Ionic Size Induced Defects in Lead Titanate-Zirconate Perovskite Studied by TDPAC Method *

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Time differential perturbed angular correlation (TDPAC) measurements were carried-out on $PbZr_{0.8}Ti_{0.2}O_3$ as a function of temperature. A broad distribution of electric field gradient (EFG) was observed in all cases with a second site for ^{181}Hf-^{181}Ta probes in the R3c phase. The results were analyzed in terms of a model which simulates an attraction of the ions by the smaller Ti ions. The EFG was calculated within the point charge approximation, by averaging over a large number of configurations generated by random distribution of the Ti ions in an ensemble of lattice cells. It was verified that the model reproduces qualitatively the broadening of the TDPAC frequencies as well as explains the second component EFG observed experimentally.

Key words: $PbZr_xTi_{1-x}O_3$; Perovskites; Crystal Defects; TDPAC Measurements.

Introduction

The perovskites based on lead titanate-zirconate (PZT) are important technological materials due to their high sensitivity as piezo-electric or pyro-electric devices. In a large number of applications these materials are prepared by combining Ti and Zr near the 50–50 atom percent with a small zirconium excess where the system becomes optimized.

The system $PbZr_xTi_{1-x}O_3$ crystallizes in a variety of phases depending on temperature and on the relative concentration of Ti and Zr. The compounds possess many types of electric polarization properties related with the structure as well as with small microscopic modifications like the deformations and tilting of the oxygen octahedra [1]. It was found recently that in PZT, with titanium contents exceeding 15%, an order-disorder phase transition occurs where an oxygen octahedron rotation changes between ordered and disordered states, affecting the electric polarization characteristics of the material [1].

TDPAC studies on the terminal compounds $PbZrO_3$ [2, 3] and $PbTiO_3$ [4] have been performed in order to investigate the nature of the phase transitions. In these cases, well defined electric field gradients are observed in accordance with the crystallographic data. In the present work a TDPAC study with ^{181}Hf-^{181}Ta probes in PZT with the 80/20 Zr/Ti ratio is reported. Two EFG's were observed with strikingly large distributions. These results can be related to the disordered state of the oxygen octahedron tilt. From a microscopic point of view an oxygen octahedron tilt changes the fractional volume occupied by the Zr/Ti ion in PZT [5]. Since a Ti ion possesses a smaller radius than a Zr ion, it is reasonable to suppose that the oxygen octahedron around a Ti ion will have a different tilting configuration as compared with an octahedron around a Zr ion in order to accommodate the two different ionic volumes. We believe that this could be a possible mechanism responsible for the observed disordered phase in PZT.

Experiment

The samples were prepared by mixing the oxides PbO, TiO_2 and ZrO_2 in the required proportions and calcining at 1173 K. The samples were then compressed into pellets and sintered at 1473 K in an atmosphere rich in PbO. The sintered pellets were then ground and analyzed by X-ray and neutron diffraction. For TDPAC measurements the samples were irradiated with thermal neutrons in the IEA-R1 reactor to produce the ^{181}Hf isotope from the hafnium present as impurity in zirconium. Table 1 shows the results of the Rietveld neutron diffraction profile anal-

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Table 1. Crystal lattice parameters for $PbZr_{0.8}Ti_{0.2}O_3$ at room temperature resulting from Rietveld neutron powder diffraction profile refinement. Space Group R3c. Cell parameters $a=5.8238(16)$ $c=14.3657(70)$.

Atom coordinates	Pb	Zr/Ti	O
x	0	0	0.1525(14)
y	0	0	0.3457(13)
z	0.2830(11)	0.01365(19)	1/12
Thermal factors $\langle u^2\rangle$ (Å^2)	0.0166(40)	0.0075 (30)	0.0155(30)

ysis of the $PbZr_{0.8}Ti_{0.2}O_3$ at room temperature with the GSAS code [6].

The TDPAC measurements were carried out with the well known 133–482 keV gamma cascade of ^{181}Ta in the β^- decay of ^{181}Hf. A set up consisting of four BaF_2 scintillation detectors provided the simultaneous acquisition of eight TDPAC spectra with a conventional fast-slow coincidence electronic system. The time resolution of the system was 0.9 ns.

