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Effects of MnO_2 additive on the properties of $PbZrO_3$–$PbTiO_3$–$PbCu_{1/4}Nb_{3/4}O_3$ ferroelectric ceramic system

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Abstract

The modifications (soft or hard doping) in lead zirconate titanate ceramics (PZT) lead to the creation of undesirable stoichiometric defects due to a lack of compensation in some of the components. Frequently, the complexed doping (with two or more elements) is used in order to obtain better results on PZT ceramics than that of single doping. We have investigated the $PbZr_{0.50}Ti_{0.44}(Cu_{1/4}Nb_{3/4})_{0.06}$(PZT–PCN), a ferroelectric ternary system where copper and niobium ions replace the Zr^{4+} or Ti^{4+} in B sites of the structure. The effects of MnO_2 additions on the piezo and ferro-electric properties have been studied. We have analyzed the ac response of both undoped and doped PZT–PCN ceramic samples in a wide temperature range, especially above the Curie point. The MnO_2 addition did not change the Curie temperature of the system and higher resistivity values have been observed in MnO_2 doped ceramics which could be associated to the substitution of copper by manganese ions in the B-sites of the perovskite structure. At the same poling conditions, the electromechanical coupling factors were relatively lower in doped ceramics and the mechanical quality factor gave us an important difference between undoped and doped PZT–PCN system

Keywords: Doping; Ferroelectric properties; Impedance spectroscopy; $Pb(Zr,Ti,Cu,Nb)O_3$; PZT

1. Introduction

The dielectric properties of ceramic materials are becoming more important as the field of solid state devices rapidly expands. Ferroelectric ceramics such as $BaTiO_3$, $PbTiO_3$ and $Pb(Zr,Ti)O_3$ are frequently used in high frequency devices, resonators, electromechanical transducers and electric capacitors, where their properties, particularly the high dielectric constant and low dielectric loss, give the material distinct advantages over traditional systems.

Lead titanate zirconate $Pb(Zr,Ti)O_3$, PZT, has been one of the most widely investigated systems. The crystal structure assumes the perovskite structure (ABO_3) with a pronounced maximum in dielectric constant and piezoelectric effects in the proximity of the morphotropic transformation at Zr/Ti ratio between 0.52 and 0.55.[1,2] The study of PZT modified with some additives is studied widely in order to improve their properties. However the modifications generally lead to the creation of undesirable defects due to a lack of compensation in some of the components.

It is known in $Pb(Zr,Ti)O_3$ that cation vacancies are formed in consequence of Pb vaporization during firing, a *p*-type conduction occurs.[1,3] These can play the role of the center of negative electric charges and each one offers an acceptor level and two holes (acceptor impurity in semiconductors). The soft doping ions (La^{3+}, Nd^{3+}, Sb^{3+}, Bi^{3+}, Th^{4+}, Nb^{5+}, W^{6+}, etc.) can occupy the A and B sites in the perovskite structure which depends on their ionic radii. They create Pb vacancies on account of the requirements of electroneutrality and can play the role of a center of positive electric charges which can bind an electron (donor impurity in semiconductors). On the other hand, Mg^{2+}, Fe^{2+}, K^{1+}, Mn^{2+} and Mn^{3+} doping ions produce the hardening effect creating

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oxygen vacancies in the perovskite structure. They are considered acceptors and can occupy both the A- and B-sites depending on their ionic radii. Usually they have a lower chemical valence than that of the ion replaced in the host lattice and oxygen vacancies are created to ensure electroneutrality. This doping case increases the centers of negatives charges and hole carriers which induce an internal field that may inhibit domain motion. Therefore, the dielectric losses are reduced and mechanical and electrical quality factors are enhanced.[3–5]

Frequently. the "complexed doping" (with two or more elements) is used for better results on PZT ceramics over a "single doping". As an example, we have investigated the $PbZr_{0.50}Ti_{0.44}(Cu_{1/4}Nb_{3/4})_{0.06}O_3$ (PZT–PCN),[6,7] a ferroelectric ternary system where copper and niobium ions replace the Zr^{4+} or Ti^{4+} in B sites of the structure. This system has been prepared totally compensated (without vacancies). Previous papers [4,5] have reported that the MnO_2 addition ameliorates mechanical vibration losses in PZT ceramics, i.e. increases the mechanical quality factor -Q_m- (hard doping effect). This behavior receives special attention in several practical applications. The increase in Q_m is ascribed to the formation of dipole of the doping ions and lattice defects.[4] Mn^{4+} occupies the B-sites of the structure and reduces to Mn^{2+} and Mn^{3+} during sintering, which leads to the creation of oxygen vacancies to keep the electrical neutrality. They pin down the rotation of the spontaneous polarization resulting in lower mechanical losses. The mechanism was explained by Lambeck et al.,[8] the manganese ions and oxygen vacancies form a dipole moment inducing lower mechanical vibration in the domain wall. Our purpose, in this paper, is to study the MnO_2 addition effects on the piezo- and ferro-electric properties, and the ac response of the PZT–PCN system. It has been known [9,10] that Mn ions change their chemical valence more easily than do Ti or Zr ions and that the Mn^{2+} is the more stable state. These ions occupy the B-sites in the perovskite structure because their ionic radii are similar to Ti^{4+} or Zr^{4+} (see Table 1).[11]

