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Effect of the composition and sintering process on the electrical properties in $Pb(Mg_{1/3}\ Nb_{2/3})O_3$–$PbTiO_3$ ceramics

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Abstract

The effects of the composition and the sintering process on the ferroelectric, dielectric and electromechanical properties in $(1\text{–}x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ ceramics with $0.1 \leqslant x \leqslant 0.4$ were investigated. It was found that the densification process was strongly dependent on the amount of PT. For the lowest concentration of PT the microstructure of the both hot-pressed and conventional sintered samples were very similar, reflecting in almost identical electrical properties. Nevertheless, it was noticed that the higher amount of PT higher was the deviation of the electrical properties between the conventional and the hot-pressed samples. The gradual decreasing of the physical properties of the conventional sintered ceramics was related to the gradual decrease of the density and inhomogeneous microstructure. The results also revealed that for the lower concentration of lead titanate a relaxor behavior is noticed with a high electrostrictive effect, which was almost hysteretic free. However, higher amount of lead titanate led to a ‘‘normal’’ ferroelectric behavior.

Keywords: Electrical properties; Hot pressing; Microstructure-final; Perovskites; Sintering

1. Introduction

Several advances on the development of the functional ceramic materials have recently opened a wide range of possible technological applications. For instance, piezoelectric and electrostrictive actuators for ultraprecision positioning[1] as well as high dielectric constant capacitors[2] have been extensively developed. Undoubtedly, among all materials, the complex perovskite lead magnesium niobate lead titanate (PMN–PT) has emerged as a high quality material due to its excellent electrical and electromechanical properties.[3,4] However, it is well known that composition diagram and microstructure play an important role to understand and improve the physical properties of the ferroelectric materials for practical purposes.[2] It has been reported that PMN–PT presents a variety of structural phase transitions covering rhombohedral, tetragonal and finally pseudo-cubic phases depending on the amount of PT.[5] However, recently, the existence of a monoclinic phase in this system was reported.[6] Thus, the possible crystal symmetries can result in either a well-known ferroelectric relaxor or in a ‘‘normal’’ ferroelectric. Additionally, another point that must be considered in the study of the PMN–PT ceramics is the relationship between the densification process and the physical properties. It is well known that grain size and porosity play a fundamental role on the dielectric and electromechanical behavior.[7] Doubtless, the microstructure characteristic can be controlled through the densification process. Although there are well-established methods of sintering, a suitable choice of parameters such as time of sintering, temperature and pressure (for pressure assisted processes) for each composition are fundamental to obtain stoichiometry samples and secondary phase free. Therefore, intrinsic (i.e. crystal symmetry) and extrinsic (i.e. porosity, grain size) factors govern the physical properties of the ferroelectric ceramics as a whole, thus it being necessary for their complete control in order to produce high quality materials.

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The objective of this work is to investigate the influence of the composition and sintering processes on the ferroelectric, dielectric and electromechanical properties in $(1-x)PbMg_{1/3}Nb_{2/3}O_3$–$(x)PbTiO_3$ ceramics with $0.1 \leqslant x \leqslant 0.4$ densified through conventional sintering or by uniaxial hot-pressing.

2. Experimental procedure

$(1–x)PbMg_{1/3}Nb_{2/3}O_3$–$(x)PbTiO_3$ ceramic powders, with $x=0.1$ and 0.3 (rhombohedral) and 0.4 (tetragonal), were prepared through the columbite method. Two distinct densification procedures, i. e., conventional sintering and hot-pressing technique were employed in this study. The ceramics will be labeled hereafter as PMN–0.1PT-CON, PMN–0.3PT-CON and PMN–0.4PT-CON for the samples sintered conventionally and PMN–0.1PT-HP, PMN–0.3PT-HP and PMN–0.4PT-HP for the hot-pressed samples. 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, then ball milled for 10 h and dried. The conventional ceramics were sintered at 1473 K for 3 h in a saturated PbO atmosphere. The hot-pressed ceramics were also densified at 1473 K for 3 h under a pressure of $\sim$5 MPa in a controlled oxygen atmosphere. X-ray diffraction analysis (not shown here) revealed only the perovskite phase for $x=0.1$ and 0.4, while traces of the pyroclore phase ($Pb_3Nb_4O_{13}$) were observed in the composition for $x=0.3$. Scanning electron micrographs (SEM) showed that all obtained samples have a homogeneous and crack free microstructure. Excluding the PMN–0.3PT-CON, no segregated phase could be identified in the SEM analysis. The relative density was around 98 and 92% for the hot-pressed and conventional samples, respectively. The sintered ceramic bodies were cut into a bar shape of $\sim 5\times4$ mm^2 and polished to a thickness of $\sim$0.5 mm for the dielectric, ferroelectric and electrostrictive measurements. 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. Hysteresis loops were measured in a Sawyer–Tower set up applying a triangular electric field of amplitude of 15–25 kV/cm at 1 Hz. This frequency is low enough to avoid the self-heating, which can change drastically the ferroelectric response.[8] The samples were immersed in silicone oil and the measurements were made at room temperature. Computer assisted dielectric characterization, as a function of frequency (from 1 kHz to 1 MHz), were made employing an Impedance Analyzer HP 4194A from $\sim$100 to $\sim$600 K using a home-made furnace and a cryogenic refrigeration system (APD Cryogenics Inc.). The electric field-induced strain measurements were performed employing a MTI-2000 Fotonic^{TM} Sensor, applying a triangular electric field of amplitude of 15 kV/cm at 100 mHz and at room temperature.

