Modified lead titanate zirconate system: preparation techniques and properties

A. PELÁIZ BARRANCO*, A. HUANOSTA TERA, L. BAÑOS, J. GUZMÁN MENDOZA
Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360 México D.F. 04510, México

O. PÉREZ MARTÍNEZ, F. CALDERÓN PIÑAR
Facultad de Física, Universidad de La Habana, San Lázaro y L, Vedado. La Habana 10400, Cuba
E-mail: pelaiz@ffuh.fmq.uh.edu.cu

The development of ferroelectric ceramics is driven by the need for functional ceramics. The most striking properties of these materials are strong coupling effects, strong hysteresis in the field polarization response, and extremely high dielectric permittivity. These properties render them desirable for manufacture of electromechanical transducers, actuators and electric capacitors [1].

Lead titanate zirconate (PZT) is one of the ferroelectric ceramics most commonly utilized in the electroceramic industries, owing to its excellent properties [2]. Although various modifications of PZT and the effects of additives on piezoelectric properties have been studied extensively, the solid solution of complex compounds with perovskite structure have been studied very little to improve the piezoelectric properties [1, 3].

Ceramic materials prepared by a mixed oxide route have spatial fluctuations in their compositions. The extent of the fluctuation depends on the characteristics of the starting powders as well as on the processing schedule. Such process variables as the mode and the extent of mixing of the powders, calcination temperature and time, compaction pressure, sintering atmosphere, time and temperature, have all been found to have a significant effect on the homogeneity of the ceramic systems. The fluctuations usually have an undesirable effect on the properties. Better homogeneity has been reported in samples in which powders made by processes such as sol-gel or coprecipitation have been used [4, 5].

In this report, the $PbCuNbO_3$-$PbTiO_3$-$PbZrO_3$ ferroelectric ceramic system was prepared by hot pressing and standard ceramic techniques in order to compare the main properties for both methods. The nominal composition considered was: $PbZr_{0.50}Ti_{0.44}(Cu_{1/4}Nb_{3/4})_{0.06}O_3$ with 0.5 mol % MnO_2 additions in order to increase the quality factor (Q_m). Table I shows the most important parameters for both techniques.

The crystallographic and microstructural analyses were realized using an X-ray diffractometer, SIEMENS D500 (35 kV, 30 mA) and CuK_α radiation, and a Leika Cambridge (Stereoscan 440 model) scanning electron microscope (SEM), respectively. The diffraction patterns showed a perovskite structure from both preparation techniques. A mixture of two phases: tetragonal (TP) and rombohedral (RP) was obtained [6]. The ratio TP/RP was 5.6 and 0.4 for ceramic (CS) and the hot-pressed (HPS) samples, respectively. These results depend on the processing schedules of the samples and these have an important effect on the properties of each sample.

Fig. 1 shows the micrographs for both samples. It can be seen that the HPS has a more homogeneous grain structure and a larger average grain size than the CS. The HPS have the highest density (ρ), electromechanical coupling coefficients (k_p, k_{31}), quality factor (Q_m) and maximum permittivity (ε_m), as shown in Table II. The dielectric losses are lower in this case.

Fig. 2 shows the dependence of the dielectric losses on temperature for both techniques, obtained using a PM6303 RLC bridge. They are lower for the HPS, but in each case a gradual increment of the dielectric parameter and a small relative maximum at Curie point (343 °C) is observed. This dependence

TABLE I Parameters for both methods of preparation

Method	Calcination		Compaction pressure (MPa)	Sintering	
	T (°C)	Time (h)		T (°C)	Time (h)
Ceramic	800	1	300	1220	2
Hot pressing*	600	3	6	1000	1

*For this technique, the calcination and milling were carried out simultaneously using a ball mill and the ceramics were sintered under a pressure of 6 MPa.

