Electronic structure of the orthorhombic and tetragonal phases of Tl_3PbBr_5

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Trithallium lead pentabromide, Tl_3PbBr_5, is recognized as a new low-phonon energy host material operating in mid-IR and far-IR regions. Two polymorphous forms, namely orthorhombic low-temperature (LT) and tetragonal high-temperature (HT), have been detected for this compound: the *LT*-Tl_3PbBr_5 phase crystallizes in the space group $P2_12_12_1$, with the lattice parameters a = 15.397 Å, b = 9.061 Å, and c = 8.537 Å, whilst the *HT*-Tl_3PbBr_5 phase possesses the lattice parameters a = b = 15.486 Å and c = 8.903 Å (space group $P4_1$). The non-central space groups adopted by both polymorphous forms of the Tl_3PbBr_5 compound make it a very prospective material for optoelectronics and non-linear optics devices (lasers, luminophors, narrow-band optical filters). In the present work, X-ray photoelectron core-level and valence-band spectra for pristine and Ar^+-ion irradiated surfaces of a Tl_3PbBr_5 single crystal grown by the Bridgman-Stockbarger method have been measured. Our X-ray photoelectron spectroscopy (XPS) results reveal high chemical stability of Tl_3PbBr_5 single crystal surface. Total and partial densities of states of constituent atoms of the orthorhombic *LT*-Tl_3PbBr_5 and tetragonal *HT*-Tl_3PbBr_5 phases have been calculated using the first-principles full potential linearized augmented plane wave (FP-LAPW) method. The FP-LAPW data reveal that contributions of the Br 4p-like states dominate in the valence band of the both phases of Tl_3PbBr_5; they contribute mainly into the top and the central portion of the valence band with also significant contributions throughout the whole valence-band region. The bottom of the valence band of the orthorhombic and tetragonal phases of Tl_3PbBr_5 is composed mainly of the Tl 6s-like states. Additionally, the unoccupied Pb 6p- and Tl 6p-like states in almost equal proportion dominate at the bottom of the conduction band of *LT*-Tl_3PbBr_5, whilst the unoccupied Pb 6p-like states are the dominant contributors at the bottom of the conduction band of the *HT*-Tl_3PbBr_5 phase. Our theoretical data reveal that the orthorhombic *LT*-Tl_3PbBr_5 and tetragonal *HT*-Tl_3PbBr_5 phases are indirect-gap materials with band gap of 3.05 and 2.26 eV, respectively. The theoretical predictions are confirmed by the XPS measurements carried out for the both phases of Tl_3PbBr_5.