3. Results and discussion

Fig. 1 (a)–(f) shows the fracture surface micrographs of all compositions and sintering processes. It is clear that, for the conventional processed ceramic, the PT amount induces microstructural changes in the PMN material. Smaller average grain size and higher porosity level was found as PT was increased. For the hot pressed PMN–PT ceramics, the microstructure is almost independent of PT content. Since all the samples were processed under the same conditions of temperature and time, it can be concluded that the pressure assisted process accelerated the sintering mechanisms and leaded PMN–PT ceramic bodies to the final sintering stage. It can be presumed that longer sintering times (> 3 h) or higher sintering temperatures (> 1473 K) can provide

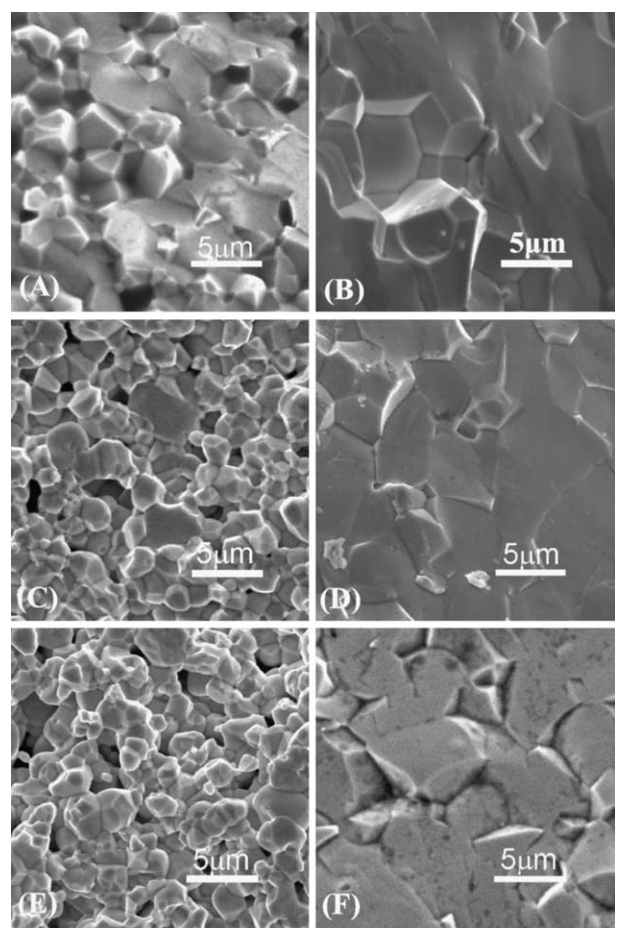

Fig. 1. Microstructure dependence on the composition and the sintering process for: (a) PMN–0.1PT-CON; (b) PMN–0.1PT-HP; (c) PMN–0.3PT-CON; (d) PMN–0.3PT-HP; (e) PMN–0.4PT-CON; (f) PMN–0.4PT-HP.

denser ceramics in the case of the conventionally processed PMN–PT ceramics, especially for $x = 0.3$ and 0.4.

