Available online at www.sciencedirect.com

Journal of the European Ceramic Society 23 (2003) 1337–1343

www.elsevier.com/locate/jeurceramsoc

Influence of synthesis process on the AC response of PLZT (8/65/35) ferroelectric ceramics

A. Peláiz Barranco[a,c], A. Huanosta Tera[a], R. Valenzuela Monjaras[a], J. Antonio Eiras[b,*], D. Garcia[b], F. Calderón Piñar[c], O. Pérez Martínez[c]

[a]Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, Apartado Postal 70-360 Mexico, D.F. 04510, Mexico
[b]Universidad Federal de São Carlos, Depto. de Física, Rod. Wash. Luis, km. 235, 13.565-905- São Carlos-SP, Brazil
[c]Facultad de Física-Instituto de Materiales y Reactivos, Universidad de La Habana, San Lázaro y L, Vedado, La Habana 10400, Cuba

Received 19 May 2001; received in revised form 28 July 2002; accepted 7 August 2002

Abstract

AC conductivity measurements have been carried out to study the dielectric characteristics of a ferroelectric PLZT (8/65/35). The initial powders were synthesized by two different methods: conventional mixed oxides and a chemical coprecipitation method. In both cases, the final ceramic bodies were obtained by an uniaxial hot-pressing step. The grain and grain boundary responses have been separated and a mixture of ionic-electronic conductivity was evaluated from the Arrhenius dependence. The preparation techniques led to different absolute conductivity values for each contribution (grain, σ_g, or grain boundary, σ_{gb}). The samples prepared by the mixed oxide method (MO) showed a higher bulk conductivity than those prepared by the coprecipitation method (CP). This result was explained taking into account the different concentration of charge carriers in MO than CP samples, influenced by the PbO content in the grain boundary. The dielectric analyses showed classical ordinary relaxor-dielectrics with a diffuse phase transition, which was markedly larger in the oxide-milled method (MO). The conductive mechanisms and their influence on the dielectric behavior were studied and led to the conclusion that they affect the dielectric permittivity measurements. The dielectric permittivity without the conductivity component showed a phase transition with lower dispersion for both preparation techniques.

Keywords: AC response; Dielectric properties; Electrical conductivity; Ferroelectrics properties; PLZT

1. Introduction

An appropriate control of the physical properties of synthetic solids has been attempted in the last few years by means of different routes of synthesis. The aim is to get high quality materials capable of maintaining their performance characteristics for long periods of time, even under severe working conditions.

The Pb(Zr,Ti)O_3 (PZT) ferroelectric system has been studied intensively for technological applications. These compounds crystallize in the ABO_3 perovskite structure type, where the A and B-sites are occupied by Pb^{2+} and (Zr^{4+},Ti^{4+}) ions, respectively. The additions of modifiers that are soluble into the lattice provide the possibility to control their electrical properties.[1,2]

A wide range of compositions of (Pb,La;Zr,Ti)O_3 (PLZT) ferroelectric ceramics have been investigated with emphasis on dielectric, piezoelectric and pyroelectric properties.[3] It has also been observed that this system exhibits a diffuse phase transition and relaxation behavior for several compositions.

AC methods have become a useful method for the characterization of ferroelectric systems; in these techniques, the electric response is collected over a wide frequency range. A particular advantage is gained in the case of polycrystalline specimens, whose electrical response is naturally more complex to analyze than that from a single crystal. AC methods may allow a separation of the electric behavior of grains, from that of grain boundaries, and also from the electrode region.[4]

In this paper we report the ac response of PLZT ceramics using conventionally mixed oxides and chemical coprecipitation techniques to obtain the ceramic composition. In both cases, the final ceramic bodies

---

* Corresponding author. Tel.: +55-16-260-8227; fax: +55-16-261-4835.

E-mail addresses: eiras@df.ufscar.br or josea.eiras@terra.com.br (J. Antonio Eiras).

PII: S0955-2219(02)00288-1

were obtained by an uniaxial hot-pressing step. The purpose of the paper is to compare the two different processing methods concerning the ac response.

