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

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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 $^\circ\text{C}$. 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 $^\circ\text{C}$ 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.

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