*Permanent address: Facultad de Física, Universidad de La Habana, San Lázaro y L, Vedado. La Habana 10400, Cuba.
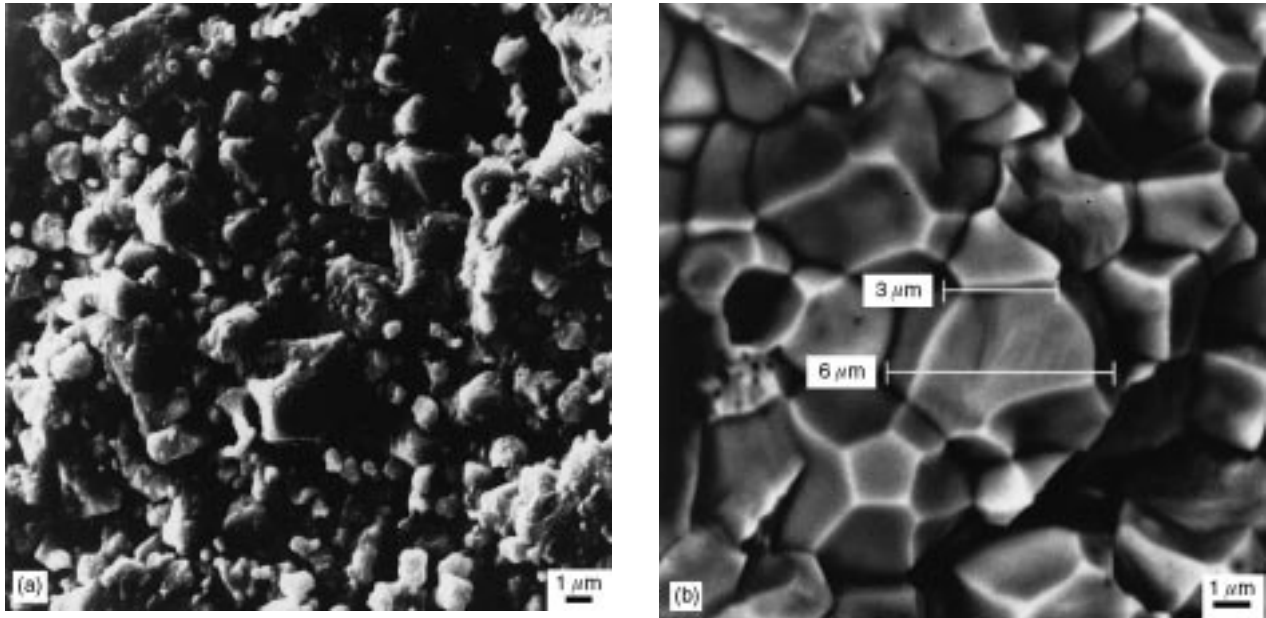
Figure 1 SEM micrographs for (a) ceramic sample, (b) hot-pressed sample. The hot-pressed sample shows a larger average grain size than that of the ceramic sample.

TABLE II Dielectric and piezoelectric properties for both preparation techniques

Method	ρ (g cm^{-3})	k_p	k_{31}	Q_m	$\tan\delta$ (25 °C)	ε_m ($T_c = 343$ °C)
Ceramic	7.21	0.24	0.14	284	0.02	7948
Hot pressing	7.61	0.40	0.23	886	0.004	14858

Note: k_p, k_{31} and Q_m were calculated at the resonance–antiresonance frequencies. $E_p = 3$ kV mm^{-1} (poling field).
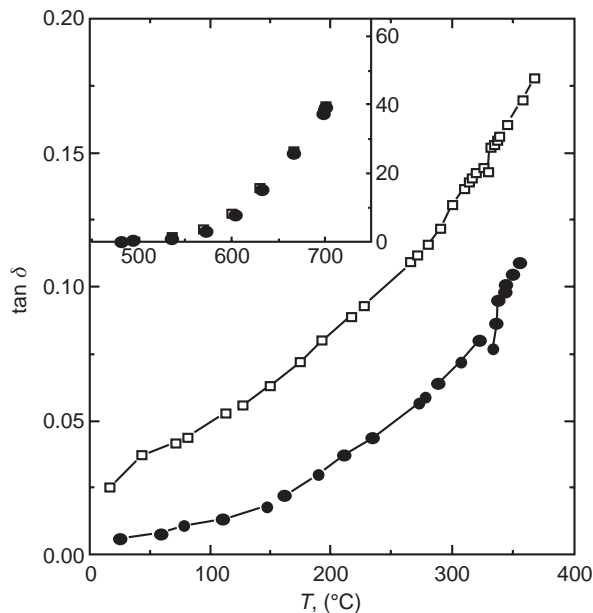

Figure 2 Temperature dependence of dielectric losses for (□) ceramic, (●) hot-pressed samples. They are lower for the hot-pressed sample, but in each case a gradual increment of the dielectric parameter and a small relative maximum at the Curie point (343 °C) is observed.

suggests an undesirable ohmic conductivity effect associated with the mobile particles.