Fig. 2 (a)–(c) shows the dielectric permittivity dependence on the temperature for all compositions and densification procedures at 1 kHz. The insets in each part of the figure show the frequency dependence of the electrical permittivity for the hot-pressing sintering process. It is verified that the composition containing 10% of PT shows a strong relaxor behavior, while a slight relaxor characteristic is still noticed for the composition with 30% of PT. However, this feature disappears for 40% of PT and the material becomes a "normal" ferroelectric. The same behavior is verified for the conventional sintered samples. Consequently, the phase transition temperature, T_{max}, is higher and the transition is less diffuse for the tetragonal sample. Additionally, it is also verified in Fig. 2 that for each respective composition the samples obtained through the uniaxial hot-pressing method present a lower temperature phase transition in relation to samples obtained by the conventional sintering process. Remarkably, the data reveal that the higher the amount of PT the smaller is the difference between the temperature phase transition for the respective samples. Since no lead oxide atmosphere control was made during the hot-pressing, stoichiometric variation can be responsible for that T_{max} difference, especially for the lower PT content composition, in which PbO volatilization is higher. On the other hand, small grain size and high porosity level of the highest PT content in the conventional sintered ceramics, as shown in Fig. 1, led to relative low dielectric constants.

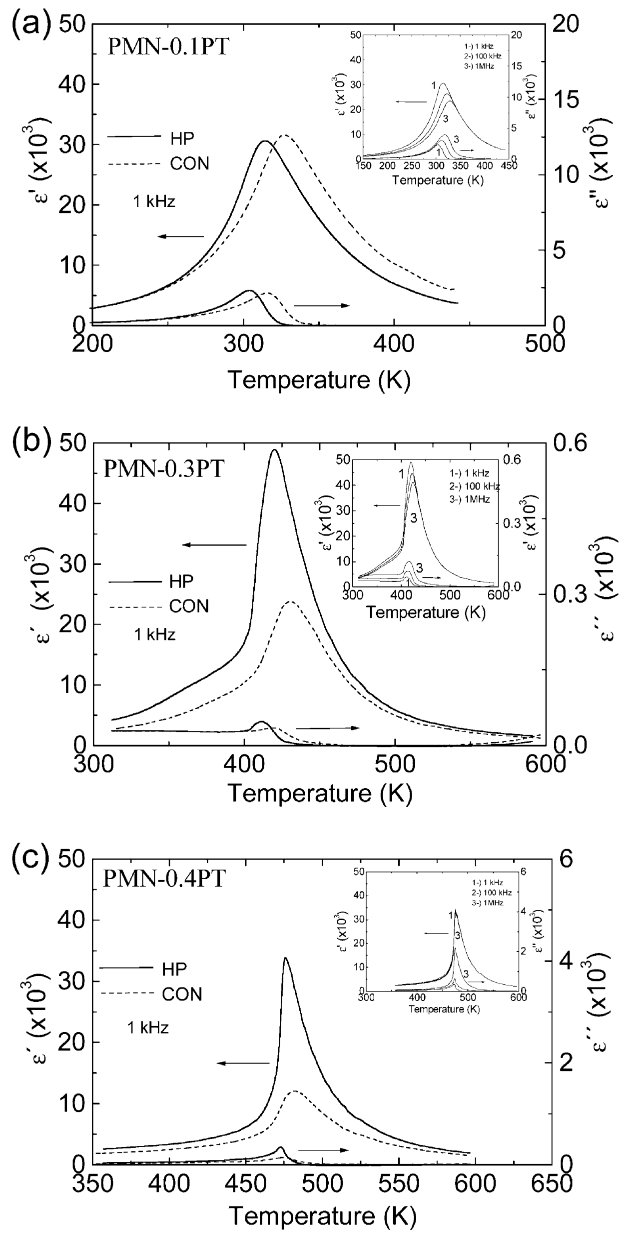

Fig. 2. Dielectric permittivity dependence on the temperature for all compositions and densification procedures: (a) PMN–0.1PT; (b) PMN–0.3PT; (c) PMN–0.4PT. The insets in each figure show the frequency dependence of the electrical permittivity for the hot pressing sintering process.

