Materials Research, Vol. 7, No. 2, 369-372, 2004.

# Temperature Coefficient of Piezoelectric Constants in $Pb(Mg_{1/3}\ Nb_{2/3})O_3$ - $PbTiO_3$ Ceramics

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Received: May 29, 2003; Revised: December 7, 2003

In this work, the thermal stability of piezoelectric constants of PMN-PT ceramics in the tetragonal and rhombohedral phases were investigated in a wide range of temperatures. The results showed that the tetragonal PMN-PT presented higher thermal stability and, consequently, the temperature coefficients for the piezoelectric constants were approximately zero. This result revealed to be much better than that commonly found for PZT ceramics. Although the rhombohedral PMN-PT presented a slight lower thermal stability, the values found for the coupling factor were significantly higher than the tetragonal composition.

**Keywords:** *temperature coefficient, PMN-PT, hot pressing, coupling factor*

## 1. Introduction

It is well known that the field of electroceramics is driven by technology and device applications. Doubtless, among the vast number of ferroelectric ceramic systems, that one based on $Pb(Mg_{1/3}\ Nb_{2/3})O_3$ - $PbTiO_3$ (PMN-PT) certainly shows one of the broadest range of technological applications. For instance, it includes ultra-precision positioners, high dielectric constant capacitors and ultrasonic motors[1,2].

Over the last decades piezoelectric ceramics have been introduced into microelectronic products. However, their thermal stability, which means the independence of the piezoelectric properties in relation to the temperature, is a fundamental parameter required for practical purposes. It is important that piezoelectric ceramics have low temperature coefficients (TC), where zero value is highly desirable. Studies conducted on lead zirconate titanate ferroelectric ceramics, $Pb(Zr, Ti)O_3$ or PZT, have suggested that TC is dependent on the Zr/Ti ratio[3]. These investigations have been centered in the temperature coefficient of the frequency constant (TCN). It has been reported that the sign and the magnitude of TC can change abruptly for compositions near the morphotropic phase boundary (MPB)[3], which is the region in the phase diagram separating the rhombohedral, monoclinic and tetragonal symmetries in the case of PZT and PMN-PT. Near the MPB ferroelectric systems exhibit outstanding electromechanical properties[4,5]. It is also attributed that the ceramic processing or the poling condition can shift the expected crystalline phase to another in the vicinity of MPB (due to changes in the stoichiometric) or induce phase transition, respectively.[3] In addition, it is reported that for PZT based ceramics TCN is positive for the tetragonal phase and negative for the rhombohedral phase, respectively[6,7].

TCN has been considered a reference to determine the thermal stability of piezoelectric ceramics. When TCN is zero due to some specific ceramic processing or poling condition, it is supposed that all temperature coefficients are minimized. However, it has been observed that almost all published works are focused on the temperature coefficient of the frequency constant in PZT ceramics.

The aim of this work is to investigate the thermal stability of piezoelectric constants of $PbMg_{1/3}Nb_{2/3}O_3$ -$PbTiO_3$ ceramics in the tetragonal and rhombohedral phases. To conduct this work, piezoelectric characterizations were performed in order to determine the temperature depend-

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Articles presented at the XV CBECIMAT, Natal - RN, November de 2002.

ence of the coupling factor ($k_{31}$), the frequency constant ($N_{31}$) and the elastic constant ($s_{11}^{E}$) in a temperature range from 213 K to 333 K. The results are compared and discussed in relation to those observed and predicted for PZT ceramics taking into account the crystalline phase.

