



Concentration Dependence of the Electric Field Gradient in $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ Ceramics

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Abstract. The concentration dependence of the electric field gradient (EFG) in PZT ceramics was studied by Time Differential Perturbed Angular Correlations (PAC) using the ^{181}Ta radioactive probe in samples with $x = 0.3, 0.5$ and 0.8 at room temperature. This phase presents two sites, probably related to defects close to probes, caused by oxygen and lead vacancies. We can also state that both the paraelectric and ferroelectric phases of these systems have two sites with different characteristics and that the high-frequency quadrupolar frequency site presents the highest fraction. The concentration dependence revealed by our results is discussed by comparing the latter with previous PAC studies.

1. Introduction

Lead titanate zirconate or PZT ($\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$) is one of the most intensively studied ferroelectric materials mainly due to its technological applications. In the course of time, PZT has been the subject of many experimental and theoretical research efforts. This system presents an interesting concentration–temperature (x – T) phase diagram and its physical properties can be associated with the several structural modifications found in. The x – T phase diagram determined by Jaffe *et al.* [1] presents a variety of phase transitions among ferroelectric, antiferroelectric and paraelectric phases. Increasing the Ti composition progressively yields the following phases: an antiferroelectric orthorhombic (AO) phase for $x \leq 0.05$, a ferroelectric rhombohedral-low temperature (FR(LT)) phase for $0.05 \leq x \leq 0.37$, another ferroelectric rhombohedral-high temperature (FR(HT)) phase for $0.37 \leq x \leq 0.47$, and finally, a tetragonal ferroelectric (FT) phase for x larger than 47%. The high-temperature phase of this solid solution in all compositions is the paraelectric cubic (PC) perovskite structure.

PZT type ceramics belong to the general class of ceramics classified as perovskites and have an ABX_3 composition in which A and B are metallic cations and X is the non-metallic anion. Their structure is cubic, with B located in the cube's center, A in the 8 corners and X occupying the center of each of the cube's faces.

Ideal perovskites show a cubic centro-symmetric structure; however, some compounds derived from perovskites through slight structural distortions have great technological significance owing to their strong piezoelectric and ferroelectric effects [2–8].

In this work we used the time differential angular correlations technique (PAC), which requires a radioactive element to be introduced into the sample. This paper reports on the extension of a systematic program which we have initiated [9].

2. Experimental

The samples were prepared by mixing the oxides PbO, TiO₂ and ZrO₂ in the required proportions and calcining at 1173 K. They were then compressed into pellets and sintered at 1473 K in an atmosphere rich in PbO. The structure was confirmed by the X-ray powder-diffraction technique, at room temperature. ¹⁸¹Ta was used as a probe for the PAC and was produced by thermal neutron irradiation of the ¹⁸⁰Hf contained in the samples as an impurity in naturally abundant zirconium. The PAC measurements were taken with two BaF₂ detectors automatic spectrometer using conventional nuclear electronic equipment. The time differential gamma–gamma spectra were obtained at 90, 180 and 270 degrees using the 133–482 keV cascade from the excited states of ¹⁸¹Ta and a time resolution of 0.7 ns. This cascade displayed the interference of the 346–136 keV cascade ($T_{1/2} = 50$ ps) from ¹⁸¹Ta, as well as the 561–204 keV cascade ($T_{1/2} = 0.76$ ns) coming from the ⁹⁵Nb daughter of ⁹⁵Zr, ($T_{1/2} = 64,0$ d). Both cascades contribute with a peak at $t = 0$ which is over the coincidence of interest and, therefore the first nanosecond was not used in the A_{22} fitting.

3. Results and discussion

Figure 1 shows the fitted spectra the PbZr_{0.2}Ti_{0.8}, or PZT 20–80, at several temperatures. Figure 2 shows the correspondent fitted hyperfine parameters as function of temperature. In spite of the PZT crystal structure having only one crystallographic Z-site, a two-site model was necessary to obtain good fits.

The phase transition temperature are marked in this figure with vertical traced lines, according to the PZT phase diagram [1]. The tetragonal ferroelectric phase, F_T, extends up to 450°C while the paraelectric cubic phase, P_c, occurs above this temperature.

