EXAFS study of lead-free relaxor ferroelectric BaTi$_{1-x}$Zr$_x$O$_3$ at the Zr K-edge

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Extended X-ray absorption fine structure (EXAFS) experiments at the Zr K-edge were carried out on perovskite relaxor ferroelectrics BaTi$_{1-x}$Zr$_x$O$_3$ (BTZ) ($x = 0.25, 0.30, 0.35$), and on BaZrO$_3$ for comparison. Structural information up to 4.5 Å around the Zr atoms is obtained, revealing that the local structure differs notably from the average Pm3m cubic structure deduced from X-ray diffraction. In particular, our results show that the distance between Zr atoms and their first oxygen neighbors is independent of the Zr substitution rate $x$ and to that measured in BaZrO$_3$, while the X-ray cubic cell parameter increases linearly with $x$. Furthermore, we show that the Zr atoms tend to segregate in Zr-rich regions. We propose that the relaxor behavior in BTZ is linked to random elastic fields generated by this particular chemical arrangement, rather than to random electric fields as is the case in most relaxors.

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I. INTRODUCTION

The perovskite-type barium zirconate titanate, BaTi$_{1-x}$Zr$_x$O$_3$ (BTZ), has attracted considerable attention as a possible lead-free ferroelectric material to replace the current industry standard lead-based ferroelectrics. The particularity of BTZ is the continuous change of its properties from a ferroelectric behavior at low Zr substitution rates to a relaxor ferroelectric (relaxor) behavior at higher substitution rates ($0.25 \leq x \leq 0.5$). The low substitution regime has been mainly studied for its interest in lead-free ferroelectric memories. However, due to the recent report of outstanding electro-mechanical properties in relaxor-based ferroelectric solid solutions, it is rather the relaxor regime of BTZ which currently attracts a large research effort.

Relaxors are characterized by a broad and frequency-dependent dielectric anomaly as a function of temperature, instead of a sharp and frequency-independent divergence as in classical ferroelectrics. In a relaxor such as PbMg$_1/3$Nb$_2/3$O$_3$ (PMN), the anomaly surprisingly occurs in a cubic average structure which remains centrosymmetric (non-polar) at all temperatures. It is generally admitted that the peculiar properties of relaxors are related to the presence of nano-scaled polar regions, due to different cation shifts in different parts of the structure.

Two necessary ingredients are often cited for a relaxor ferroelectric: (i) the presence of Pb$^{2+}$ or Bi$^{3+}$ cations (showing large displacements due to their lone-pair) and/or (ii) a heterovalent cationic disorder (generating random local electric fields that break long-range polar correlations). They are both present in the extensively studied model relaxor PMN (e.g., Refs. [14,15,16,17,18,19,20]). On the other hand, BTZ relaxors present a homovalent Zr$^{4+}$/Ti$^{4+}$ substitution, which does not give rise to such random electric fields. Therefore, another mechanism has to be considered in order to account for the break of long-range correlated displacements in BTZ. It has been proposed that random elastic fields, induced by the difference in size of Zr$^{4+}$ and Ti$^{4+}$ cations, play an important role. Yet it is not known how, and on which scale such random elastic fields build up. The BaTi$_{1-x}$Zr$_x$O$_3$ solid solution thus opens an interesting route towards the comprehension of the relaxor behavior, and raises much interest.

The average crystal structure of the BTZ relaxors ($0.25 \leq x \leq 0.5$) is cubic (space group Pm3m) at any temperature. Local distortions away from the ideal cubic structure expected from the observation of the relaxation behavior are evidenced by the observation of a first-order Raman scattering, which is forbidden in a perfect primitive cubic structure. However, the latter technique does not reveal the nature of these distortions. The aim of the present study is to determine the local structure and chemical order in BTZ relaxors. For this purpose, we used EXAFS (Extended X-ray Absorption Fine Structure) spectroscopy which is a structural and chemical local probe. This technique has been proven to be a powerful tool to analyze the local distortions in ferroelectric perovskites (e.g., Refs. [22,23,30,31]). On the other hand, only a few EXAFS studies have been reported for relaxors yet [32,33,34,35,36].

In the following, we report an EXAFS study of three BTZ relaxors ($x = 0.25, 0.30$ and $0.35$) at the Zr K-edge. The local structure parameters were determined up to
distances of 4.5 Å from the Zr atoms, giving information on their local environment up to their fourth neighbors. Hence, the Zr/Ti repartition could be probed, as well as the distortions induced by the substitution of Ti atoms by Zr ones in BaTiO₃. In order to have a proper reference for the understanding of the local Zr environment, we also studied BaZrO₃ under the same experimental conditions.

II. EXPERIMENTAL METHODS

A. Samples and experiments

BaTi₁₋ₓZrₓO₃ (x=0.25, 0.30, 0.35 and 1) powders were synthesized by solid state reaction, starting from the appropriate amounts of BaCO₃, TiO₂, and ZrO₂ powders and following the method described in Ref. [3]. They were then characterized by X-ray diffraction at 300 K. All the powders were found to be single phases within the accuracy of the experiment. The cubic cell parameters are 4.054(1), 4.061(1), 4.072(1), and 4.192(1) Å for x values of 0.25, 0.30, 0.35, and 1 respectively.

EXAFS experiments at the Zr K-edge (17.998 keV) were carried out on the FAME beamline BM30B at the European Synchrotron Radiation Facility (ESRF). The X-ray absorption coefficient μ was measured in the transmission mode as a function of the incident photon energy E in the range [17.8-19.5 keV], using a Si(220) single crystal monochromator. The samples consisted of pellets made of BaTi₁₋ₓZrₓO₃ powders (with a grain size of about 1 µm) mixed with very low-absorbing boron nitride. The effective thickness e of each sample was chosen in such a way that the product µe increases approximately by 1 through the Zr K-edge. EXAFS data were collected at room temperature for all samples, as well as at 11 K for BaZrO₃ and at 11K, 90 K and 150 K for BaTi₀.₆₅Zr₀.₃₅O₃.