2. Experimental

Samples of polycrystalline PLZT 8/65/35 with nominal composition $Pb_{1-x}La_x(Zr_{1-y}Ti_y)_{1-x/4}O_3$ (with Zr/Ti ratio of 65/35, 8% La content, and assuming a B-site vacancy formula), were prepared by two different methods: the classic ceramic mixed oxide (MO) method and the coprecipitation (CP) technique.

For the first preparation method (MO), the powder was prepared using high-purity reagent grade lead, titanium, zirconium, and lanthanum oxides in the appropriate molar compositions. After milling and drying, the mixture of oxides was calcined at 950 °C for 3.5 h in air, and then ground in polyethylene bottles with water and zirconia cylinders, for 15 h. Thick discs (~10 mm of thickness) were uniaxially cold pressed and the ceramic bodies were then densified by uniaxial hot-pressing (1150 °C/2 h/3500 psi).

In the second case (CP), the previously prepared PLZT powder, with 2 wt.% of PbO excess, was dissolved in HNO_3 and then precipitated with ammonia hydroxide (pH ~ 9–10), washed with alcohol and filtered. The precipitate slurry was dried under vacuum at room temperature and calcined at 900 °C, for 3.5 h. It was then ground for 15 h in acetone. The final densification was performed by uniaxial hot-pressing (1100 °C/2 h/3500 psi). Details about preparation methods can be found in.[5]

Scanning electronic micrographs showed a mean grain size around 0.7 and 1.5 μm for MO and CP ceramics, respectively. It can be seen from the micrographs (Fig. 1) that CP sample(s) presented fully transgranular, while OM sample(s) showed intregranular as well as transgranular fracture characteristics. It is well known that intergranular fracture in ceramics occurs when in grain boundaries thin layers, as PbO liquid phase for example, are present [5,6]. In this way, it can be assumed the difference of the fracture characteristics between CP and OM samples is related to the PbO amount in grain boundaries. It is well known that PbO will have a higher activity in powders prepared through