An analysis of the results shows the presence of two sites for both phases. The adjusted ω_Q values are very distinct, with the higher value contributing with a higher fraction of approximately $70 \pm 5\%$. The low-frequency interaction (fraction of approximately $30 \pm 5\%$), reflects the collective effects of many defects. Although we expected values for EFG or ω_Q to be equal to zero in the P_c phase, no null values were found. However, it presents a much smaller value than the tetragonal phase. The same behavior was observed for other samples, PZT 90–10, 80–20 and

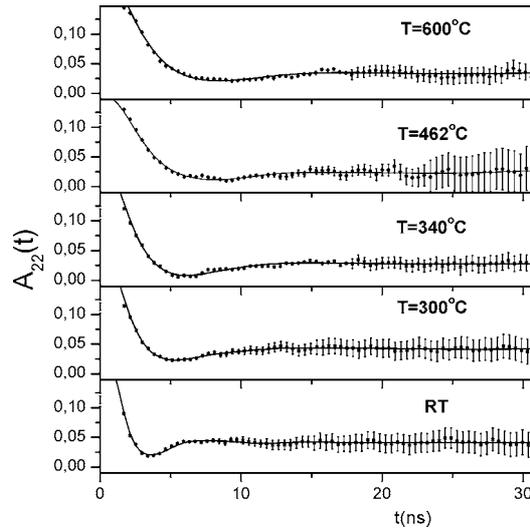


Figure 1. TDPAC spectrum of ^{181}Ta in PZT 20–80 at several temperatures.

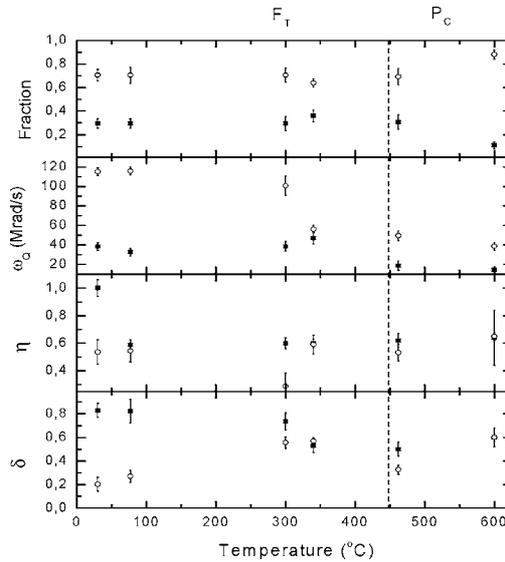


Figure 2. Temperature dependence of the PZT 20–80 hyperfine parameters. Filled squares corresponds to site 1 and open circles, to site 2.

60–40 [10]. When the Ti and Zr ions were ordered on the B-sublattice, null values were found. Most likely these ions are distributed at random, or, alternatively, the chemical differences between Hf and Zr may give rise to an apparent non-random distribution of Ti and Zr on the B-sublattice. In addition, it is well known that point defects give rise to measurable EFGs in the cubic phases for both PT and

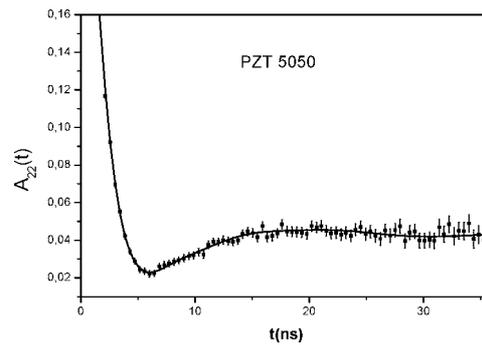


Figure 3. TDPAC spectrum of ^{181}Ta in PZT 50–50 at room temperature.

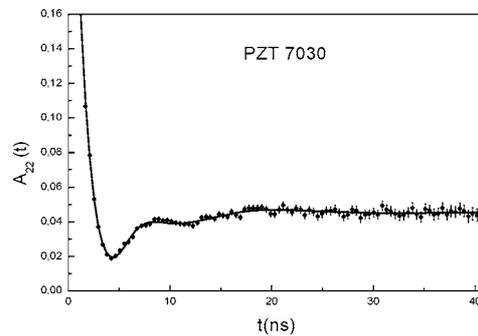


Figure 4. TDPAC spectrum of ^{181}Ta in PZT 70–30 at $T = 316^\circ\text{C}$.

PZ [10, 11], in which the question of Zr and Ti alloy ordering is not pertinent. So the origin of these defects is still unclear.

The high δ values fitted for the two sites showed that the present sample presented a high distribution of ω_Q . This fact limits the discussion about the fitted η values, as discussed by Forker *et al.* [12].

Figures 3 and 4 display the fitted spectra for the PZT 50–50 at room temperature and for PZT 70–30 at $T = 316^\circ\text{C}$. Two sites were used in the fit as well.

Figures 5(a) and (b) show the fitted parameters obtained for two sites, as a function of Ti concentration at room temperature. The parameters obtained for PZT 70–30 tetragonal phase measured at $T = 316^\circ\text{C}$ were used as well.

Alonso's results [10] are included in order to analyze the effect of concentration on the hyperfine parameters. The dashed lines in the figures indicate the phase transitions. In general, the results are coherent, indicating that the relative populations of both sites and the quadrupolar frequency at site 1 are approximately independent of the Ti concentration, while the quadrupolar frequency at site 2, primary high-frequency, presents a jump between $x = 0.1$ and 0.2 . However, the asymmetry parameter and the frequency distribution show more evident concentration dependence.

