric constant ($\epsilon \sim 2500$), low loss tangent ($\tan\delta \sim 0.031$), the highest piezoelectric coefficient ($d_{33} \sim 1500$ pC/N) and a high electrochemical coupling coefficient ($k_{33} \sim 0.82$) for $\langle 112 \rangle$ grain-oriented PMN-PT ceramics (Sun et al., 2004). The piezoelectric coefficient d_{ij} 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 $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ($x = 0$) 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 $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ 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 ($T_C = 490^\circ\text{C}$).

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 $\text{A}_2\text{B}_2\text{O}_7$ (A and B metals) represent a family of phases isostructural to the mineral pyrochlore $(\text{NaCa})(\text{NbTa})\text{O}_6\text{F}/(\text{OH})$ (Subramanian, M.A. et al., 1983). Although $\text{A}_2\text{B}_2\text{O}_7$ compounds exhibit a wide variety of interesting physical properties, in high-performance ferroelectrics such as PMN-PT these compounds should be

avoided due to their paraelectric characteristic (Kamba et al., 2007). The compound $\text{Pb}_{1.83}\text{Mg}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$ (PMN) exhibits a pyrochlore structure (space group $\text{Fd}\bar{3}\text{m}$), 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: $\text{MgO} + \text{Nb}_2\text{O}_5 \rightarrow \text{MgNb}_2\text{O}_6$ and $\text{MgNb}_2\text{O}_6 + 3\text{PbO} \rightarrow 3(\text{PMN})$. This procedure was adopted keeping in mind that the kinetics for liberating Nb_2O_5 from the MgNb_2O_6 columbite phase may be slow enough to prevent the pyrochlore phase from forming and that structure of the MgNb_2O_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_2O_6 calcination step. Thus, powders with perovskite structure have been successfully synthesized with the two-step calcination technique described, where the columbite (MgNb_2O_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

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_2O_5 powder is coated with $\text{Mg}(\text{OH})_2$ in the first step, and in the second step, the $\text{Mg}(\text{OH})_2$ -coated Nb_2O_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 power 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_2O_6 powders, which were used as precursors to produce the PMN phase, obtained by the solid-state reaction between MgNb_2O_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 $\langle 111 \rangle$ -orientation (Araújo 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 $\langle 112 \rangle$ and $\langle 001 \rangle$ 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.

References	PMN ceramics				Comments
	K_{\max} (at 1 kHz)	T_C (°C)			
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	
Sun et al. (2004)	0.30	~1500	0.82	0.51	<112> Grain-oriented ceramics
Sabolsky et al. (2001)	0.32	~1200	0.755	-	<001> Textured ceramics
	0.30	450	-	0.41	
Kelly et al. (1997)	0.33	640	-	0.43	Random-oriented ceramics
	0.35	700	-	0.44	
Park et al. (1997)	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 $x \approx 0.52$ (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 (M_A 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.

