Direct experimental evidence of hybridization of Pb states with O 2p states in ferroelectric perovskite oxides

J. C. Jan, a) H. M. Tsai, C. W. Pao, J. W. Chiou, K. Asokan, b) K. P. Krishna Kumar, and W. F. Pongc) Department of Physics, Tamkang University, Tamsui, Taiwan 251, Republic of China

Y. H. Tang and M.-H. Tsai Department of Physics, National Sun Yat-Sen University, Kaohsiung, Taiwan 804, Republic of China

S. Y. Kuo Precision Instrument Development Center, National Science Council, Hsinchu, Taiwan 300, Republic of China

W. F. Hsieh Department of Photonics and Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu, Taiwan 300, Republic of China

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This work presents the O K- and Ti L3,2-edge x-ray absorption near-edge structure (XANES) spectra of Pb,Sr1−x,532,534 TiO3 (P,STO) and Ba,Sr1−x,532,534 TiO3 (B,STO) compounds with various Pb and Ba concentrations. The result provides direct evidence that the Pb–O bonding strongly affects O 2p–Ti 3d hybridization in the TiO6 octahedron of P,STO. In contrast, the Ba–O bonding does not substantially affect O 2p–Ti 3d hybridization in B,STO. The Ti L3-edge XANES spectra show the splitting of the eg band for P,STO with x ≥ 0.5, which provides an evidence of Pb-induced tetragonal distortion in the TiO6 octahedron. In contrast, eg band splitting is absent in B,STO.

Ferroelectric perovskite oxides of the ABO3-type including BaTiO3 (BTO), SrTiO3 (STO), and PbTiO3 (PTO) are important materials because of their piezoelectric, pyroelectric, and dielectric properties. 1–3 Interestingly, these materials have tunable properties over a wide range of mixed solid solutions doped with various cations. A characteristic unit cell of these perovskites contains a TiO6 octahedron. Collective polarization of the TiO6 octahedra is believed to determine the ferroelectric characteristics. 4–6 X-ray absorption near-edge structure (XANES) measurements and first-principles calculations have been used to elucidate the role of alkaline-earth metals in perovskites, 7–9 which showed that A cations influenced the coupling between Ti and O ions and is responsible for tuning the ferroelectric properties. Kuo et al. determined the lattice constant from x-ray diffraction (XRD) data and observed a structural change from cubic to tetragonal (associated with an increase in the tetragonal distortion c/a) for Pb,Sr1−x,532,534 TiO3 (P,STO) at x=0.5 (Ref. 10) and for Ba,Sr1−x,532,534 TiO3 (B,STO) at x=0.7. 11 They also carried out Raman measurements for P,STO and B,STO and found that the splitting of longitudinal optical (LO) and transverse optical (TO) modes became stronger as the Pb content in the tetragonal phase of P,STO increases, while the splitting became weaker as the Ba content in B,STO increases. These results were explained by the covalent Pb–O bonding in P,STO and ionic Ba–O bonding in B,STO. 10–12 The present study is intended to understand the electronic structures of P,STO and B,STO solid solutions by O K- and Ti L3,2-edges XANES measurements to elucidate the role of Pb and Ba ions in M1Sr1−x,532,534 TiO3 (M=Pb and Ba).

Room-temperature XANES spectra at the O K- and Ti L3,2-edges were recorded using a high-spherical grating monochromator beamline in fluorescence and sample drain current modes, respectively, at the National Synchrotron Radiation Research Centre, Taiwan. P,STO and B,STO (where x is varied from 0 to 1) solid solutions were prepared by the sol-gel method and characterized by XRD. The details of the preparation and characterization of these samples have been reported elsewhere. 10,11

Figures 1 and 2 present the normalized O K-edge XANES spectra of P,STO and B,STO (x=0 to 1) compounds, respectively, and reference TiO2. These spectra were divided by the incident intensity I0 and normalized to the same area in the energy range between 550 and 560 eV (not fully shown). The main spectral features in the spectra of PTO (BTO) in Fig. 1 (Fig. 2) are centered at ~531 (530.5), 532, 534 (533.5), and 537 (537) eV and are labeled as A1 (A2) to D1 (D2), respectively. These features correspond to transitions from the O 1s core state to the unoccupied O 2p-derived states. According to first-principles calculations for P,STO (Ref. 13) and B,STO (Ref. 9) these states are hybridized states between O 2p and relatively narrow 3d and broader 4sp bands of the Ti ion and Pb 6sp and Sr 4d/(Ba 5d) bands. Specifically, spectral features A1, C1, and B1 are attributable to hybridized states between O 2p and Ti 3d and Pb 6sp, while features A2 and C2 are associated with O 2p–Ti 3d hybridized states. A similar two-peak structure (t2g and e g states) at the threshold of the O K-edge is commonly obtained from 3d-transition metal oxides. 14 Feature D1 (D2) in the spectra of P,STO (B,STO) is attributable to

a) Present address: National Synchrotron Radiation Research Center, Hsinchu, Taiwan 300, Republic of China.

