Difference of Electronic Structures between SrTiO$_3$ and BaTiO$_3$

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SrTiO$_3$ and BaTiO$_3$ えんきょうきょうずの差異

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1. Introduction

BaTiO$_3$ crystallizes in the tetragonal perovskite structure and belongs to the space group of Pm3m. Wanir found, in 1942, that BaTiO$_3$ indicates a ferroelectricity. This compound has been applied as an oscillator in a fish finder, a ceramic condenser and a ceramic filter since then. The ferroelectricity in BaTiO$_3$ occurs from the displacement of each ion positioning at cubic perovskite sites. The relative displacement is about 0.01 nm and a spontaneous polarization occurs. Recently, a first-principles band calculation was performed to research the nature of the numerous physical properties of BaTiO$_3$. However, it is not easy to obtain a definite chemical image from the calculation, because it was carried out using plane-waves as the basis function. On the contrary, LCAO-like approach based on chemical bonding theory is more appropriate method to analyze chemical properties of BaTiO$_3$ than the plane-wave methods.

The purpose of the present study is to provide basic informations for the electronic structures of BaTiO$_3$ and to elucidate the difference with the electronic structure of SrTiO$_3$ with cubic perovskite structure. Therefore, we performed X-ray photoemission spectroscopy (XPS) measurements for these single crystals and compared the results with the theoretical ones obtained from a molecular orbital (MO) calculation.

2. Experiment and calculation

XPS measurements were carried out using a Surface Science Laboratories model SSX–100 spectrometer with a monochromated Al K$_\alpha$ X-ray source. The XPS spectra were collected from the BaTiO$_3$ and SrTiO$_3$ single crystals fractured in situ in ultrahigh vacuum (UHV). Fracturing single crystals in situ in UHV is the only reliable way of preparing almost perfect and stoichiometric surfaces that are indispensable for obtaining highly accurate data that can be compared with the theoretical calculation. The spectrometer was calibrated utilizing the peak originating from Au 4f$_{7/2}$ (83.79 eV) and the full width at half maximum (FWHM) of Au 4f$_{7/2}$ was 1.03 eV. The single crystals were attached to copper sample holders and introduced into a measurement chamber under a pressure less than $6.5 \times 10^{-8}$ Pa. The surfaces had no C 1s XPS peaks, and their elastic scattering peaks of O 1s had symmetrical single Gaussian peaks. Since these crystals were highly resistive, the conditions of a neutralizer were optimized to obtain XPS spectra.

MO calculations were performed using a discrete-variational (DV) Xα method. The cluster models for the MO calculations were constructed on the basis of the crystal structure of perovskite. The lattice parameters were the same as those in bulk, $a = 0.3994$ nm for SrTiO$_3$ and $a = 0.3992$ nm, $c = 0.4031$ nm for BaTiO$_3$. The cluster models employed in the MO calculation were [Sr$_7$Ti$_8$O$_{60}$]$^{74-}$ and [Ba$_7$Ti$_8$O$_{60}$]$^{74-}$ clusters. The clusters were embedded in a Madelung potential generated by point charges outside the cluster. Electronic structures of the model clusters were self-consistently calculated using numerical atomic basis functions. The atomic orbitals used in the MO calculation are 1s–5s orbitals for Sr, 1s–4p orbitals for Ti, 1s–2p orbitals for O and 1s–6s for Ba, respectively. Here, Sr 4d and Ba 5d orbitals were excluded in the calculation. The total charge matrix of the [Ba$_7$Ti$_8$O$_{60}$]$^{74-}$ cluster, $–7e^–$, was obtained by summing the formal charges of the constituents, Ba$^{2+}$, Ti$^{4+}$ and O$^{2–}$.