The perturbation factor due to the interaction of the quadrupole moment of ^{181}Ta with an external electric field gradient is given by the expression [7]

$$G_{22}(t)=\sigma_{20}+\sum_{n=1}^{3}\sigma_{2n}\cos(\omega_n t),$$

where the coefficients σ_{2n} and frequencies ω_n are known functions of the main component V_{zz} of the EFG tensor and the asymmetry parameter $\eta=|V_{xx}-V_{yy}|/|V_{zz}|$. The quadrupole frequency is $\omega_Q=eQV_{zz}/[4I(2I-1)\hbar]$ where e is the charge of the electron and Q is the quadrupole moment of the nucleus ($Q=2.36\cdot 10^{-24}$ cm^2 for ^{181}Ta in the 482 keV, $5/2^+$ state) [8]. For a nuclear state with total angular momentum $I=5/2$ and $\eta=0$ one has $\omega_1=6\omega_Q$, $\omega_2=2\omega_1$ and $\omega_3=3\omega_1$. When $\eta\neq 0$ the three frequencies are not harmonic, being determined directly by solving the Hamiltonian which describes the quadrupole interaction [7]. The effects of time resolution τ_R and the distribution of EFG around a mean value with a width δ are introduced by multiplying the expression for $G_{22}(t)$ respectively by the terms $\exp(-\omega_n^2\tau_R^2/2)$ and $\exp(-\omega_n^2\delta^2t^2/2)$.

The perturbation factor is derived from the time-coincidence spectra $W(\theta,t)$, taken at the angles 90 and 180 degrees, by performing the ratio (neglecting the A_{44} term)

$$A_{22}G_{22}(t)\approx -2[W(180,t)-W(90,t)]/[W(180,t)+2W(90,t)],$$

where A_{22} is a known unperturbed angular correlation coefficient.

Figure 1 shows the TDPAC spectra of $PbZr_{0.8}Ti_{0.2}O_3$ at several temperatures. The derived quadrupole interaction parameters are given in Table 2. The compound presents two phase transitions. The low temperature phase is rhombohedral R3c and changes to an other rhombohedral symmetry R3m at 413 K, which then transforms to cubic at 578 K [9]. In each phase the quadrupole frequency decreases as the temperature increases, and quite a large distribution is observed in all the cases. Moreover, two distinct sites, characterized by different quadrupole frequencies, are observed for the R3c phase. No dynamic effects near the phase transitions have been detected.

Discussion

From the TDPAC results it is observed that an unusually broad distribution of EFG exists in $PbZr_{0.8}Ti_{0.2}O_3$ at all temperatures and phases, in contrast to the terminal compounds $PbZrO_3$ [2, 3] and $PbTiO_3$ [4] where well defined EFG are observed. For the low temperature R3c phase, two components of EFG are seen in spite of the fact that only one phase with a single crystallographic site for the Zr/Ti ions is

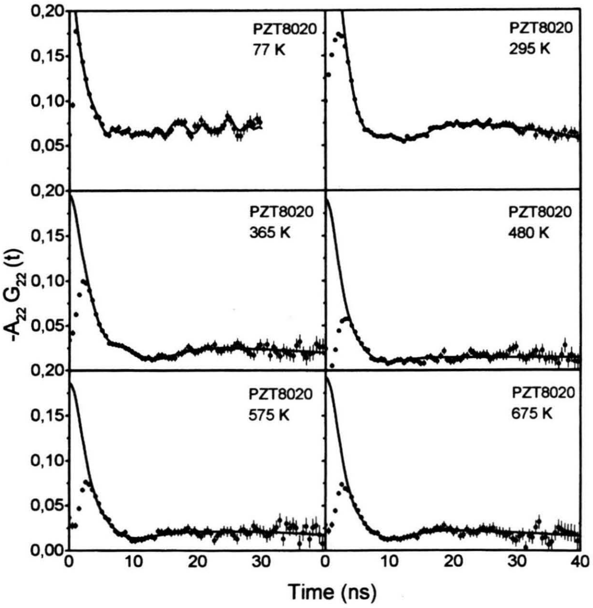

Fig. 1. TDPAC spectra with ^{181}Hf-^{181}Ta probes in $PbZr_{0.8}Ti_{0.2}O_3$ as a function of temperature.