b) Permanent address: Nuclear Science Centre, Aruna Asaf Ali Marg, New Delhi-110067, India.
c) Author to whom correspondence should be addressed; electronic mail: wfpong@mail.tku.edu.tw

to the O 2p derived states hybridized with Sr 4d (Sr 4d/Ba 5d) orbitals. The insets of Figs. 1 and 2 show magnified near-edge features with the background subtracted to highlight intensity differences. The inset of Fig. 1 shows that feature B 1 emerges between features A 1 and C 1 when the Pb content is added. Furthermore, strong hybridization between O 2p and Ti 3d/Pb 6p states increases the number of unoccupied O 2p derived states and broadens the features for P 1/STO. In contrast, the general spectral line shapes and widths in the inset of Fig. 2 are very similar for B 1/STO because Ba and Sr ions have similar valence states. The similarity of the spectra of B 1/STO also shows that substitution of Sr by Ba insignificantly affects the Ti–O bonding in B 1/STO. Feature A 2 shifts slightly to lower energy as the Ba content increases. This trend is due to the fact that the electronegativity of Ba (0.89) is slightly less than that of Sr (0.95), so that the average electronegativity of cations decreases and the negative effective charge of the O ion increases with the Ba content. The O K-edge XANES spectra of P 1/STO have more features than those of B 1/STO. This indicates that the Pb–O covalent bonding has additional contribution to the spectra and such result is consistent with the findings of Kuroiwa et al. and also in agreement with the theoretical prediction of Cohen. 4

Figure 3 plots the integrated intensities of A 1+C 1, B 1, and A 2+C 2 features in the O K-edge XANES spectra as functions of the Pb (Ba) concentration. The frequency difference data of P 1/STO (open squares) and B 1/STO (open triangles) are from Refs. 10 and 11, respectively. The inset shows a magnified view of A 1, B 1, and C 1 features and fitted result of P 1/STO at x = 0.9.

FIG. 1. Normalized O K-edge XANES spectra of the P 1/STO (x = 0–1) samples. The dashed line represents a best-fitted Gaussian shape background. The inset shows the magnified near-edge feature after background subtraction.

FIG. 2. Normalized O K-edge XANES spectra of the B 1/STO (x = 0–1) samples. The dashed line represents a best-fitted Gaussian shape background. The inset shows the magnified near-edge feature after background subtraction.

FIG. 3. Integrated intensities of A 1+C 1, B 1, and A 2+C 2 features in the O K-edge XANES spectra as functions of the Pb (Ba) concentration. The frequency difference data of P 1/STO (open squares) and B 1/STO (open triangles) are from Refs. 10 and 11, respectively. The inset shows a magnified view of A 1, B 1, and C 1 features and fitted result of P 1/STO at x = 0.9.
The intensity decreases and the energy shifts to lower energies as x increases, suggesting that the effective charge of the Ti ion increases in P_{x}STO. This finding reflects that Pb has a larger electronegativity than Ti (2.33 vs. 1.54), so that there is electron transfer from Ti to Pb, which increases the positive effective charge of Ti. In contrast, the spectra of B_{x}STO after background subtraction reveal that the intensity of the L_{3}-edge feature overall increases as the Ba content increases as shown in the inset of Fig. 5, which suggests that the Ti effective charge decrease with the increase of the Ba content. In this case, the decrease of the Ti effective charge reflects the smaller electronegativity of Ba than Ti (0.89 versus 1.54), the direction of electron transfer is from Ba to Ti, which reduces the positive effective charge of Ti.

In summary, the XANES measurements provide direct evidence that the Pb–O bonding strongly affects O 2p–Ti 3d hybridization in the TiO_{6} octahedron of P_{x}STO. In contrast, the Ba–O bonding does not substantially affect O 2p–Ti 3d hybridization in B_{x}STO. The Ti L_{3}-edge XANES spectra provide evidence of Pb-induced tetragonal distortion in the TiO_{6} octahedron for x≈0.5. In contrast, this effect is absent in B_{x}STO.

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15Table of Periodic Properties of the Elements (Sargent-Welch Scientific, Skokie, Illinois, 1980).