B. EXAFS data treatment

The scattering of the photoelectron by the neighbors of the central absorbing atom introduces oscillations in the energy dependence of the absorption coefficient μ(E) after the energy edge. The normalized experimental EXAFS signal is given by χ(k) = [μ(k) - μ₀(k)]/Δμ₀(k = 0). μ₀ is the smooth, atomic-like, absorption background, Δμ₀(k = 0) is the absorption edge jump and k is the photoelectron wave number, given by k = √(2mₑ(E - E₀)/h²) with mₑ the electron mass and E₀ the edge energy. In the present work, χ(k) was extracted from the measured absorption coefficient μ(E), by using the AUTOBK program. E₀ was taken at the first maximum of the derivative of μ(E) at the Zr K-edge. Two representative examples of normalized k²-weighted χ(k) spectra are shown in Fig. 1.

The theoretical EXAFS signal χ(k) is expressed as a sum of contributions from different paths, each path i corresponding to a given scattering process of the photo-electron:

\[
\chi(k) = -S₀² \sum_i N_i A_i(k) \frac{\bar{R}_i}{kR_i²} e^{-2k²σ_i²} e^{-2R_i/\lambda(k)} \sin(2kR_i + 2δ_i(k) + φ_i(k)),
\]

where N_i is the degeneracy of path i, R_i its half-length and A_i(k) its effective scattering amplitude. The Debye-Waller (DW) factor σ_i² is the standard deviation of the R_i distance distribution, assumed to be gaussian. The DW factor takes into account both the thermal disorder and a possible small structural disorder. δ_i(k) and φ_i(k) are phase shifts associated with the electron propagating into and out the potentials of the absorbing site and scattering sites respectively. The other parameters are the photoelectron mean-free path λ(k) and an overall amplitude factor S₀², close to 1, which accounts for many-electron effects in the excited central atom. Note that Eq. 1 includes both single (back-)scattering (SS) and multiple scattering (MS) processes. For a SS path, N_i is simply the number of chemically identical atoms situated at a given distance R_i from the central atom.

The analysis of EXAFS signals at the Zr K-edge was performed in R-space after a Fourier transform (FT) of the k²-weighted χ(k) in the k-range [3.2-14.6 Å⁻¹], using a Hanning weight function. The calculated FTs were fitted to the experimental ones using the FEFFIT program. The electronic parameters A_i(k), φ_i(k), δ_i(k) and λ(k) were calculated for both SS and MS paths with the FEFF8.00 code. The structural parameters R_i, σ_i², as well as N_i if unknown, were extracted from the fit as will be described in details in sections [III B] and [III C].
As customary, an additional parameter $\Delta E_0$ was introduced to account for the small difference between the experimental edge energy $E_0$ and its calculated value using the FEFF code. The parameter $S_0^2$ was also refined, the experimental value usually differing from the theoretical one.

III. RESULTS

A. General trends

Examples of the Fourier transforms of the experimental $k^2$-weighted $\chi(k)$ spectra are shown in Fig. 2. For all studied samples and at all temperatures, the FTs can be readily separated into two contributions, characteristic of the perovskite structure. The first neighbors of a Zr atom are six oxygen atoms (denoted hereafter as O1), which form a regular octahedron in the perfect Pm3m perovskite structure. The first contribution to the FT, at $R$ values lower than 2.5 Å, only includes a SS process by one of the O1 atoms. The second contribution, in the $R$-range [2.5-4.5 Å], results both from SS processes where the photoelectron is backscattered by either the second (Ba), third (Zr or Ti), or fourth oxygen (O2) neighbors of the Zr atom, and from several MS processes. Note that due to the $k$-dependence of the phase shifts $\phi_i(k)$ and $\delta_i(k)$, the maxima of the FT modulus occur at distances different from the real ones.

Surprisingly, the first peaks of the FTs are nearly identical at 300 K in all relaxor samples and in BaZrO$_3$ (see Figs. 2 and 3). The latter suggests very close first neighbors environment of the Zr atoms, whatever the Zr substitution rate. On the other hand, the FTs of BaZrO$_3$ and BTZ relaxors differ significantly for $R$ values larger than 2.5 Å.

The shape of the FTs suggests an analysis in two steps. Fits of the measured FTs are first performed in the $R$-range related to the Zr first oxygen neighbors (Sec. III B). In a second step, the fitted $R$-range is extended up to 4.5 Å, in order to take into account the second neighbors contributions (Sec. III C and III D). In BTZ relaxors, one has to take into account both the Zr/Ti substitution and the strong contribution of several MS paths in this $R$-range, which makes the EXAFS analysis complicated. In order to get reference parameters for the analysis of BTZ relaxors, the FT of BaZrO$_3$ is first fitted (Sec. III C). From previous EXAFS studies, the local structure of BaZrO$_3$ can be considered as a perfect cubic perovskite structure, identical to the average one deduced from X-ray diffraction (space group Pm3m).

B. Analysis of the first neighbor contribution

We already noted that the backscattering processes between Zr atoms and their first oxygen neighbors (O1) give rise to very similar contributions to the FTs of the EXAFS signals below 2.5 Å, for all samples and at all temperatures (Figs. 2 and 4). From the known structure of BaZrO$_3$, it is then reasonable to assume, as a starting point for the analysis of BTZ relaxors, that the six O1 atoms are located at the same distance from the absorbing Zr atom. Within this hypothesis, only one SS path (denoted hereafter as path 1) contributes in Eq. 1 for the considered $R$-range. The fitted parameters are, for each sample, the Zr-O1 distance $R_1$, the associated DW factor $\sigma_1^2$ and $\Delta E_0$. The number of O1 neighbors, $N_1$, is fixed to 6. The analysis of the EXAFS data for BaZrO$_3$ at 11 and 300 K allows to determine $S_0^2$ value equal to 1 ± 0.07. This parameter was then fixed to 1 for all the further analysis. The EXAFS oscillations were refined in the $R$-range [1.14-2.33 Å]; the data for $R$ lower than 1 Å are affected by the background subtraction procedure and had to be excluded from the fit. Fits of good quality could be obtained, with reliability factors less than 1%, for all samples at all temperatures (Fig. 4 and Table I).

