

X-ray absorption spectroscopy studies of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$

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We report x-ray absorption near edge spectroscopy (XANES) of Ca and O *K*-edges of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ ($x = 0, 0.01, 0.08, 1$) and understand the spectral features related to the electronic structure of these perovskites. The XANES spectra of Ca *K*-edge possess a pre-edge peak similar to other *3d* transition metals like Ti, Ni when present in perovskite structure and provides information about *p*-type or hole doping. Presence of considerable amount of *3d* states justifies the reason to consider it as a light *3d* transition metal. The O *K*-edge spectra display characteristic spectral features assigned as e_g and t_{2g} and show strong dependence on concentration.

Keywords: XANES, Titanates, Perovskites

1. Introduction

Perovskites constitute an important group of oxide crystals with broad ranges of technologically important dielectric, piezoelectric, ferroelectric, superconducting and electro-optic properties (Lines & Glass, 1977). Alkaline earth titanates are prototype perovskite compounds having many properties common to cuprates and manganites. The fascinating aspect of these perovskites is in their rich and unique anisotropic properties related to structural phase transitions (Cohen, 1992). Understanding the electronic structure of these materials remains a major challenge. X-ray absorption near edge spectroscopy (XANES) is one of the most suitable techniques to provide information about the atomic environment and they are unique to each element in materials (Stöhr, 1992). Charge carrier holes are introduced in perovskites by Ca, Sr and Ba doping and by oxygen stoichiometry. It is also known that Ca, Sr and or Ba doping produce a rich variety of physical properties including magnetism, ferroelectricity, superconductivity, a metal insulator transition, and structural transformations. Alkaline metals are thus important ingredients in perovskites structure and its role has not been understood in right perspective. The interest in the mixed compounds arises due to the possibility of 'tailoring' them for various devices. From fundamental physics point of view such compounds especially under low concentration demonstrates a progressive change in the electronic structure. We also noticed that data on Ca *K*-edge is very much limited and all these motivated us to investigate these compounds.

We have measured the XANES spectra of Ca and O *K*-edges for the compositions $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ ($x = 0, 0.01, 0.08, \text{ and } 1$) to understand the spectral features related to their electronic structure.

2. Experimental

$\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ ($x = 0, 0.01, 0.08, \text{ and } 1$) samples were prepared from reagent grade BaCO_3 , TiO_2 and CaCO_3 powders (Merck Co, Darmstat, Germany) via standard ceramic routes. These samples

were characterized by x-ray diffraction, resistivity and dielectric constants and details are given elsewhere (Lin *et al.*, 1990). Room temperature x-ray absorption spectra were obtained for Ca and O *K*-edges at the Synchrotron Radiation Research Center, Hsinchu, Taiwan, running at 1.5 GeV with a maximum stored current of 200 mA. The Ca *K*-edge spectra were recorded using Si (111) double crystal monochromator beamline in fluorescence mode. The O *K*-edge was measured in fluorescence mode using seven-element Ge detectors at high-energy spherical grating monochromator beamline under vacuum better than 10^{-9} torr.

3. Results and Discussion

The XANES spectra at the Ca *K*-edge for all compositions investigated are reported in Fig. 1(a). We identify three major XANES structures within 30 eV above the edge, which are labeled as A_1 to C_1 . The intensity of these spectral features change across the series as a function of Ca concentrations. This modification can be associated with the changes in the local environment around calcium caused by Ca substitution at the Ba site. As the energy increases, we find that the most intense resonance of the spectra corresponds to the $1s \rightarrow 4p$ transition. The main edge presents a characteristic three-peak structure (marked as B_1) changes marginally across the series and corresponds to unoccupied states mainly of Ca *4p* states and C_1 from *5s* states (Chaboy & Quartieri, 1995). These peaks may also contain unoccupied states of Ba *5sp* and Ti *4sp* states. Peaks B_1 , and C_1 whose relative intensities increase indicate that Ca substitutes mostly Ba site. All these experimental spectra show a small feature (A_1) at the pre-edge whose energy position is independent of the Ca concentrations. However, its intensity increases with Ca content indicating that Ca substitutes preferably Ba sites. Fig.(b) highlights the pre-edge feature for different Ca compositions. The spectra with $x = 0.01$ is noisy due to low concentration of Ca. Similar spectral features have been reported for Ca metal, CaF_2 , and some garnets with varying Ca content. However, no difference was observed in the pre-edge peak intensity of Ca *K*-edge XANES spectra between CaF_2 and Mn doped CaF_2 (Chaboy & Quartieri, 1995). Various assignments have been put forth for this pre-edge feature such as excitons, as a forbidden $1s \rightarrow 4s$ transition, $1s \rightarrow 3d$ transition multiple scattering (MS) resonance. It is also considered due to transition to bound final states in a molecular orbital or one electron band structure picture (Barkyoub & Mansour, 1992).

