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# Electronic structure of $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$ ferroelectric materials from Ti 2p and O 1s soft x-ray absorption spectroscopy

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The electronic structure of  $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$  (PLT) compounds for  $x$  ranging from 0 to 30 at. % of La is investigated by means of soft x-ray absorption near edge structure (XANES) at the Ti  $L_{3,2}$  and O  $K$  edges. The greatest modification in the structure of the Ti 2p XANES spectra of the PLT compounds is observed in the region of the high energy peak of the  $L_3$  edge ( $e_g$  states), which exhibits a splitting in the undoped sample. As the amount of lanthanum increases, this splitting becomes less pronounced. This modification is interpreted as a decrease in the degree of disorder of titanium atoms, which is correlated to the substitution of Pb by La atoms. The structural changes observed at the low energy peaks of the O  $K$ -edge XANES spectra of the PLT compounds may be interpreted in terms of hybridization between O 2p, Ti 3d, and Pb 6p orbitals. A decrease in the degree of hybridization observed as Pb atoms are replaced by La atoms may be related to the differences in the ferroelectric properties observed between  $x=0.0$  and  $x=0.30$  compounds. © 2006 American Institute of Physics. [DOI: 10.1063/1.2173683]

## I. INTRODUCTION

Ferroelectric perovskites have been the subject of extensive studies, for they exhibit promising electrical characteristics potentially useful in fundamental research and technological applications. Among the plethora of ferroelectric ceramic systems, considerable interest has focused on the lanthanum-doped lead titanate ceramic ( $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$  or PLT) system due to its desirable physical properties.<sup>1</sup> In this system, the isomorphic substitution of lead by lanthanum atoms has been found to induce intriguing changes in the physical properties of  $\text{PbTiO}_3$  (PT) material. When the lanthanum content is higher than 25 at. %, the ferroelectric-paraelectric phase transition displays a diffuse character.<sup>2,3</sup> Moreover, the modification in the character of the phase transition is followed by a linear decrease in the Curie temperature ( $T_c$ ) to room temperature for  $x \sim 30$  at. %.<sup>2,3</sup>

X-ray absorption spectroscopy (XAS) studies of different mixed perovskite compounds revealed that their local structure as a function of the composition is essentially disordered in compositions containing larger amounts of dopants. According to x-ray diffraction (XRD) experiments, a structural phase transition to a cubic structure occurred in this case.<sup>4-6</sup>

Recently, we studied the composition resulting from the substitution of the Pb ion by La in the  $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$  system for  $x$  ranging from 0 to 30 at. % using XAS and XRD techniques.<sup>7</sup> Our XRD results indicated that all our samples possessed a tetragonal structure except the one containing 30 at. % of La, which exhibited a cubic unit cell. XRD refinements also confirmed the existence of only A-site vacancies. On the other hand, x-ray absorption near edge spectroscopy (XANES) measurements at the Ti  $K$  edge indicated that the local structure around the Ti atoms had a different compositional dependence from the one indicated by XRD, mainly in the case of the sample containing 30 at. % of La. According to our XANES data, a local distortion around the Ti atoms persisted in the sample with 30 at. % of La.<sup>7</sup>

Although the use of x-ray absorption spectroscopy to study  $\text{ABO}_3$  and mixed perovskite compounds has been limited mainly to the analysis of  $K$ -edge spectra, the electronic structure of the transition metals in these compounds has recently been studied by soft x-ray absorption spectroscopy measurements of Ti  $L_{3,2}$  and O  $K$  edges.<sup>8-14</sup> When applied to mixed perovskite compounds, these studies proved very useful in shedding light on how compositional substitution influences the electronic structure of these systems.<sup>11-13,15</sup>

Theoretical calculations have shown that hybridized states of Ti 3d and O 2p and covalent bonding of Pb–O

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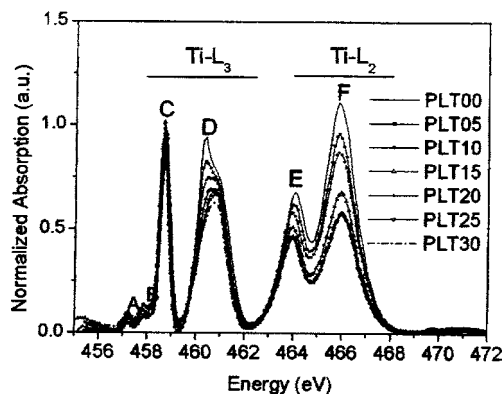


