

Dielectric Response of BaTiO₃ Electronic States under AC Fields via Microsecond Time-Resolved X-Ray Absorption Spectroscopy

The electronic states of a ferroelectric BaTiO₃ thin film under AC electric fields are investigated in order to clarify the correlated contributions of each constituent atom to dielectric properties. Since the observation of the electronic states at the instant of polarization reversal is a key issue in our study, we developed microsecond time-resolved X-ray absorption spectroscopy (TR-XAS) techniques synchronized with external AC fields. In addition to the well-identified orbital hybridization between Ti and O atoms, an electronic correlation was found between Ba and Ti atoms. This also contributes to polarization reversal of BaTiO₃.

Ferroelectric materials are widely used in various practical applications such as multilayer ceramic capacitors, piezoelectric devices, and memory cells. Dielectric properties of a typical dielectric material, ATiO₃, are affected significantly by A-site cations: for example, BaTiO₃ and PbTiO₃ have spontaneous electric polarizations, while SrTiO₃ and CaTiO₃ do not. Previous related literature primarily focused on the off-center displacement of Ti ions, which is a major cause of polarization. The Ti off-center displacement is accompanied by Ti-3*d* and O-2*p* hybridization in BaTiO₃ and PbTiO₃. Therefore, it is evident that orbital hybridization is closely linked to the dielectric properties of ATiO₃ [1, 2].

Since spontaneous polarization of ferroelectric materials can be switched by external electric fields, direct observation of the electronic states under electric fields is an appropriate approach to investigate the dielectric properties. In this study, we investigated the polarization reversal response of atomic bonds in BaTiO₃ under AC electric fields. Using time-resolved X-ray absorption spectroscopy (TR-XAS), we observed the electronic correlation between Ba and Ti ions in addition to Ti-O hybridization. This is the first experimental verification of Ba contributions to polarization reversal of BaTiO₃.

A microsecond TR-XAS technique was employed to detect tiny time variations under AC fields. In comparison with the conventional DC scans, the use of time stamps of a silicon drift detector (SDD) brings the advantage of enhanced sensitivity of faint features, since at each photon energy the experimental conditions, such as beam intensity, Joule heating, and fatigue, are the same. In this study, a TR-XAS system was established on the beamline BL-15A1. The system was realized by an independent digital signal processing (DSP) system. It could easily be combined with various sample conditions such as quick-scanning XAS, and it has a time resolution of sub-microsecond order.

The sample was a BaTiO₃ thin film with a thickness of 650 nm prepared by pulsed laser deposition. Ti K-edge spectra were measured in partial fluorescence yield mode, as illustrated in Fig. 1. X-rays were incident on the top electrode of the sample. The detected fluorescence X-rays were converted to digital signals and recorded with time information by the DSP. We used signals only in the Ti K α region to obtain partial fluorescence spectra.

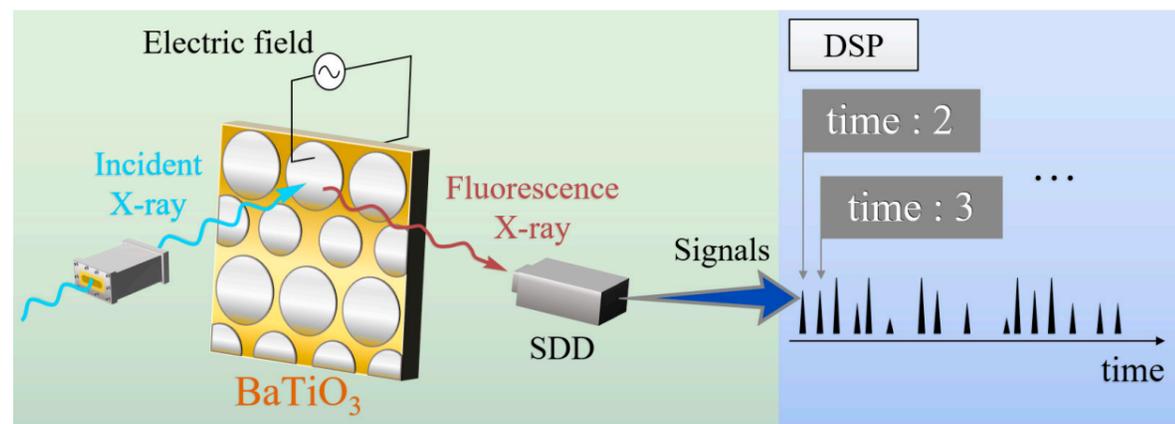


Figure 1: Schematic diagram of the time-resolved X-ray absorption spectroscopy synchronized with external electric fields.