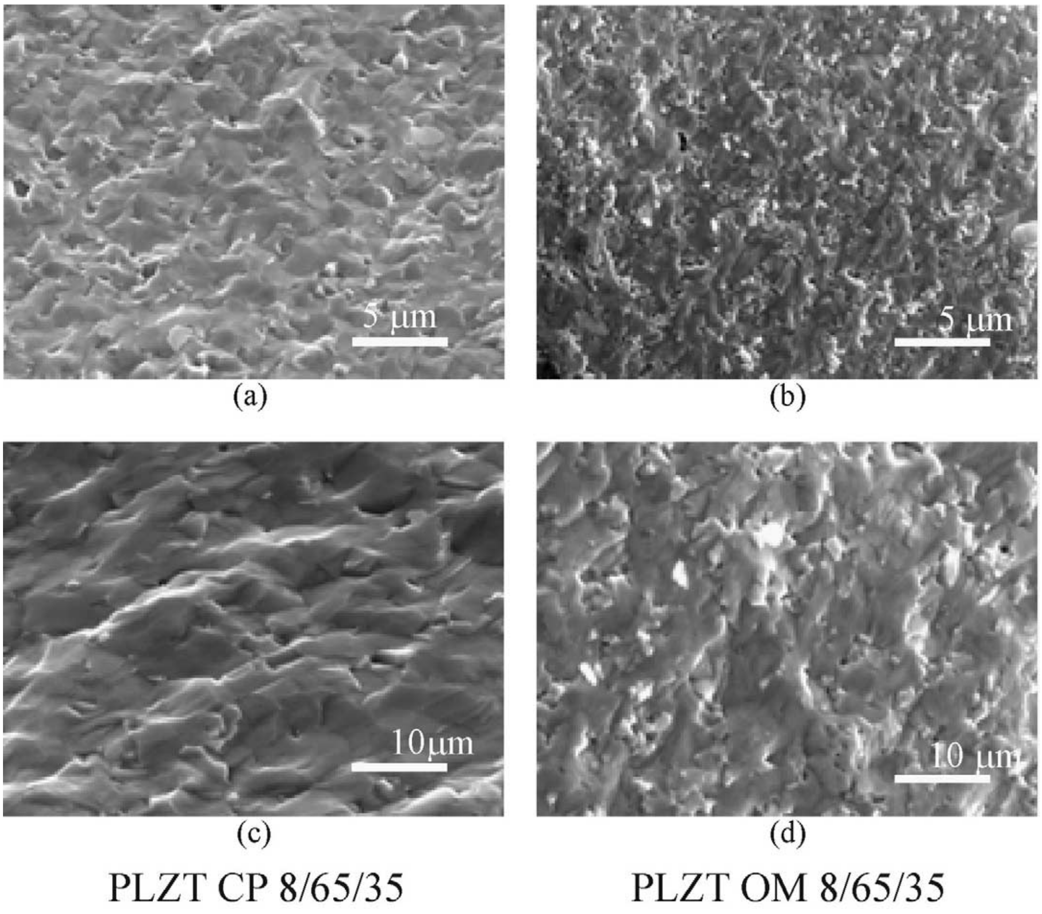

Fig. 1. Fracture micrographs of PLZT 8/65/35: (a), (c) CP and (b), (d) OM ceramics.

chemical routes. Therefore, it is expected a greater PbO loss for CP sample(s), resulting in lesser PbO content in grain boundaries, as compared to OM sample(s).

Flat specimens were used for dielectric property measurements, with approximate dimensions 1×3×4 mm. Electrodes were fabricated on the largest parallel faces by using Au strips and an organogold paste. They were then placed inside a vertical furnace, where the temperature varies ±2 °C with respect to the preset value. By using the two-probe configuration, impedance data was collected over the frequency range 5 Hz–13 MHz, under an applied voltage of 1V, with a Hewlett Packard 4192A Impedance Analyzer. Measurements were carried out isothermally allowing thermal equilibrium by leaving the furnace at the preset temperature 60–90 min before each frequency run. Measurements provide the real and imaginary parts of impedance as frequency-dependent values.

3. Results and discussion

Cole-Cole plots, Z'' (Z'), of both types of samples showed evidence of more than one overlapping semicircle above 400 °C (Fig. 2) because the responses in the impedance plane exhibited deformed semicircles whose center appears below the real axes. Below that temperature it was not possible to obtain resolved semicircles because the sample conduction was below the sensitivity of our equipment. Polycrystalline materials show irregular semicircles because of the overlapping response of the different microstructural components. In these cases RC circuit simulations can be helpful to separate each contribution. Once that is done the RC parameters are calculated as in a single-phase material. The analysis is complicated by the fact that different element arrangements can describe the same electrical response.[4] Different arrangements of elements were accordingly analyzed which could describe the electrical response of the samples.

Two parallels RC connected in series form the selected equivalent electrical circuit; Fig. 2 shows the simulated curves for the CP sample as example obtained by using a non-linear least-squares program.[7] This evaluation is supported by the frequency dependence[8] of the imaginary part of impedance (Fig. 3) which shows two contributions for the studied samples. The values of the corresponding circuit elements can be extracted as follows: the resistor values (R) are the diameters. At the top of each semicircle, the impedance of the resistive and the capacitance arms are equal ($R = 1/\omega_x C$, where ω_x is the angular frequency, $\omega_x = 2\pi f_x$). Since this frequency can be derived from Z'' (f) plots (where it appears as a maximum), C (capacitance) can be straightforwardly calculated. The order of magnitude of equivalent capacitance and its temperature dependence make it conventional to associate [9] the high-frequency response with the impedance contributions from grains and the low frequency response with the grain boundaries contribution. The conductivity of both types of samples, for the grain and grain boundary contributions, all exhibited an Arrhenius behavior when plotted in the form log σ vs $1/T$, Fig. 4. The activation energy values (Ea) for the grain and grain boundary responses have not been affected by the sample preparation techniques. These results are in the same order as those of other reports on PZT ceramics.[10]