FIG. 1. Titanium  $L_{3,2}$ -edge XANES spectra of the  $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$  compounds.

crucially affect ferroelectric stability in the  $\text{PbTiO}_3$  compound.<sup>16,17</sup> Different features observed in the O  $K$ -edge spectra of mixed perovskite ferroelectric compounds have also been interpreted in terms of hybridization between O  $2p$  and Ti  $3d$ , and O  $2p$  and Pb  $6p$  orbitals.<sup>12</sup>

On the other hand, the features observed at the Ti  $L_{3,2}$  edges in different  $\text{ABO}_3$  and in mixed perovskite compounds have been attributed to various factors, some of which are controversial.<sup>18–20</sup>

To better understand the structural results obtained from the Ti  $K$  edge, we conducted an experimental study of the electronic structure of the  $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$  system for  $x$  ranging from 0 to 30 at. %. The electronic structure was investigated by measuring the soft XANES at the Ti  $L_{3,2}$  and O  $K$  edges.

## II. EXPERIMENTAL DETAILS

Seven PLT powder samples, with a nominal composition of  $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$  with  $x=0.0, 5, 1, 15, 20, 25,$  and  $30$  at. % (abbreviated as PLT $x$ , from PLT00 to PLT30), were prepared by a conventional mixed oxide method. Details of the samples' preparation are reported elsewhere.<sup>7</sup> Room temperature XANES measurements were taken on the spherical grating monochromator (SGM) beam line for Visible Ultraviolet (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 between 100–160 mA. The Ti  $L_{3,2}$  edge (455–470 eV) and O  $K$ -edge (520–555 eV) XANES spectra were measured by collecting the total electron yield current from the samples with an energy resolution of around 0.5 eV. The energy scale of the Ti  $L_{3,2}$  and O  $K$  edges was calibrated based on the energy scale of  $\text{TiO}_2$  and  $\text{SrTiO}_3$  compounds.

## III. RESULTS

### A. Ti $L_{3,2}$ XANES results

Figure 1 shows the titanium  $L_{3,2}$  normalized absorption spectra of the PLT compounds for  $x$  varying from 0.0 to 0.30 at. %. As can be seen, the main difference in the absorption spectra of the PLT compounds is a modification in the shape of the  $D$  peak.

The first two small peaks in the XANES spectra (dubbed A and B) represent a transition which is normally forbidden

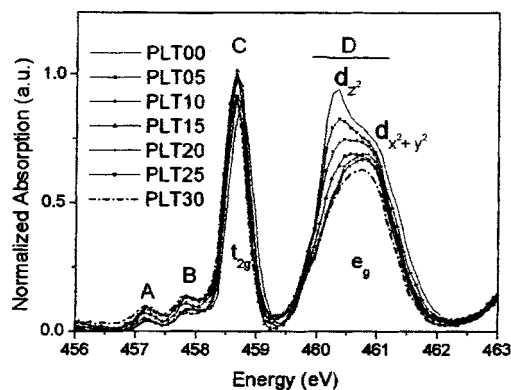


FIG. 2. Low energy region of Ti  $L_{3,2}$ -edge XANES spectra of the  $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$  compounds.

in  $LS$  coupling, but become allowed in this case because of the multipole  $pd$  interactions.<sup>18</sup> The separation between the  $L_3$  and  $L_2$  edges is attributed to Ti  $2p_{3/2}(L_3)$  and  $2p_{1/2}(L_2)$  spin orbit splitting, which is around 5.3 eV and is comparable to that observed in  $\text{TiO}_2$  and other mixed perovskite compounds.<sup>8–14</sup> The crystal field at both the  $L_3$  and  $L_2$  edges splits the  $3d$  band into  $t_{2g}$  and  $e_g$  subbands.<sup>21</sup> The split observed at the  $D$  peak, shown in greater detail in Fig. 2, reflects the splitting of the  $e_g$  states. A similar splitting of the  $e_g$  states in the  $F$  peak also occurs at the  $L_2$  edge, although it is not well resolved due to the lifetime-related broadening of the  $L_2$  edge. 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.<sup>15</sup> Consequently, the splitting of  $e_g$  states indicates the degree of distortion from the octahedral symmetry.

