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Short-range structure of Pb$_{1-x}$Ba$_x$Zr$_{0.65}$Ti$_{0.35}$O$_3$ ceramic compounds probed by XAS and Raman scattering techniques

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Ti K-edge x-ray absorption near-edge spectroscopy (XANES) and Raman scattering were used to study the solid solution effects on the structural and vibrational properties of Pb$_{1-x}$Ba$_x$Zr$_{0.65}$Ti$_{0.35}$O$_3$ with 0.0 < $x$ < 0.40. Compared with x-ray diffraction techniques, which indicates that the average crystal symmetry changes with the substitution of Pb by Ba ions or with temperature variations for samples with $x$=0.00, 0.10, and 0.20, local structural probes such as XANES and Raman scattering results demonstrate that at local level, the symmetry changes are much less prominent. Theoretical XANES spectra calculation corroborate with the interpretation of the XANES experimental data.

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I. INTRODUCTION

Lead zirconate titanate oxide (PbZr$_{1-x}$Ti$_x$O$_3$ or PZT) compounds are one of the most studied ferroelectric materials, not only due their technological applications but also due to their usefulness in fundamental research.$^{1,2}$ It is well known that the substitution of Pb atoms by Ba atoms in PZT system induces important changes, mainly on the electrical properties, with a linear decrease in $T_m$ ($T_m$=maximum of the relative dielectric permittivity temperature), which tends to room temperature as the amount of Ba increases. Moreover, depending on the amount of Ba atoms, a diffuse behavior and a large frequency dependence of the relative dielectric permittivity are observed.$^{1,2}$ Materials presenting these behaviors are denominated relaxor ferroelectrics. They present a characteristic temperature $T_m$ that is no longer a crystal phase transition temperature and shows strong frequency dependence.

The Pb$_{1-x}$Ba$_x$Zr$_{0.65}$Ti$_{0.35}$ (PBZT) compositions with $x$ < 0.30, whose long-range order structure probed by x-ray diffraction (XRD), were characterized by low symmetric rhombohedral phase, present, at room temperature, a normal ferroelectric behavior.$^3$ The ferroelectric property in this case is well explained by the formation of well-defined microdomains and wall domain structures when they are cooled from paraelectric to ferroelectric phase. On the other hand, for compositions which present a relaxor character, $x$ ≥ 0.30, an average long-range cubic symmetry was observed at room temperature.$^3$ It is well accepted that the relaxor character of these compounds can be attributed to the existence of nanometric polar regions immersed in a high polarizable host lattice.$^4$

Although the long-range order structure of normal and relaxor PBZT ferroelectric ceramic compounds was recently well established,$^3$ to the best of our knowledge, we did not found in the literature any report concerning the short-range structure of this set of samples.

In the last decade, x-ray absorption spectroscopy (XAS) and Raman spectroscopy have become important tools to study the structural short-range order of normal and relaxor ferroelectric materials.$^3$–$^{14}$

X-ray absorption near-edge structure (XANES) studies have provided interesting information of the local structure of disordered crystalline compounds as well as their phase transition mechanism.$^3$–$^{11}$ These studies have shown that local structure remains distorted even on the relaxor samples well characterized as cubic according XRD measurements.

While XANES probes the local structure, with order or disorder, around a selected atom (Ti atom in this case), Raman scattering probes the structure in the medium range, within a few lattice parameters. On the other hand, XRD probes averaged long-range order distances within the complete set of lattice parameters. So, it is expected that each technique may lead to different results when analyzing the same sample, especially if there is a certain amount of structural disorder, and the correct interpretation of the results obtained by these different probes may lead to a better understanding of the material behavior.

In this work, XANES and Raman spectroscopy were used to probe the short- and medium-range structures in PBZT system in order to elucidate how the substitution of Pb by Ba atoms acts on the local structure, mainly around titanium atoms. These results are also confronted with XRD data already published.$^3$ To correlate the Ti K-edge XANES spectral features which appear on the pre-edge region spectra.
and their behavior as Pb atoms are substituted by Ba atoms, we have also carried out model calculations of $x=0.0$ sample as a function of the temperature using the full multiple-scattering calculations with the FEFF 8.2 code.\textsuperscript{15}

\section*{II. EXPERIMENTAL AND METHOD OF CALCULATION}

PBZT samples of nominal composition Pb$_{1-x}$Ba$_x$Zr$_{0.65}$Ti$_{0.35}$ with $0.0 \leq x \leq 0.40$ were prepared by conventional mixed oxide method.\textsuperscript{3,4} The oxides and carbonates, PbO, BaCO$_3$, ZrO$_2$, and TiO$_2$, weighed according to the stoichiometry, were mixed by ball milling in distilled water for 10 h. The slurry was dried and calcined in a covered alumina crucible at temperatures between 1300 and 1373 K for 3 h. Ceramic bodies were then conformed by isostatic pressure and fired at $\sim$1450 K for 3 h. The sintering occurred in closed Al$_2$O$_3$ crucibles at saturated PbO atmosphere and the highest density samples were chosen for the physical characterization.