Fig. 3(a)–(c) shows the electric field induced-strain results obtained for all compositions and densification processes. In accordance with the dielectric behavior presented in Fig. 2(a), the electric field induced-strain results for the samples with 10% PT reveal an electrostrictive feature that is typical of the relaxor materials. It is verified that the conventional sample presents a reasonable similar performance in relation to the hot-pressed one, although a lower value and a slightly more pronounced hysteresis are noticed. On the other hand, the strain curve butterfly-like shape, observed in Fig. 3(b) and (c) reflect the "normal" ferroelectric characteristic due to a higher amount of PT added in the PMN, which enables the formation and coarsening of macro domains. For the highest amount of PT (40%), which corresponds to the tetragonal phase, the electric field induced-strain shows higher coercive field and the strain curves tend to be much less saturated than for the composition with 30% of PT. Again, the effect of the densification route is remarkable. The results show that the samples sintered conventionally, present a smaller electric induced-strain than the respective counterpart composition.

Fig. 4(a) and (b) shows the hysteresis loops for the PMN–0.3PT and PMN–0.4PT, respectively. The results reveal that the hot-pressed samples present higher values for the polarization than the conventional ones. In addition, the rhombohedral composition shows a more squared curve with a lower coercive field.

The effect of the densification process on the physical properties seems to be stronger for a higher concentration of PT. As verified in Fig. 1, for 10% of PT the microstructure for the hot-pressed and the conventional samples are very similar and the data show that the physical properties for both sintering methods do not reveal a sensitive difference between them. Nevertheless, a higher amount of PT seems to deviate the results obtained for the conventional sintering from the results obtained for the hot pressing process. It is noticed that the higher the amount of PT for the conventional samples, the lower the density and the grain size distribution. Therefore, the relative inferior quality of the physical properties of the conventional sintered ceramics can be associated with the gradual decrease in the density, and perhaps some non-stoichiometry, promoted by the continuous addition of PT. For instance, the electrostrictive property is directly related to the dielectric permittivity, which is highly microstructure sensitive.[7] Therefore, the fact that the conventional sintered samples present smaller densification rate and, consequently, higher porosity levels, justify the lower ϵ' values, thus reducing the strain values in comparison with the hot-pressed ones. Another fact that must be considered is the presence of the depolarizing fields induced, for example, by space charges.[7,9] It is reported that the space charges density increases decreasing the average grain size or increasing the porosity.[7] Therefore, the possible high concentration of the space chargers in the conventional sintered samples, which induce depolarizing fields, can be related to the lower electrical permittivity values[7] and higher temperature of the phase transition,[10] as observed in Fig. 2.

The continuous addition of PT in the PMN induces a transformation from a nanodomain to macrodomain, which means, from relaxor to "normal" ferroelectric behavior.[11] Thus, for the lower amount of PT, the PMN–PT sample presents exclusively a short-range order, allowing a diffuse phase transition being strongly frequency dependent [Fig. 2(a)]. These kinds of materials have slim quadratic hysteresis loop [Fig. 3(a)], which develop piezoelectric properties only under DC bias.[12]