The ferroelectric ceramics are widely studied below T_c; however, at present not many studies have been conducted to investigate the high-temperature electrical behavior of these materials in paraelectric state. We will analyze the ac response of both undoped and doped PZT–PCN ceramic samples in a wide temperature range, especially above the Curie point.

Table 1
Ionic radii of doping metal ions

Ions	Coordinate number	Ionic radii (Å)
Pb^{2+}	12	1.63
Zr^{4+}	6	0.86
Ti^{4+}	6	0.74
Cu^{+}	6	0.91
Nb^{5+}	6	0.78
Mn^{2+}	6	0.81
Mn^{3+}	6	0.72
Mn^{4+}	6	0.67

2. Experimental procedure

Samples of PZT–PCN type were made from powders mixed to give an overall composition of $PbZr_{0.50}Ti_{0.44}(Cu_{1/4}Nb_{3/4})_{0.06}O_3$. In order to analyze the effects of MnO_2 addition, samples with 0.5 mol% of this additive, were also prepared.

Ceramic bodies were fabricated from high purity reagents [$PbCO_3$: 99.5% (Merck), ZrO_2: 99.4% (Johnson and Matthey), TiO_2: 99.2% (Reachim), Nb_2O_5: 99.5% (Johnson and Matthey), Cu_2O: 99% (Reachim), MnO_2: 99% (Aeasar)], milled for 2 h and later fired at 800°C for 1 h in air atmosphere with a heating rate of 50°/min. They were milled again for 1 h, pressed at 300 MPa using a hydraulic press and sintered at 1220°C for 2 h in air. The powder samples were examined by XRD using a Siemens D500 X-ray diffractometer. The voltage and currents ratings used were 35 kV and 30 mA, respectively, and CuK_α radiation was used. The diffraction data were collected from 15 to 70° 2θ with an X-ray scan speed of 0.5°/min. SEM studies were conducted using a Leica Cambridge (Stereoscan 440) scanning electron microscope on fractured samples.

Disk-like specimens were obtained from sintered block. Au electrodes were deposited on the surfaces by heat treatment at 600°C for 20 min with a heating rate of 50°/min. Dielectric permittivity and loss tangent of the materials were measured directly by a PM 6303 RLC digital meter at 1 kHz.

The complex impedance (ac response) of unpoled samples was measured using a HP 4192A impedance analyzer operated at 1 V, which covers a frequency range between 5 Hz and 13 MHz. and a micro-computer as control system and data collection. The studies were carried out from ferroelectric to paraelectric state in a wide temperature range from room temperature to 700°C.

The temperature programmed reduction measurement (TPR) in H_2 atmosphere was carried out in the powder samples by using an ISRI, model Rig-100 and the registering conditions of thermoconduction cell (TC) was 100°C, 100 mA and a flux of 25 cc/min of 10%-vol. H_2/Ar.

To evaluate piezoelectric properties, the samples were poled at 2 kV/mm and 140°C in silicon oil. Resonance frequency, anti-resonance frequency, and impedance at resonance frequency were measured by a TESLA BM 507 impedance analyzer meter. The radial and transversal electromechanical coupling factors (k_p,k_{31}), and mechanical quality factor (Q_m) were calculated by resonance–antiresonance method.[6]

3. Results and discussion

3.1. Structural and dielectric analysis

Room temperature X-ray diffraction patterns for powders of samples undoped and doped with MnO_2 are shown in Fig. 1. All of the sintered samples were thought to be a perovskite structure, but there is a mixture of rombohedral and tetragonal phases, as can be observed in the inset of the figure. The amount of tetragonal phase tends to increase with MnO_2 additions from the higher definition of (200)T and (002)T peaks for the doped PZT–PCN ceramics. Undesirable second phases were not detected in the samples.