In general, spectral features within ~ 10 eV of the edge threshold are due to electronic transitions to unoccupied states near the Fermi level and are sensitive to the spatial and electronic details of the potential. Thus, this feature reflects that effective charge and the site symmetry of Ca ion changes across the series. This feature is commonly attributed to transitions from *1s* energy levels to bound *3d* or O *2p* molecular orbital (Ravel & Stern, 1995). In this picture, the transitions are discrete, with broadening due to core-hole lifetime and instrumental resolution. This feature is attributed to a $1s \rightarrow 3d$ transition, which is forbidden unless some *d-p* mixing is operating. It is also known that in many transition-metal compounds and complexes and in other calcium compounds, this pre-edge originates from a $1s \rightarrow 3d$ transitions. The intensity of $1s \rightarrow 3d$ transition in first-row transition metals will be stronger in compounds that are distorted from centrosymmetry (Ravel & Stern, 1995; Grunes, 1983).

Distortions around the Ca atom are likely to occur among the oxygen near neighbors. Physically, feature A_1 originates from MS of the photoelectron by the nearest anion neighbor, oxygen. In the sense that the Ca ions are, adjacent to the O ions and well separated from Ti ions and in the relaxed structure shows considerable buckling and distortion. Thus, change in the intensity of feature A_1 in the Ca

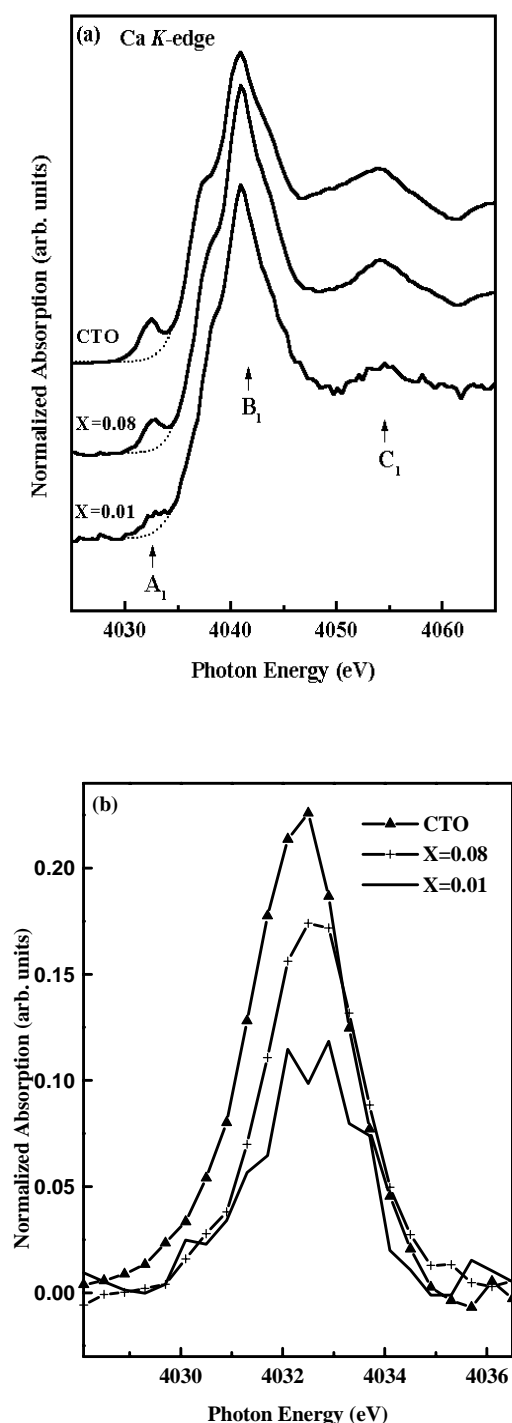


Figure 1

(a) Normalized x-ray absorption spectra of Ca *K*-edge taken in fluorescence mode for $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ compounds: (i) CTO, (ii) $x = 0.08$, and (iii) $x = 0.01$. (b) Highlights the pre-edge feature of Ca *K*-edge with different Ca concentrations.

spectra may arise from oxygen near neighbor configuration. It is appropriate to mention that Farges *et al.*, proposed that pre-edge can be attributed to MS effects and outlined a method for determining coordination numbers of cations from this pre-edge information

