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Electronic structure of $\text{Pb}_{1-x}\text{Ba}_x\text{Zr}_{0.65}\text{Ti}_{0.35}\text{O}_3$ ferroelectric compounds probed by soft x-ray absorption spectroscopy

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Abstract

O K and Ti $L_{2,3}$ x-ray absorption near-edge spectra (XANES) of $\text{Pb}_{1-x}\text{Ba}_x\text{Zr}_{0.65}\text{Ti}_{0.35}\text{O}_3$ (PBZT) ferroelectric ceramic compounds with x varying from 0.0 to 0.40 were obtained. The XANES spectra at the O K edge were compared with *ab initio* calculations based on the structures obtained by x-ray diffraction, using the FEFF 8.2 code. The different features observed in the XANES spectra of PBZT samples were quite well reproduced with the calculations, especially for $x \leq 0.20$. However, for $x > 0.20$ the *ab initio* calculations do not match the experimental spectra, indicating that for these Ba concentrations, the structural model deduced from powder x-ray diffraction does not reflect the actual local structure around oxygen atoms. Based on calculations of the local partial electron density of states (DOS), the main features of the O K-edge experimental spectra were assigned primarily to the hybridization between O 2p–Ti 3d, Pb 6p and Ba 5d orbitals. The differences in the ferroelectric character of the end-member $x = 0.0$ and 0.40 sample compositions has been interpreted as due to the decrease of the hybridization between Pb 6p and O 2p orbitals caused by the substitution of Pb^{2+} by Ba^{2+} atoms.

1. Introduction

$\text{Pb}_{1-x}\text{Ba}_x\text{Zr}_{0.65}\text{Ti}_{0.35}\text{O}_3$ (hereafter referred to as PBZT) ferroelectric ceramic compounds present interesting variations in their physical properties as the lead atoms are replaced by barium [1, 2]. It is well known that PBZT samples with $x < 0.30$ present a classic ferroelectric character, whereas samples with $x \geq 0.30$ present a ferroelectric relaxor character,

characterized by a diffuseness and a significative frequency dependence of the relative dielectric permittivity versus temperature [1].

Previous x-ray diffraction studies shows that at room temperature samples with $x \leq 0.20$ (classic ferroelectric) were characterized as rhombohedral, whereas samples with $x \geq 0.30$ (relaxor ferroelectric) were characterized as cubic [1]. On the other hand, Ti K-edge XANES studies of PBZT samples with $0.0 \leq x \leq 0.40$ revealed a local distorted structure around Ti at all sample compositions for both long-range order symmetries [2]. The impossibility of observing the local distortion around titanium atoms by x-ray diffraction has been attributed to disorder effects and crystallographic averaging [3–6]. According to the literature, such a kind of local disorder, which was observed in classic and relaxors ferroelectric compounds, is related to hybridization between electronic states of cations and the 2p states of oxygen [3].

To better understand the relationship between local disorder and electronic structure, ABO_3 ($A = \text{Pb, Ba, Ca}$ and $B = \text{Ti, Zr}$) and more complex ferroelectric perovskite compounds has been studied in detail by soft x-ray absorption spectroscopy measurements [7–10]. The analysis of x-ray absorption near-edge structure (XANES) spectrum in combination with *ab initio* quantum theoretical calculations has been used to study the relationship between the electronic structure of the oxygen and the B-site transition metal and the ferroelectric property.

By measuring the XANES spectra at the O K edge and Ti $L_{2,3}$ edges, the purpose of the present work is to verify the role of the substitution of Pb^{2+} by Ba^{2+} atoms on the electronic structure of $\text{Pb}_{1-x}\text{Ba}_x\text{Zr}_{0.65}\text{Ti}_{0.35}\text{O}_3$ (PBZT) ferroelectric ceramic compounds with $0.0 \leq x \leq 0.40$. To better understand the XANES spectral features observed in the O K-edge XANES experimental spectra, we also carried out calculations using the full multiple-scattering (FMS) approaches of the FEFF 8.2 code [11]. The correlation between the projected electronic density of states (DOS), the O K-edge XANES experimental spectra and the ferroelectric character of PBZT samples is presented.