In BaTi$_{0.65}$Zr$_{0.35}$O$_3$ and BaZrO$_3$ samples, no significant temperature dependence of the Zr-O1 distance is
detected, within the experimental accuracy of the EXAFS technique. More surprisingly, the Zr-O1 distance hardly varies with the Zr substitution rate \( x \), and keeps values very close to that found in BaZrO\(_3\).

The refined values of the \( \sigma_1^2 \) DW factors in BaZrO\(_3\) at 11 and 300 K are in good agreement with those reported in Ref. 43. In BTZ relaxors, systematically higher \( \sigma_1^2 \) values are obtained. From the definition of the DW factor, this increase depicts either a stronger static disorder, or enhanced vibration amplitudes (associated with a decrease of the Zr-O1 bond stiffness). As a matter of fact, the static and dynamic contributions can be separated, by analyzing the thermal evolution of the measured DW factor. In the absence of a static disorder, the DW factor only accounts for thermal vibrations and can be written, in the Einstein model, as:

\[
\sigma_{1,\text{therm}}^2(T) = \frac{k_B^2}{2B M R \theta_E} \coth\left(\frac{\theta_E}{2T}\right),
\]

where \( k_B \) is the Boltzmann constant, and \( M \) the reduced mass of all atoms involved in the scattering path. The Einstein temperature \( \theta_E \), characterizing the bond strength, increases with the bond stiffness. Given our hypothesis of a perfect Pm\( \overline{3} \)m perovskite local structure in BaZrO\(_3\), the two \( \sigma_1^2 \) values measured at 11 and 300 K in this sample were fitted to Eq. 2. An Einstein temperature of 606 K ± 14 K was then obtained for the Zr-O1 bond. In Ba\(_{1-x}\)Ti\(_x\)Zr\(_{0.35}\)O\(_3\), the thermal evolution of \( \sigma_1^2 \) is consistent with the same \( \theta_E \) value, provided that a constant \( \Delta \sigma_1^2 = +0.0007 \) Å\(^2\) is added to Eq. 2 (Fig. 4). This result gives evidence for the existence of a static distribution of the Zr-O1 distances in Ba\(_{1-x}\)Ti\(_x\)Zr\(_{0.35}\)O\(_3\), which is temperature-independent within the experimental accuracy. The full width at half maximum of a gaussian distribution of distances would be equal to \( 2\sqrt{2}\ln 2\Delta \sigma_1^2 = 0.06 \) Å. This small value justifies a posteriori the use of only one SS path in Eq. 1, the DW factor \( \sigma_1^2 \) taking into account the small disorder that cannot be resolved in R-space.

The mean square deviation of the \( R_1 \) distance linked to a static disorder, \( \Delta \sigma_1^2 \), is intended to describe a gaussian static distribution of distances in Eq. 1 with \( \sigma_1^2 = \sigma_{1,\text{therm}}^2(T) + \Delta \sigma_1^2 \). However, a measured non-zero value of \( \Delta \sigma_1^2 \) can describe other distance distributions (discrete or continuous), provided their width remains small. In the present case, the distribution of the Zr-O1 distances could be due to a distortion of the ZrO\(_6\) units, coming from the Zr/Ti chemical disorder, and/or to a displacement of Zr atoms in their octahedral cages. To evaluated the magnitude of such a displacement, we calculated the FT of the EXAFS signals for Zr atoms in a perfect octahedron, weakly displaced either along the [100], [110], or [111] cubic axis. We then performed fits on the calculated signals in the same conditions as described above for the measured signals. From these simulations, we conclude that the refined DW factors presented in Table 1 for Ba\(_{1-x}\)Ti\(_x\)Zr\(_{0.35}\)O\(_3\) could correspond to a Zr

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**FIG. 3:** Modulus and imaginary part of the FT of \( k^2 \chi(k) \) at 300 K. The dots represent measured data and the solid lines their best fit, obtained with the parameters values given in Table I. Measured data for \( R < 1 \) Å are affected by the background subtraction procedure and were excluded from the analysis.

**TABLE I:** Structural parameters deduced from the EXAFS analysis in the R-range [1.14-2.33 Å] for BaZrO\(_3\) and BTZ relaxors. \( R_1 \) is the length of the bond between an absorbing Zr atom and its first oxygen neighbor, and \( \sigma_1^2 \) the associated Debye-Waller factor. RF is the reliability factor of the fit. The uncertainties are of the order of ±0.01 Å and ±0.0004 Å\(^2\) for \( R_1 \) and \( \sigma_1^2 \) respectively. The energy shift \( \Delta E_0 \) was found equal to 1.4 ± 0.8 eV for all fits.

| sample         | T  | \( R_1 \) | \( \sigma_1^2 \) | RF  |
|----------------|----|-----------|-----------------|-----|
| BaZrO\(_3\)    | 300| 2.11      | 0.0039          | 0.61|
|                | 11 | 2.11      | 0.0029          | 0.62|
| Ba\(_{1-x}\)Ti\(_x\)Zr\(_{0.35}\)O\(_3\) | 300| 2.10      | 0.0048          | 0.58|
|                | 150| 2.10      | 0.0038          | 0.46|
|                | 90 | 2.10      | 0.0038          | 0.96|
|                | 11 | 2.10      | 0.0035          | 0.48|
| Ba\(_{1-x}\)Ti\(_x\)Zr\(_{0.30}\)O\(_3\) | 300| 2.10      | 0.0048          | 0.55|
| Ba\(_{1-x}\)Ti\(_x\)Zr\(_{0.25}\)O\(_3\) | 300| 2.10      | 0.0043          | 0.47|
displacement of 0.07 Å, in any of the three directions cited above.

A static distribution of Zr-O1 distances is also expected in the two other relaxor samples, BaTi$_{0.70}$Zr$_{0.30}$O$_3$ and BaTi$_{0.75}$Zr$_{0.25}$O$_3$, from the $\sigma_i^2$ values measured at 300 K and by analogy with the case of BaTi$_{0.65}$Zr$_{0.35}$O$_3$.