Table 2. Measured quadrupole interaction parameters for $PbZr_{0.8}Ti_{0.2}O_3$ with ^{181}Hf-^{181}Ta probes

T(K)	Group	ω_{Q1} (Mrad/s)	η_1*	δ_1	f_1	ω_{Q2} (Mrad/s)	η_2*	δ_2	f_2
77	R3c	35.8	0	0.59	0.79	129	0	–	0.03
295	R3c	33.0	0	0.36	0.70	92.1	0	0.15	0.17
365	R3c	30.0	0	0.34	0.66	108	0	0.13	0.11
480	R3m	34.3	0	0.49	0.79	–	0	–	–
575	R3m	30.7	0	0.31	0.72	–	0	–	–
675	Pm3m	35.2	0	0.50	0.78	–	0	–	–
720	Pm3m	26.8	0	0.38	0.74	–	0	–	–

(* assumed to be 0)

observed from X-ray and neutron diffraction measurements. In each phase the lower EFG component decreases as the temperature increases as is expected from the lattice expansion with temperature.

It is known that large distributions of EFG are mainly due to imperfections in the lattice. It is believed that the defects in $PbZr_{0.8}Ti_{0.2}O_3$ occur primarily as displacements of ions caused by differences in the radii of two elements that are expected to form a solid solution. As Ti and Zr occupy one crystallographic site and the radii of these ions are quite different (0.68 and 0.79 Å for titanium and zirconium, respectively), they induce different dislocations in the neighboring ions. In a local environment probed by the TDPAC method these displacements may be sufficient to cause appreciable changes in EFG. A computer simulation of the defects caused by Ti ions in $PbZr_{0.8}Ti_{0.2}O_3$ due to their smaller radii as compared with Zr ions was carried-out by applying the Monte-Carlo method.

Initially a computation of the EFG at the Zr/Ti position was made by the point charge model in the undisturbed $PbZr_{0.8}Ti_{0.2}O_3$ R3c structure by taking the parameters shown in Table 1. It was assumed that the expected ionic charges for the lead, zirconium, titanium and oxygen ions are concentrated at points and are respectively $+2e$, $+4e$, $+4e$ and $-2e$, where e is the charge of the electron. The numerical summation was extended to the ions up to a distance of 120 Å from the Zr/Ti ion. The ^{181}Ta Sternheimer anti-shielding factor is $1-\gamma_\infty=62$ [10]. The calculated EFG at ^{181}Ta occupying Zr/Ti sites in $PbZr_{0.8}Ti_{0.2}O_3$ yielded $2.67 \cdot 10^{21}$ Volt/m^2 and $\eta=0$, whereas the value derived from experiment is $3.68 \cdot 10^{21}$ Volt/m^2. The discrepancy may be attributed to the inadequacy of the point charge model in describing the charge distribution of the ions in the structure. However, this discrepancy will not affect the following discussion since we are concerned with the effects caused by the defects and we will compare the EFG computed for a lattice with an without the defects.

As a second step in the calculations, the EFG was estimated after introducing displacements of ions in a way that simulates attraction by titanium ions due to their smaller radii as compared with zirconium. All ions around one Ti ion are displaced toward Ti by the amount given by $\Delta r = -A \cdot \exp(-r/d)$ where A is the magnitude of the displacement, r is the original distance of the ion from Ti and d is a parameter that measures the extent of the disturbance caused by Ti. As d increases, the farther ions are more affected by the presence of Ti. This approach does not simulate the tilting of oxygen octahedra but reduces the volume fraction of Ti ions as the tilting does. In this context it is considered that these displacements are equivalent to the octahedron tilts and similar effects on the EFG are expected.

In the computations, 20% of the Zr/Ti sites in the lattice were substituted by sites which attract the neighboring ions, and the EFG was calculated for the resulting ion configuration. With the computed EFG, the three hyperfine frequencies were derived. This process was repeated for a number (≈ 5000) of different configurations, and the final averaged frequency and TDPAC spectra were obtained.

Figure 2 shows the results of the simulations for various values of A and d. These figures show the frequency as well as the corresponding time spectra of the hyperfine interaction at the ^{181}Ta site resulting from the simulations. In Fig. 2a only the three narrow peaks due to a single EFG are depicted for the case where no ion displacements are performed. In the cases when $d=1$ Å, shown in Figs. 2b and 2c, the frequency spectra broaden and new frequency distributions appear. The positions of these new frequencies are roughly proportional to A. The extra peaks are due to the second component EFG and are still discernible despite the broadening. For the cases where $d=2$ Å, shown in Figs. 2d and 2e, similar effects arise but the peaks are broader than for the $d=1$ Å case, resulting in considerable overlap. The presence of the