2. Experimental procedure

Polycrystalline $\text{Pb}_{1-x}\text{Ba}_x\text{Zr}_{0.65}\text{Ti}_{0.35}\text{O}_3$ with $x = 0.0, 0.10, 0.20, 0.30$ and 0.40 nominal compositions were prepared by a conventional mixed-oxide method [1, 2]. Room-temperature XANES measurements were taken on the spherical grating monochromator (SGM) beam line for VUV and soft x-ray spectroscopy of the Brazilian synchrotron light source (LNLS), operating with an electron beam energy of 1.36 GeV and a current in the range 150–250 mA. The O K (520–555 eV) and Ti $L_{2,3}$ (450–470 eV) XANES spectra were measured by collecting the total electron yield current from the powder samples with an energy resolution around 0.5 eV. The energy scales of the O K edge and Ti $L_{2,3}$ edges were calibrated based on the energy scale of the TiO_2 compound. The spectra were normalized to the maximum intensity after a constant background subtraction.

3. Results and discussion

Figure 1 shows the normalized O K-edge soft x-ray absorption spectra of PBZT compounds measured at room temperature. The XANES spectra are composed of four main features, referred to as A, B, C and D. When the amount of barium atoms replacing the lead atoms increases, we observe that the first peak denoted as A becomes more symmetric, the intensity of peak B increases, a shoulder appears on peak C and the intensity of the peak labelled D decreases. Similar trends have been observed in the O K-edge XANES spectra of different mixed ferroelectric perovskite compounds [7–10]. The O K-edge XANES spectra basically reflect transitions from the O 1s core state to the unoccupied O 2p-derived states [7–10].

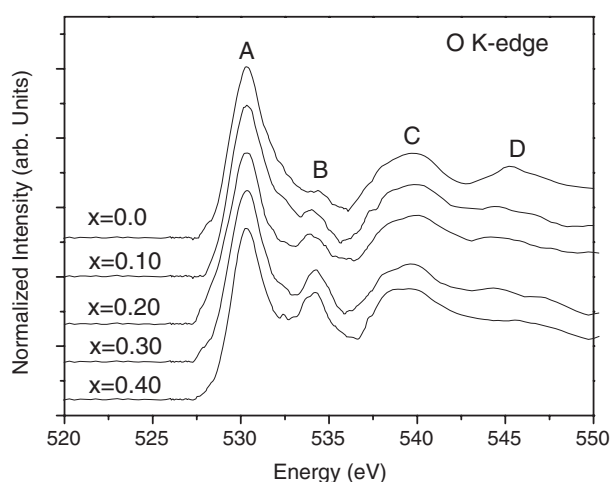


Figure 1. Normalized O K-edge XANES spectra of PBZT compounds.

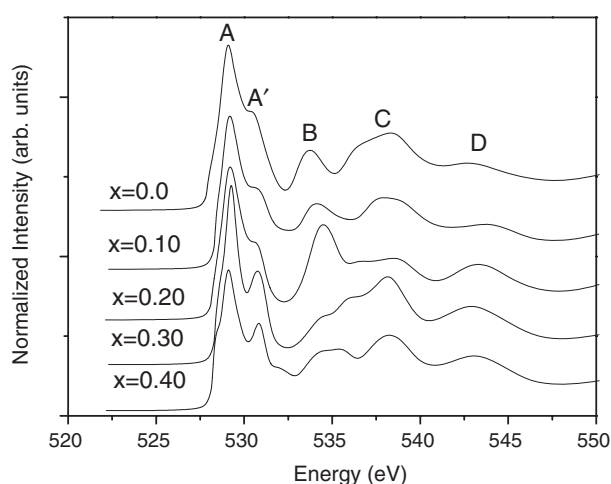


Figure 2. Calculated XANES spectra of PBZT compounds using the FEFF 8.2 code.

In figure 2, we present theoretical O K-edge spectra of PBZT compounds obtained from the FEFF 8.2 code [11]. O K-edge XANES spectra were calculated in terms of a cluster derived from the average structure of PBZT compounds determined from previous x-ray diffraction (XRD) measurements [1]. Clusters with size of up to eight shells around the absorber (oxygen atom) were used. The calculation was performed according to the default setting of the FEFF 8.2 code. Only 12 interactions or fewer were needed to achieve the self-consistency in Fermi energy. The calculations of the PBZT XANES spectra were undertaken by the replacement of Pb by Ba atoms according to the sample stoichiometry. The best approach to simulating the XANES spectrum on a solid solution material like the PBZT system involves running the FEFF code many times [12]. Each time, we replace a different set of randomly selected Pb by Ba atoms, each time saving the result. This set of computed spectra was then averaged and compared to the experimental spectra. The Fermi energy obtained from the calculations was around -7.0 eV.