Titanium $K$-edge XANES spectra were collected at the LNLS (National Synchrotron Light Laboratory) facility using the D04B-XAS1 beam line. The LNLS storage ring was operated at 1.36 GeV and 180–250 mA. The sample pellets, obtained after sintering, were grounded for XAS measurements. XANES data were collected at the Ti $K$-edge (4966 eV) in transmission mode at room temperature using a Si(111) channel-cut monochromator. Ionization chambers filled with helium gas were used to detect the incident and the transmitted flux. XANES spectra at the Ti $K$-edge were recorded for each sample between 4910 and 5100 eV using energy steps of 0.3 eV around the edge. To provide good energy reproducibility during the XANES data collection, the energy calibration of the monochromator was checked during the collection of the sample using a Ti metal foil. The XANES spectrum of $x=0.0$ sample was recorded below and above $T_C$ (343 K) at 293 and 430 K. The XANES spectrum of $x=0.40$ sample was recorded at 20, 100, 120, and 293 K, which are temperatures below and above $T_m$ (215 K).

Raman scattering measurements were performed using a Jobin-Yvon T64000 triple monochromator with a charge coupled device detector. The 514 nm line of an argon laser was used as exciting light, with the power kept below 1 mW, measured after the 50$\times$ objective. For the low temperature measurements, in the 10–300 K, a helium closed cycle cryostat was used, while for high temperature, in the 300–750 K range, an optical microfurnace was used.

Calculation of XANES spectra was performed using the \textit{ab initio} FEFF8 code with the self-consistent and full multiple-scattering options.\textsuperscript{15} XANES spectra of $x=0.0$ sample, which correspond to PbZr$_{0.65}$Ti$_{0.35}$O$_3$, were calculated in terms of a cluster derived from the average structure determined from previous XRD data.\textsuperscript{3} Clusters with a size up to eight shells, containing at least 110 atoms in an $R=9$ Å radius, around the absorber (titanium atom) were used to calculate the XANES spectra based on the $x=0.0$ rhombohedral (below $T_C$) and cubic (above $T_C$) crystallographic phases. The calculation was performed according to the default setting of FEFF8 code and no experimental broadening was taken into account.\textsuperscript{15} PbZr$_{0.65}$Ti$_{0.35}$O$_3$ is a disordered system where Zr ions are substituted by Ti in randomly distributed sites. The best approach to simulate the theoretical XANES spectrum of such a disordered structure implies the calculation of many spectra with various random Ti site distributions.\textsuperscript{16} This set of computed spectra is averaged. New calculations are performed with an additional set of Ti distributions and added to the running average until the result stops changing.

\section*{III. RESULTS AND DISCUSSION}

\subsection*{A. Ti $K$-edge XANES spectra}

Figure 1 shows the Ti $K$-edge XANES spectra of PBZT samples at room temperature as well as the detailed pre-edge region. In transition metal oxides which crystallize in centrosymmetric structures, the pre-edge peak denoted as $A$ is very small or absent, while in noncentrosymmetric structures it can be quite intense. According to the literature, the physical origin of this $K$ pre-edge peak is due to the transition between the 1$s$ Ti core level and a final state which can be described in two different but equivalent manners.

\begin{enumerate}
\item The final state can be interpreted as an unfilled bond 3$d$ state.\textsuperscript{17} This dipole-forbidden electronic transition is enhanced by hybridization with $p$-character orbitals from surrounding oxygen atoms. This $p$-$d$ hybridization occurs when the local structure is distorted.
\item The final state can also be interpreted as the result of multiple scattering of the Ti $K$ edge photoelectron by the Ti neighbors. Such multiple-scattering path resonances are lowered by destructive interferences when the local structure is regular and centrosymmetric and enhanced by the local distortions.
\end{enumerate}