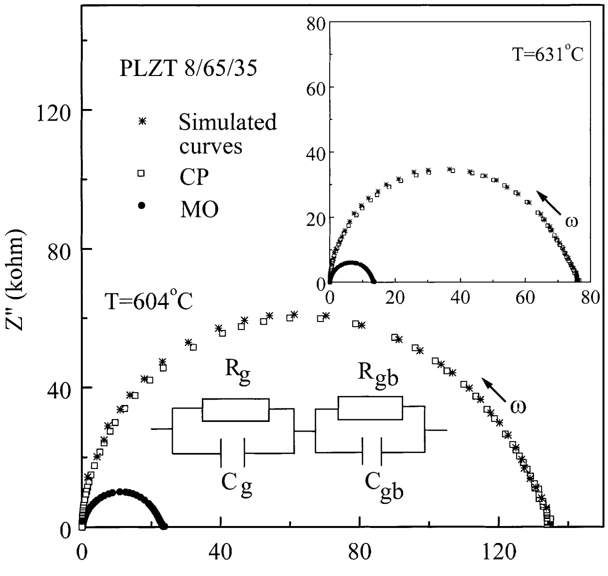

Fig. 2. Complex plane of MO and CP types of samples at two selected temperatures. The equivalent circuit is shown. The simulated curves for the CP sample is also shown.

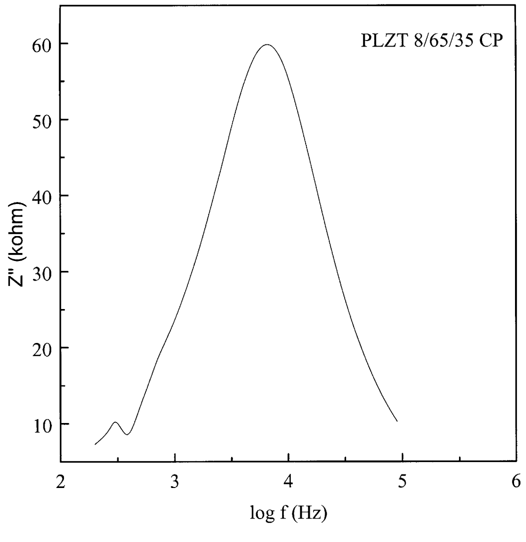

Fig. 3. Frequency dependence of the imaginary component of the impedance for the CP sample, measured at 604 °C. Both OM and CP samples show the same behavior, although present different absolute values.

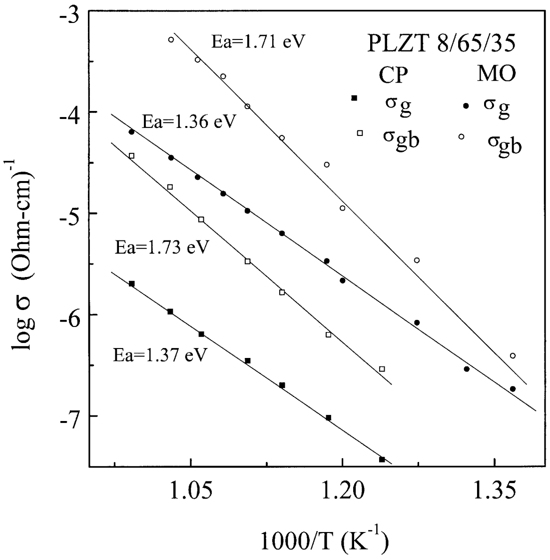

Fig. 4. Arrhenius plots for grain boundary and grain contributions, for both MO and CP types of samples.

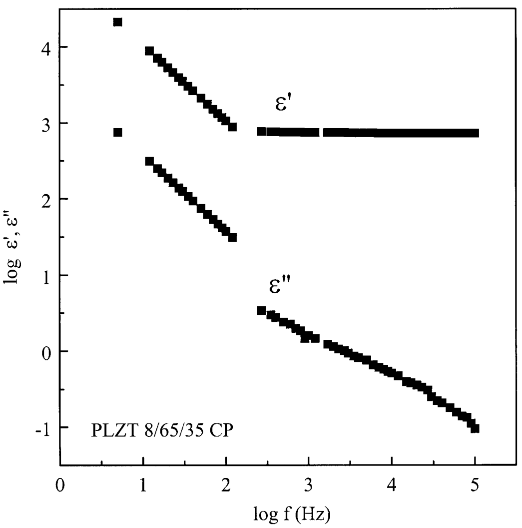

Fig. 5. Frequency dependence of the relative real and imaginary parts of the dielectric permittivity in a log-log plane at a selected temperature (361 °C) for the CP sample. Both MO and CP samples show qualitatively the same behavior.

