Ti K-XANES Analysis of the Cation Distribution in the CaTi$_{1-x}$Zr$_x$O$_3$ Solid Solutions

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Abstract. The effects of local B-cation distribution and octahedral tilting on the pre-edge structure in the Ti X-ray absorption $K$-spectra of the CaTi$_{1-x}$Zr$_x$O$_3$ perovskite solid solutions were investigated. Experimental spectra for the disordered CaTi$_{1-x}$Zr$_x$O$_3$ samples revealed a systematic variation of the pre-edge peak intensities with the $x$-values. Multiple scattering calculations using 75-atom clusters Ti(TiO$_6$)$_{6-n}$(ZrO$_6$)$_n$Ca$_8$O$_{24}$ were conducted to interpret these differences. The calculations reproduced the experimental spectra and demonstrated that the differences in the pre-edge feature intensities are dominated by the probability of finding a Zr atom in the 1st B-cation coordination sphere around the absorbing Ti. The pre-edge structure appeared to be sensitive to even small changes in the value of this probability, so that the pre-edge intensities could be used effectively to compare the extent of local B-site order in perovskite solid solution samples having similar chemical composition but processed differently.

Keywords: perovskite-like solid solutions, pre-edge structure, cation distribution.

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INTRODUCTION

Many complex metal oxides crystallizing with perovskite-like structures exhibit exploitable functional properties. Commonly, these properties are sensitive to slight variations in lattice distortions and chemical/displacive atomic ordering; therefore, understanding of structure-properties relations becomes critical for a development of new and optimization of the existing materials. Despite numerous examples of functional responses in perovskite-like solid solutions being dominated by the details of local atomic arrangements, the understanding of structural behavior at this scale remains incomplete largely because of the difficulties associated with local structure measurements.

Local deviations from the average structure are manifested in the details of diffuse X-ray/neutron scattering and XAFS. Unlike typical diffraction data, structural information contained in XAFS is element-specific. For perovskites based on 3$d$ and 4$d$ metal ions, a pre-edge XAFS in transition metal $K$-edge spectra carries information about local distortions of the oxygen coordination environment and distribution of the neighboring 3$d$ and 4$d$ cations. In the present study, we addressed this issue by analyzing the effects of B-cation distribution and octahedral tilting on the Ti $K$-pre-edge structure in the perovskite solid solutions CaTi$_{1-x}$Zr$_x$O$_3$.

All considered CaTi$_{1-x}$Zr$_x$O$_3$ crystallize with similar structures having orthorhombic $Pbnm$. The deviations from the ideal perovskite symmetry are caused by the $a'b'b'$ octahedral tilting.

Recent EXAFS and PDF analyses of local structures in the CaTi$_{1-x}$Zr$_x$O$_3$ revealed that both Zr-O and Ti-O distances in the solid solutions remain close to their respective values in the end-compounds [1]. Semi-quantitative analyses supported a near-random distribution of Zr and Ti over octahedral B-sites. However, accurate analyses of short-range B-site order using EXAFS were precluded by the strong correlations among the occupational probability and the octahedra tilting angles. In this contribution, we examined the sensitivity of a Ti $K$-pre-edge XAFS to the short-range B-site order in transition metal-based perovskites.

EXPERIMENTAL

The CaTi$_{1-x}$Zr$_x$O$_3$ powder samples with $x$=0, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$ were prepared by conventional solid state synthesis and equilibrated by multiple heating (with intermediate grinding) at 1500 °C for a total of 300 h. The equilibrium was inferred from the lack of change in the X-ray line broadening.

The Ti $K$-XANES were measured at the X23A2 beamline of the NSLS in transmission modes. The
double crystal monochromator was operated with a pair of Si (311) crystals; a detuning was used to minimize the effect of harmonics.

CALCULATION PROCEDURE

Ti K-absorption spectra were calculated using a full multiple scattering method implemented in the XKDQ computer code which utilizes a muffin tin cluster potential and includes both dipole and quadrupole parts of electron-photon interactions [2]. The potentials of all atoms in the cluster but the absorbing one were calculated from the electron densities of the free neutral atoms using a Hermann-Skillman procedure. The model of incomplete screening, with the screening charge of $0.8\, e$ added to the lowest unoccupied orbital of the ionized atom, accounts for the core-hole effect.

RESULTS AND DISCUSSION

![Absorption coefficient vs. Energy](image1)

**FIGURE 1.** The pre-edge part of Ti K-edge spectra of CaTi$_{1-x}$Zr$_x$O$_3$ solid solutions with $x=0, \frac{1}{4}, \frac{1}{2},$ and $\frac{3}{4}$.

The Ti K-pre-edge structures summarized in Fig. 1 were aligned according to the positions of peak A and the low-energy side of peak B. Detailed interpretation of the pre-edge features in Ti K-spectra of several perovskite-like structures has been reported previously [1]. According to these analyses, peak A is caused primarily by the quadrupole excitation of $1s$ electron to the $t_{2g}$ orbitals of the absorbing [TiO$_6$] octahedron, whereas peak B arises from the excitation of $1s$ electron to the $e_g$ orbitals of the same octahedron and contains both quadrupole and dipole (caused by the $p-d$ mixing) contributions. While Ti atoms in CaTiO$_3$ occupy centrosymmetrical positions, thermal vibrations ($\Delta u=0.1\, \text{Å}$) induce a $p-d$ mixing sufficient to account for the observed magnitude of peak B. The intensity of this peak remains nearly constant across the solid solutions thus indicating that the Ti atoms retain their centrosymmetric environment over the entire compositional range.