## 2. Experimental

(1-x)$PbMg_{1/3}Nb_{2/3}O_3$ – (x)$PbTiO_3$ ceramic powders, with x = 0.3 (rhombohedral) and x = 0.4 (tetragonal), were prepared through the columbite method. These samples will be labeled as PMN-0.3PT and PMN-0.4PT, respectively, hereafter. The experimental procedure is described in details in a previous work[8]. Briefly, the analytical graded precursor oxides were mixed in a ball mill using isopropyl alcohol as solvent and stabilized $ZrO_2$ balls as grinding medium. After that, the powder was calcined at 1173 K for 4 h, ball milled for 10 h and dried. The hot-pressed ceramics were densified at 1523 K for 3 h under a pressure of ~5 MPa in controlled oxygen atmosphere. X-ray diffraction analysis revealed only the perovskite phase for x = 0.4, while weak traces of the pyroclore phase ($Pb_3Nb_4O_{13}$) were observed in the composition x = 0.3. Scanning electron microscopy (SEM) showed that both samples have a homogeneous and crack free microstructure and that the average grain size lies between 2 - 3 µm for the ceramics of both compositions. The relative apparent density determined by the Archimedes' method was around 98%. The sintered ceramic bodies were cut in a bar shape with ~7 × 3 mm$^2$ and polished to a thickness of ~ 0.5 mm. After that, they were annealed at 900 K for 1 h to release mechanical stresses introduced during polishing. In order to make the measurements, gold electrodes were sputtered onto the sample surfaces. The samples were poled under optimized poling conditions: an electric field of 10 kV/cm (for the PMN-0.3PT) and 25 kV/cm (for the PMN-0.4PT), during 0.5 h at 350 K[8]. These conditions guarantee a complete ferroelectric domain reorientation in the electric field direction, which leads to a macroscopic polarization and, consequently, the induction of the piezoelectric effect in the ferroelectric ceramic[9, 10]. The piezoelectric measurements were performed in a temperature range from 213 K to 333 K. The results presented below are an average of 16 measurements. The thermal variation of generic piezoelectric constant ($\Delta X$) was determined in relation to the room temperature ($X_{(293\ K)}$) with the formula:

$$\Delta X = [(X_{(T)} - X_{(293\ K)})100\%] / X_{(293\ K)} \qquad (1)$$

where $X_{(T)}$ is the generic piezoelectric constant at a certain temperature.

The temperature coefficient of the piezoelectric constant ($TCX_{(ppm/K)}$) was computed in the temperature range whole investigated, supposing a linear temperature dependence, i.e.:

$$TCX_{(ppm/K)} = X_{(T)} - X_{(293\ K)} / 110X_{(293\ K)} \qquad (2)$$

## 3. Results and Discussions

The piezoelectric characterization performed at room temperature showed that tetragonal and rhombohedral PMN-PT compositions have high piezoelectric constants, as summarized in Table 1. The found constants are similar to those reported in other works for ceramics with similar compositions[11, 12], revealing the high quality of the samples. It is observed that in general the PMN-0.3PT presents higher piezoelectric constants than that of the PMN0.4PT . This result may be related to the fact that the composition of the PMN-0.3PT is nearest to the monoclinic phase[13], in which the piezoelectric properties are maximized[13, 14].

Figure 1 shows the temperature dependence of the coupling factor, $k_{31}$, for both compositions. It is observed that the $k_{31}$ for the PMN-0.3PT presents an excellent thermal stability, showing practically no changes in the whole temperature range investigated. On the other hand, for the PMN-0.4PT, the $k_{31}$ does not present a well-defined feature, having positive and negative variations. However, the maximum oscillation is limited only to 3.7 %.

Figure 2 shows the thermal variation of the frequency constant, $N_{31}$, for the PMN-0.3PT and PMN-0.4PT ceramics. On the contrary to that observed in Fig. 1 for the $k_{31}$, the frequency constant for the PMN-0.3PT ceramic reveals some variation. It can be seen a quasi-linear decreasing with the increase of the temperature, while the $N_{31}$ for the PMN-0.4PT is almost temperature independent. These values are comparable to those obtained for PZT near the MPB[15].

The thermal variation of the elastic constant $s_{11}^{E}$ for both PMN-PT ceramics is shown in Fig. 3. Analogously to that verified for the frequency constant in Fig. 2, the tetragonal composition (PMN-0.4PT) reveals a high thermal stability in the whole temperature range investigated. However, the rhombohedral composition shows a reasonable linear increasing of the $s_{11}^{E}$ with the increase of the temperature.