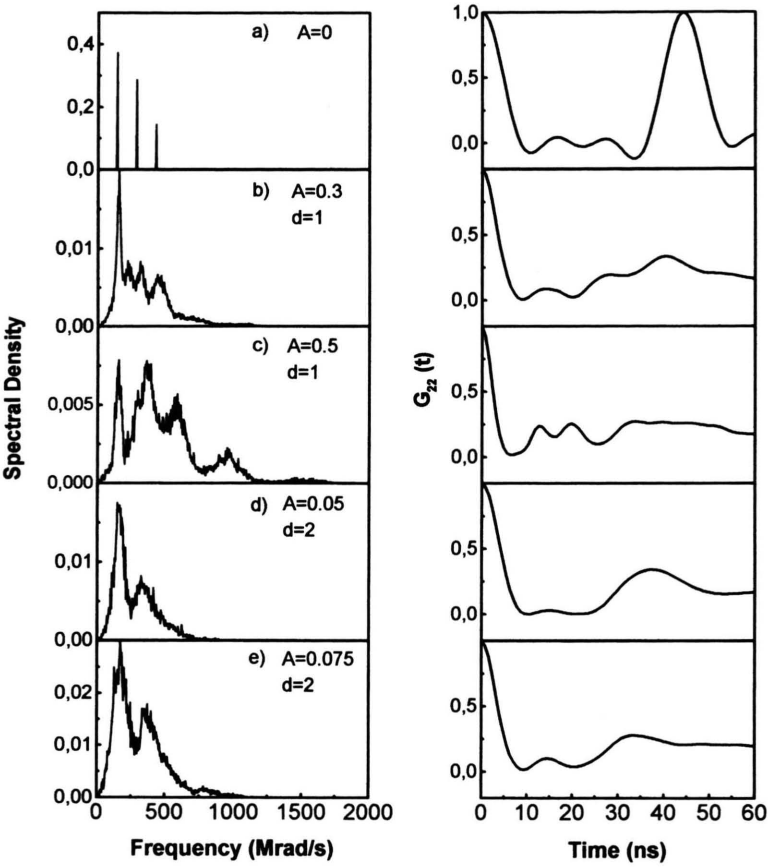

Fig. 2. TDPAC frequency and time spectra resulting from computer simulations of Ti ions acting as attraction centers of neighboring ions in $PbZr_{0.8}Ti_{0.2}O_3$. The parameter A represents the magnitude of the shift of an ion towards Ti, in Angstroms, and d measures the extent of the perturbation caused by Ti (Å). The absolute displacement is given by $\Delta r = -A^* \exp(-r/d)$, where r is the original distance of one ion from Ti.

higher EFG component can be visualized as a distribution around 800 Mrad/s in Figure 2e. In a rough way, one can see that the parameter d has the main effect of broadening the frequency spectra, whereas the parameter A defines the magnitude of the second component EFG.

The first three successive shells of ions around a Zr/Ti site in $PbZr_{0.8}Ti_{0.2}O_3$ are: oxygen ions at 2.06 Å, lead ions at 3.57 Å and Zr/Ti ions at 4.13 Å. Thus, for the case where $d = 1$ Å practically only the first neighbor oxygen ions are dislocated from the equilibrium positions in amounts proportional to the value of A. For example, when $A = 0.3$ Å the first neighbor oxygen ions were dislocated by 0.038 Å, the second neighbor lead ions by 0.008 Å and the third neighbor Zr/Ti ions by 0.005 Å. In the cases where $d = 2$ Å and $A = 0.075$ Å, the oxygen ions are dislocated by 0.027 Å, Pb by 0.013 Å and Zr/Ti by 0.010 Å. This case has the best qualitative agreement with the experimentally determined time spectrum for $PbZr_{0.8}Ti_{0.2}O_3$ at 295 K or 365 K, as can be compared with Figure 1.

Conclusions

The present simulations of the dislocations of ions toward the smaller Ti ions reproduce qualitatively the observed broadening of the TDPAC frequency spectra and give a possible explanation for the second site. The required shifts of the ions toward Ti are small and quite acceptable, producing only a small contraction of the volume occupied by the Ti ions in the structure, which simulates the volume change in the tilting of the oxygen octahedra. An observation which also supports the idea of the existence of such displacements is that the mean square deviations of ions resulting from neutron diffraction measurements, shown in Table 1, are unusually high, specially for oxygen and lead.

For higher temperatures, $T > 365$ K in the present study, we did not observe a second component of EFG in the TDPAC experiments. This may be an indication that the ionic shifts performed in the present work may represent the disordered octahedron tilt state in PZT since it transforms to an ordered state at $T \cong 438$ K [1].

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