From the Arrhenius behavior for σ_{gb} (Fig. 4) it can be observed that the preparation techniques led to different absolute conductivity values. These results could be explained by a higher concentration of charge carriers in MO than CP sample, which was influenced by the PbO content in the grain boundary. The same explanation could be extended to the σ_g behavior. The different content of PbO surrounding the grains, which occurred between the samples (as commented in the experimental part), could generate different defects (charge carriers) concentration into the grain. In this way, samples prepared by the mixed oxide method have a higher bulk conductivity than those prepared by the coprecipitation method.

The relative real and imaginary parts of the dielectric constant, ε' and ε'', as a function of frequency (ω), can be obtained from the real (Z') and imaginary (Z'') parts of the impedance,[11] as follows:

$$\varepsilon'(\omega)=\left(\frac{g.f}{\varepsilon_o}\right)\left(\frac{1}{\omega Z''\left(1+\left(\frac{Z'}{Z''}\right)^2\right)}\right) \quad (1)$$

$$\varepsilon''(\omega)=\left(\frac{g.f}{\varepsilon_o\omega}\right)\left(\frac{Z'}{(Z')^2+(Z'')^2}\right) \quad (2)$$

where $g.f$, ε_o and ω are the geometrical factor, the vacuum dielectric constant and the angular frequency ($2\pi f$, f-frequency), respectively.

Fig. 5 shows the frequency dependence of the relative real and imaginary parts of the dielectric permittivity at a selected temperature (361 °C). Both MO and CP samples show the same frequency dependence for the dielectric permittivity, although they present different absolute values, therefore only the dependence for the CP sample is showed. It can be see that the low-frequency part follows a power law[12] and there is no loss peak. This is a characteristic behavior of a material in which mobile charge carriers such as ions or hopping electrons dominate the dielectric response.[12]

A family of curves showing the temperature dependence of $\varepsilon'(\omega)$ appears in Fig. 6 a,b. All of them behave as expected for a ferroelectric material, and their maxima announce the occurrence of a phase transition. The absolute values of the maximum dielectric constant [$\varepsilon'(\omega)_{max}$], smaller than some reported for the same PLZT composition, can be attributed mainly to the grain size of our samples. It was shown that $\varepsilon'(\omega)_{max}$ for ferroelectric materials can be decreased three to four times, when the grain size decreases from 4 to 1 μm.[13,14]

The T_m, which is the temperature of maximum permittivity, shifts toward high temperatures with increasing measuring frequency, especially in MO samples, and the temperature dependence of $\varepsilon''(\omega)$ shows its maxima below T_m (also calculated but not shown here). Both behaviors are classical of the ordinary relaxor-dielectrics, which show a broad-diffuse phase transition. The diffuseness of the phase transition means that the phase change does not take place in the whole specimen volume at a strictly determined Curie temperature (T_c), but in a certain zone ΔT_c. The dielectric permittivity peaks at T_m but, because of the dispersion in the T_c, can only be defined with reference to the frequency at which measurements are made. Table 1 shows the variation of T_m for the same frequencies as those in Fig. 6, included 100 Hz. MO samples exhibit a larger temperature shift

