Supplemental Material

Changes in the electronic structure of $BaTiO_3$ due to ferroelectric phase transition investigated via polarization-dependent hard x-ray photoemission spectroscopy

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Table S1 Photoionization cross-sections per electron (σ) for valence orbitals of the Ba, Ti, and O atoms with 6 keV E(H)- and E(V)-x-rays in our experimental geometry. The unit is given in barn.

Element	Orbital	Cross section (σ) E(H) 6 keV	 E(V) 6 keV
Ba	6*s*	30.5	0.376
	5*p*	184	16.3
	5*d*	23.0	5.89
Ti	4*s*	31.2	0.422
	4*p*	0.0767	0.0222
	3*d*	0.365	0.251
O	2*s*	53.2	1.06
	2*p*	0.353	0.299

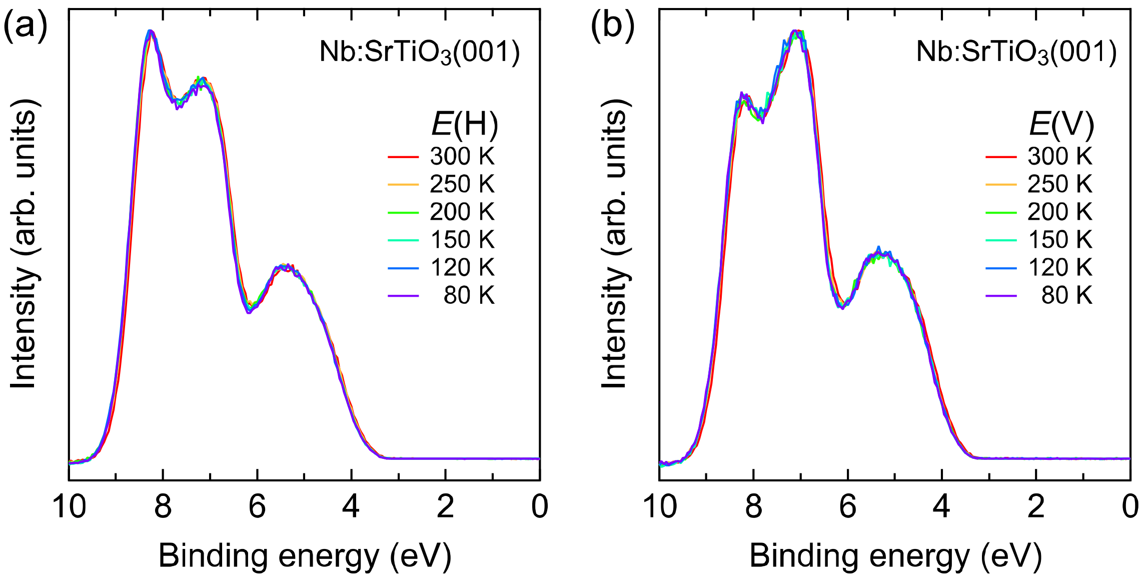

Figure S1 Temperature dependence of (a) *E*(H)-VB and (b) *E*(V)-VB spectra of $SrTiO_3(001)$ doped with niobium ($Nb:SrTiO_3$).