The results showed that the PMN-0.4PT ceramic presents

**Table 1.** Room temperature piezoelectric (coupling factor $K_{31}$ and frequency constant $N_{31}$), elastic ($S_{11}$) and dielectric ($\varepsilon_{33}$) constants for the PMN-0.3PT and PMN-0.4PT ceramics (24 h after the poling process).

| Sample | $k_{31}$ | $N_{31}$ Hz.m | $\varepsilon_{33}$ 1 kHz | $s_{11}^{E}10^{-12}$ m$^2$/N |
|---|---|---|---|---|
| PMN-0.3PT | 0.43 | 1728 | 3020 | 4.6 |
| PMN-0.4PT | 0.28 | 1747 | 2600 | 4.3 |

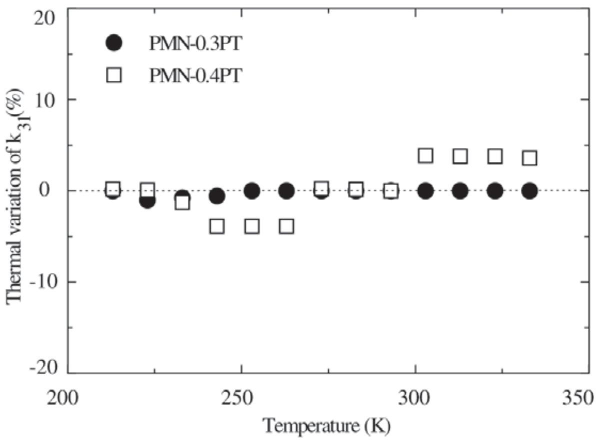

**Figure 1.** Thermal variation of the coupling factor ($k_{31}$) for the PMN-0.3PT and PMN-0.4PT ceramics.

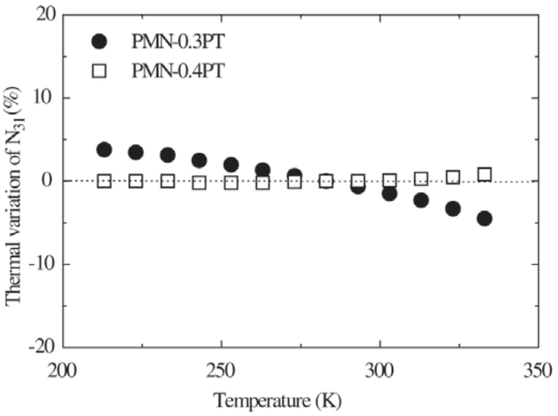

**Figure 2.** Thermal variation of the frequency constant ($N_{31}$) for the PMN-0.3PT and PMN-0.4PT ceramics.

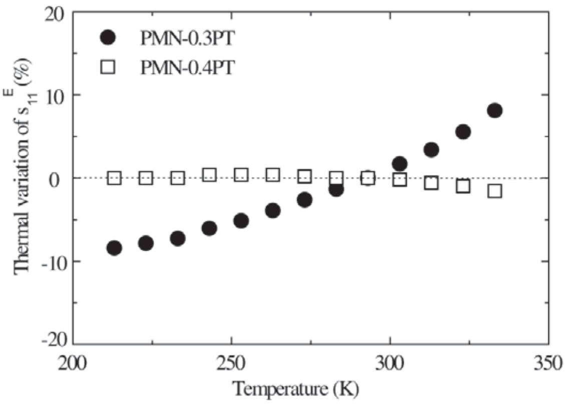

**Figure 3.** Thermal variation of the elastic constant $s_{11}$ for the PMN-0.3PT and PMN-0.4PT ceramics.

higher thermal stability than the PMN-0.3PT ceramic and, consequently, the temperature coefficients for all piezoelectric constants were approximately zero even taking into account the small fluctuations observed in the $k_{31}$. The results also bring two contrasts when they are compared to those observed for other piezoelectric ceramics. First, according to the literature[3,16], it is expected that piezoelectric ceramics in the tetragonal phase show a positive TC for $N_{31}$, which was not verified here. These results remarkably reveal that piezoceramics in the tetragonal phase do not have necessarily a positive TC, thus being a specific characteristic of each material. Second, as reported in the introduction, anomalies in the TC can be related to changes in crystalline phase induced by applying a high electric field, as previously verified for PZT ceramics[3,16]. Therefore, it is also possible to conclude that a shift to the rhombohedral phase was not induced in the PMN-04PT during poling process. This fact can be explained assuming either the PMN-04PT needs higher electric field to induce a phase transition or the compositions investigated in the PZT case were very close to the MPB, where low electric fields are able to induce a phase transition. The second hypothesis seems to be more reasonable since saturation conditions were applied in the poling process of the PMN-0.4PT.

