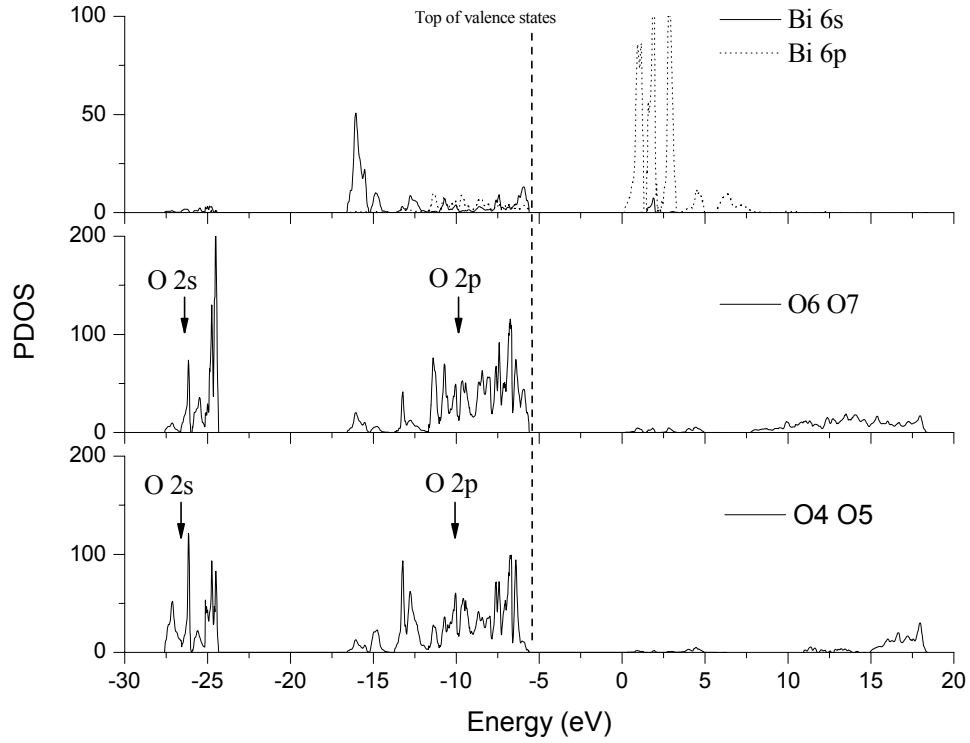

Fig. S1 The l-momentum projected densities of states (PDOS) for Bi 6s (top, solid line), Bi 6p (top, dotted line), O6O7 (middle, solid line) and O4O5 (bottom, solid line) orbitals for BiB_3O_6.

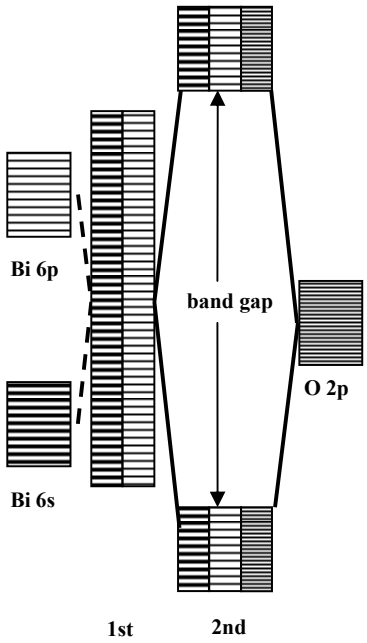

Fig. S2 Bi 6s-6p hybridized orbitals are formed first in the primary interaction (1st; dashed lines; allowed in a non-centrosymmetric environment) and subsequently participate in covalent bonding and antibonding with O 2p orbitals in the secondary interaction (2nd; solid lines). Bi 6s-6p hybridization demands that the Bi 6p states should be mixed with the Bi 6s states over the shared energy region. However, this model is inconsistent to the fact that no Bi 6p states are found in the same energy region as Bi 6s states from -16.6 eV to -14.5 eV (**Fig. S1**). Therefore the classic viewpoint due to VSEPR which demands the hybridization of central atomic s and p orbitals is not correct for BiB_3O_6. Bi 6s, Bi 6p and O 2p states are represented by rectangles filled with three different patterns. The content of each of the three states is schematically weighted by the width of the corresponding pattern.