By comparing the theoretical and experimental spectra of $x = 0.0, 0.10$ and 0.20 samples, we observe that the A, B, C and D features were reasonably reproduced. The asymmetry observed on the right side of the first peak of the experimental spectra corresponds to a well-discriminated shoulder of the calculated spectrum (A'). However the intensity of the B features of the calculated spectra varies in a totally different way than the experimental spectra. This disagreement observed in the intensity behaviour of feature B as the amount of barium increases can be related to the difficulty of simulating the structural distribution of the Pb substitution by Ba correctly. The most important information given by our result presented in figure 2 is the complete disagreement between theory and experience for $x > 0.20$ samples. This important mismatch between theory and experience can be explained as follows: while other structural and spectroscopic methods revealed a local distorted structure, the structural model derived from XRD refinement used to build the cluster around oxygen atoms in the $x = 0.30$ and 0.40 samples supposes a cubic symmetry [2]. As we discussed in section 1, Ti K-edge XANES results of PBZT samples show the existence of a local disorder around Ti atoms independently of the crystallographic structure. Thus, the present comparison between experimental and *ab initio* calculation O K-edge spectra is another proof that the XRD cubic structure for $x > 0.20$ is only an average structure between randomly distributed distorted local structures.

In order to better assign the different features observed in the O K-edge XANES spectra of PBZT samples, we undertook *ab initio* quantum-theoretical calculations. Calculations of the electronic structure of similar ferroelectric ceramic systems suggested that peaks A and B are primarily contributed by O 2p–Ti 3d t_{2g} and e_g hybridized states with smaller contributions from O 2p and hybridized states of other atoms that compose the sample [7–9].

Figure 3 presents the local density of states (s-, p-, d- and f-projected DOS) of the constituents oxygen, titanium, lead, zirconium and barium, which are compared to the experimental O K-edge XANES spectrum of the $x = 0.10$ compound. The DOS calculations were developed in equivalent conditions to those used to calculate the theoretical XANES spectrum of the $x = 0.10$ compound. We calculated the projected DOS of the $x = 0.10$ sample to evaluate the local density contribution of states of all atoms, including barium atoms. The energy scale of the local DOS is as calculated by FEFF 8.2 code and the experimental XANES spectrum was then shifted to be aligned to the O 2p-projected DOS in order to compare the specific peak positions.

As observed in the literature for similar perovskite ferroelectric compounds, the O 2p-projected DOS resembles the experimental O K-edge XANES spectrum of the $x = 0.10$ sample [7–9]. Moreover, we observe that the first peak in the O p DOS between -7.0 and -2.0 eV coincides with the position of the maxima of Ti 3d DOS, indicating that peak A results mainly from the transitions of the O 1s orbital to antibonding O 2p states hybridized with the Ti 3d orbitals. Note that in figure 3 the Ti 3d DOS intensity is divided by 10 in order to compare the shape of the symmetry-projected DOS on a common intensity scale. We also observed a contribution of the hybridization between O 2p and Pb 6p and Zr 4d states [7–9, 13]. Based on these calculations, we can also infer that peak B arises mainly with O 2p hybridized with Ti 3d, Zr 4d and Ba 5d; peaks C and D arise from a hybridization of O 2p with Ti 4spdf, Pb 6s/5d4f, and Zr 4spdf states.