Thus, the height of this pre-edge peak can be used to study the TiO$_6$ local distortion in these samples. Such study can be done either experimentally by comparison of the XANES spectra of model compounds with known crystal structures and those of the unknown species, or by theoreti-
cal modeling, using *ab initio* codes. In the early XAS works on this perovskite family, it was impossible to extend post-edge *ab initio* XAS calculations to the pre-edge region because the multiple scattering extension approximations introduced by these codes was not accurate in the pre-edge spectral range. The full multiple scattering codes available now allow to calculate the XANES spectra in the full energy range with a good accuracy. This is why most papers referenced in this work used only empirical comparison to experimental XANES spectra of model compounds. At present, theoretical codes are efficient and accurate enough, even in the pre-edge region and it is possible to compare experiments and theoretical models.

From the experimental point of view, EuTiO$_3$, whose structure presents regular TiO$_6$ octahedra, is considered as a prototype perovskite with a cubic and regular structure. CaTiO$_3$ is also a good model compound for XANES studies because it is an example of an almost regular TiO$_6$ octahedral site within a noncubic crystal structure (orthorhombic). In the XANES spectra of these two different prototype compounds, the pre-edge feature is similarly very weak, while their post-edge XANES structures are completely different.

Among our samples, none have pre-edge peak amplitude similar to these undistorted models (Fig. 1). On the contrary, their amplitudes are closer to the pre-edge structure of PbTiO$_3$, which is a typical Ti off-center structure. Moreover, the amplitude of the pre-edge peak does not show any dependence with sample composition. In the $x=0.0$ sample Ti atoms are coordinated in the first coordination shell by six oxygen atoms in two different sets of distances in a distorted octahedra (three Ti–O bonds at 1.87 Å and three Ti–O bonds at 2.30 Å). According to these results, it appears that the distortion of the TiO$_6$ octahedra observed in the $x=0.0$ sample did not vary significantly when the amount of barium increases. According to our XANES data, this local distorted structure is preserved even for the $x=0.30$ and $x=0.40$ samples for which XRD analysis showed a cubic structure and a regular TiO$_6$ octahedra.

Dealing with the relationship between pre-edge peak $A$ height and the Ti off-center structure, our results for PbZT are in agreement with previous XANES studies of PZT materials by Ravel and Stern and by Cao et al. They have concluded, based on the fact that changes in the pre-edge peak of the Ti $K$-edge spectra are relatively smaller, that Ti local structure in their PZT samples is only weakly dependent on the sample composition and crystallographic phase.

On the other hand, significant changes are observed in the XANES spectra beyond the edge (Fig. 1). As the amount of barium increases, $B$ peak disappears and $C$ and $D$ peaks become more broadened. This region of the XANES spectra is related to the medium-range order structure around titanium atoms. The $x=0.40$ sample shows the most significant changes in this region, which could be attributed to the substitution of a large amount of Pb$^{2+}$ by Ba$^{2+}$ atoms or to the crystal structure changes induced by this substitution. Although Pb and Ba atoms have the same valence (2+), the ionic radius of Pb$^{2+}$ (1.19 Å) is smaller than that of Ba$^{2+}$ (1.35 Å). Figure 2 compare the experimental XANES spectra of $x=0.0$ and $x=0.40$ samples measured at room temperature with that of the BaTiO$_3$ model compound. This simple empirical comparison of experimental spectra allows us to verify that although the presence of 40% Ba substituting Pb atoms, the structure represented by the XANES spectrum of $x=0.40$ sample is not a simple mixing of $x=0.0$ and BaTiO$_3$ structures, since peak $B$ is dramatically enhanced in BaTiO$_3$ and almost absent in the spectrum of $x=0.40$ sample.

In order to better understand the structural origin of the after edge features, we have performed theoretical calculations based on crystal structures of PbZT samples determined from our previous XRD measurements. First, we calculated the XANES spectrum of $x=0.0$ sample (rhombohedral) as a function of the cluster size $R$ (Fig. 3). It appears clearly that the pre-edge peak $A$ is present with a noticeable height even when we only consider the first oxygen coordination shell around the Ti atom ($R<3$). On the other hand, peaks B–D can be correctly reproduced if the cluster size is bigger than 6 Å. It can be observed that peak $B$ appears when the coordination shell containing Pb and Ba atoms is considered in the calculation, meaning that the disappearance of this peak as the amount of barium increases could be in part attributed to the substitution of Pb by Ba atoms.