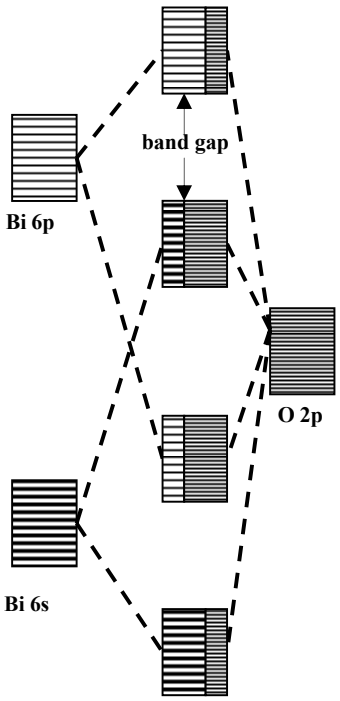

Fig. S3 Bi 6s and Bi 6p individually form covalent bonds with O 2p in the primary interaction (dashed lines). The lowest unoccupied states, *i.e.*, the top states shown here, should involve only Bi 6p and O 2p states, whereas the small amount of Bi 6s states virtually appear at ≈2 eV rather than at the lowest unoccupied level (**Fig. S1**); on the other hand, the highest occupied states, *i.e.*, the middle two states shown here, should contain some amount of separate Bi 6s states and Bi 6p states, whereas the continuously mixed Bi 6s-6p states virtually stay between -13.5 eV and -5.6 eV (**Fig. S1**). In addition, this model may lead to a too small band gap. Bi 6s, Bi 6p and O 2p states are represented by rectangles filled with three different patterns. The content of each of the three states is schematically weighted by the width of the corresponding pattern.

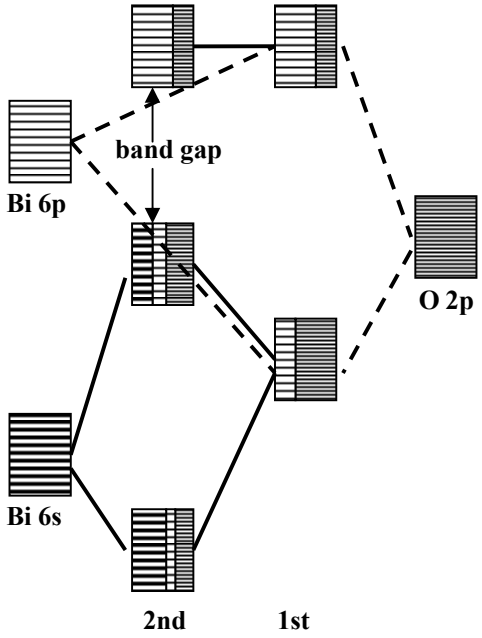

Fig. S4 Bi 6p-O 2p covalent occupied bonding and unoccupied antibonding orbitals are formed first in the primary interaction indicated by the dashed lines (1st), and the former resultant filled bonding orbitals subsequently take the further coupling with Bi 6s orbitals in the secondary interaction indicated by the solid lines (2nd). The lowest unoccupied states should involve only Bi 6p and O 2p states, and the lowest occupied states should contain some components of Bi 6p states mixed with pronounced Bi 6s states. However, it disagrees with the findings that the small amount of Bi 6s states virtually appears at the higher unoccupied level at ≈2 eV and no Bi 6p orbitals are distributed in the Bi 6s region between -16.6 eV and -14.5 eV (**Fig. S1**). Bi 6s, Bi 6p and O 2p states are represented by rectangles filled with three different patterns. The content of each of the three states is schematically weighted by the width of the corresponding pattern. The 1st also labels the intermediate states produced by the primary interaction and the 2nd the final states by the secondary interaction.