In conclusion, the length and strength of the bond between a Zr atom and its first oxygen neighbor are found to be independent of the Zr substitution rate in BaTi$_{1-x}$Zr$_x$O$_3$ samples. Only a small temperature-independent distribution of the Zr-O1 distances is detected in BaTi$_{0.65}$Zr$_{0.35}$O$_3$, in opposition to the single distance in the regular octahedron present in BaZrO$_3$. These fluctuations of the Zr-O1 distance can be due to Zr displacements in their octahedra, but can also result from distortions of the ZrO$_6$ octahedra induced by the Zr/Ti chemical disorder.

C. Analysis of the further neighbor contribution: BaZrO$_3$

For $R$ values up to 4.5 Å, the FT of the EXAFS signal involves scattering processes beyond the first oxygen neighbors. The amplitudes and phases of all the possible paths have been calculated by using the FEFF8.00 code, for an atomic cluster of 145 atoms representative of the BaZrO$_3$ Pm3m perovskite structure. The scattering processes with relative weight lower than 2.5 % have been neglected. The single backscattering processes on the second (Ba), third (Zr), and fourth (O2) neighbors of the Zr central atom must be considered, as well as several collinear MS paths and only two non-linear MS paths. One of the two latter paths involves Ba atoms. The other one is a triple scattering path within the ZrO$_6$ octahedron, which corresponds to a $R$-range between the two main peaks of the FTs. We verified that it does not affect the fit, and did not consider it further. The retained paths for the EXAFS analysis are listed in Table III. Note that the half-lengths of all the collinear MS paths are equal to the Zr-Zr distance. As a consequence, these MS paths contribute to the FT in the same $R$-range as the single backscattering path by a Zr atom, which makes the analysis complex.

Assuming a perfect Pm3m cubic structure, all $N_i$ are known and the $R_i$ parameters for the ten paths can be expressed as a function of $R_1$, the distance between the central absorbing Zr atom and O1 (see Table III). The number of $\sigma_i^2$ parameters needed could be decreased using the expression of the DW factor:

$$\sigma_i^2 = \frac{1}{4}\langle\sum_j(\mathbf{u}_j \mathbf{u}_j - \mathbf{u}_j \mathbf{u}_j)\cdot \mathbf{R}_{jj+1}\rangle$$

where $t$ is the time, $j$ represents an atomic site of the scattering path $i$, $\mathbf{u}_j$ is the displacement vector of the $j$ atom, and $\mathbf{R}_{jj+1}$ is the directing unit vector between $j$ and $j+1$ atoms at equilibrium. The resulting relations between the $\sigma_i^2$ parameters in BaZrO$_3$ are given in Table III.

For the fit of the measured FT, in the $R$-range [1.14-4.52 Å], seven parameters were then refined: $\Delta E_0$, $R_1$, $\sigma_0^2$, $\sigma_2^2$, $\sigma_3^2$, $\sigma_4^2$, $\sigma_5^2$, and $\sigma_6^2$. Although they have already been determined in Sec. III B, and the strongly correlated parameter $\Delta E_0$ were refined, all distances up to 4.5 Å being functions of $R_1$. On the other hand, the $S_0^2$ and $\sigma_7^2$ parameters were fixed to the previously refined values. The obtained parameters at 11 K and 300 K are presented in Table III. During the refinement process, the $\sigma_8^2$ and $\sigma_9^2$ values were found to have no influence on the RF factor. These two DW factors are related to paths 4, 6, and 9, which give rise to very large, and relatively weak contributions in $R$-space. Consequently, $\sigma_8^2$ and $\sigma_9^2$ values do not affect significantly the amplitude and shape of these contributions and cannot be precisely determined.

### Table II: SS and MS paths used to analyze BaZrO$_3$ EXAFS data.

| index | scattering process | $N_i$ | $R_i$ | $\sigma_i^2$ |
|-------|-------------------|------|-------|-------------|
| 1     | Zr$_c$ → O1 → Zr$_c$ | 6    | $R_1$ | $\sigma_1^2$ |
| 2     | Zr$_c$ → Ba → Zr$_c$ | 8    | $\sqrt{3}R_1$ | $\sigma_2^2$ |
| 3     | Zr$_c$ → Zr → Zr$_c$ | 6    | $2R_1$  | $\sigma_3^2$ |
| 4     | Zr$_c$ → O1’ → O1 → Zr$_c$ | 6    | $2R_1$  | $\sigma_4^2$ |
| 5     | Zr$_c$ → Zr → O1 → Zr$_c$ | 12   | $2R_1$  | $\sigma_5^2$ |
| 6     | Zr$_c$ → O1’ → Zr$_c$ → O1 → Zr$_c$ | 6    | $2R_1$  | $\sigma_6^2$ |
| 7     | Zr$_c$ → O1 → Zr → O1 → Zr$_c$ | 6    | $2R_1$  | $\sigma_7^2$ |
| 8     | Zr$_c$ → O1 → Zr → O1 → Zr$_c$ | 6    | $2R_1$  | $\sigma_8^2$ |
| 9     | Zr$_c$ → O1 → Ba → Zr$_c$ | 48   | $\frac{\sqrt{2}}{2}R_1$ | $\sigma_9^2$ |
| 10    | Zr$_c$ → O2 → Zr$_c$ | 24   | $\sqrt{5}R_1$ | $\sigma_{10}^2$ |

### FIG. 4: Thermal evolution of the measured DW factor for the Zr-O1 bond (symbols). The solid line represents Eq. 2 with $\theta_E = 606$ K. The dashed line corresponds to the same function shifted by 0.0007 Å$^2$.
The calculated FTs are in very good agreement with the measured ones (Fig. 6). The DW factors for the Zr-Ba ($\sigma_2^2$), Zr-Zr ($\sigma_3^2$) and Zr-O$_2$ ($\sigma_{10}^2$) bonds are consistent with those reported in Ref. 43. Their thermal evolution was fitted to Eq. 2, resulting in Einstein temperatures equal to 194 ± 8 K, 263 ± 10 K, and 296 ± 50 K for the Zr-Ba, Zr-Zr, and Zr-O$_2$ bonds respectively.

