Experimental and Calculated Ti K-Edge XANES Spectra of Pb$_{1-x}$La$_x$TiO$_3$ Ferroelectric Ceramic Compounds

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Abstract. The X-ray absorption near-edge structures (XANES) at the Ti K-edge of Pb$_{1-x}$La$_x$TiO$_3$ ferroelectric ceramic compounds are analyzed as a function of the sample composition. The calculated XANES spectra using the FEFF8.2 code are compared with experimental data. Experimental results show that the local distortion around Ti atoms has different composition dependence as compared to the crystallographic structure. Moreover, this distortion is also observed in samples presenting a crystallographically cubic phase. The agreement between experimental XANES spectra and theoretical ones deduced from the XRD results was good only for undoped and weakly doped samples. The use of structural models based on the XRD technique for samples containing higher amounts of lanthanum is not appropriate to describe correctly the local order around Ti atoms in this system.

Keywords: XANES, ferroelectric materials, local disorder, FEFF

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INTRODUCTION

It is well known that the replacement of Pb$^{2+}$ by La$^{3+}$ atoms in PbTiO$_3$ induces significant changes of the electrical properties of this material [1,2]. A linear decrease in the temperature of the maximum of the relative dielectric permittivity is observed as the amount of La increases. Moreover, depending on their amount, a diffuse phase transition and a large frequency dependence on the relative dielectric permittivity are observed [1,2]. Materials presenting the last behavior are denominated ferroelectric relaxors.

In the Pb$_{1-x}$La$_x$TiO$_3$ (PLT) system, to keep the neutrality of charge since the replacement of Pb by La atoms is aliovalent, site vacancies are created in the Pb site [3]. For compositions which present a normal ferroelectric behavior (x < 0.25), the long range order structure, probed by X-ray diffraction (XRD), is characterized by a low symmetric crystalline phase [3]. The ferroelectric property of these samples is well explained by the existence of well-defined ferroelectric domain structures which are formed during cooling from the paraelectric to the ferroelectric phase. On the other hand, for compositions which present a relaxor behavior (x > 0.25), an average long range cubic symmetry was observed in all cases [3].

In this work, titanium K-edge XANES spectra of the Pb$_{1-x}$La$_x$TiO$_3$ (PLT) system were collected in order to better understand the main effect on the local structure around Ti atoms when Pb is replaced by La atoms. To correlate the XANES spectral features that appear as the amount of La increases, we have also carried out model calculations using the one-electron multiple-scattering approaches using the FEFF 8.2 code [4].

EXPERIMENTAL PROCEDURE

Pb$_{1-x}$La$_x$TiO$_3$ samples with 0.0 ≤ x ≤ 0.30 were prepared by using the conventional mixed oxide method [3]. Ceramic bodies were conformed by isostatic pressure and fired at ~1450 K during 3 h.

Titanium K-edge XANES spectra were collected at the LNLS (National Synchrotron Light Laboratory, Campinas, Brazil) facility using the D04B-XAS1 beam line. The LNLS storage ring was operated at 1.36 GeV and 150-250 mA. The ceramic bodies were grounded for Ti K-edge (4966 eV) XANES measurements in transmission mode at room temperature using a Si(111) channel-cut monochromator and energy steps of 0.4 eV. Ionization chambers were used to detect the incident and the transmitted flux. To provide good energy
reproducibility during the XANES data collection, the XANES spectrum of a Ti metal foil was collected simultaneously.

Calculation of XANES spectra were performed using the *ab-initio* full multiple scattering FEFF8.2 code [4]. XANES spectra of the PLT and PBZT samples were calculated in terms of a cluster derived from the average structure determined from previous XRD measurements [3]. Clusters with a size up to 8 shells around the absorber (titanium atom) were used. The calculation was performed according to the default setting of the FEFF8.2 code [4].

RESULTS AND DISCUSSION

Figure 1 shows the Ti K-edge XANES spectra of the samples.

The pre-edge region of the K-edge XANES spectra of some transition metal oxides are characterized by a pronounced feature several eV before the main rising edge. In transition metal oxides that crystallize in centrosymmetric structures, this pre-edge feature is very small or absent; in non centrosymmetric structures as in the PbTiO3 compound it can be quite large [5,6].