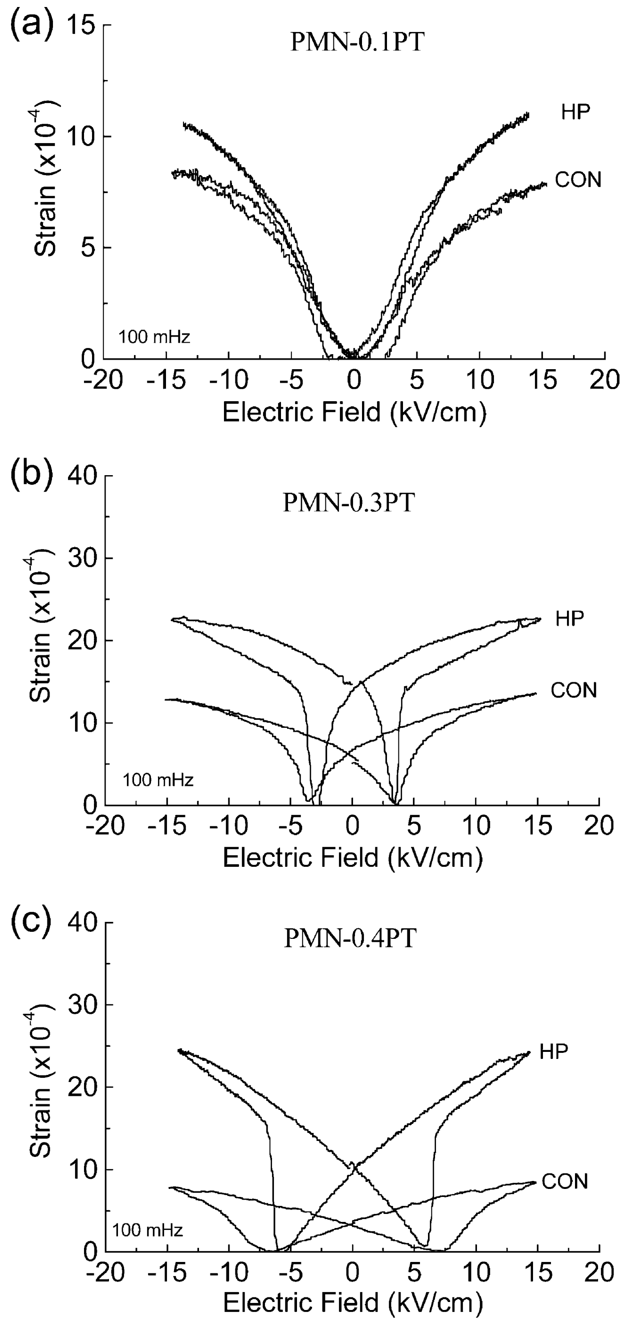

Fig. 3. Electric field induced-strain results obtained from all compositions and sintering processes: (a) PMN–0.1PT; (b) PMN–0.3PT; (c) PMN–0.4PT.

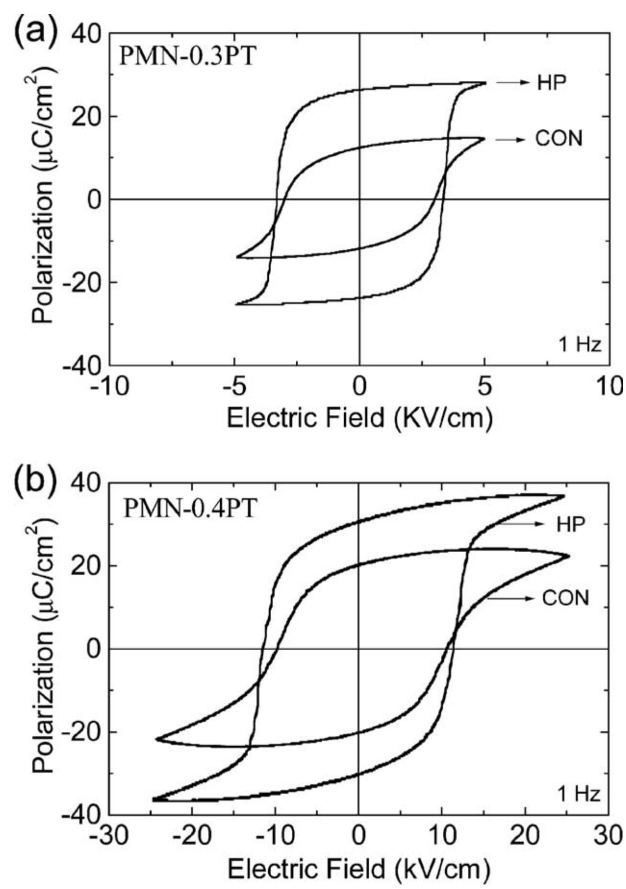

Fig. 4. Ferroelectric hysteresis loops for the: (a) tetragonal phase; (b) rhombohedral phase.

However, the macrodomain state induces a "normal" ferroelectric state, reflecting in the physical properties. Indeed, Figs. 2 and 3(b) and (c) show this behavior. It is noticed that the rhombohedral composition, although still having a subtle relaxor behavior, presents a butterfly-like curve with lower coercive field in comparison with the tetragonal composition. Additionally, the higher coercive field observed in the tetragonal composition can be related to the internal stress, which is associated with the lattice distortion.[13] The high distortion found in the tetragonal compositions induces a considerable stress, thus increasing sensitively E_C.[14]

4. Conclusion

This work was to investigate the influence of the composition and sintering process on the ferroelectric, dielectric and electromechanical properties in the PMN–PT ceramics densified through conventional sintering and by uniaxial hot-pressing. For the lowest concentration of PT the microstructure and the electrical properties for the hot-pressed and the conventional samples were almost identical, while a deviation of the electrical properties was noticed for higher concentration of PT. Dielectric relaxor behavior for the rhombohedral sample was found to lower concentration of lead titanate, where high electrostrictive effect was observed. A higher amount of lead titanate induced a normal ferroelectric behavior with high polarization values and high electric field induced-strain.

Acknowledgements

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