The analysis of the EXAFS oscillations in BaZrO$_3$ gives information on the relative contributions of the different paths to the FTs in the $R$-range [2.5-4.5 Å], which will help to analyze BTZ samples (see Fig. 6). Only the backscattering path on Ba atoms (path 2 in Table III) contributes in the $R$-range [3.0-3.6 Å], which allows a precise determination of the Zr-Ba distance and the associated DW factor. The contributions in the $R$-range [3.6-4.2 Å] mainly arise from the MS linear paths that involve the third neighbor Zr atoms (paths 5 and 8 in Table III). The backscattering path on Zr atoms (path 3) also contributes in the same $R$-range, but it is much less important. The remaining MS paths (paths 4, 6, 7, and 9 in Table III) correspond to weak contributions to the FTs, but it is necessary to take them into account in order to obtain good quality fits. The DW factors of paths 4, 6, and 9 were shown to have no influence on the fit. Finally, the backscattering path on O$_2$ atoms (path 10) contributes over a very large $R$-range [3-4.6 Å]. It is then compulsory to keep this path in the analysis, as it cannot be separated from the other contributions to the FTs.

D. Analysis of the further neighbor contribution: BaTi$_{1-x}$Zr$_x$O$_3$ relaxors

In the following analysis, we shall introduce two different models of the local structure in BTZ relaxors. In a first step, we show that a model with aligned Zr, O$_1$, and (Zr/Ti) atoms in the perovskite structure cannot account for the measured EXAFS signals. In a second step, we introduce a buckling angle for the Zr-O$_1$-(Zr/Ti) bonds.
1. Basic model for the BTZ analysis

The BaZrO$_3$ model (see Sec. III C) is used as a starting point to analyze BTZ samples. To take into account the Ti third neighbors, we also calculated the amplitudes and phases of the scattering paths within a hypothetical cluster of BaTiO$_3$ in the Pm$ar{3}$m cubic perovskite structure, with a single Zr impurity as the absorbing atom. For the paths that do not involve Ti atoms, the calculated amplitude and phase remain strictly identical to those calculated for the BaZrO$_3$ structure. Thus, we only consider three extra paths 3’ (Zr$_c$ → Ti → Zr$_c$), 5’ (Zr$_c$ → Ti → O1 → Zr$_c$), and 8’ (Zr$_c$ → O1 → Ti → O1 → Zr$_c$), in addition to those presented in Table II. The k-dependence of these path amplitudes differs significantly from that of the corresponding paths 3, 5, and 8 of the BaZrO$_3$ model. Thus, the EXAFS technique allows the refinement of structural parameters for Zr and Ti atoms with limited correlations effects, despite similar Zr-Zr and Zr-Ti distances. A new parameter $N_{2Zr}$ has to be introduced, which is the average number of Zr third neighbors of the central atom Zr$_c$. The degeneracy of paths 3, 5, and 8 is then multiplied by $N_{2Zr}$/6, and that of paths 3’, 5’, and 8’ by $(6-N_{2Zr})$/6. A unique $\sigma_3^2$ parameter is attached to the paths 3’, 5’, and 8’, according to Eq. 3.

Zr atoms being larger than Ti ones, they likely cause local distortions in the BaTiO$_3$ matrix. This difference in size is taken into account by introducing independent Zr-O1, Zr-Ba, Zr-Ti, and Zr-O2 distances. The O1 atoms lying between Zr$_c$ and (Zr/Ti) atoms in this first model, the Zr-Zr and Ti-O1 distances are defined using the expressions $d_{Zr-Zr} = 2d_{Zr-O1}$ and $d_{Ti-O1} = d_{Zr-Ti} - d_{Zr-O1}$. The DW factors $\sigma_{1Zr}^2$ and $\sigma_{2Zr}^2$ were fixed to the same values as in BaZrO$_3$, since they are not expected to affect the fit (see Sec. III C). Furthermore, the relations between the DW factors presented in Table II remain correct, so that only $\sigma_{2Zr}^2$, $\sigma_{3Zr}^2$, $\sigma_{1Ti}^2$, and $\sigma_{1O}^2$ DW factors were refined. The Zr-O1 distance ($R_3$) and $\sigma_3^2$, as well as $\Delta E_0$ and $S_0^2$, were fixed to the values refined in the R-range [1.14-2.33 Å] (see Table II).

Within this model, the fitting procedure over the R-range [1.14-4.52 Å] yields non-physical values of the $\sigma_3^2$ and $\sigma_{3Zr}^2$ parameters (0.033 and -0.0008 respectively, at 11 K). In fact, the calculated contribution of paths linked to Zr atoms (paths 3, 5, and 8 in Table II) are completely damped (see top of Fig. 7). Only paths involving Ti atoms then contribute to the calculated signal, in the R-range [3.4-3.9 Å]. Fixing $\sigma_{2Zr}^2$ to its value in BaZrO$_3$ made impossible a good agreement between calculated and experimental signals. In particular, the shift of the FT’s imaginary part in the R-range [3.6-3.9 Å] indicates an overestimated Zr-Zr distance (see bottom of Fig. 7). Hence, we deduce that $d_{Zr-Zr}$ must be smaller than $2d_{Zr-O1}$.

2. Determination of the buckled local structure in BTZ relaxors

The hypothesis of aligned Zr$_c$, O1 and Zr atoms being not valid in BTZ samples, a new model has to be built, where the O1 atoms are no longer aligned with Zr ones. In order to get all different possible configurations, one can introduce two mean buckling angles, $\Theta_{Zr}$, and $\Theta_{Ti}$, defined as 180° - ZrO1Zr and 180° - ZrO1Ti respectively. All the possible paths and their parameters were calculated in the preceding BaZrO$_3$ and BaTiO$_3$ clusters, moving the O1 atoms out of their collinear sites with varying values of the buckling angle $\Theta$. The only effect of the O1 atom displacements is the damping of the
amplitudes of the MS paths in which these atoms play a focusing role, i.e. paths 5, 5′, 8, and 8′ (Table II). As an example, we show the evolution of the amplitude of path 5 as a function of Θ on Fig. 8. This evolution can be expressed by expanding the scattering amplitude of the focusing paths about Θ = 0:

\[ A(k, \Theta) \approx A(k, 0) \left[ 1 - b(k) \Theta^2 \right]^n, \]

where n is the number of scattering processes by the off-centered focusing atom (O1). For each of the paths 5, 5′, 8, and 8′, the coefficients b(k) were determined for various buckling angles and averaged. Eq. 4 is found to be correct for buckling angles values below 20°.