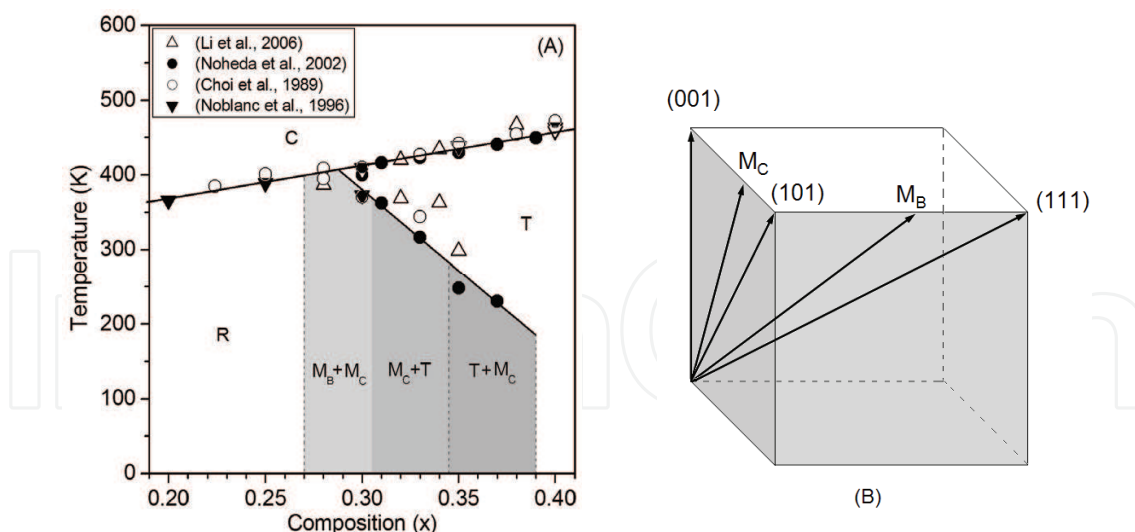


Fig. 1. A) Modified x - T phase diagram of PMN-PT around the MPB, adapted from Noheda et al. (Noheda et al., 2002a), Noblanc et al. (Noblanc et al., 1996), Choi et al. (Choi et al., 1989) and Li et al. (Li et al., 2006). The MPB includes the phase coexistences M_B+M_C ($Cm+Pm$), M_C+T ($Pm+P4mm$) and $T+M_C$ ($P4mm+Pm$) 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 rhombohedral 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 ($Cm+Pm$) 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 \mathbf{P} . In the space group $Pm3m$ cubic phase, $P_x=P_y=P_z=0$. If the polarization \mathbf{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 $P_x=P_y \neq P_z$ with $P_z > P_x$, for the M_B phase $P_x=P_y \neq P_z$ with $P_x > P_z$ and for the M_C phase $P_x=0$ and $P_y \neq P_z$ (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 \mathbf{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 ν_1 -(Nb-O), ν_1 -(Ti-O) and ν_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:

$$I = \sum_i I_0 \frac{AW_i}{(\omega - \omega_f)_i^2 + W_i^2}, \quad (1)$$

where I_0 is the constant, ω is the experimental frequency, ω_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 ($B = \text{Mg, Nb and Ti}$), 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: ν_1 -stretching at higher-frequency and lower-frequency ν_2 -torsion, ν_3 -bending and ν_4 -cation-(BO_3) vibrations. These arguments justify the use of three lorentzian functions for analyzing ν_1 -stretching within the $400\text{-}1000 \text{ cm}^{-1}$, since the ν_2 , ν_3 and ν_4 vibrations are located in the far infrared region. The ν_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 ν_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:

$$F(T) = -kT + \varepsilon(T), \quad (2)$$

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 $\bar{\nu}(T)$ can be expressed as:

$$\bar{\nu}(T) = \sqrt{C_1 - C_2 T^2}, \quad (3)$$

in which C_1 and C_2 are constants. This equation describes the behavior of the ν_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 ν_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 ν_1 -(Ti-O) mode between 230 K and 300 K, where $\bar{\nu}(T)$ 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 *monoclinic* (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 ν_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 ν_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