On the other hand, for the rhombohedral composition, the $N_{31}$ shows the standard characteristic, which means a negative TC. Although the value found for $TCN_{31}$ is 4.8 ppm/K, it is much lower than that found for PZT ceramics[3,15]. The composition PMN-0.3PT is close to the MPB[13] but no anomalies were observed in the $TCN_{31}$, which means that no different phases were induced by preparation or poling processes. In addition, the value found for the $TCs_{11}$ is 1380 ppm/K that is much higher than that found for the other constants.

The data reveal that for the tetragonal composition the thermal variation and TC are approximately zero for all eletromechanical constants. However, this feature is not followed by the rhombohedral composition. It is commonly considered that the optimization of the piezoelectric ceramics for practical purposes is reached when $TCN_{31}$ tends to zero. Nevertheless, our results show that this is not general true because it was found for PMN-PT ceramics that the suppression of $TCN_{31}$ does not mean the suppression of other temperature coefficients. In order to obtain a high performance of an electrical device it is imperative to know what is the piezoelectric constant of interest to determine specifically its thermal stability. Although the PMN-0.4PT ceramics presented lower constants for the electromechanical properties compared to the PMN-0.3PT ceramics, these coefficients are still comparable to those of PZT ceramics with the advantage of presenting much better thermal stability. Therefore, PMN-0.4PT is certainly a promising material to be widely employed in the electronic industry.

## 4. Conclusion

The thermal stability of the piezoelectric constants of tetragonal and rhombohedral PMN-PT ceramics shows that the tetragonal composition is thermally more stable, consequently the temperature coefficients for the piezoelectric constants are approximately zero. The rhombohedral PMN-PT presents a slight lower thermal stability, but it is still similar to that observed for the PZT ceramics. Therefore, these results show the high quality of the samples and their high potential to be applied in electronic industry.

## Acknowledgements

The authors thank FAPESP and CNPq for the financial support.

## References

1. Uchino, K. *Ferroelectric Devices - Marcel Dekker*, Inc., 2000.
2. Takagi, H.; Sakata, K.; Takenaka, T. *Jnp. J. Appl. Phys.*, v. 32, p. 4280, 1993.
3. Liang, C.K.; Wu, L.; Wu, *T.S. Ferroelectrics*, v. 120, p.185, 1991.
4. Guo, R.; Cross, L. E.; Park, S-E.; Noheda, B.; Cox, D. E.; Shirane, G. *Phys. Rev. Lett.*, v. 84, p. 5423, 2000.
5. Park, S-E; Hackenberger, W. *Curr. Opin. Solid, St. M.*, v. 6, p. 11, 2002.
6. Thomann, H.; Wersing, W. *Ferroelectrics*, v. 40, p.189, 1982.
7. Wersing, W. *Ferroelectrics*, v. 37, p. 611, 1981.
8. Lente, M. H.; Zanin, A. L.; Assis, S. B.; Santos, I. A.; Garcia, D.; Eiras, J.A. *J. Eur. Ceram. Soc,* v. 24, p. 1529, 2004.
9. Lente, M. H.; Eiras, J.A. *J. Appl. Phys.*, v. 89, p.5093, 2001.
10. Lente, M. H.; Eiras, J.A. *J. Appl. Phys.*, v. 92, p. 2112, 2002.
11. Chen, Y.; Hirose, S.; Viehland, D.; Takahashi, S.; Uchino, K. *Jnp. J. Appl. Phys.*, v. 39, p. 4843, 2000.
12. Chen, Y. W.; Uchino, K.; Shen, M.; Viehland, D. *J. Appl. Phys.*, v. 90, p.1455, 2001.
13. Noheda, B.; Cox, D. E.; Shirane, G.; Gao, J.; Ye, Z. *G. Phys. Rev. B*, v. 66, p.054104, 2002.
14. Noheda, B.; Cox, D. E.; Shirane, G.; Guo, R.; Jones, B.; Cross, L. E. *Phys. Rev. B*, v. 63, p. 014103, 2001.
15. Lente, M.H.; Eiras, J.A. *Anais do 38° Congresso Brasileiro de Cerâmica* v.1, p.132, 1994. In portuguese.
16. Liao, J.H.; Cheng, S.Y.; Wang, C.M. *Ferroelectrics*, v. 106, p.357, 1990.