The expressions for Zr-Zr and Ti-O1 distances are now given by:

\[ d_{Zr-Zr} = 2d_{Zr-O1} \cos(\Theta_{Zr}/2), \]

\[ d_{Ti-O1} = \sqrt{d_{Zr-Ti}^2 - d_{Zr-O1}^2 \sin^2 \Theta_{Ti} - d_{Zr-O1} \cos \Theta_{Ti}}, \]

from which the lengths of paths 1 to 8 can be easily derived. The path length R9 splits into several different values, due to the misalignment of the O1 oxygen atoms. This effect can be modeled by an increase of the corresponding DW factor σ2, but we already showed that this parameter does not affect the fit quality. Thus, we determined the mean distance R9 with the expression given in Table IV using the the σ2 value of BaZrO3.

The length of path 10 splits as well, depending on the size and shape of the octahedra next to the central one Zr6O6. This information being out of the scope of this study, we assigned to this path an average value of the Zr-O2 distances, R10. In that case, σ102 is expected to take into account both thermal and static disorders. In the absence of an adequate model for the O2 repartition, the values obtained for R10 and σ102 will not be interpreted. Concerning the DW factors, the linearity of paths 5, 5′, 8 and 8′ is broken by the off-centering of O1 atoms with respect to Zr-(Zr/Ti) bonds, so that the relations σ52 = σ5′2 = σ82 and σ8′2 = σ8′2 are no longer exact. However, we postulated their validity for the buckled paths, in order to limit the number of free parameters. The buckling angles ΘZr and ΘTi were determined separately, as preliminary fits using the same buckling angle for both Zr6-O1-Zr and Zr6-O1-Ti bonds did not yield a good agreement between experimental and calculated signals (see Fig. 9). Ten parameters were then refined: R2, R3, R10, NZr, ΘZr, ΘTi, σ2, σ2, σ3′2, and σ102. The σ3′2 and σ3′2 parameters were found to reach very low (non-physical) values when not fixed. Like NZr, ΘTi, and ΘZr, these two DW factors determine the signal amplitude in the R-range [3.4-3.9 Å]. Strong correlation effects exist between these five parameters and various sets of their values give rise to similar, very good fits.

To go further in the analysis, we assume that σ2 and σ3′2 in BTZ relaxors are equal to σ2 in BaZrO3, which is determined for all temperatures using Eq. 4 with the Einstein temperature of 263 K reported in Section III C. Values of refined parameters in this hypothesis are presented in Table IV and fits are shown on figure III for the three BTZ relaxors. The fits are not very sensitive to the variations of ΘTi in the range [0-10°]. ΘTi values larger than 10° are excluded since they do not yield satisfactory agreements. Note that the Zr-Ba distance and the associated DW factor σ2 are accurately defined, the contribution of path 2 to the FTs being well separated from the others.

One needs to estimate the consequences of fixing σ2 and σ3′2 for the analysis of BTZ relaxors. For this purpose, we performed several fits for various, not necessarily equal, values of σ2 and σ3′2, in a range of ±0.0010 Å2 around the σ2 value in BaZrO3. The ΘZr, NZr, and R3′ values were found to vary by ±1.5°, ±0.2, and ±0.01 Å respectively. Furthermore, the refined values of ΘZr, being at the limit of the validity range of Eq. 4 one expects an error of ±1° on its determination. The uncertainties given in Table IV are those determined by the FEFFIT code, augmented by the preceding amounts. Note that in the case of BaTi0.65Zr0.35O3, the refined value of NZr is found to be independent of the temperature, as it should be. This confirms a posteriori that the hypothesis of an identical thermal evolution of σ2 and σ3′2 in BTZ samples and σ2 in BaZrO3 is reasonable.

3. Fit results

For all the relaxor samples investigated, the refined values of the buckling angle ΘZr range from 18 to 20°, ΘTi being smaller (less than 10°), the Zr6O6 octahedra are therefore distorted differently depending on the type of the third neighbors (Zr or Ti) of the Zr central atom.

In BTZ relaxors, the existence of a nearly constant buckling angle whatever the Zr substitution rate x, together with the invariant Zr-O1 distance (Sec. III B) result in a Zr-Zr distance of the order of 4.15 Å, which
TABLE IV: Structural parameters deduced from the EXAFS analysis in the \( R \)-range [1.14-4.52 Å], for BTZ relaxors. The path half-lengths are denoted \( R_i \), and the associated DW factors \( \sigma_i^2 \). \( \Theta_{Zr} \) is the buckling angle of the Zr-O1-Zr bonds, defined as 180° - ZrO1Zr, and \( N_{Zr} \), the mean number of Zr third neighbors of the Zr atom. \( R_3 \) is deduced from \( R_1 \) (Table II) and \( \Theta_{Zr} \). The uncertainties are of the order of \( \pm 0.006 \) Å, \( \pm 0.0004 \) Å², \( \pm 5^\circ \), \( \pm 0.04 \) Å, \( \pm 0.02 \) Å, \( \pm 0.04 \) Å, \( \pm 0.005 \) Å², and \( \pm 1.0 \) for \( R_2, \sigma_{Zr}^2, \Theta_{Zr}, R_3, R_3', R_{10}, \sigma_{10}^2 \) and \( N_{Zr} \) respectively.