The fact that peak A becomes more symmetric and the intensity of peak B increases as the amount of barium increases can be interpreted as a modification of the degree of hybridization between O 2p–Ti 3d states and O 2p–(Zr 4p, Pb 6p, Ba 5d) states respectively. In agreement with previous works, we observe a significant influence on the substitution of Pb and Ba cations in the coupling between Zr/Ti–O atoms, which have a direct relationship with the ferroelectric character of PBZT samples [7–9]. Miyazawa *et al* studied the relation between

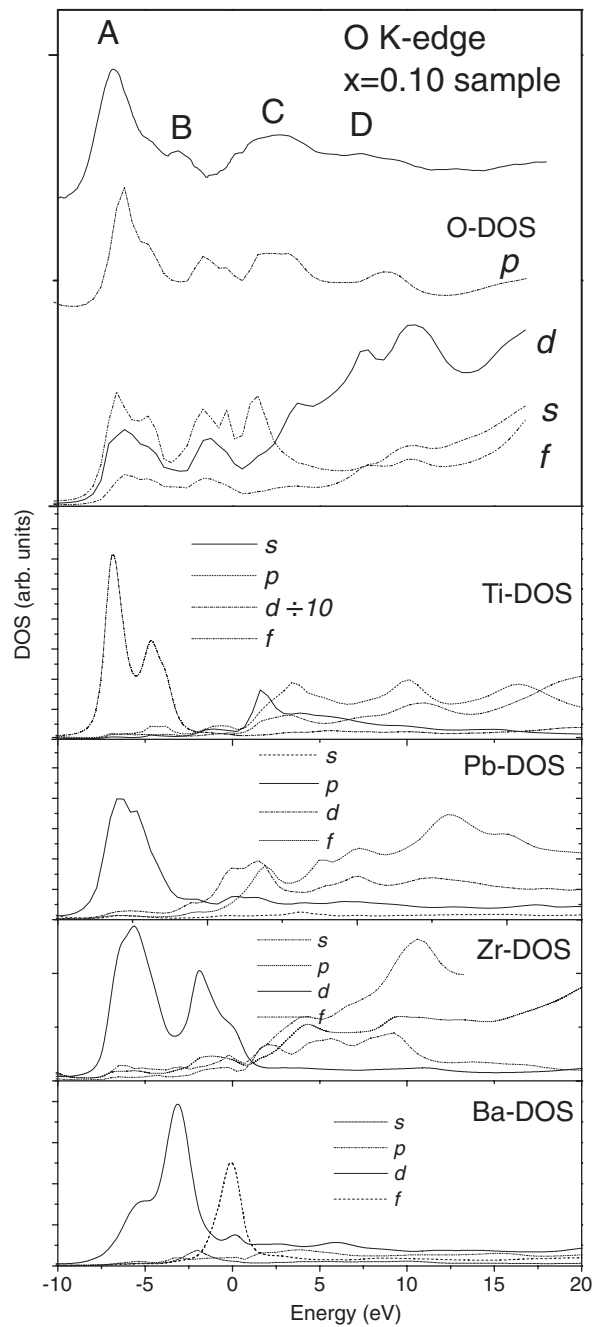


Figure 3. O K-edge XANES spectrum of the $x = 0.10$ sample and s-, p-, d- and f- projected DOS of the constituents elements.

B-site transition metal and ferroelectricity in a series of ABO_3 perovskite-type compounds with A = Pb, Ba and K and B = Ti, Zr, Nb, Hf and Ta [14]. They noted that the hybridization between Pb 6p and O 2p is crucial for the high ferroelectricity observed in the $PbTiO_3$ compound.

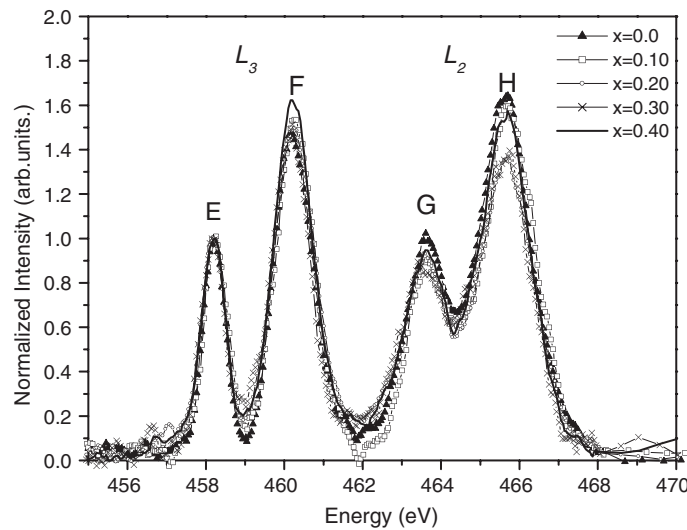


Figure 4. Normalized Ti $L_{2,3}$ absorption spectra of PBZT compounds for x varying from 0.0 to 0.40 at. %.