The additive examined increases the density of PZT–PCN ceramics ($\rho = 7.18$ and 7.60 g/cm^3 for undoped and doped ceramic system, respectively). Fig. 2 shows the SEM micrographs results. The specimens with MnO_2 show smaller average grain size (2 μm) compared with undoped samples (1 μm), i.e. the grain growth was slightly suppressed by the manganese inclusion.

The temperature dependence of the real part of dielectric permittivity (ε) at 1 kHz is shown in Fig. 3 for undoped and doped ceramics. The MnO_2 addition does not change the Curie temperature of the PZT–PCN system ($T_c = 345$°C) and both compositions show a first order-like transformation. ε-values of the MnO_2-doped PZT–PCN remain lower than that of undoped PZT–PCN for all temperature range (from ferroelectric to paraelectric phase). The same behavior was obtained for the dielectric losses (tanδ), as can be observed in Fig. 4. These results could be suggested another contribution to the dipolar behavior (conductive mechanism) which could induce the higher values of ε in the undoped samples. Note that heating activates the charge carriers movements and they may be slowed down through another phase or interfaces. A space charge polarization is induced and could manifest as an increment in the dielectric permittivity. Above 400°C, the dielectric losses increase rapidly in both samples showing a different conductive mechanism above Curie point.

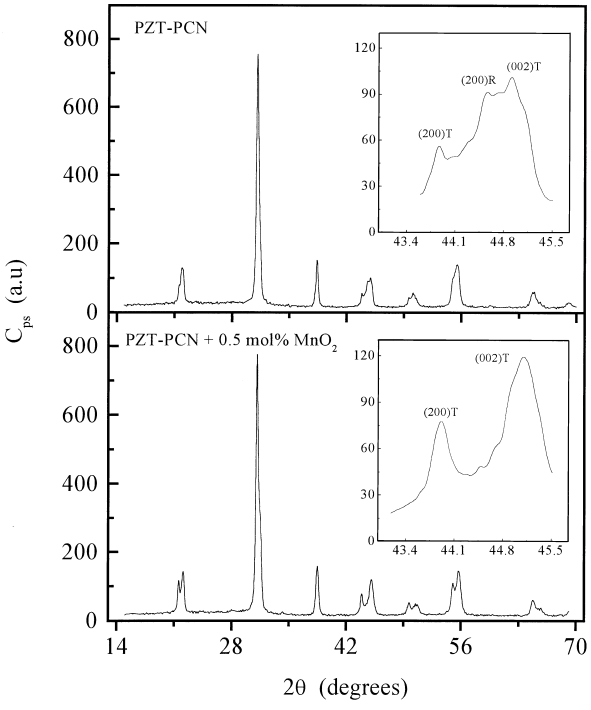

Fig. 1. Room temperature X-ray diffraction patterns for powders of undoped and doped PZT–PCN ceramic system.

3.2. AC response

In single phase systems, the electrical response in a complex impedance plane exhibits a regular semicircle which can be associated to a *RC* parallel arrangement. *R* and *C* values can be calculated by standard methods,[12–14] i.e. resistance (*R*) is usually determined from the low frequency intercept of the semicircle on the real Z' axis and capacitance (*C*) values is estimated from the maximum of the semicircle, knowing that $\omega_{max}RC = 1$, where $\omega_{max} = 2\pi f_{max}$ (f_{max} being the instantaneous frequency at the maximum of the semicircle). Polycrystalhine materials show irregular semicircies because of the overlapping response of the different components; also the center of the arcs could be below the real axis. In these cases more complex simulations are necessary and the parameters are calculated by a similar way described for the single phase material. Different arrangements of elements could describe the electrical response [12,13] and the approach to the true equivalent circuit can only be made by using the criterion of simplicity; the circuit in which the changes are simplest and/or closest to the theoretical expectation should certainly generally be preferred.

The impedance planes were obtained at several temperatures. Below 400°C, all samples showed a non-defined arc in the impedance plane. At higher temperatures irregular semicircles were obtained for undoped and MnO_2 doped samples as we can observe at 600°C (Fig. 5). We analyzed different arrangements of elements which could describe the electrical response of the samples, and we finally proposed an equivalent circuit consisting of three and two *RC* parallel arms in series, respectively (see Fig. 5). The theoretical simulation was carried out by using a non-linear least-squares program[15] in order to obtain their separate contributions, i.e. their corresponding *R* and *C* values. This simulation gave us the parameters of two and three overlapping semicircles with a very good fitting. Fig. 5 shows measured and simulated curves using the proposed equivalent circuits.