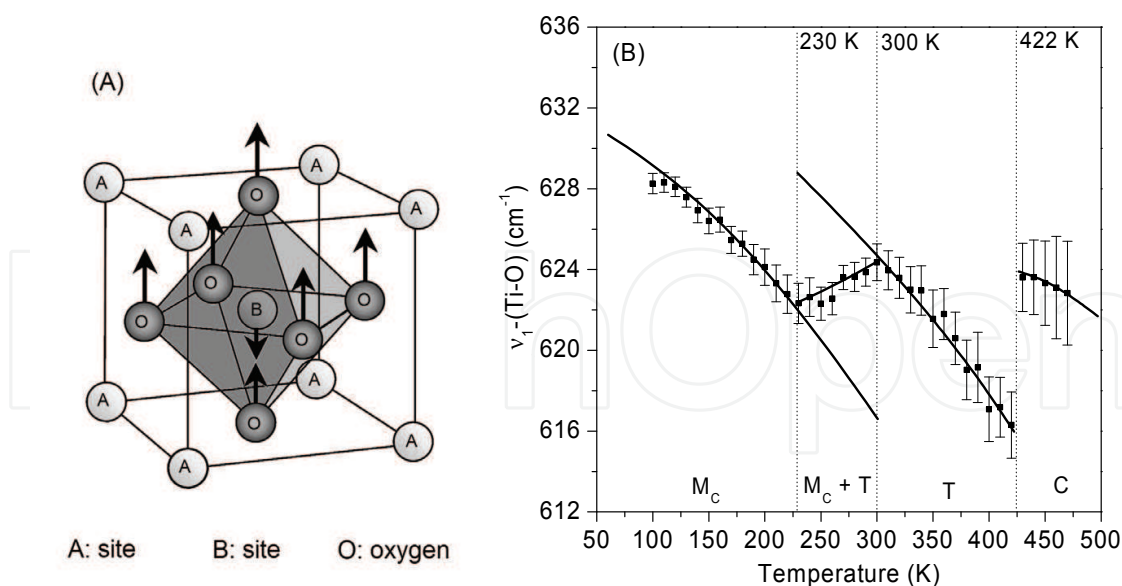


Fig. 2. (A) Schematic infrared-normal active higher-frequency ν_1 -stretching vibration of the BO₆ octahedra in the perovskite structure. (B) Behavior of the ν_1 -(Ti-O)-stretching mode in the BO₆ octahedron in ABO₃ structure of the PMN-PT as a function of the temperature. (Adapted from Araújo et al., 2008).

tetragonal-monoclinic (T-M_C) and tetragonal-monoclinic (T-M_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_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_B or M_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_B and M_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_{1/3}Nb_{2/3})O₃-PbTiO₃ (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 PbTiO₃ 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 richness 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.

5. Acknowledgment

The author is grateful to Brazilian agencies FAPESP, CNPq and CAPES for the financial support for the correlated research. My special thanks to Pró-Reitoria de Pós-Graduação da

UNESP (PROPG) and Fundação para o Desenvolvimento da UNESP (FUNDUNESP) for their financial support for this work.

6. References

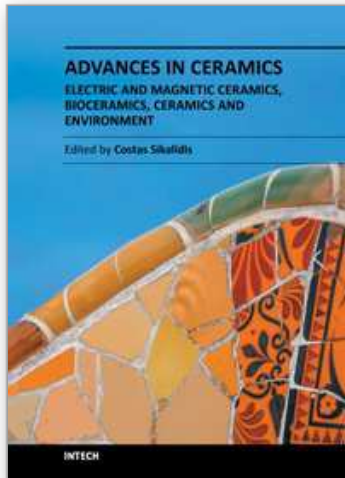
- Ahart, M. et al. (2008). Origin of morphotropic phase boundaries in ferroelectrics. *Nature* 451, 545-549. ISSN 0028-0836
- Araújo, E.B. et al. (2007). Synthesis of slightly <111>-oriented 0.65Pb(Mg_{1/3}Nb_{2/3})O₃-0.35PbTiO₃ ceramic prepared from fine powders. *Materials Chemistry and Physics* 104, 40-43. ISSN 0254-0584
- Araújo, E.B. et al. (2008). Structural phase transition studies on PMN-0.35PT using Infrared Spectroscopy. *Ferroelectrics* 369, 35-42. ISSN 1563-5112
- Arigur, P. & Benguigui, L. (1975). Direct determination of coexistence region in solid-solutions Pb(Zr_xTi_{1-x})O₃. *Journal of Physics D: Applied Physics* 8, 1856-1862. ISSN 1361-6463
- Babooram, K. et al. (2004). Phase formation and dielectric properties of 0.90Pb(Mg_{1/3}Nb_{2/3})O₃-0.10PbTiO₃ ceramics prepared by a new sol-gel method. *Ceramics International* 30, 1411-1417. ISSN 0272-8842
- Baek, J.G. et al. (1997). Synthesis of pyrochlore-free 0.9Pb(Mg_{1/3}Nb_{2/3})O₃-0.1PbTiO₃ ceramics via soft mechanochemical route. *Journal of the American Ceramic Society* 80, 973-981. ISSN 1551-2916
- Bellaiche, L. et al. (2000). Finite-Temperature properties of Pb(Zr_{1-x}Ti_x)O₃ alloys from first principles. *Physical Review Letters* 84, 5427-5430. ISSN 1079-7114
- Bhattacharyya, S. et al. (2008). Direct high-resolution transmission electron microscopy observation of tetragonal nanotwins within the monoclinic M_C phase of Pb(Mg_{1/3}Nb_{2/3})O₃-0.35PbTiO₃ crystals. *Applied Physics Letters* 92, 1429041-1429043. ISSN 1077-3118
- Bokov, A.A. & Ye, Z.G. (2004). Domain structure in the monoclinic Pm phase of Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ single crystals. *Journal of Applied Physics* 95, 6347-6359. ISSN 1089-7550
- Bokov, A.A. & Ye, Z.G. (2006). Recent progress in relaxor ferroelectrics with perovskite structure. *Journal of Materials Science* 41, 31-52. ISSN 1573-4803
- Chen, K.P. et al. (2002). Electric-field-induced phase transition in <001>-oriented Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ single crystals. *Journal of Physics: Condensed Matter* 14, L571-L576. ISSN 1361-648X
- Chen, S.Y. & Chen, I.W. (1994). Temperature-time texture transition of Pb(Zr_{1-x}Ti_x)O₃ thin films: II, Heat treatment and compositional effects. *Journal of the American Ceramic Society* 77, 2337-2344. ISSN 1551-2916
- Choi, S.W. et al. (1989). Morphotropic phase boundary in Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ system. *Materials Letters* 8, 253-255. ISSN 0167-577X
- Cruz, L.P. et al. (2002). An easy way to Pb(Mg_{1/3}Nb_{2/3})O₃ synthesis. *Materials Research Bulletin* 37, 1163-1173. ISSN 0025-5408
- Dkhil, B. et al. (2009). Intermediate temperature scale T* in lead-based relaxor systems. *Physical Review B* 80, 064103-064109. ISSN 1550-235x
- Du, X.J. et al. (1998). Crystal orientation dependence of piezoelectric properties of lead zirconate titanate near the morphotropic phase boundary. *Applied Physics Letters* 72, 2421-2423. ISSN: 1077-3118