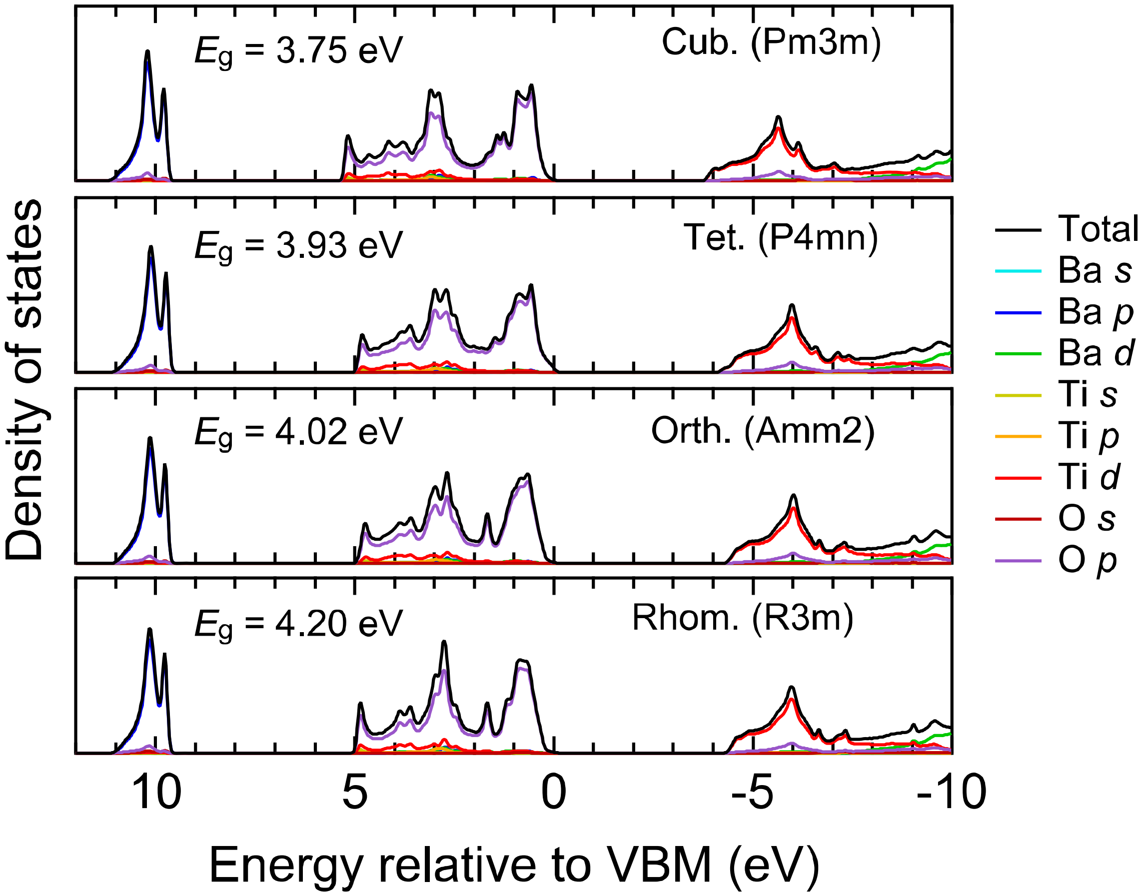

Figure S2 Wide-range total and projected densities of states of $BaTiO_3$ for cubic (Cub.), tetragonal (Tet.), orthorhombic (Orth.), and rhombohedral (Rhom.) phases. The energy is referred to the valence band maximum (VBM). The bandgap (E_g) for each phase is shown in the inset.