From capacitance values and their temperature dependences we can obtain information related to these semicircles. *C*-values of 10^{-10}–10^{-9} F showing a Curie–

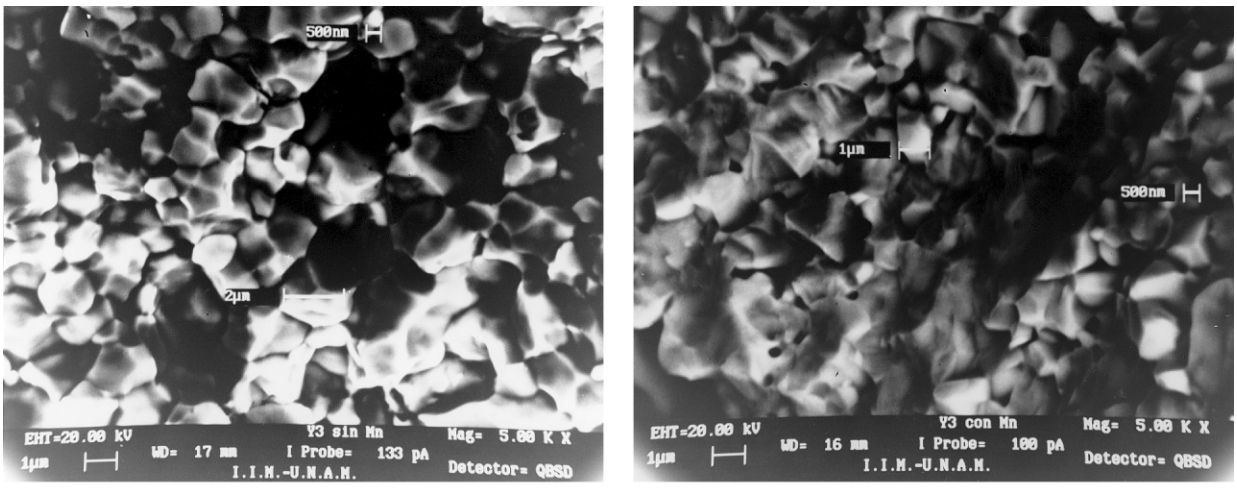

Fig. 2. SEM micrographs results for (a) undoped and (b) MnO_2 doped PZT–PCN.

Weiss behavior were obtained for the high-frequency arm (R_GC_G) which was associated to the ferroelectric bulk response (or grains). The low frequency arm ($R_{GB}C_{GB}$) showed capacitance values of 10^{-9}–10^{-8} F which not shown any temperature dependence;[16] this response was associated to the grain boundary contribution. The third contribution for the undoped specimens is assigned to the electrode-sample interface ($R_{EL}C_{EL}$) which showed C-values in the μF scale which increase with the temperature. The absent electrode contribution in the doped PZT–PCN could be associated to their resistivity values respect to the pure PZT–PCN. On the other hand, the analyzed frequency range could limit the electrode response in the impedance plane too.

As the temperature increases, the resistance values of each contribution decrease as a thermally stimulated process (Arrhenius behavior). From the Arrhenius plots, which were constructed by using the resistance values calculated from the semicircles in the complex impedance plane. the activation energy values (E_a) were obtained above the Curie point. Below this temperature

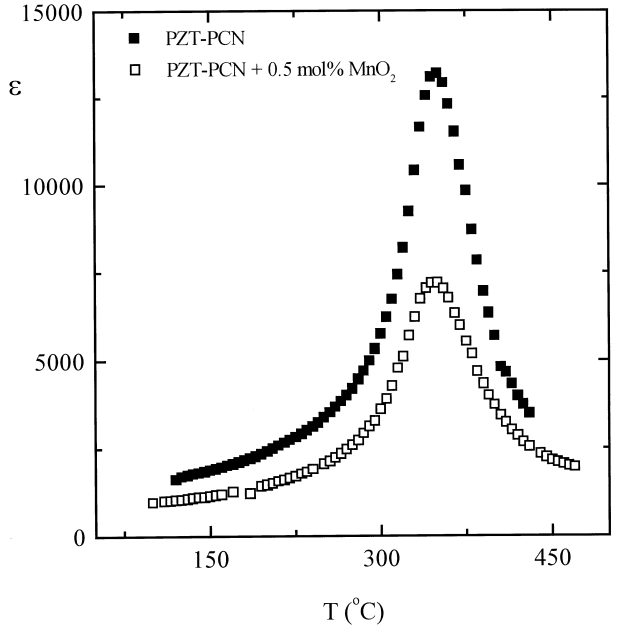

Fig. 3. Temperature dependence of the real part of the dielectric permittivity (ε) at 1 kHz for undoped and MnO_2 doped PZT–PCN. The MnO_2 addition doesn't change the Curie temperature of the PZT–PCN system ($T_c = 345$°C). The values of ε of the MnO_2 doped PZT–PCN is lower than that of undoped PZT–PCN from room temperature to 700°C.