- Frantti, J. et al (2008). Evidence against the polarization rotation model of piezoelectric perovskites at the morphotropic phase boundary. *Journal of Physics: Condensed Matter* 20, 472203-472203. ISSN 1361-648X
- Fu, H.X. & Cohen, R.E. (2000). Polarization rotation mechanism for ultrahigh electromechanical response in single-crystal piezoelectrics. *Nature* 403, 281-283. ISSN 0028-0836
- Guerra, J.D.S. et al. (2009). Investigation on dielectric response of PMN ceramics around paraelectric-ferroelectric diffuse phase transition. *Materials Science and Technology* 25, 1316-1320. ISSN 1743-2847
- Gu, H. et al. (2003). Single-calcination synthesis of pyrochlore-free $0.9\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.1PbTiO_3 and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ceramics using a coating method. *Journal of the American Ceramic Society* 86, 217-221. ISSN 1551-2916
- Guo, R. et al. (2000). Origin of the high piezoelectric response in $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$. *Physical Review Letters* 84, 5423-5426. ISSN 1079-7114
- Hatch, D.M. et al. (2002). Antiferrodistortive phase transition in $\text{Pb}(\text{Ti}_{0.48}\text{Zr}_{0.52})\text{O}_3$: Space group of the lowest temperature monoclinic phase. *Physical Review B* 65, 212101-212103. ISSN 1550-235x
- Hlinka, J. et al. (2006). Infrared dielectric response of relaxor ferroelectrics. *Phase Transitions* 79, 41-78. ISSN 1029-0338
- Hlinka, J. et al. (2006). Anisotropic dielectric function in polar nanoregions of relaxor ferroelectrics. *Physical Review Letters* 96, 027601-027604. ISSN 1079-7114
- Johnson, D.W. (1985). Sol-gel processing of ceramics and glass. *American Ceramic Society Bulletin* 64, 1597-1602. ISSN 1551-2916
- Jin, Y.M. et al. (2003). Adaptive ferroelectric states in systems with low domain wall energy: Tetragonal microdomains. *Journal of Applied Physics* 94, 3629-3640. ISSN 1089-7550
- Kamba, S. et al. (2007). Quantum paraelectric behavior of pyrochlore $\text{Pb}_{1.83}\text{Mg}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$. *Physical Review B* 76, 054125-054131. ISSN 1550-235x
- Takegawa, K. & Mohri, J. (1977). A compositional fluctuation and properties of $\text{Pb}(\text{Zr,Ti})\text{O}_3$. *Solid State Communications* 24, 769-772. ISSN 0038-1098
- Kelly, J. et al. (1997). Effect of composition on the electromechanical properties of $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$ ceramics. *Journal of the American Ceramic Society* 80, 957-964. ISSN 1551-2916
- Khachatryan, A.G. (2010). Ferroelectric solid solutions with morphotropic boundary: Rotational instability of polarization, metastable coexistence of phases and nanodomain adaptive states. *Philosophical Magazine* 90, 37-60. ISSN 1478-6443
- Kong, L.B. et al. (2001). Preparation of PMN powders and ceramics via a high-energy ball milling process. *Journal of Materials Science Letters* 20, 1241-1243. ISSN 1573-4811
- Kreisel, J. et al. (2009). Phase transitions and ferroelectrics: revival and the future in the field. *Phase Transitions* 82, 633-661. ISSN 1029-0338
- Kutnjak, Z. et al. (2006). The giant electromechanical response in ferroelectric relaxors as a critical phenomenon. *Nature* 441, 956-959. ISSN 0028-0836
- Kwon, S. et al. (2005). High strain, $\langle 001 \rangle$ textured $0.675\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.325PbTiO_3 ceramics: Templated grain growth and piezoelectric properties. *Journal of the American Ceramic Society* 88, 312-317. ISSN 1551-2916
- Last, J.T. (1957). Infrared-absorption studies on barium titanate and related materials. *Physical Review* 105, 1740-1750. ISSN 1536-6065