The details in Fig. 2 reveal that the splitting of  $e_g$  orbitals became less conspicuous with increasing amounts of lanthanum, indicating that the degree of distortion from the octahedral symmetry decreased.

The existence of a similar split in the Ti  $L_{3,2}$  absorption spectra of  $\text{Pb}_{1-x}\text{Ca}_x\text{TiO}_3$  (PCT) ferroelectric compounds in samples up to  $x=0.4$  was attributed by Jan *et al.* to the fact that Ti atoms are displaced from the center of the octahedral site.<sup>12</sup> These authors observed that this splitting disappeared in the samples containing high concentrations of Ca and suggested a restoration of the Ti ion to the center of the octahedron. Thus, they correlated the changes observed in the  $L_3$   $e_g$  peak to the structural changes in the first oxygen atoms around titanium atoms.

Figure 3 shows the  $L_{3,2}$  titanium absorption spectra of the  $\text{SrTiO}_3$  compound, which possessed a practically perfect octahedral site symmetry for titanium atoms, and hence no splitting at the  $e_g$  states ( $D$  peak) is expected. Although the  $D$  peak was slightly asymmetric, it could be fitted by a simple Gaussian function. On the other hand, the best fit for the PLT30 sample, which presented a broader  $D$  peak, was achieved through two Gaussian functions. These results indicate that, although the distortion on the titanium site decreased when Pb atoms were replaced by La atoms, a perfect octahedral symmetry such as that of  $\text{SrTiO}_3$  compound was not discernible. This analysis is in good agreement with the Ti  $K$ -edge XAS results.<sup>7</sup>

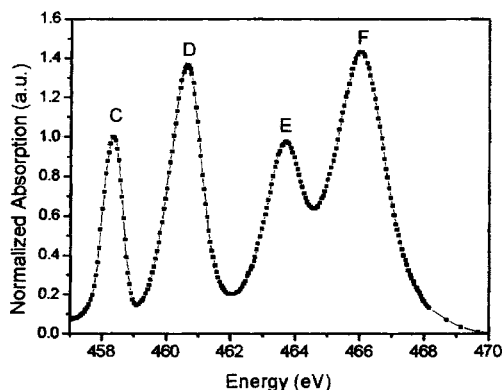


FIG. 3. Titanium  $L_{3,2}$ -edge XANES spectrum of the  $\text{SrTiO}_3$  compound.

The origin of this splitting in the  $e_g$  states is a controversial subject in the literature.<sup>8–14,18–20</sup> In their first paper, De Groot *et al.*<sup>18</sup> proposed that the different distortions from  $O_h$  symmetry observed in the Ti  $2p$  XANES spectra of  $\text{TiO}_2$  compounds produced dissimilar splitting of the  $e_g$  orbitals. However, according to Crocombette and Jollet,<sup>20</sup> who calculated the Ti  $2p$  x-ray absorption edge of these compounds by a configuration interaction code, the existence of this splitting cannot be attributed to differences between the titanium oxides in the first coordination shell of the cation. These authors argued that the relatively good congruence between the calculated and experimental curves, in the case of the rutile sample obtained by De Groot, was achieved using incorrect crystal-field parameters. Based on their work, Crocombette and Jollet proposed that the splitting originated from a medium-range order effect at least-second-neighbor interactions and that the Ti  $2p$  XAS spectral shape cannot be entirely explained by arguments about local order.<sup>20</sup>

Brydson *et al.* proposed that the splitting of the  $e_g$  band may be attributed to the dynamic Jahn-Teller effect due to the coupling of the electronic and vibrational states.<sup>19</sup> However, according to Kucheyev *et al.*, who studied the electronic structure of titania compounds, the values of splitting observed in optical absorption experiments of  $\text{Ti}^{3+}$  ions in the octahedral environment in different systems and attributed to the Jahn-Teller effect are much lower than the relatively large separation observed in the splitting of the  $e_g$  band in titania compounds.<sup>14</sup> Moreover, in those studies, no significant change in the peak position was observed with temperature decreases of upto 77 K, as would be expected were the splitting due to the Jahn-Teller effect. Thus, it was concluded that the Jahn-Teller effect was not the major contributing factor for the splitting of the  $e_g$  related band in Ti  $L_{3,2}$  XANES spectra of  $\text{TiO}_2$  polymorphs.