(Farges *et al.*, 1997). Wu *et al.*, have demonstrated that the variation of the width and intensity of the pre-edge is associated with the occupation of the *d* band and linked with the higher-neighboring atomic structure (Wu *et al.*, 1988). From the electronic configuration of Ca, *3d* electrons are empty and a basic feature of Ca-O bonding is its strong covalent character. This has to be considered while understanding this feature and it is similar to *3d* metals like Ni *K*-edge where pre-edge gives information on the presence and the amount of the hole states (Garcia *et al.*, 1995). The lattice distortion that originates from doping Ca introduces the hole band on the Ti-O. The pre-edge intensity thus indicates that the hole doping in the system and drives them as *p*-type. This suggests that change in the intensity of pre-edge peak of alkaline-earth core levels can be a common measure of the hole concentrations for perovskites. This spectral feature thus may be assigned as ligand hole with corresponding notation of $3d^1L$. Ca doping introduces a local structural distortion and hole doping through the oxygen and provides a unifying approach of relating the pre-edge features. Above reasons strengthens to consider Ca in the series of light *3d* transition metals.

The molecular orbitals, which contain O *2p* states, can be observed in the O *K*-edge absorption spectrum. The information on unoccupied oxygen *p* states in these compositions are of great importance to understand the hybridization of Ti and O states in TiO_6 octahedral which forms the basic structural unit in these compounds. The O *K*-edge absorption spectra of all samples are presented in Fig. 2. These spectra contain electronic states depending upon the energy and symmetry. All major spectral features are marked A_2 to E_2 in the increase in energy. The first two peaks A_2 and B_2 are similar to TiO_2 with a splitting of ~ 2.5 eV. These are attributed to the unoccupied O *2p* states, which are covalent, mixed with the Ti *3d* states: t_{2g} and e_g states (Brydson *et al.*, 1989, de Groot *et al.*, 1993). The e_g states are directed towards the O and therefore have a higher energy than the t_{2g} states. The distortion of the Ti site from octahedral to lower symmetry results in an asymmetric broadening of the peaks assigned to e_g states. The spectral features at C_2 and D_2 arise due to O *2p* states that are mixed with Ba and Ca of *5sp* and *4sp* states respectively. This feature is absent in TiO_2 . The structure marked as E_2 is seen in all samples and due to Ti *4sp* states (de Groot *et al.*, 1993).

Note that it is shifted towards lower energy side with reference to TiO_2 after doping Ca. Some of the features in doped system are broad when compared to TiO_2 and BaTiO_3 due to the many body effects. It is evident that there is finite hybridization of O *2p* states with Ti *3d* wave functions in the ground state for all compositions apart from mixing of *sp* states from Ca or Ba. Local distortions of the TiO_6 octahedra appear after the introduction of Ca or Ba and they play an important role in determining the complex ferroelectric and structural phase behavior. The presence of alkaline earth metals is essential for many of these interesting properties in perovskites.

4. Conclusion

We have reported the Ca and O *K*-edge spectra of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$. The intensity of pre-edge of Ca *K*-edge increases with Ca content and this feature is similar to *3d* transition metals. It provides information about *p*-type or hole conduction induced by substitution of Ca. Ca and O *K*-edge data suggest a new approach for studying the physical properties relating the role of alkaline earth metals in perovskites.

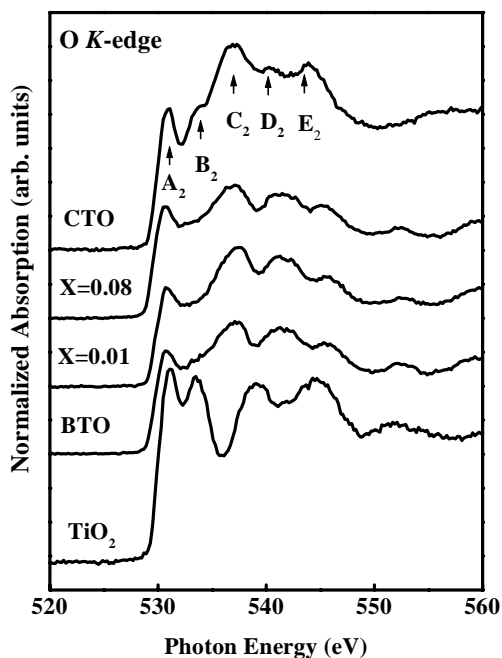


Figure 2
Normalized x-ray absorption spectra of O K-edge measured in fluorescence mode for $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ compounds: CTO, $x = 0.08$, $x = 0.01$, BTO, and TiO_2 .

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