- Li, J.B. et al. (2006). Structural transition in unpoled (1-x)PMN-xPT ceramics near the morphotropic boundary. *Journal of Alloys and Compounds* 425, 373-378. ISSN 0925-8388
- Mergen, A. & Lee, W.E. (1997). Fabrication, characterisation and formation mechanism of $\text{Pb}_{1.83}\text{Mg}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$ pyrochlore. *Journal of the European Ceramic Society* 17, 1033-1047. ISSN 0955-2219
- Mishra, S.K. et al. (1996). Effect of phase coexistence at morphotropic phase boundary on the properties of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ceramics. *Applied Physics Letters* 69, 1707-1709. ISSN 1077-3118
- Noblanc, O. et al. (1996). Structural and dielectric studies of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 ferroelectric solid solutions around the morphotropic boundary. *Journal of Applied Physics* 79, 4291-4297. ISSN 1089-7550
- Noheda, B. et al. (1999). A monoclinic ferroelectric phase in the $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ solid solution *Applied Physics Letters* 74, 2059-2062. ISSN 1077-3118
- Noheda, B. et al. (2001). Tetragonal-to-monoclinic phase transition in a ferroelectric perovskite: The structure of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$. *Physical Review B* 61, 8687-8695. ISSN 1550-235x
- Noheda, B. et al. (2001). Stability of the monoclinic phase in the ferroelectric perovskite $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$. *Physical Review B* 63, 014103-014112. ISSN 1550-235x
- Noheda, B. et al. (2002). Phase diagram of the ferroelectric relaxor $(1-x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ - $x\text{PbTiO}_3$. *Physical Review B* 66, 054104-054114. ISSN 1550-235x
- Noheda, B. (2002). Structure and high-piezoelectricity in lead oxide solid solutions. *Current opinion in solid state & materials science* 6, 27-34. ISSN 1359-0286
- Noheda, B. & Cox, D.E. (2006). Bridging phases at the morphotropic boundaries of lead oxide solid solutions. *Phase Transitions* 79, 5-20. ISSN 1029-0338
- Panda, P.K. & Sahoo, B. (2005). Preparation of pyrochlore-free PMN powder by semi-wet chemical route. *Materials Chemistry and Physics* 93, 231-236. ISSN 0254-0584
- Pandey, D. & Ragini (2003). On the discovery of new low temperature monoclinic phases with Cm and Cc space groups in $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$: an overview. *Zeitschrift Fur Kristallographie* 218, 1-7. ISSN 0044-2968
- Pandey, D. et al. (2008). Stability of ferroic phases in the highly piezoelectric $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ ceramics. *Acta Crystallographica Section A* 64, 192-203. ISSN 0108-7673
- Park, S.E. & Shrout, T.R. (1997). Characteristics of relaxor-based piezoelectric single crystals for ultrasonic transducers. *IEEE Transactions on Ultrasonics, Ferroelectrics and Frequency Control* 44, 1140-1147. ISSN 0885-3010
- Pechini, M. (1967). Method of preparing lead and Al-alkaline-earth titanates and niobates and coating method using the same to form a capacitor. U.S. Pat. N° 3 330 697.
- Perry, C.H. et al. (1964). Infrared studies of perovskite titanates. *Physical Review* 135, A408-A412. ISSN 1536-6065
- Randall, C.A. et al. (1998). Intrinsic and extrinsic size effects in fine-grained morphotropic-phase-boundary lead zirconate titanate ceramics. *Journal of the American Ceramic Society* 81, 677-688. ISSN 1551-2916
- Ranjan, R. et al. (2002). Antiferrodistortive phase transition in $\text{Pb}(\text{Ti}_{0.48}\text{Zr}_{0.52})\text{O}_3$: A powder neutron diffraction study. *Physical Review B* 65, 060102-060106. ISSN 1550-235x