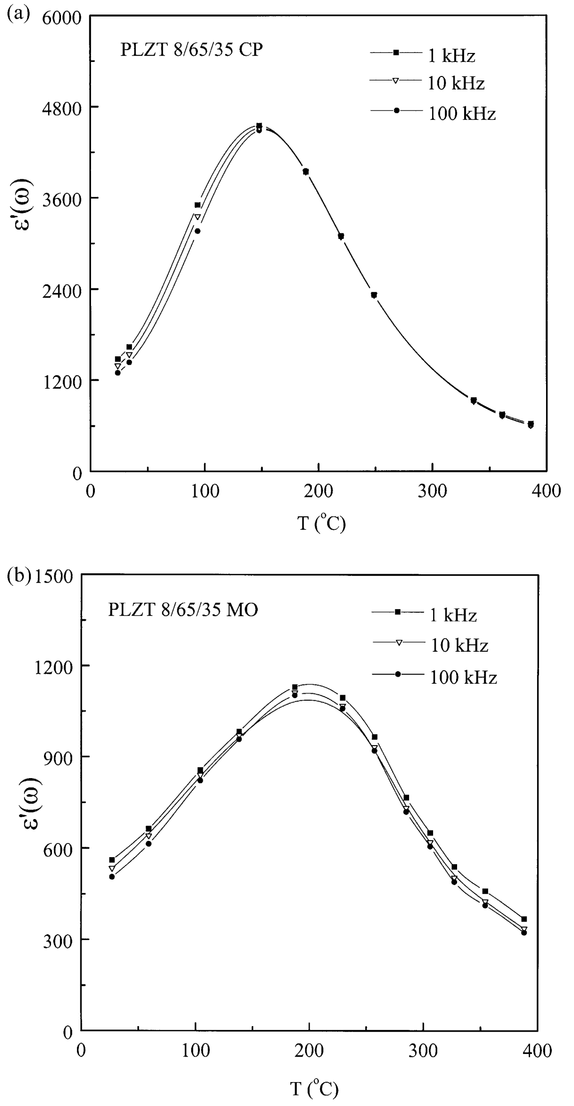

Fig. 6. Thermal behavior of the relative real permittivity for several constant frequency measurements, for both types of samples.

of T_m ($\Delta T = 17$ °C) from 100 Hz–100 kHz than that of the CP samples ($\Delta T = 5$ °C). Thus, the MO samples have a greater degree of dispersion ($\eta_{MO} = 15\%$, $\eta_{CP} = 9\%$ at 200 °C) taken as the measure of dispersion at a determined temperature as follows:

$$\eta = \frac{\varepsilon'_{1kHz} - \varepsilon'_{100kHz}}{\varepsilon'_{1kHz}} 100\% \qquad (3)$$

It could be inferred that, as a consequence of the smaller grain size, comparing Fig. 6a and b, the diffuseness of the phase transition is higher for the MO than for the CP samples.

Also, a clear deviation from the Curie–Weiss law was observed in the studied frequencies, especially at 100 Hz and 1 kHz. On the other hand, a Curie–Weiss behavior was observed from the grains response for both preparation methods with the same critical temperature (extrapolation value at $1/C_g \approx 0$). This result indicates that the intrinsic ferroelectric interactions are the same for CP and MO ceramics, in spite of different T_m values of the bulk responses at the measuring field frequencies. As pointed out, the ac response of all samples showed the grain and grain boundary contributions in the complex impedance plane, and both may contribute to the transition of the material.

Table 1
Variation of T_m for the same frequencies than those in Fig. 5, included 100 Hz.

	T_m (°C)	
Frequency	MO	CP
100 Hz	158	171
1 kHz	163	173
10 kHz	172	175
100 kHz	175	176

The diffusion of the ferroelectric phase transition was shown to exist in such ferroelectrics where ions of different type occupy equivalent sites of the lattice, resulting local composition fluctuations and a distribution of Curie temperature.[15] It has been found[16] that the macro-temperature width (ΔT) could be broadened by compositionally modifying the A-site of the perovskite structure by using lanthanum, which in addition, inhibits grain growth. Substitution of Pb^{2+} ions by La^{3+} ions creates vacancies in the A-site and also, could create vacancies in the B-sites of the perovskite ABO_3 structural lead zirconate titanate ferroelectric ceramics (PZT). The incorporation of La ions and vacancies in the lattice is believed to break the long-range interaction between ferroelectrically active oxygens in octahedra containing B-sites cations.