Figure 4 shows the titanium $L_{2,3}$ normalized absorption spectra of PBZT compounds for x varying from 0.0 to 0.40 at.%. The separation between the L_3 (features E and F) and L_2 (features G and H) edges is attributed to Ti $2p_{3/2}$ (L_3) and $2p_{1/2}$ (L_2) spin-orbit splitting. The crystal field at both the L_3 and L_2 edges splits the 3d band into t_{2g} and e_g subbands.

The e_g states, which consist of d_z^2 and $d_{x^2-y^2}$ orbitals, are directed toward ligand anions and are therefore more sensitive to deviations from Ti octahedral symmetry. A splitting of e_g states in the Ti L_3 -edge spectrum has been observed in different simple and complex ferroelectric ceramic systems where Ti atoms are displaced from their central symmetric positions [7–10].

According to our previous Ti K-edge XAS measurements of PBZT samples, Ti atoms are displaced from their central symmetric positions in all sample compositions, even in those characterized as cubic according to XRD results [2]. Based on this result, a splitting of e_g states in the Ti L_3 -edge spectrum is expected for all PBZT samples. However, as presented in figure 4, a symmetric peak is observed for all compositions, and feature F, which is related to the e_g states, does not show a clear peak splitting even in the $x = 0.0$ sample where the Ti first coordination shell is formed by three long and three short Ti–O bonds [1]. A similar behaviour has been observed when La atoms substitute Pb atoms in $Pb_{1-x}La_xZr_{0.65}Ti_{0.35}$ (PLZT) thin films and Ba atoms are substituted by Sr atoms in the $Ba_{1-x}Sr_xTiO_3$ (BST) ceramic system [8, 15]. In that case of the BST system, the absence of e_g splitting was attributed to an insignificant tetragonal distortion or a lower c/a ratio [8]. However, we should emphasize that in the PBZT system the Ti off-centre displacement is along the $[111]_c$ direction (the subscript c indicates pseudocubic notation) and thus a direct comparison with the results obtained in the BST system is irrelevant [16]. Looking the results presented in the literature, it seems a trend that the short-range disorder in lead-based ferroelectric ceramic materials is easily observed in systems which present a significant tetragonal distortion. A possible relationship between the displacement of Ti atoms along the $[111]_c$ direction and the non-observation of a e_g splitting in the PBZT samples is not clear, and calculations of the Ti $L_{3,2}$ XANES spectra should help in better understanding this particular behaviour. The present version of FEFF, based on the multiple scattering of photoelectrons theory, is not suitable for the first-row transition metal L_{II} – L_{III} edge theory. Calculations using ligand field and multiplet theory are under development.

4. Conclusions

We measured the O K-edge XANES spectra of $\text{Pb}_{1-x}\text{Ba}_x\text{Zr}_{0.65}\text{Ti}_{0.35}\text{O}_3$ compounds and compared them with *ab initio* calculations using the FEFF 8.2 code. The different features observed in the XANES spectra of samples with $x \leq 0.20$ could be reproduced from calculations. The difference between experience and theory for $x > 0.20$ is a new indication that, for these Ba concentrations, the actual structures of the compound, and especially the distortions around Ti and O atoms, are not correctly modelled by the average structure obtained from XRD. Based on the assignment of the DOS, we verify that the main changes observed in the O K-edge spectra of PBZT samples as the amount of barium increases are related to the hybridization between O 2p states hybridized with the Ti 3d, Pb 6p and Zr 4d orbitals, whereas the intensity variation observed in peak B is correlated mainly with the hybridization between O 2p and Ti 3d and Ba 5d states. These modifications seem to be directly correlated to the variation of the ferroelectric character of PBZT samples from a classic ferroelectric to a relaxor as the amount of barium increases. Although significant structural variations were observed in the O K-edge XANES spectra as the amount of barium increases, the e_g band at the Ti L_3 -edge spectra of PBZT compounds does not present a splitting normally observed in systems where Ti atoms are displaced from their central symmetric positions.

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