We undertook two other theoretical calculations with the same objective: first, we assumed that the XANES spectra of $x=0.40$ sample could be reproduced by considering the same structure of $x=0.0$ compound (rhombohedral) with the Pb atoms replaced by Ba atoms according the $x=0.40$ stoichi-
omentry. In a second calculation, we assumed that the XANES spectra of \( x = 0.40 \) sample could be reproduced by considering a cubic structure as determined from previous XRD results\(^3\) with Ti atoms displaced from their centrosymmetric position. The two additional theoretical spectra (figure not shown) derived from these hypothetical structures are in complete disagreement with the observed \( x = 0.40 \) XANES spectra. Thus, up to now, we are unable to propose a satisfying structural model which could explain the XANES features above the Ti \( K \)-edge and their changes versus Ba concentration mainly for \( x > 0.20 \) samples.

We also undertook a structural study of a normal (\( x = 0.0 \)) and relaxor (\( x = 0.40 \)) ferroelectrics as a function of the temperature considering the dielectric permittivity behavior of these samples.\(^4\) Figures 4(a) and 4(b) show, respectively, the XANES spectra of \( x = 0.0 \) and \( x = 0.40 \) samples as a function of temperature. In both cases, we observed only a very slight decrease on the pre-edge peak A as the temperature increases (\( x = 0.0 \)) or decreases (\( x = 0.40 \)). In the case of \( x = 0.0 \) sample, according to the PZT phase diagram proposed,\(^3\) when the temperature increases, at 300 K a structural phase transition from \( R3m \) to \( R3c \) is observed, while a structural phase transition from rombohedral (\( R3c \)) to cubic is observed at 620 K. This temperature corresponds to the Curie (\( T_C \)) temperature. Thus, even for a normal ferroelectric sample, well above \( T_C \) (paraelectric phase), where, according XRD refinement, the long-range structure was characterized as cubic, the presence of the pre-edge A peak on the XANES spectra clearly shows that titanium atoms are yet located out of center of symmetry.

Concerning the \( x = 0.40 \) sample, according to XRD results, this sample does not show any structural phase transformation from 10 to 450 K. It is characterized as cubic in the whole interval, above and below \( T_m \) (290 K).\(^3\) XANES results presented on Fig. 4(b) clearly shows that in all range of temperature where the long-range order structure was characterized as cubic, the short-range order around Ti atoms is not affected by the temperature variation and titanium atoms are located out of center in the TiO\(_6\) octahedron in spite of the cubic long-range order.\(^3\)

Figure 5 presents the \( ab \) initio XANES calculated spectra for the \( x = 0.0 \) sample based on the rhombohedral and cubic phases. It can be observed that the calculated XANES spectra of \( x = 0.0 \) sample based on the rhombohedral phase reproduce quite well the pre-edge and post-edge XANES structures presented on the experimental spectra of \( x = 0.0 \) collected below 620 K (below \( T_C \)), which corresponds experimentally to the rhombohedral phase [Fig. 3(a)]. On the other hand, the calculated XANES spectra based on the cubic phase, which corresponds to the experimental XANES spectra collected above 620 K (above \( T_C \)), show that the pre-edge feature A is totally removed and the features present at the edge and after the edge shows a significative change in their intensities.

However, as can be clearly seen on Fig. 4(a), the XANES spectra of \( x = 0.0 \) sample collected above \( T_C \) (cubic structure according XRD) present a pre-edge feature characteristic of distorted TiO\(_6\) octahedron. Thus, the calculation based on the cubic structure shows that the structural model obtained from XRD for temperatures above \( T_C \) is not appropriate to describe the short- and medium-range order structures of this sample. These results are in good agreement with our previous experimental and theoretical calculations on the Pb\(_{1-x}\)La\(_x\)TiO\(_3\) ferroelectric system.\(^5\) Our theoretical
study is also in agreement with the work of Cabaret et al. who showed the same kind of disagreement between experimental XANES spectra and ab initio calculations based on the XRD structures of perovskite compounds.\textsuperscript{12}

Concerning the pre-edge structure, both the experimental and theoretical calculations could be interpreted unambiguously: XANES results presented on this paper show that it does not matter if the sample is a ferroelectric or a relaxor material and the long-range order presents a low or a high symmetric phase, the local distortion on the TiO\textsubscript{6} octahedron exists in any cases and is not affected by changing the composition, crystallographic symmetry, and by the temperature.