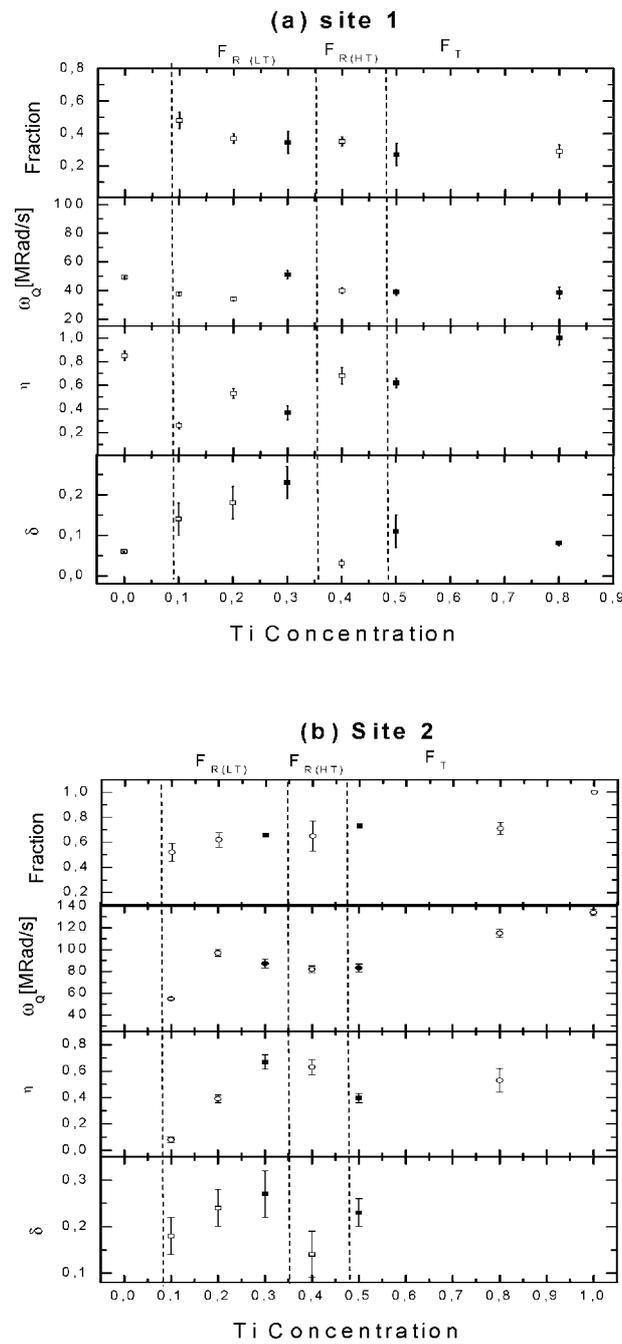


Figure 5. Concentration dependence of the hyperfine parameters of sites 1 and 2. Open symbols correspond to the results obtained by Alonso *et al.* [10].

4. Conclusion

The PZT systems presents two sites, probably related to defects close to probes, caused by oxygen and lead vacancies. We can also state that both the paraelectric and ferroelectric phases of these systems have two sites with different characteristics and that the high-frequency ω_Q site presents higher fraction.

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References

1. Jaffe, B., Cook, W. R. and Jaffe, H., *Piezoelectric Ceramics*, London, Academic, 1971.
2. Michael, C., Moreau, J. M., Achenbach, G. D., Gerson, R. and James, W., *Solid State Commun.* **7** (1969), 865.
3. Kumada, A., *Jpn. J. Appl. Phys.* **24** (1985), 739.
4. Uchino, K., *Bull. Am. Ceram. Soc.* **65** (1986), 647.
5. Wood, V. E., Busch, J. R., Ramamurthi, S. D. and Swartz, S. L., *J. Appl. Phys.* **71** (1992), 4557.
6. Preston, K. D. and Haertling, G. H., *Appl. Phys. Lett.* **60** (1992), 2831.
7. Hsueh, C. C., Tamagawa, T., Helgelson, A. and Polla, D. L., *Integr. Ferroelect.* **3** (1993), 21.
8. Petrovsky, V. I., Sigov, A. S. and Vorotilov, K. A., *Integr. Ferroelect.* **3** (1993), 59.
9. Mestnik Filho, J., Carbonari, A. W., Motta, E. F., Moralles, M., Saxena, R. N., Olzon-Dionysio, M. and de Souza, S. D., *Zeitschrift für Naturforschung* **53A** (1998), 318.
10. Alonso, R. E., López García, A., Ayala, A. and de la Presa, P., *J. Phys.: Condens. Matter* **10** (1998), 2139.
11. Catchen, G. L., Wukitch, S. J. and Spaar, D. M., *Physical Review B* **42**(4) (1990), 1885.
12. Forker, M. and Hammesfahr, A., *Z. Phys.* **255** (1972), 196.