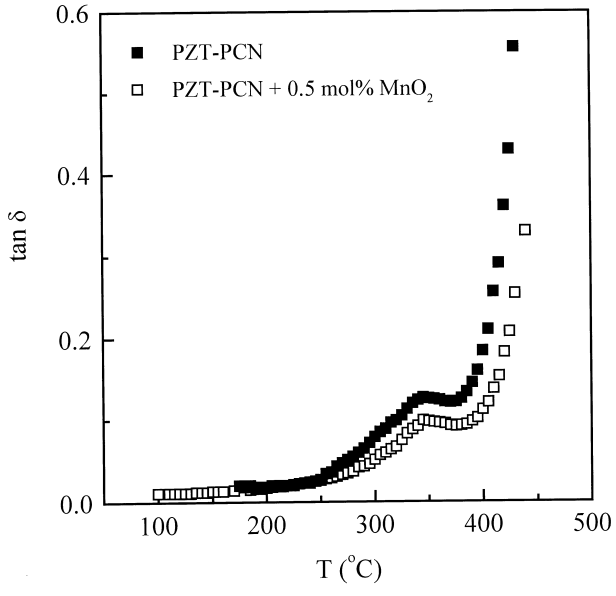

Fig. 4. Temperature dependence of dielectric losses at 1 kHz for undoped and doped PZT–PCN ceramic system. These are higher in the pure PZT–PCN from ferroelectric to paraelectric phase. Both samples show a relative maximum at Curie point and then increase rapidly above 400°C.

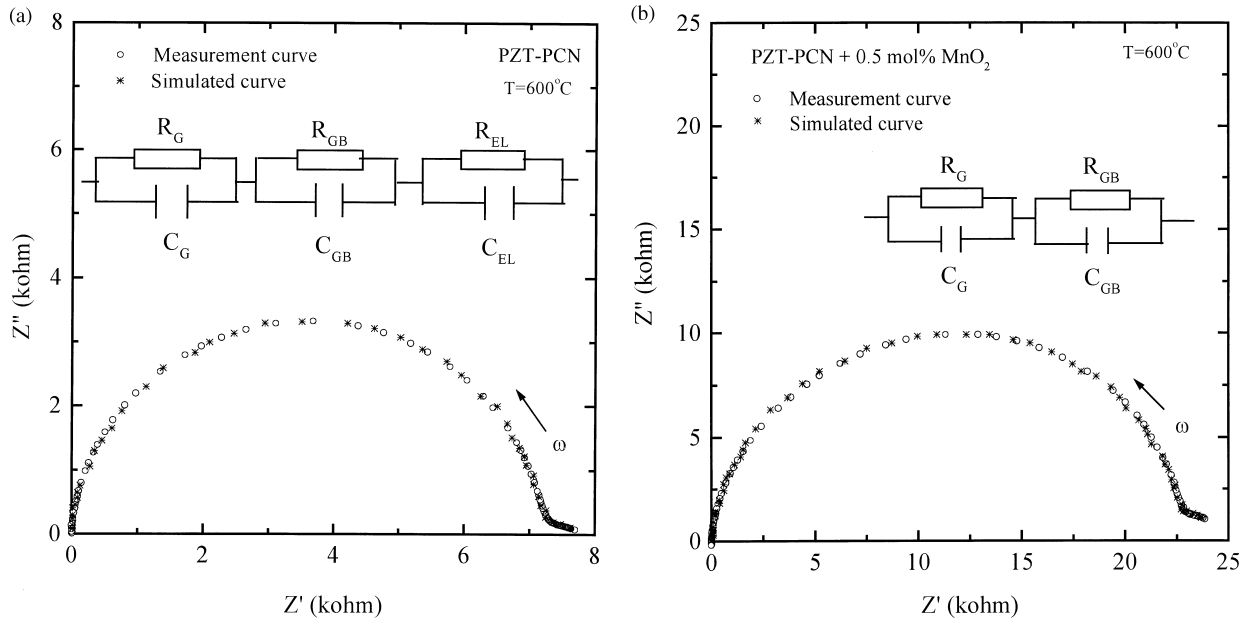

Fig. 5. A Cole–Cole plot, constructed from impedance data taken at 600°C (simulated and measured curves), for (a) undoped and (b) MnO_2 doped PZT–PCN. Three and two semicircles were found for undoped and MnO_2 doped samples, respectively, instead of a single one. Equivalent circuits formed by three and two RC parallel arms in series, respectively, were used to modeled the responses. The high-frequency arm (R_GC_G) was associated to the ferroelectric bulk response (or grains) and $R_{GB}C_{GB}$, with the grain boundary response. The third contribution for the undoped specimens is assigned to the electrode-sample interface ($R_{EL}C_{EL}$).

the resistance values ($R = Z'$) of the gram response were estimated extrapolating geometrically in order to calculate its activation energy value in the ferroelectnc state from 200°C to the Curie point ($T_c = 343$°C).