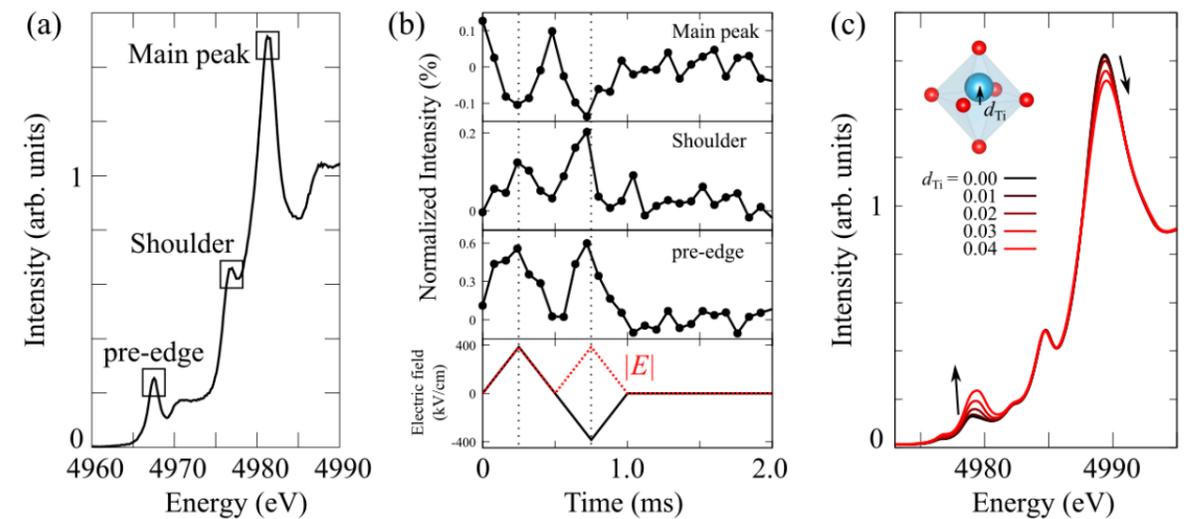


Figure 2: (a) Non-TR Ti K-edge spectrum of the BaTiO₃ thin film at room temperature. (b) Time variation of the intensities of the main peak, shoulder, and pre-edge peak under a triangular AC electric field. (c) Simulated Ti K-edge spectra of BaTiO₃ for various Ti off-center displacements (d_{Ti}) performed by FEFF9.6 codes.

A non-TR Ti K-edge spectrum of the BaTiO₃ is shown in Fig. 2(a). The absorption profile above the sharp main peak at 4985 eV corresponds to the density of states of the unoccupied Ti 4*p* states, whereas small features in the pre-edge region (4965–4975 eV) represent the Ti 3*d* states. The intensity of the pre-peak increases as the local distortion in a TiO₆ octahedron increases because the hybridization between the Ti-3*d* and O-2*p* orbitals becomes more pronounced [3]. The shoulder structure at 4980 eV is a characteristic of BaTiO₃ because its intensities and broadness are different with different A-site ions in ATiO₃.

The time variation of the integrated intensities of the pre-edge peak, the shoulder structure, and the main peak are presented in Fig. 2(b). Intensities of the pre-edge peak and the shoulder structure increase with an increase in the amplitude of the applied electric field, while that of the main peak decreases.

To provide a theoretical background for the interpretation of the TR-XAS results, the experimental spectra were compared with the simulated spectra obtained by FEFF 9.6 codes [4]. The simulated results are shown in Fig. 2(c), wherein the Ti off-center displacement (d_{Ti}) was varied from $d_{Ti} = 0$ to 0.04 in atomic units. It was assumed that larger displacements would make the spectral changes clearer. The intensity of the pre-edge peak increases with increasing d_{Ti} , which reflects the enhanced Ti 3*d*-O 2*p* hybridization, whereas the intensity of the main peak decreases with increasing d_{Ti} . In

contrast, the shoulder structure is not affected by the Ti off-center displacement, which clearly indicates a different physical origin for the shoulder structure. As previously mentioned, the shoulder structure was attributed to the A-site contribution. Therefore, it can be stated that orbital hybridization is not restricted to Ti and O ions but also involves Ba ions, or at least, that Ba ions also play an important role in the formation of the valence band. This is the first experimental verification of the electronic contribution of Ba to polarization reversal [5].

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