B. Raman scattering results

Figure 6 shows the Raman spectra of the five PBZT samples at low temperature (10 K). In the high frequency region, the peak at 680 cm\textsuperscript{-1}, present only for $x=0.0$, 0.10, and 0.20, may be considered as an assignment of the rhombohedral phase. This peak is drastically reduced or even absent in the Raman spectra of the samples with $x=0.30$ and 0.40. In the low frequency region, below 500 cm\textsuperscript{-1}, the exchange of Pb by Ba leads to a broadening of the Raman peaks, indicating an increase in the structural disorder. This effect was and is still subject of many discussions in perovskite materials. An interesting discussion was done by Comes et al.\textsuperscript{20} since 1968, where the authors showed, by analyzing the diffuse scattering of x rays, that BaTiO\textsubscript{3} is “naturally” disordered in the cubic, tetragonal, and orthorhombic phases. In our samples, the addition of Zr atom certainly leads to increase the structural disorder, as corroborated by the Raman results.

For temperatures around 300 K (Fig. 7), a similar behavior as described above was observed in the high frequency region of the Raman spectra. On the contrary, in the low frequency region it can be seen an important increase in the relative intensity of the peaks at about 130, 300, and 430 cm\textsuperscript{-1} as the Ba concentration increases. These changes in the Raman spectra may be indicative of changes in the medium-range order.

Figure 8 displays the Raman spectra of the five samples at temperatures in which they should be in the cubic phase according to XRD results.\textsuperscript{3} The Raman results show that the five samples present basically similar Raman spectra; although in the cubic phase the perovskite-type materials should not exhibit any Raman peaks. It is clear that it is not the case, since it is possible to identify the three broadened main peak characteristics of the overall perovskite structure around 250, 550, and 750 cm\textsuperscript{-1}. This result is strongly indicative that at medium range, at least within distances containing a few unit cells, the structure is not cubic. This observation was already reported in other perovskites, using Raman scattering, as (Pb,La)TiO\textsubscript{3}, for example.\textsuperscript{21,22} Recent work of Itié et al.\textsuperscript{23} presented a high pressure XANES measurement at the Ti K-edge of BaTiO\textsubscript{3} perovskite compound. They observed that above 10 GPa the Ti atom is at the center of the oxygen octahedron and the Raman activity remains unchanged. Thus, they pointed out that the observation of nonallowed broad Raman peaks in the cubic phase of these compounds at high pressures could not be directly correlated only to the fact that Ti atoms are in an off-center position. They attributed the existence of these broad bands to a second order Raman scattering effect. In the present case of PBZT samples, there are an important chemical disorder in both sites A and B, hence it is expected an important local structural disorder, which may also lead to the breakdown of the Raman selection rules. Ykeuchi et al.\textsuperscript{24} also observed a quasielastic scattering and a few internal modes on Ti-rich Pb(Zr\textsubscript{x}Ti\textsubscript{1−x})O\textsubscript{3} ceramic samples above $T\textsubscript{C}$ (Curie tempera-
tured). Based on the fact that the intensity of these modes decreases as the temperature increases, they attributed the origin of this modes to a first order transition Raman scattering due to local breakdown of cubic symmetry by some kind of disorder.

IV. CONCLUSIONS

In the present paper Ti K-edge XANES and Raman scattering spectra were used to study the temperature and cation substitution effects on the structural and vibrational properties of Pb$_{1-x}$Ba$_x$Zr$_{0.65}$Ti$_{0.35}$, with 0.0 < x < 0.40.

XANES results showed that at very short-range order, within the first coordination sphere around the Ti ion, any change can be observed in the spectrum by changing Pb by Ba ion or changing the temperature, contrary to the XRD data, which indicate rhombohedral to cubic phase transition for x = 0.0, 0.10, and 0.20. Theoretical XANES calculations corroborate with the XANES experimental data. After edge, XANES spectrum displays significative differences between samples with different Ba amounts, mainly for the peak at around 4982 eV, indicating changes within distances longer than the first coordination shell (medium-range order). On the other hand, Raman scattering results showed that even in their high Ba concentration (x = 0.30 and 0.40) and/or high temperature conditions (cubic phase from the XRD point of view) the Raman spectra present broad bands similar of the tetragonal phase. These results are strongly indicative that at short and medium ranges, the local symmetry is preserved, although the overall symmetry may change depending on the Ba concentration and/or on the temperature, that is, it does not matter if the material is in the ferroelectric or in the paraelectric phase, the local distortion on the TiO$_6$ octahedron exists in both cases.

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