Table 2 shows the activation energy values for the grain response below and above Curie point. These results suggest an extrinsic conduction mechanism because of the manganese doping produces an important change in the activation energy values. It has been known that virtually there is no ionic transport in the perovskite lattice due to the low mobility of the cation vacancies (Pb, Ti, Zr).[3]

Therefore, are the oxygen ions which may show a certain motion in perovskite ceramics. The energy values of the grain response in the doped ceramic suggest a majority movement of oxygen ions by a vacancy mechanism below and above the Curie point. However, for the undoped system we can deduce that this is not the most important contribution to the total conductivity because of its activation energy values.[17] This suggests an electronic contribution in the undoped system and could be an important influence in the dielectric losses results and the resistivity values in the pure PZT–PCN. The detailed analysis of the conductive mechanisms is the purpose of another paper.[18] Fig. 6 shows the temperature dependence of the bulk electric resistivity, calculated from R_G-values, showing higher values in doped samples.

Table 2
Activation energy values of the grain response for undoped and MnO_2 doped ceramics

System	E_a (eV) ($200°C < T < T_c$)	E_a (eV) ($T > T_c$)
PZT–PCN	1.61	1.67
PZT–PCN + 0.5 mol% MnO_2	0.91	1.23

3.3. TPR results

The temperature programmed reduction (TPR) technique has been used for us to study possible changes of the oxidation state with the Mn-addition. This technique shows a variation of the thermal conductivity with temperature by changes in the H_2 concentration due to a chemical reaction where the formation of H_2O occurs. Fig. 7 shows a TPR in the H_2 atmosphere for undoped and Mn-doped ceramics. A Cu^{2+}/Cu^{+} or Cu^0 and Cu^{+}/Cu^0 reduction process are assigned to the reaction around 450 and 550°C, respectively. This observation is in agreement with the easy order of reduction that it has known for $Cu^{2+}/Cu^{+} < Cu^{+}/Cu^0$.[9,19] These processes are in perfect sequence with previous reports.[10] The small change in temperature of each one has been studied[20] and it has been associated to experimental conditions.

The change in the TPR curves from undoped to doped ceramics could be associated to the manganese entering the lattice displacing Cu^{+} ions (note that copper and manganese ions occupy the same crystallographic site, B-sites, in the perovskite structure) which induces

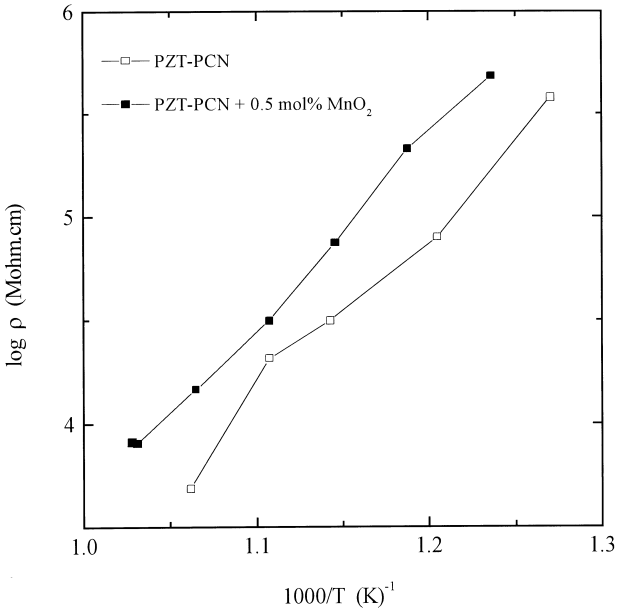

Fig. 6. Temperature dependence of the bulk electric resistivity for doped and not doped $PbZr_{0.50}Ti_{0.44}(Cu_{1/4}Nb_{3/4})_{0.06}O_3$. There are appreciable higher values in doped samples.

