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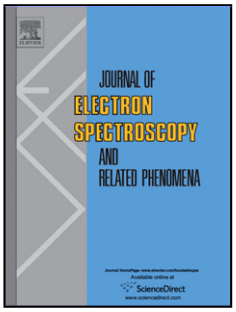

Title: The valence band electronic structure of rhombohedral-like and tetragonal-like $BiFeO_3$ thin films from hard X-ray photoelectron spectroscopy and first-principles theory

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The valence band electronic structure of rhombohedral-like and tetragonal-like $BiFeO_3$ thin films from hard X-ray photoelectron spectroscopy and first-principles theory

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Abstract

We investigate the electronic structure of rhombohedral-like (R) and tetragonal-like (T) $BiFeO_3$thin films using high energy X-ray photoelectron spectroscopy and first-principles electronic structure calculations. By exploiting the relative elemental cross sections to selectively probe the elemental composition of the valence band, we identify a strong Bi 6*p* contribution at the top of the valence band in both phases, overlapping in energy range with the O 2*p* states; this assignment is confirmed by our electronic structure calculations. We find that the measured occupied Bi 6*p* signal lies closer to the top of the valence band in the T phase than in the R phase, which we attribute, using our electronic structure calculations, to lower Bi-O hybridization in the T phase. We note, however, that our calculations of the corresponding densities of states underestimate the difference between the phases, suggesting that matrix element effects resulting from the different effective symmetries also contribute. Our results shed light on the chemical nature of the stereochemically active Bi lone pairs, which are responsible for the large ferroelectric polarization of $BiFeO_3$.

Keywords: hard x-ray photoelectron spectroscopy, multifunctional materials, multiferroics, electronic structure, density functional theory, bismuth ferrite
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