| sample                  | \( T \) (K) | \( R_2 \) (Å) | \( \sigma_{Zr}^2 \) | \( \Theta_{Zr} \) (°) | \( R_3 \) (Å) | \( R_3' \) (Å) | \( R_{10} \) (Å) | \( \sigma_{10}^2 \) | \( N_{Zr} \) | RF factor (%) |
|-------------------------|-------------|---------------|---------------------|-----------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| BaTi_{0.65}Zr_{0.35}O_3 | 300         | 3.557        | 0.0070             | 18                    | 4.15        | 4.07        | 4.61        | 0.018       | 3.4         | 1.09        |
| BaTi_{0.70}Zr_{0.30}O_3 | 150         | 3.554        | 0.0048             | 17                    | 4.15        | 4.06        | 4.60        | 0.014       | 3.4         | 0.81        |
| BaTi_{0.75}Zr_{0.25}O_3 | 11          | 3.554        | 0.0037             | 18                    | 4.14        | 4.06        | 4.60        | 0.012       | 3.3         | 0.51        |

FIG. 9: Modulus and imaginary part of the FTs of the observed (dots) and refined (solid line) \( k^2 \chi(k) \) for BaTi_{0.65}Zr_{0.35}O_3 at 11 K. The modulus of the FT for paths 3 (dashed line) and 3' (dotted line), which describe the backscattering on Zr and Ti atoms respectively, are also represented. We show the best fit obtained in the hypothesis of a single buckling angle for Zr-O1-Zr and Zr-O1-Ti bonds, for reasonable values of \( \sigma_{Zr}^2 \) and \( \sigma_{Ti}^2 \) parameters. The missing amplitude in the \( R \)-range [3.3-3.7 Å], characteristic of the path 3', indicates an overestimated buckling angle for the Ti bonds.

hardly varies with \( x \). Of course, the Zr-Zr distance is smaller in BTZ samples than in BaZrO_3, since the oxygen atoms are aligned with the Zr-Zr bonds in the latter compound. The Zr-Ti distance (4.07 Å) does not change with \( x \), and is found to be significantly smaller than the Zr-Zr distance. The Zr-Ba distance, on its turn, increases with \( x \). From the Zr-Ti distance and the buckling angle of the Zr-O1-Ti bond, we can derive the Ti-O1 distance value at 300 K in BTZ relaxors, which is of the order of 1.98 Å. This corresponds to the shortest Ti-O distance in the quadratic BaTiO_3 at 300 K^{19}.

We now consider the temperature dependence of \( \sigma_{Zr}^2 \) in BaTi_{0.65}Zr_{0.35}O_3 sample. As shown on Fig. 11, it can be
described following Eq. 2 with an Einstein temperature equal to 231 ± 4 K, instead of 194 ± 8 K in BaZrO$_3$. This result indicates an increase of Zr-Ba bond strength with increasing Ti-content. In addition, a constant $\Delta \sigma^2$ = 0.0019 Å$^2$ must be added to Eq. 2, revealing the presence of static disorder. The full width at half maximum of the corresponding gaussian distance distribution would be equal to $2\sqrt{2 \ln 2} \Delta \sigma^2 = 0.10$ Å. However, let us remind that other distance distributions can be expected (see Sec. III B). The possible distribution of the Zr-Zr and Zr-Ti bond lengths is out of the scope of this study, since $\sigma_3^2$ and $\sigma_2^2$ parameters had to be fixed during the refinement process.

The mean number of Zr third neighbors around a Zr atom $N_{Zr}$, brings information on the distribution of the Zr and Ti atoms in BTZ relaxor samples. $N_{Zr}$ is found to be equal to 2.7, 3.1, and 3.4 in BaTi$_{0.65}$Zr$_{0.35}$O$_3$, BaTi$_{0.70}$Zr$_{0.30}$O$_3$, and BaTi$_{0.60}$Zr$_{0.40}$O$_3$ samples respectively. Despite the large uncertainty attached to $N_{Zr}$ (± 1.0), the measured values are higher than those expected for a random distribution of Zr and Ti atoms: 1.5, 1.8, and 2.1. This observation indicates a tendency of Zr atoms to segregate in Zr-rich regions. However, the EXAFS technique giving only an average of the local structure, we cannot conclude on the Zr concentration in the Zr-rich regions, and hence on the sizes of these regions.

In summary, in all the BTZ relaxors investigated the shape of a ZrO$_6$ octahedra depends on the nature of its neighboring octahedra (ZrO$_6$ or TiO$_6$), the oxygen atoms being differently off-centered with respect to the Zr-Zr and Zr-Ti bonds. The Zr-Zr and Zr-Ti distances do not depend on $x$, Zr-Ti distances being significantly shorter than Zr-Zr ones. The Zr-Ba bond length increases with the Zr-content, and is affected by a strong static disorder. Finally, the EXAFS analysis reveals a tendency of Zr atoms to segregate. Note that in the case of BaTi$_{0.65}$Zr$_{0.35}$O$_3$, the Zr environment is found to be remarkably stable with temperature. Therefore, no important changes of the local structure are observed around Zr atoms in the temperature range of the maximum of the dielectric permittivity.

IV. CONCLUDING DISCUSSION

A. Microstructural picture of BTZ relaxors

In the preceding sections we have described quantitatively the local structural features of the Zr environment in BTZ relaxors. It is now interesting to discuss how this local structure contrasts with the average, long-range cubic structure evidenced by X-ray diffraction (XRD). The interatomic distances deduced from EXAFS are compared to those determined from XRD on Fig. 11. The two techniques yield quite different values of distances. On one hand, the XRD measurements show that the unit cell dimensions of BTZ samples follow the Vegard’s law, i.e., the cell volume linearly increases from its value in BaTiO$_3$ (64.286 Å$^3$) to that in BaZrO$_3$ (73.665 Å$^3$). In the cubic relaxor samples, all the average distances then linearly increase with the Zr substitution rate $x$. On the other hand, the distances deduced from the EXAFS analysis systematically exceed those expected in the average structure and, with the exception of the Zr-Ba distance, are found to be independent of $x$. Considering that EXAFS probes the structure on a very local scale, the latter observation is direct evidence that the local structure is different from the average structure.