- Ranjan, R. et al. (2005). Comparison of the Cc and R3c space groups for the superlattice phase of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$. *Physical Review B* 71, 092101-092104 (2005). ISSN 1550-235x
- Sabolsky, E.M. et al. (2001). Piezoelectric properties of <001> textured $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 ceramics. *Applied Physics Letters* 78, 2551-2553. ISSN 1077-3118
- Sekar, M.M.A. & Halliyal, A. (1998). Low-temperature synthesis, characterization, and properties of lead-based ferroelectric niobates. *Journal of the American Ceramic Society* 81, 380-388. ISSN 1551-2916
- Shrout, T.R. & Swartz, S.L. (1983). Dielectric-properties of pyrochlore lead magnesium niobate. *Materials Research Bulletin* 18, 663-667. ISSN 0025-5408
- Singh, A.K. & Pandey, D. (2001). Structure and the location of the morphotropic phase boundary region in $(1-x)[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]$ - $x\text{PbTiO}_3$. *Journal of Physics: Condensed Matter* 13, L931-L936. ISSN 1361-648X
- Singh, A.K. et al. (2002). Powder neutron diffraction study of phase transitions in and a phase diagram of $(1-x)[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]$ - $x\text{PbTiO}_3$. *Physical Review B* 66, 0541011-0241019. ISSN 1550-235x
- Singh, A.K. & Pandey, D. (2003). Evidence for M_B and M_C phases in the morphotropic phase boundary region of $(1-x)[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]$ - $x\text{PbTiO}_3$: A Rietveld study. *Physical Review B* 67, 064102-064114. ISSN 1550-235x
- Singh, A.K. & Pandey, D. (2006). Powder neutron diffraction study of phase transitions in and a phase diagram of $(1-x)[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]$ - $x\text{PbTiO}_3$. *Physical Review B* 74, 024101-024119. ISSN 1550-235x
- Singh, A.K. et al. (2007). High-resolution synchrotron x-ray diffraction study of Zr-rich compositions of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ($0.525 \leq x \leq 0.60$): Evidence for the absence of the rhombohedral phase. *Applied Physics Letters* 91, 192904-192907. ISSN 1077-3118
- Singh, A.K. et al. (2008). Origin of high piezoelectric response of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ at the morphotropic phase boundary: Role of elastic instability. *Applied Physics Letters* 92, 022910-022913. ISSN 1077-3118
- Souza, A.G. et al. (2000). Monoclinic phase of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ ceramics: Raman and phenomenological thermodynamic studies. *Physical Review B* 61, 14283-14286. ISSN 1550-235x
- Souza, A.G. et al. (2002). Raman scattering study of the $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ system: Rhombohedral-monoclinic-tetragonal phase transitions. *Physical Review B* 66, 132107-132111. ISSN 1550-235x
- Subramanian, M.A. et al. (1983). Oxide pyrochlores - A review. *Progress in Solid State Chemistry* 15, 55-143. ISSN 0079-6786
- Sun, S. et al. (2004). Fabrication and electrical properties of grain-oriented $0.7\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.3PbTiO_3 ceramics. *Applied Physics Letters* 84, 574-576. ISSN 1077-3118
- Swartz, S.L. & Shrout, T.R. (1982). Fabrication of perovskite lead magnesium niobate. *Materials Research Bulletin* 17, 1245-1250. ISSN 0025-5408
- Swartz, S.L. et al. (1984). Dielectric properties of lead-magnesium niobate ceramics. *Journal of the American Ceramic Society* 67, 311-315. ISSN 1551-2916
- Spitzer, W.G. et al. (1962). Far infrared dielectric dispersion in BaTiO_3 , SrTiO_3 and TiO_2 . *Physical Review* 126, 1710-1962. ISSN 1536-6065