3. Results and discussion

The valence band XPS spectrum for the SrTiO$_3$ single crystal is shown in Fig. 1 (a). The valence band (VB) spectrum of as-fractured SrTiO$_3$ exhibited two large peaks: P1 at around 4.35 eV and P2 at around 6.25 eV arising from the O 2p$_x$ and O 2p$_y$ bonding orbitals, respectively. The experimental width of valence band, determined from both intercepts of linear fits to right shoulder of the lowest binding energy peak and left shoulder of the highest peak with zero line of the samples, was 5.8 eV. These features of the VB
spectrum of as-fractured SrTiO₃ are in agreement with those reported by XPS and ultraviolet photoemission spectroscopy (UPS) measurements. The apparent maxima P3 and P4 are at around 4.0 and 5.75 eV and correspond to the O 2pₓ and O 2pᵧ bonding orbitals, respectively.

We performed a partial density of states (PDOS) calculation for each atomic orbital component in order to reveal the difference of the electronic structures between SrTiO₃ and BaTiO₃. In the PDOS calculations of [Sr₇Ti₈O₆₀]⁷⁴⁻ and [Ba₇Ti₈O₆₀]⁷⁴⁻ clusters, the atomic orbitals were used as the basis functions. For broadening the discrete energy eigenvalues, each DOS curve is represented by the Gaussian functions with 0.3 eV full width at half maximum (FWHM). MO energies are aligned so as to make the highest occupied MO (HOMO) zero.

Figure 2 shows the calculated total density of states (TDOS) and PDOS for [Sr₇Ti₈O₆₀]⁷⁴⁻ cluster. The theoretical TDOS in the VB region reproduce well the experimental XPS spectrum in width and shape. The energy gap between HOMO and the lowest unoccupied MO (LUMO) was 4.24 eV. O 2p orbitals have a large DOS in the VB region and hybridize with Ti 3d orbitals. This result is agreeing well with the calculation result that was obtained regarding TiO₂. However, the hybridization of Sr 5s orbitals with O 2p orbitals is very weak. This indicates that for a Sr–O bonding the ionic contribution is predominant because of a large electronegativity of oxygen and small ionization energy of a strontium atom. Figure 3 shows the DOS curves obtained for [Ba₇Ti₈O₆₀]⁷⁴⁻ cluster. The energy gap between HOMO and LUMO decreased to 3.88 eV. It should be noted that O 2p orbitals hybridize with Ba 5p orbitals, while do not almost hybridize with atomic orbitals of Sr atom. This means that the nature of the chemical bonding
of Ba–O is more covalent than that of Sr–O in SrTiO$_3$.

Figure 4(a) displays the overlap population diagrams for Sr–O and Ti–O bonds obtained for the [Sr$_7$Ti$_8$O$_{60}$]$^{74-}$ cluster. The right part shows the bonding contribution and the left part the anti-bonding contribution. The nearest neighbors in the cluster (Sr–O: 0.2761 nm, Ti–O: 0.1952 nm) were used in the overlap population analysis. The Ti–O interaction is including both of the contributions of bonding and anti-bonding in the VB region. The major part of the Sr–O interaction can be assigned to the anti-bonding contribution. In addition, it is found that the Sr–O bond is less significant than the Ti–O bond. Subsequently, the similar calculation was implemented for the [Ba$_7$Ti$_8$O$_{60}$]$^{74-}$ cluster. The anti-bonding interaction between Ba and O atoms is fairly observed and is comparatively strong, as shown Fig. 4(b). In the [Ba$_7$Ti$_8$O$_{60}$]$^{74-}$ cluster, it should be very noticeable that the bonding contribution of the Ti–O bond strengthens and the anti-bonding contribution weakens, compared with the [Sr$_7$Ti$_8$O$_{60}$]$^{74-}$ cluster. In fact, bond overlap population defined as a sum of the overlap population of occupied of the nearest Ti–O is estimated to be 0.077 for the [Ba$_7$Ti$_8$O$_{60}$]$^{74-}$ cluster and 0.028 for the [Sr$_7$Ti$_8$O$_{60}$]$^{74-}$ cluster. These calculation results are consistent with the first-principles band calculation.\(^{16}\)

Fig. 4. Overlap population diagrams for (a) [Sr$_7$Ti$_8$O$_{60}$]$^{74-}$ and (b) [Ba$_7$Ti$_8$O$_{60}$]$^{74-}$ clusters.

References

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