We have shown in Sec. III D 3 that Zr-atoms tend to segregate in BTZ relaxors. The latter result is in agreement with previous speculations based on Raman scattering. If we assume that the Zr-rich regions consist of BaZrO$_3$ spherical inclusions in a BaTiO$_3$ matrix, one can calculate the mean number of segregated atoms. It is estimated to 27, 15, and 10 in BaTi$_{0.65}$Zr$_{0.35}$O$_3$, BaTi$_{0.70}$Zr$_{0.30}$O$_3$, and BaTi$_{0.75}$Zr$_{0.25}$O$_3$ respectively, which corresponds to diameters of 14.1, 11.5, and 10.8 Å.

The EXAFS study of BTZ relaxors at the Zr K-edge allowed us to evidence local structural deviations from the average cubic structure, as well as chemical inhomogeneities. In the following, we shall propose a microstructural picture of BTZ relaxors and discuss its origin and implications on the relaxor behaviour. In order to expose the possible basic physical mechanisms in a clear and simple manner, we will assume that the segregation of Zr atoms consists of small inclusions of BaZrO$_3$ in a BaTiO$_3$ matrix. However, the real repartition of the Zr atoms could be much more complex (see Sec. III D 3).

Such BaZrO$_3$ inclusions in BTZ relaxors must be submitted to a chemical pressure from the BaTiO$_3$ environment, which has a smaller unit cell volume than BaZrO$_3$. 

FIG. 11: Thermal evolution of the measured DW factor for the Zr-Ba bond (symbols). The solid line represents Eq. 2 with $\theta_E = 194$ K. The dashed line corresponds to the same equation with $\theta_E = 231$ K, and shifted by 0.0019 Å$^2$. 

Ba$_{0.65}$Zr$_{0.35}$O$_3$ 

BaZrO$_3$ 

Temperature (K) 

$\sigma^2$ (Å$^2$) 

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 

8.0x10^-3 7.0x10^-3 6.0x10^-3 5.0x10^-3 4.0x10^-3 3.0x10^-3 2.0x10^-3 1.0x10^-3 

BaTi$_{0.65}$Zr$_{0.35}$O$_3$ 

BaZrO$_3$
It is first interesting to note that the Zr-O distance in BTZ relaxors is almost insensitive to this chemical pressure, since it is the same as in BaZrO₃ (Fig. 12a). On the other hand, the Zr-Ba distance decreases with increasing Ti-content (Fig. 12b) and hence, is more sensitive to the chemical pressure. This latter difference in \( a/2, a\sqrt{3}/2, \) and \( a \) respectively, where \( a \) is the cubic cell parameter.

polyhedra more rigid than \( \text{AO}_2 \) ones\(^{34}\). Furthermore, it has been proposed in the literature that BaZrO₃ undergoes a pressure-induced phase transition to the tilted \( a^- a^- a^- \) perovskite structure\(^{52} \) (Glazer’s notation\(^{52} \). Assuming that the BaZrO₃ inclusions adopt the latter structure in BTZ relaxors, the tilt angle calculated from the buckling angle of the Zr-O-Zr bonds is about 11°, which is a reasonable value for a tilted perovskite\(^{54,55,56} \). In summary, within our simplified picture, BaZrO₃ inclusions do not adopt the cubic bulk structure of BaZrO₃ but present considerable distortions away from it. The Zr environment in BTZ relaxors appears to be determined by both the high stiffness of the ZrO₆ octahedra and chemical pressure effects.

Let us now discuss the structure around the inclusions. Given that the Zr-Zr distance is approximately 2% larger than the average \( B-B \) cation distance deduced from XRD (Fig. 12c), we expect a significant strain at the interface of the BaZrO₃ inclusions and the BaTiO₃ matrix. The TiO₆ octahedra adjacent to the inclusions likely accommodate the structural misfit between BaZrO₃ inclusions and the BaTiO₃ matrix. Considering that the cell volume of BaZrO₃ is larger than that of BaTiO₃, we expect that these adjacent TiO₆ octahedra are submitted to a tensile strain. Although their deformation shape remains an open question, different Ti\(^{4+} \) displacements (and thus polarity) are expected in the adjacent regions when compared to the BaTiO₃ matrix.

**B. Comparison to PZT**

We have already mentioned in the introduction that the ferroelectric PbZr\(_{1-x}\)Ti\(_x\)O\(_3\) (PZT), similar to BTZ, does surprisingly present no relaxation, making the comparison of BTZ to PZT insightful. First, we note that in both BTZ and PZT, the mean Zr-O distance is almost unaffected by the Ti-content, and the observed Zr-O distance distribution is of the same order of magnitude. As a consequence, the relaxor properties of BTZ cannot be linked to the first neighbour environment of Zr atoms. A key feature for understanding the different behaviors of BTZ and PZT could lie in the local chemical order, which is known to play a determinant role for relaxor properties (e.g. the so-called 1:1 Mg/Nb order on the nanometer scale in PMN\(^{10,11} \)). In that context, it is interesting to note that BTZ cannot be synthesized in the region \( 0.5 < x < 1 \) (Ref. 7), which suggests an important internal chemical strain which inhibits the formation of BTZ across the whole composition range. We speculate that the local phase segregation observed for BTZ relaxors is a precursor for the macroscopic phase separation observed for higher Zr substitution rates. Such an internal chemical strain does not seem to exist for PZT since it forms a solid solution whatever the Zr/Ti ratio. The distribution of elastic fields is thus expected to differ significantly from BTZ to PZT. In particular, the strain around the local phase separation in BTZ can be...
regarded as the source of the elastic random fields which have been proposed earlier by Farhi et al.\textsuperscript{21} Such elastic random fields (similarly to electric random fields in common relaxors) are then considered to lead to particular local pattern of polar regions, which become the source of relaxor properties.

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weak first-order Raman spectrum (see C. Chemarin and al, J. Sol. State Chem., 149, 298 (2000)). Our purpose being to set reference parameters for the analysis of BTZ, these minor distortions can be safely neglected here.

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