- Topolov, V.Yu. (2009). Monoclinic phases and stress-relief conditions in $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{TiO}_3$ - $x\text{PbTiO}_3$ solid solutions. *Journal of Alloys and Compounds* 480, 568-574. ISSN 0925-8388
- Isupov, V.A. (1975). Comments on the paper "x-ray study of the pzt solid solutions near the morphotropic phase transition". *Solid State Communications* 17, 1331-1333. ISSN 0038-1098
- Viehland, D. et al. (2001). Piezoelectric instability in $\langle 011 \rangle$ -oriented $\text{Pb}(\text{B}_{1/3}\text{B}_{2/3}^{\text{II}})\text{O}_3$ - PbTiO_3 crystals. *Applied Physics Letters* 79, 1006-1009. ISSN 1077-3118
- Viehland, D. et al. (2004). Domain structure changes in $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$ with composition, dc bias, and ac field. *Journal of Applied Physics* 96, 3379-3381. ISSN 1089-7550
- Vanderbilt, D. & Cohen, M.H. (2001). Monoclinic and triclinic phases in higher-order Devonshire theory. *Physical Review B* 63, 094108-094117. ISSN 1550-235x
- Wang, H.C. & Schulze, W.A. (1990). The role of excess magnesium oxide or lead oxide in determining the microstructure and properties of lead magnesium niobate. *Journal of the American Ceramic Society* 73, 825-832. ISSN 1551-2916
- Woodward, D.I. et al. (2005). Review of crystal and domain structures in the $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ solid solution. *Physical Review B* 72, 104110-04118. ISSN 1550-235x
- Ye, Z.G. & Dong, M. (2000). Morphotropic domain structures and phase transitions in relaxor-based piezo-/ferroelectric $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$ single crystals. *Journal of Applied Physics* 87, 2312-2320. ISSN 1089-7550
- Ye, Z.G. et al. (2001). Monoclinic phase in the relaxor-based piezoelectric/ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 system. *Physical Review B* 64, 184114-184119. ISSN 1550-235x
- Yokota, H. et al. (2009). Crystal structure of the rhombohedral phase of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ ceramics at room temperature. *Physical Review B* 80, 104109-104121. ISSN 1550-235x
- Yoon, K.H. et al. (1995). Characteristics of lead magnesium niobate thin-film prepared by sol-gel processing using a complexing agent. *Journal of the American Ceramic Society* 78, 2267-2270. ISSN 1551-2916
- Zhao, X.Y. et al. (2003). Effect of a bias field on the dielectric properties of $0.69\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.31PbTiO_3 single crystals with different orientations. *Journal of Physics: Condensed Matter* 15, 6899-6908. ISSN 1361-648X



**Advances in Ceramics - Electric and Magnetic Ceramics,
Bioceramics, Ceramics and Environment**

Edited by Prof. Costas Sikalidis

ISBN 978-953-307-350-7

Hard cover, 550 pages

Publisher InTech

Published online 06, September, 2011

Published in print edition September, 2011

The current book consists of twenty-four chapters divided into three sections. Section I includes fourteen chapters in electric and magnetic ceramics which deal with modern specific research on dielectrics and their applications, on nanodielectrics, on piezoceramics, on glass ceramics with para-, anti- or ferro-electric active phases, of varistors ceramics and magnetic ceramics. Section II includes seven chapters in bioceramics which include review information and research results/data on biocompatibility, on medical applications of alumina, zirconia, silicon nitride, ZrO₂, bioglass, apatite-wollastonite glass ceramic and b-tri-calcium phosphate. Section III includes three chapters in applications of ceramics in environmental improvement and protection, in water cleaning, in metal bearing wastes stabilization and in utilization of wastes from ceramic industry in concrete and concrete products.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Eudes Borges Araújo (2011). Recent Advances in Processing, Structural and Dielectric Properties of PMN-PT Ferroelectric Ceramics at Compositions Around the MPB, *Advances in Ceramics - Electric and Magnetic Ceramics, Bioceramics, Ceramics and Environment*, Prof. Costas Sikalidis (Ed.), ISBN: 978-953-307-350-7, InTech, Available from: <http://www.intechopen.com/books/advances-in-ceramics-electric-and-magnetic-ceramics-bioceramics-ceramics-and-environment/recent-advances-in-processing-structural-and-dielectric-properties-of-pmn-pt-ferroelectric-ceramics->

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the [Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License](#), which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.

IntechOpen

IntechOpen