There is a consensus in the literature that, in  $\text{La}^{3+}$ -modified  $\text{PbTiO}_3$  materials,  $\text{La}^{3+}$  replaces  $\text{Pb}^{2+}$  rather than  $\text{Ti}^{4+}$ .<sup>7,21</sup> To maintain the neutrality of the charge, since that replacement is aliovalent, vacancies in the Pb site are created. Earlier XRD studies on these compounds confirmed the existence of only Pb-site vacancies.<sup>7</sup> On the other hand, XAS studies show that the local structure of the titanium site is only slightly dependent on the crystallographic phase.<sup>7</sup> Thus, the changes observed in the  $e_g$  states of Ti  $L_{3,2}$  XANES spectra of the PLT samples, such as the amount of lanthanum

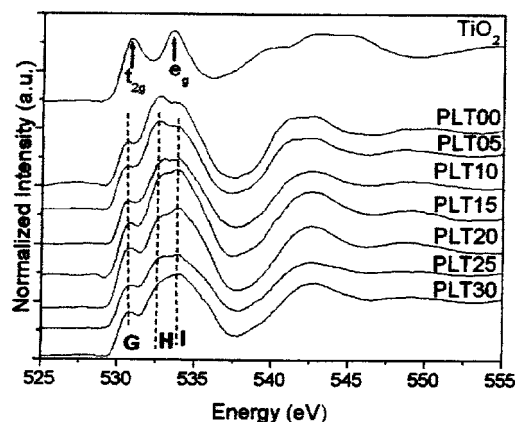


FIG. 4. Oxygen  $1s$  XANES spectra of the  $\text{TiO}_2$  and  $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$  compounds.

increases found in this work, can be attributed primarily to the replacement of Pb atoms by La atoms and to the subsequent creation of vacancies on Pb site. Comparing our results with those obtained by Jan *et al.*<sup>12</sup> for the PCT system, we find that whereas the splitting of  $e_g$  states in the PLT sample with 30 at. % of La is less conspicuous, this splitting in the PCT sample with 30 at. % of Ca is clearly visible. Thus, the vacancies created in the Pb site of the PLT system in response to the substitution of Pb by La atoms appear to cause a relaxation in the degree of distortion of Ti atoms.

The above analysis supports the proposition that the splitting of  $e_g$  states can be attributed principally to effects of medium-range order and, particularly, to the influence of Ti atom interactions with the second neighbor shell, as proposed by Crocombette and Jollet.<sup>20</sup>

## B. O $K$ -edge XANES results

The O  $K$ -edge XANES spectra basically reflect transitions from the O  $1s$  core state to the unoccupied O  $2p$  derived states, which are hybridized states with the relatively narrow  $3d$  and broader  $4sp$  bands of the  $3d$  transition metal ion alkaline earth metal bands.<sup>13</sup>

Figure 4 shows the oxygen  $1s$   $K$ -edge XAS spectra of the  $\text{TiO}_2$  and PLT samples. The XANES spectra of the  $\text{TiO}_2$  compound is comparable to that obtained in previous XANES studies.<sup>12,14</sup> Figure 4 shows a significant change, mainly in the lower energy region of the spectra, with increasing amounts of lanthanum. Figure 5 shows this low energy region in greater detail. Note the slight shift of peak  $G$  to higher energies with increasing amounts of lanthanum. A similar shift in the  $\text{TiO}_2$  compounds was attributed a larger band gap of the anatase than the rutile phase.<sup>14</sup>

The  $G$  and  $H$  peaks in the  $\text{TiO}_2$  compound have been attributed to hybridization between O  $2p$  and Ti  $3d$   $t_{2g}$  and  $e_g$  orbitals.<sup>12,13</sup> The Ti  $e_g$  orbitals are directed toward the O ions; hence, their coupling with O  $2p$  orbitals is stronger and their antibonding hybridized states are at higher energies than those of the  $t_{2g}$  orbitals.<sup>13</sup> The crystal-field splitting measured in the  $\text{TiO}_2$  compound was found to be equal to 2.7 eV, which is very similar to that reported in the literature.<sup>12–15</sup> In the PLT compounds, peak  $G$  intensity remained practically constant as the amount of lanthanum in-