In addition to peaks A and B, the Ti K-pre-edge structure exhibits the bulkhead C and the peak D which both, unlike peaks A and B, display a pronounced dependence on the Zr content. We calculated difference spectra among the solid solution samples to isolate those pre-edge features which vary with the $x$-value. These spectra, calculated by subtracting the spectra of CaTi$_{1-x}$Zr$_{x}$O$_3$ from those of CaTi$_{1-x}$Zr$_x$O$_3$ ($x=0, \frac{1}{4}, \frac{1}{2}$) yield two peaks between 0 eV and 6 eV (Fig. 2). The lower energy difference peak occurs at the location of bulkhead C and can be attributed to the dipole excitations of photoelectrons ejected from the absorbing Ti atom to the $t_{2g}$ orbitals of neighboring [TiO$_6$] octahedra. These are the lowest unfilled orbitals that are not affected by the core-hole potential. The higher energy difference peak presumably reflects contributions of dipole excitations of a photoelectron to the $e_g$ and $t_{2g}$ orbitals of the neighboring [TiO$_6$] and [ZrO$_6$] octahedra, respectively.

![Absorption difference vs. Energy](image2)

**FIGURE 2.** The difference Ti pre-edge spectra calculated from the experimental spectra of CaTi$_{1-x}$Zr$_x$O$_3$ and CaTi$_{1-x}$Zr$_x$O$_3$ for the following $x$-pairs: (0-\(\frac{1}{4}\))-solid line, (\(\frac{1}{4}\)-\(\frac{1}{2}\))-dashed line, and (\(\frac{1}{2}\)-\(\frac{3}{4}\))-dotted line.

Fig. 3 compares the experimental Ti K-pre-edge structure for CaTiO$_3$ with that calculated using 75- and 200-atom clusters. Calculated spectra are in a good agreement with each other and with the experimental one in the pre-edge and main edge regions. This coincidence suggests that the 75-atom cluster is sufficient for reproducing the experimental spectra of CaTiO$_3$. 
Variations of the pre-edge structure in with Zr-content could be caused by change in the probability, \( p_{Zr} \), of finding a Zr atom on the six neighboring B-sites around the absorbing Ti and change in the octahedra tilting angles which increase monotonically with increasing Zr-content. The extent of these two effects on the Ti K-pre-edge structure was examined using a series of clusters Ti\((\text{TiO}_6)_{6-n}\)(\text{ZrO}_6)^n\text{Ca}_8\text{O}_{24}. The solid solution clusters were generated by replacing the \([\text{TiO}_6] \) octahedra in the cluster built for CaTiO\(_3\) with the \([\text{ZrO}_6] \) octahedra extracted from the CaZrO\(_3\) structure. Thus, the solid solution clusters accounted for a variation of the local tilting angles with the change in the nature of the neighboring B-cations.

The difference spectra calculated for the pairs of \( p_{Zt} \) \((\frac{1}{2}-\frac{1}{4}), (\frac{1}{4}-\frac{1}{2}), (\frac{1}{4}-0) \) (Fig. 4) reproduce those calculated from the experimental spectra for the analogous compositions. A good agreement between the difference trends in the calculated and experimental spectra, while providing a further support for a near-random distribution of Zr and Ti in the presently studied solid solutions, indicates that our calculations capture the main physics underlying the Ti pre-edge structure in perovskites.

The pre-edge structure calculated for solid solutions with definite compositions but different order parameters \( \alpha \) reveal a significant systematic variation of the pre-edge intensities with \( \alpha \). Thus, the Ti K pre-edge structure can be used as a sensitive tool for a semi-quantitative comparison of the short-range B-cation order parameters in the samples having the same chemical composition but processed differently. For example, this technique can be attractive for studying the effect of processing on the Ti/Zr distribution in the thin films of industrially-relevant PbTi\(_{1-x}\)Zr\(_x\)O\(_3\) whose functional properties have been reported as sensitive to the short-range B-cation order.

**CONCLUSIONS**

The effects of B-site short-range order and octahedral tilting on the pre-edge structure of the Ti-K-absorption spectra of the prototype perovskite solid solutions CaTi\(_{1-x}\)Zr\(_x\)O\(_3\) were studied both experimentally and theoretically using full multiple-scattering calculations. The Ti K-spectra were calculated for a series of the 75-atom clusters Ti\((\text{TiO}_6)_{6-n}\)(\text{ZrO}_6)^n\text{Ca}_8\text{O}_{24} with different concentrations of Zr \( p_{Zt} \) in the 1\(^{st} \) B-cation coordination shell around the absorbing Ti atom. The systematic differences in the pre-edge structure observed among the samples having different \( x \)-values were established to correlate closely with a \( p_{Zt} \) value. According to our XANES calculations, the Ti K-pre-edge structure is highly sensitive to the \( p_{Zt} \)-value thus providing an attractive tool for a semi-quantitative comparison of the degree of short-range B-site order in perovskite solid solution samples have identical average chemical composition.

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**REFERENCES**