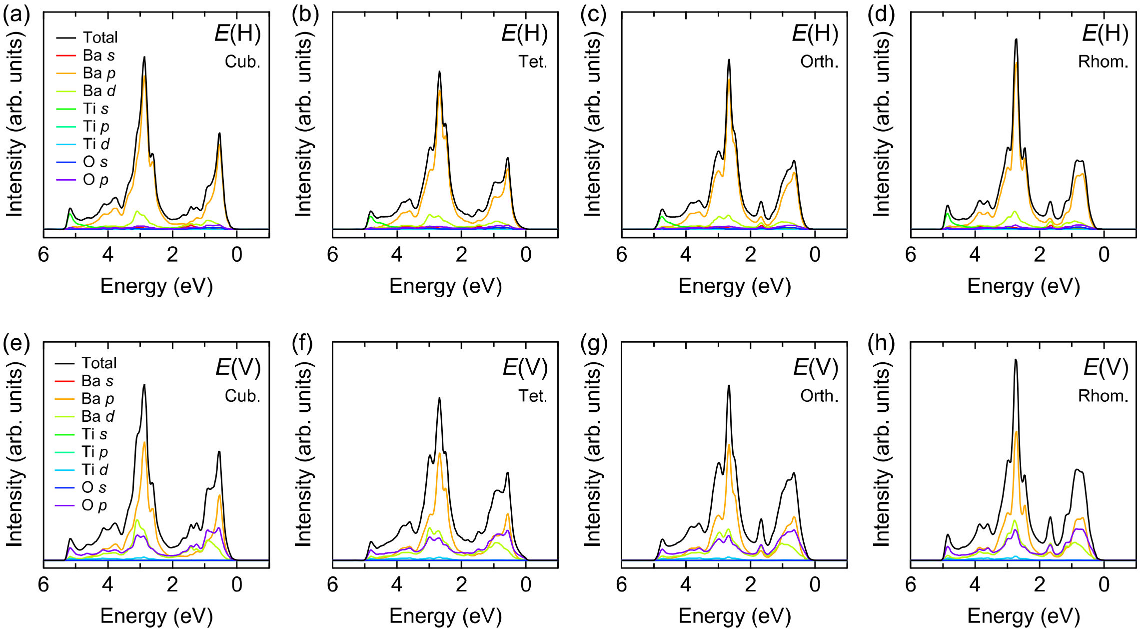

Figure S3 Cross-section weighted total and projected densities of states, which are proportional to the photoemission intensity, for (upper) *E*(H)-VB and (bottom) *E*(V)-VB spectra in (a,e) cubic (Cub.), (b,f) tetragonal (Tet.), (c,g) orthorhombic (Orth.), and (d,h) rhombohedral (Rhom.) phases, respectively. The energy is referred to the valence band maximum.

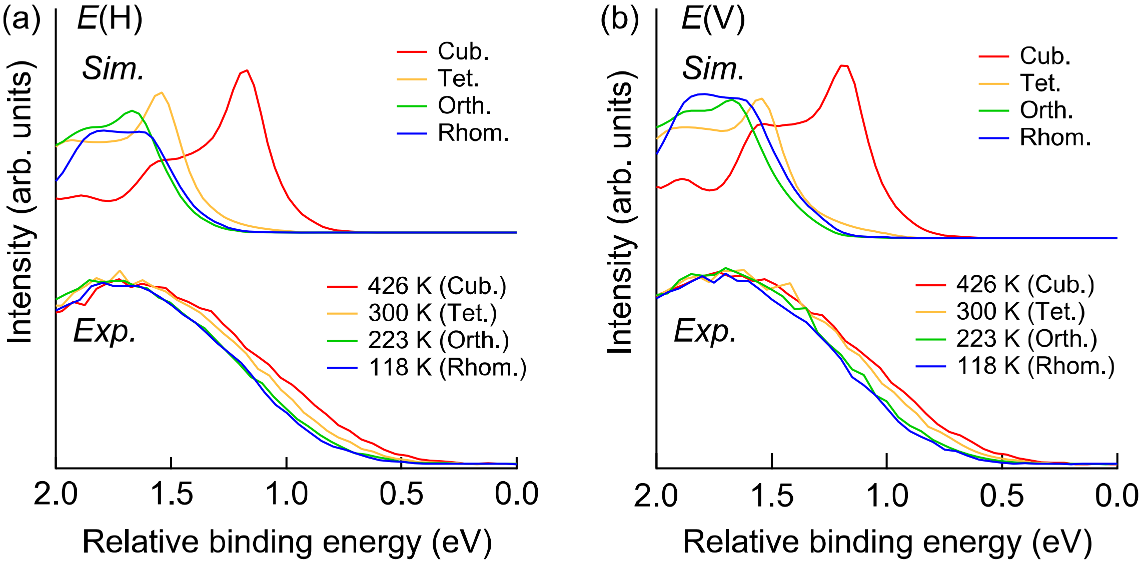

Figure S4 Zoomed-in simulated and experimental VB spectra in the vicinity of the top of VB using (a) *E*(H) and (b) *E*(V) X-rays.