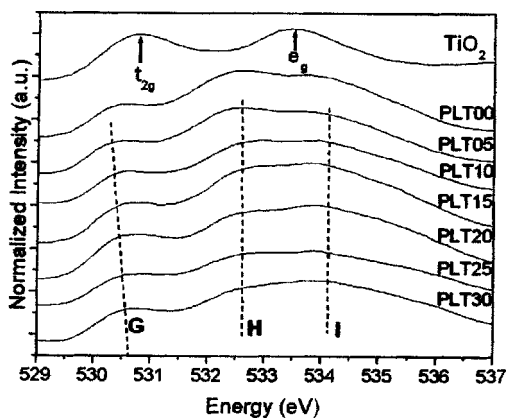


FIG. 5. Low energy region of oxygen 1s XANES spectra of the  $\text{TiO}_2$  and  $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$  compounds.

creased. However, while the PLT00 sample showed two peaks, *H* and *I*, the PLT30 sample displayed only one large broad peak.

The variation of *H* and *I* peak intensities in the O *K*-edge XANES spectra of the PLT compounds may be interpreted in terms of orbital hybridization.<sup>12</sup> Jan *et al.* calculated the O *2p*, Ti *3d*, Pb *6sp*, and Ca *3d* derived states of the  $\text{Pb}_{0.5}\text{Ca}_{0.5}\text{TiO}_3$  compound to elucidate the O *2p*–Ti *3d*, O *2p*–Pb *6sp*, and O *2p*–Ca *3d* hybridizations and identify the contributions to the O *K*-edge XANES features of  $\text{Pb}_{0.5}\text{Ca}_{0.5}\text{TiO}_3$  compound.<sup>12</sup> They observed a strong hybridization between O *2p*–Ti *3d*  $t_{2g}$  and  $e_g$  and O *2p*–Pb *6p* orbitals, which they interpreted as giving rise, respectively, to the *G*, *I*, and *H* peaks depicted in Figs. 4 and 5.<sup>12</sup> They observed that the substitution of the Pb cation by Ca decreased the hybridization of O *2p*–Ti *3d* and O *2p*–Pb *6p* because Ca is less electronegative than the other two cations. In our case, La also exhibited lower electronegativity (1.1) than did the Pb (2.33) and Ti (1.54) atoms. Thus, following their analysis, electron charge is transferred from the La cation to both Pb and Ti ions in the PLT samples, reducing the positive effective charges on Pb and Ti ions. The attractive Coulomb potentials at the Pb and Ti sites are reduced, which raises the energies of Pb and Ti orbitals and reduces the hybridization of O *2p*–Ti *3d* and O *2p*–Pb *6p*. According to Miyazawa *et al.*, the hybridization between the O *2p* and Pb *6p* orbitals is the main reason for large oxygen displacements and high ferroelectricity in the  $\text{PbTiO}_3$  compound.<sup>16</sup> The reduction of the O *2p*–Ti *3d* and O *2p*–Pb *6p* hybridizations in the PLT samples as the amount of lanthanum increases could therefore be related to the modification observed in the ferroelectric behavior of the PLT samples with increasing amounts of lanthanum.

#### IV. CONCLUSIONS

Our analysis of the Ti  $L_{3,2}$ -edge results indicated that, although the distortion at the titanium site decreased as Pb

atoms were replaced by La atoms, a perfect octahedral symmetry was not discernible even in the PLT30 sample in which, according to our XRD results, titanium atoms moved to the central symmetric position. The decreasing disorder with increasing amounts of lanthanum is congruous with previous XAS results obtained at the Ti *K* edge. The structural variations observed in the splitting of the  $e_g$  state in Ti  $L_{2}$ -edge XANES spectra may be attributed to the effects of Ti second neighbor interactions. The O *K*-edge XANES spectra of the PLT compounds displayed characteristic features resulting predominantly from hybridization of the O *2p* with Ti *3d*  $t_{2g}$  and  $e_g$  states and Pb *6p* states. The changes in the low energy peaks (dubbed *G*, *H*, and *I*) were attributed to a decrease in the hybridization between the O *2p* and Ti *3d* and Pb *6p* orbitals. The decrease in the degree of hybridization as Pb atoms were replaced by La atoms may have been related to the differences observed between the PLT00 and PLT30 compounds.

#### ACKNOWLEDGMENTS

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