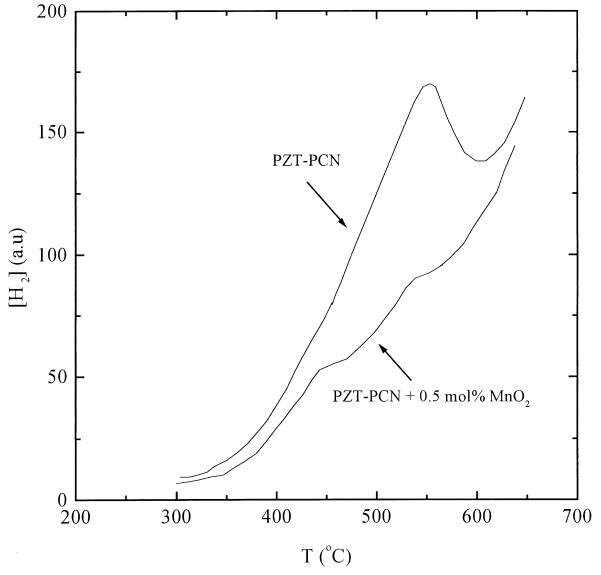

Fig. 7. The temperature programmed reduction (TPR) in the H_2 atmosphere. A Cu^{2+}/Cu^{+} or Cu^0 and Cu^{+}/Cu^0 reduction processes are assigned to the reaction around 450 and 550°C. respectively.

the formation of CuO. It could be presented as a segregated phase. Then we could conclude that the manganese occupy the B-sites. The bigger negative free energy of formation of the other oxides give us elements to conclude that it's not probably their reduction in the studied temperature zone.

In air conditions, which are our experimental condition for the electrical measurements, a Cu^{+}/Cu^{2+} oxidation process occurs in the ceramics with and without MnO_2, but due to the entrance of manganese in the lattice the Cu^{+} concentration decreases as we have pointed out by using TPR. Then, a lower contribution to the conductive mechanism is obtained in doped system than that of undoped ceramic from this oxidation process, which induces a higher resistivity values in this case.

Table 3
Dielectric and piezoelectric properties for doped and not doped $PbZr_{0.50}Ti_{0.44}(Cu_{1/4}Nb_{3/4})_{0.06}O_3$

System	tanδ (25°C)	ε (25°C)	k_p[a]	k_{31}[a]	Q_m[a]
PZT–PCN	0.039	1083	0.41	0.24	85
PZT–PCN + 0.5 mol% MnO_2	0.017	722	0.21	0.12	311

[a] Calculated from the resonance–antiresonance frequencies.[6]

3.4. Piezoelectric properties

Table 3 shows some dielectric and piezoelectric properties for both specimens after poling process. Dielectric permittivity and loss tangent exhibit the same behavior as we discussed above in unpoled conditions. Electromechanical coupling factors (k_p, k_{31}) are relatively lower in doped ceramics; however, mechanical quality factor gives us an important difference between undoped and doped PZT–PCN system (almost 4 times). This is in agreement with other reports [3–5] where ternary ceramic systems with Mn^{2+} doping have an enhanced Q_m while k_p is almost unchanged.

From Q_m results, we can deduce lower mechanical vibration losses in domain motion for the doped PZT–PCN system. Note that the main origin of the mechanical vibration losses is the domain structure.[21] The spontaneous polarization near the domain wall rotates when an alternative electric field is applied (poling field), and the friction during the movement corresponds to both electric and mechanical vibration losses. The mechanical quality factor is an inverse proportion to total losses which decrease with progress of poling. Therefore, lower losses are obtained in PZT–PCN + 0.5 mol% MnO_2 because of its higher mechanical quality factor than those of the undoped ceramics at the same poling conditions.

4. Conclusions

- From XRD studies, a mixture of tetragonal and rhombohedral phases was observed. The amount of tetragonal phase tends to increase with the MnO_2 addition.
- The MnO_2 addition doesn't change the Curie temperature of the PZT–PCN system ($T_c = 345$°C). The values of ε and tanδ of the MnO_2 doped PZT–PCN were lower than those of undoped PZT–PCN for all temperature ranges.

- Higher resistivity values were observed in MnO_2 doped ceramics which could be associated to the substitution of Cu^+ by manganese ions in the B-sites of the perovskite structure.
- At the same poling conditions, the electromechanical coupling factors were relatively lower in doped ceramics. Mechanical quality factor gave us an important difference between undoped and doped PZT–PCN system. The manganese ions in B-site and oxygen vacancies form a dipole moment inducing lower mechanical vibration in the domain wall. Lower dielectric losses were obtained in PZT–PCN + 0.5 mol% MnO_2 because of its higher mechanical quality factor than that of the undoped ceramics at the same poling conditions.