The PLZT 8/65/35 has been known as a relaxor ferroelectric ceramic with a diffuse phase transition,[17] as we could studied from the temperature dependences $\varepsilon'(\omega)$. The grain response shows the same critical temperature, but the inhomogeneties because of the lanthanum-doping, which segregate to the grain boundary affect the bulk dielectric response, resulting in a diffuse phase transition. This effect is markedly larger in the oxide-milled method (MO). Taking into account the conductivity analysis, the loss factor has been subtracted from the dielectric permittivity in order to obtain the "true" dielectric response, without the influence of the conductive mechanisms, which could affect the dielectric results even at low temperatures. Fig. 7 shows this analysis from room temperature to around 400 °C ($T >> T_m$). There are very important comments:

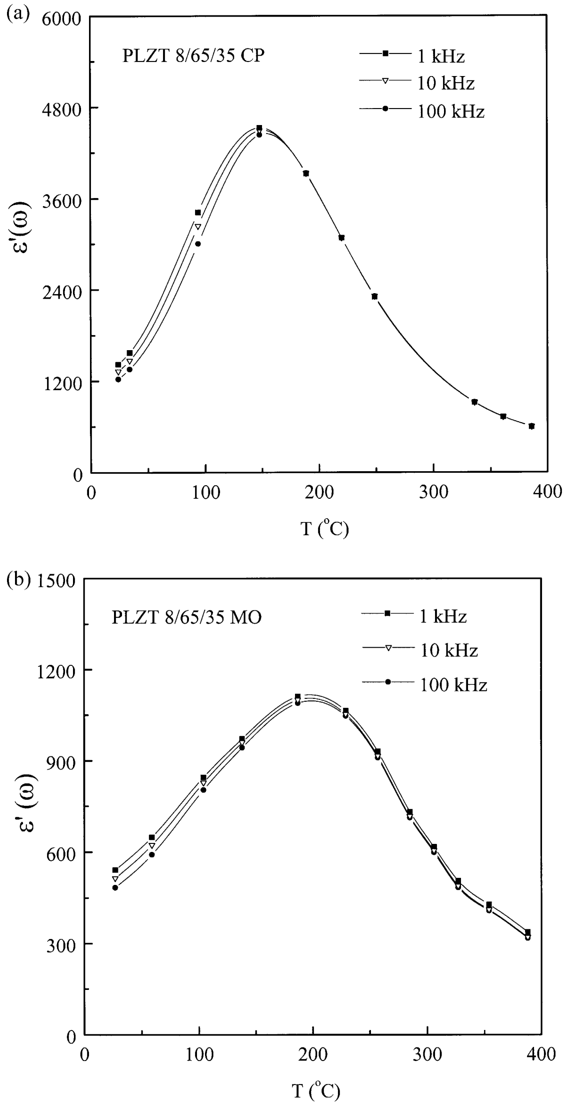

Fig. 7. Temperature dependence of the relative real dielectric permittivity free of loss factor for the same frequencies than those in Fig. 4.

both dependencies show a lower dispersion of the permittivity values with increasing measuring field frequency. There is not a markedly variation of T_m ($\Delta T < 5$ °C in both cases) and the degree of dispersion is very small ($\eta < 1\%$). Also a Curie–Weiss behavior was observed. Then the conductive mechanisms affect the dielectric permittivity measurements; when these are subtracted from the experimental results a lower dispersion phase transition is obtained for both preparation processes.

4. Conclusions

By using the impedance spectroscopy technique the grain and grain boundary responses have been separated in PLZT 8/65/35 ferroelectric ceramics. The preparation techniques led to different absolute conductivity values for each contribution (σ_g or σ_{gb}). The samples prepared by the mixed oxide method showed a higher bulk conductivity than those prepared by the coprecipitation method. This behavior was explained taking into account the different concentration of charge carriers in MO than CP sample, influenced by the PbO content in the grain boundary.