In order to obtain some insight into this phenomenon, the a.c. measurements were performed using an HP 4192A impedance analyzer controlled by an HP85 microcomputer. At temperatures below the Curie point in the impedance plots only a fraction of an arc is observed for each sample. Above that temperature a single semicircle is observed in the HPS. A parallel RC equivalent circuit was assigned to this response and capacitance values in the order of hundreds of pF were calculated using the NLLS-fit program [7]. This result was associated with the bulk grain properties [8]. The CS showed two contributions as the temperature rises in the complex impedance plane. In the same way, it was assumed that the ceramic response could be approximated by two RC parallel equivalent circuits [7]. Fig. 3 shows both measured and simulated curves using the proposed equivalent circuit at a selected temperature for both preparation techniques (532 °C). The a.c. response of the two techniques (ceramic and hot pressing) was markedly different, particularly that part associated with the low frequency: only the CS shows a second semicircle ($R_2 C_2$). However, in some systems, an intergranular blocking phase of different composition to the bulk crystals may give another contribution to the bulk crystal in the a.c. data planes [9], there is no evidence for such a second phase here. That is, on extended exposure, X-ray diffraction patterns taken from the solid bulk samples showed that there was no evidence of a second phase. Using the relation $\omega RC = 1$, which holds at the maximum of an ideal semicircle, the capacitances of the high (C_1) and low (C_3) semicircles
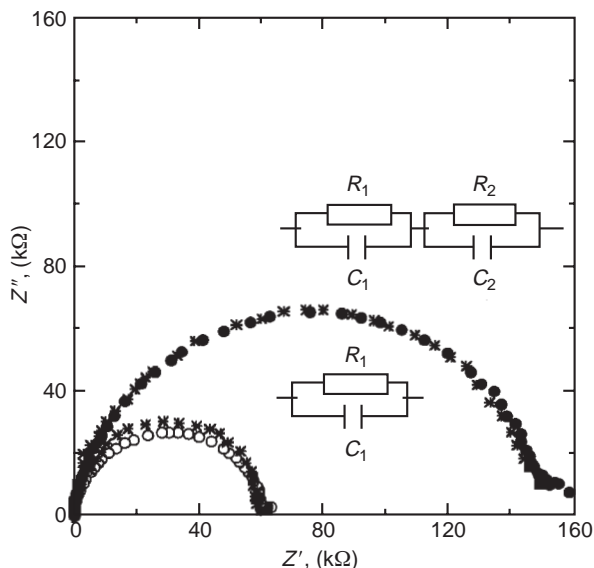
Figure 3 Both measured and simulated (∗) curves using the proposed equivalent circuit at a selected temperature for both preparation techniques (532 °C). A parallel RC equivalent circuit was assigned to the hot-pressed response (○) (bulk response). Two RC parallel equivalent circuits were associated to the ceramic response (●) (bulk and grain boundary response). The subscripts 1 and 2 are assigned to the bulk and grain boundary response, respectively.

were calculated and their temperature dependences were plotted (Fig. 4). The parameter C_1 decreases when the temperature increases (Curie–Weiss behavior) and C_2 remains almost constant. Then, the first semicircle is associated with the ferroelectric bulk ($R_1 C_1$) whereas the second depends on the grain boundary polarization ($R_2 C_2$), respectively.

Around 600 °C a poorly resolved arc appears for both cases and approximate calculations gave capacitance values in the order of μF, which means that the response comes from the electrode region.
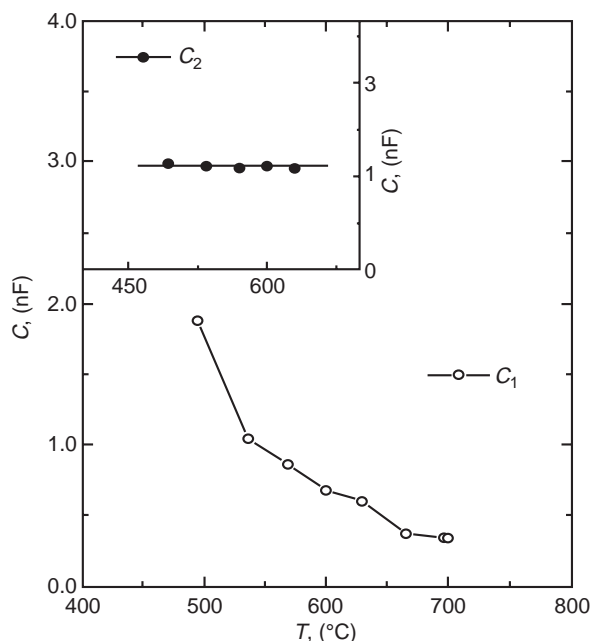

Figure 4 Temperature dependence of the bulk and grain boundary capacitance of ceramic sample. Bulk capacitance values decrease when the temperature increases and grain boundary capacitance remains almost constant. The subscripts 1 and 2 are assigned to the bulk and grain boundary response, respectively.

Ideal blocking behavior at the electrode-sample interface, which is signified by a limiting low frequency, vertical spike in the complex impedance plane, was not observed with the present ferroelectric system. A detailed study of the electrode-sample response has not been made although some preliminary observations were made.

In a previous report [10], we concluded qualitatively that the grain boundary contribution may be treated as a separate or partly resolved second semicircle in the complex plane plots, depending on the relative magnitudes of the resistivity for the bulk and grain boundary. This depends on the grain size. The CS exhibits a lower grain size and an inhomogeneous microstructure; this shows the grain boundary response. The HPS showed an anomalous effect above 450 °C (paraelectric phase), where the dielectric permittivity at 1 kHz increased as the temperature increased [8]. This phenomenon was associated with electrode effects even below 600 °C, but there was no grain boundary response in any temperature range and the electrode effect was barely observed above 600 °C in the impedance plots. The grain size and an homogeneous grain structure limit the grain boundary contribution in the complex impedance plane.

The resulting bulk resistivity values transformed into electric conductivity (σ) show results ranging from 10^{-7}–10^{-4} $\Omega\,cm^{-1}$ for both samples from ferroelectric to paraelectric phase, which are characteristics of semiconductor materials. Thus, the presence of the electrode region in the electric response and the electric conductivity values support our own results of the temperature dependence of dielectric losses even at low temperatures because of the σ values.

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