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References

1. Jaffe, B. and Cook, W., *Piezoelectric ceramics*. Academic Press, London/New York, 1971 pp. 135–171.
2. Noheda, B., Cox, D. E., Shirane, G., Gonzalo, J. A., Cross, L. E. and Park, S. E., A monoclinic ferroelectric phase in the $Pb(Zr_{1-x}Ti_x)O_3$ solid solution. *Applied Physics Letters*, 1999, **74**(14), 2059–2061.
3. Xu, Y., *Ferroelectric Materials and Their Applications*. Elsevier Science Publishers B.V, The Netherlands, 1991 pp. 101–162.
4. Izaki, T. and Watanabe, A., Influence of the electronic state of dopants on the piezoelectric properties of PZT doped with transition ions. In *Proceedings of European Ceramic Society Fourth Conference Vol. 5*, ed. G. Gusmano and E. Traversa. Gruppo Editoriale Faenza Editrice S.p.A, Italy, 1995, pp. 33–38.
5. Izaki, T., Haneda, H., Watanabe, A., Uchida, Y. and Tanaka, J., Effects of Mn ions on the piezoelectric properties of PLZT. *The Sumimoto Search*, 1993, **53**, 29–32.
6. Peláiz Barranco, A., *Sistemas Ternarios Basados en $PbTiO_3$–$PbZrO_3$ (PZT)*. Licenciatura thesis, Facultad de Física, Universidad de la Habana, La Habana, Cuba, 1995.
7. Calderón Piñar, F., Pérez Martínez, O., Peláiz Barranco, A. and Font Hernández, R., Estudio de cerámicas ferroeléctricas obtenidas por el método de prensado en caliente combinado con la reacción de la molienda a altas temperaturas. *Revista Mexicana de Física*, 1996, **42**(1), 82–85.
8. Lambeck, P. V. and Jonker, G. H., *Ferroelectrics*, 1978, **22**, 729–732.
9. Huheey, J. E., *Química Inorgánica. Principio de Estructura y Reactividad*, 2nd edn. Harla, Mexico, 1981 pp. 314–357.
10. Hurst, W. N., Gentry, J. S., Janes, A. and Mcnicol, B. D., Temperature programmed reduction. *Catal. Rev. — SCI, Eng.*, 1982, **24**(2), 233–309.
11. Huheey, J. E., *Química Inorgánica. Principio de Estrucrura y Reactividad*, 2nd edn. Harla, Mexico, 1981 pp. 55–119.
12. Macdonald, J. R. (ed.), *Impedance Spectroscopy*. John Wiley & Sons, New York, 1987, pp. 1–132.
13. Irvine, J., Sinclair, D. and West, A., Electroceramics: characterization by impedance spectroscopy. *Advanced Materials*, 1990, **2**(3), 132–138.
14. Peláiz, A., Huanosta, A., Calderón, F., Perez, O. & de los Santos, J., Bulk conductivity and a.c behavior of the ferroelectric $PbTiO_3$–$PbZrO_3$–$PbCuNbO_3$ sintered by a hot pressing method. In *XIV Latin-American Symposium of Solid State Physics*, SLAFES'98. Oaxaca. México. 1998.
15. Boukamp, B. A., *Equivalent Circuit (equiver.pas.), Users Manual*, 2nd edn. Department of Technology, University of Twente, Netherlands, 1989 pp. 26–29.
16. Peláiz Barranco, A., Huanosta Tera, A, Baños, L., Guzmán Mendoza, J., Pérez Martínez. O. and Calderón Piñar, F., Modified lead titanate zirconate system: preparation techniques and properties. *Journal of Material Science Letters*, 1998, **17**(12), 1033–1035.
17. Bauerle, J. E., Study of solid electrolyte polarization by a complex admittance method. *Journal of Physics and Chemistry of Solids*, 1969, **30**(12), 2657–2670.
18. Torres García, E., Peláiz Barranco, A., Vázquez. C., Calderón Piñar, F. and Pérez Martínez. O., Oxidation kinetic study of copper I in ceramic ferroelectric [$PbTiO_3$–$PbZrO_3$–$PbCuNbO_3$] system by high resolution thermogravimetric analysis. *Thermochimica Acta*, 2001, in press.
19. Torres Garcia, E., Cu^{2+}/Cu^+ and Cu^+/Cu^0 reduction processes (unpublished).
20. Fierro, J., Jacono, M., Lo, Inversi, M., Porta, P., Lavecchia, R. and Ciocio, F., A study of anomalous temperature programmed reduction profiles of Cu_2O, CuO and CuO–ZnO catalysts. *Journal of Catalysis*, 1994, **148**, 709–721.
21. Gethsen, P., Hardtl, K. H. and Schmidt, N. A., Correlation of mechanical and electrical losses in ferroelectric. *Journal of Applied Physics*, 1980, **51**(2), 1131–1134.