The influence of the preparation techniques was analyzed for the dielectric properties showing behavior of classical ordinary relaxor-dielectrics with a diffuse phase transition, which was markedly larger in the oxide-milled method (MO). The conductive mechanisms and their influence on the dielectric behavior were studied and it could conclude that they affect the dielectric permittivity measurements. The dielectric permittivity without the conductivity component showed a less pronounced relaxor phase transition behavior for both preparation techniques.

Acknowledgements

M.Sc. A. Peláiz-Barranco acknowledges partial support from the University of Mexico (IIM-UNAM and DGIA-UNAM) for the leave of absence. Special acknowledges to Third World Academy of Science (TWAS) for partial financial support. The authors wish to thanks to ICTP, Trieste-Italy for financial support of Latin-American Network of Ferroelectric Materials (NET-43) and to the CyTED Network of Electroceramic Materials (Sub-program XIII F).

References

1. Jaffe, B., Cook, W. and Jaffe, H., *Piezoelectric Ceramics*. Academic Press, London-New York, 1971.
2. Xu, Y., *Ferroelectric Materials and their Applications*. Elsevier Science Publishers B.V., 1991.
3. Landolt, X. and Bornstein, X., *Ferroelectric and Related Substances, vol.16*. Springer-Verlag, Berlin, Heildelberg, New York, 1981.
4. Ross Macdonald, J. (Ed), *Impedance Spectroscopy*. John Wiley Sons, 1987.
5. Garcia, D., Síntese e Caracterização de Cerâmicas Ferroelétricas Transparentes do Sistema (Pb,La)(Zr,Ti)O_3. PhD thesis, Physics Institute, São Carlos Federal University, Brasil, 1995.
6. Kingery, W. D., Bowen, H. K. and Uhlmann, D. R., *Introduction to Ceramics, 2nd Edn*. John Wiley & Sons, NY, 1975.
7. Boukamp, B. A., *Equivalent Circuit (equiver.pas). Users Manual. 2nd Ed.* University of Twente, Dept. Chemical Technology, Netherlands, 1989.
8. Gerhardt, R., Impedance and dielectric spectroscopy revisited: distinguishing localized relaxation from long-range conductivity. *Journal of Physics and Chemistry of Solids*, 1994, **55**(12), 1491–1506.
9. West, A.R., *Solid State Chemistry and its Applications*. John Wiley and Sons, 1984.

10. Dih, J. J. and Fulrath, R. M., Electrical conductivity in lead zirconate-titanate ceramics. *J. Am. Ceram. Soc.*, 1978, **61**(9–10), 448–451.
11. Peláiz Barranco, A., Orientación granular, propiedades dieléctricas y mecanismos de pérdidas en cerámicas ferroeléctricas. Master Degree Thesis, Physics Faculty, Havana University, Cuba, 1996.
12. Jonscher, A. K., Dielectric relaxation in solids. *Journal of Physics D: Applied Physics*, 1999, **32**, R57–R69.
13. Okazaki, K. and Nagata, K., Effects of grain size and porosity on electrical and optical properties of PLZT cermics. *J. Am. Ceram. Soc.*, 1972, **56**(2), 82–86.
14. Randall, C. A., Kim, N., Kucera, J. P., Cao, W. and Shrout, T. R., Intrinsic and extrinsic size effects in fine-grained morphotropic-phase-boundary lead zirconate titanate ceramics. *J. Am. Ceram. Soc.*, 1998, **81**(3), 677–688.
15. Smolenskii, G. A., Physical phenomena in ferroelectric with diffused phase transition. *Journal of Physics Society of Japan*, 1970, **28**(Supplement), 26–30.
16. Kim, N., Huebner, N., Jang, S. J. and Shrout, T. R., Dielectric and piezoelectric properties of lanthanum modified lead magnesium niobate ceramics. *Ferroelectrics*, 1981, **93**, 341–349.
17. Dai, X., Xu, Z., Li, J. F. and Viehland, D., Effects of lanthanum modification on rombohedral $Pb(Zr_{1-x}Ti_x)O_3$ ceramics: part I. Transformation from normal to relaxor ferroelectric behaviors. *Journal Materials Research*, 1996, **11**(3), 618–625.