As can be seen in Figure 1, the increase of lanthanum content to x=0.10 leads to a significant decrease in the intensity of the A feature. A further increase of lanthanum to x=0.30 promotes a very slight variation in the A feature intensity only. On the contrary feature B is not affected by the lanthanum amount over the entire x range. Previous XRD results showed a tetragonal symmetry for PLT samples with x < 0.25 and a cubic structure for x = 0.30 [3]. Based on the analysis of the intensity of pre-edge feature A, we can affirm that none of the samples present a pre-edge feature characteristic of a regular TiO₆ octahedron.

In good agreement with previous XAS studies [5,6], the analysis of the XANES spectra shows that the local distortion does not follow the compositional dependence of the crystallographic structure.

Figure 3 and 4 present the *ab initio* XANES calculated spectra for the 0.0 ≤ x ≤ 0.30 PLT compounds. The calculation of the PLT XANES spectra was undertaken by the replacement of Pb by La atoms according to the sample stoichiometry. The best approach to simulating the XANES spectrum on a doped material like the PLT system involves running the FEFF code many times [7]. Each time, we replace a different set of randomly selected Pb by La atoms each time saving the result. This set of computed spectra was then averaged. New calculations were made and added to the running average until the result stopped changing.

![FIGURE 1.](image1.png) **FIGURE 1.** Experimental Ti K-edge XANES spectra of the Pb₁ₓLaₓTiO₃ compounds.

![FIGURE 2.](image2.png) **FIGURE 2.** Theoretical XANES spectra of Pb₁₋ₓLaₓTiO₃ samples with 0.0 ≤ x ≤ 0.15.

![FIGURE 3.](image3.png) **FIGURE 3.** Theoretical XANES spectra of Pb₁₋ₓLaₓTiO₃ samples with 0.20 ≤ x ≤ 0.30.

The calculated XANES spectrum of the x=0.0 sample, which corresponds to the PbTiO₃ compound,
reproduces quite well the XANES structure present in the experimental spectrum. All the structures from A to F are well reproduced. As has been previously observed by Ravel [7], the XANES spectrum of the PbTiO$_3$ compound can be described when 6 coordination shells around titanium are considered. Compared to the experimental spectrum, the energy position of the pre-edge feature is misplaced by a few electron volts probably due to problems with the underlying model potential [7].

For the sample with 5% mol% of La (x=0.05), theoretical calculations also reproduce quite well the experimental spectrum above and below the edge. However, for the x=0.10 and highest concentrated samples, a large discrepancy is observed between experimental and calculated spectra. For the calculated ones we observe an important decrease in the intensity of the pre-edge feature A which is totally removed for the x=0.30 sample. As can be clearly seen in Figure 1, any of XANES spectrum, including the one of x=0.30, presents a pre-edge feature characteristic of a distorted TiO$_6$ octahedron.

The calculation results show that the structural models obtained from XRD are not appropriate to describe the short and medium-range order structure for samples containing more than 5 at.% of lanthanum.

Figure 4 shows the comparison between theoretical XANES spectra of the x=0.10 sample where Pb atoms were or were not replaced by La atoms. As can be seen, the replacement of Pb by La atoms does not introduce significant changes in the pre-edge spectra or in the post-edge region of the XANES spectrum. Thus, as has been observed previously by others [7], we can assume that the substitution of a high Z element by others of comparable atomic number produces only slight modifications to the pre-edge region.

CONCLUSIONS

The analysis of experimental XANES spectra at the titanium K-edge shows that the nature of the pre-edge feature is only slightly dependent of the sample concentration. For the sample which presents a relaxor behavior and a crystallographic cubic symmetry, the pre-edge feature remains stronger than expected for a sample containing a regular TiO$_6$ octahedron. This shows that the long range cubic symmetry is only an average on a macroscopic scale.

The analysis of the theoretical XANES spectra shows that the structural models obtained from XRD analysis can only be applied to describe the local order correctly for undoped samples and for samples with x ≤ 0.05 of lanthanum. For samples with x ≥ 0.10, the calculation shows that the structural models provided by XRD are not appropriate to describe correctly the local and medium range order structure in these disordered perovskite materials. In such disordered crystalline compounds, the local distortions can be revealed only by local probes like XANES.

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