Supporting Information Available: Four additional figures are individually listed for the reference of scalar-relativistic and correlation effects. Figure 1 (non-relativistic B3PW) and Figure 2 (scalar-relativistic HF) are densities of optical transitions for the total and individual units within BiB_3O_6 and illustrate the optical transition of 6s-6p within single Bi cations. Figure 3 (non-relativistic B3PW) and Figure 4 (scalar-relativistic HF) are crystal orbital overlap populations for Bi 6s-O 2p, Bi 6p-O 2p and B-O bonds.

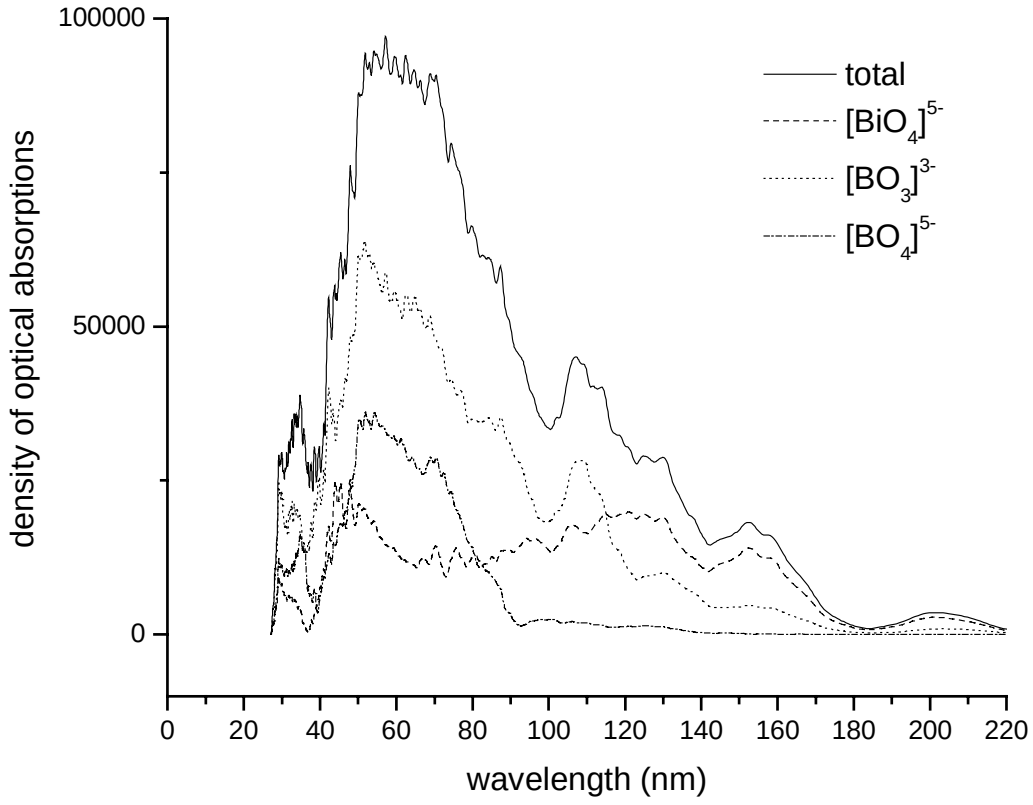

Figure 1 The density of optical absorptions for the total BiB_3O_6 (solid line), $[BiO_4]^{5-}$ (dash line), $[BO_3]^{3-}$ (dot line) and $[BO_4]^{5-}$ (dash-dot line) at non-relativistic B3PW level.

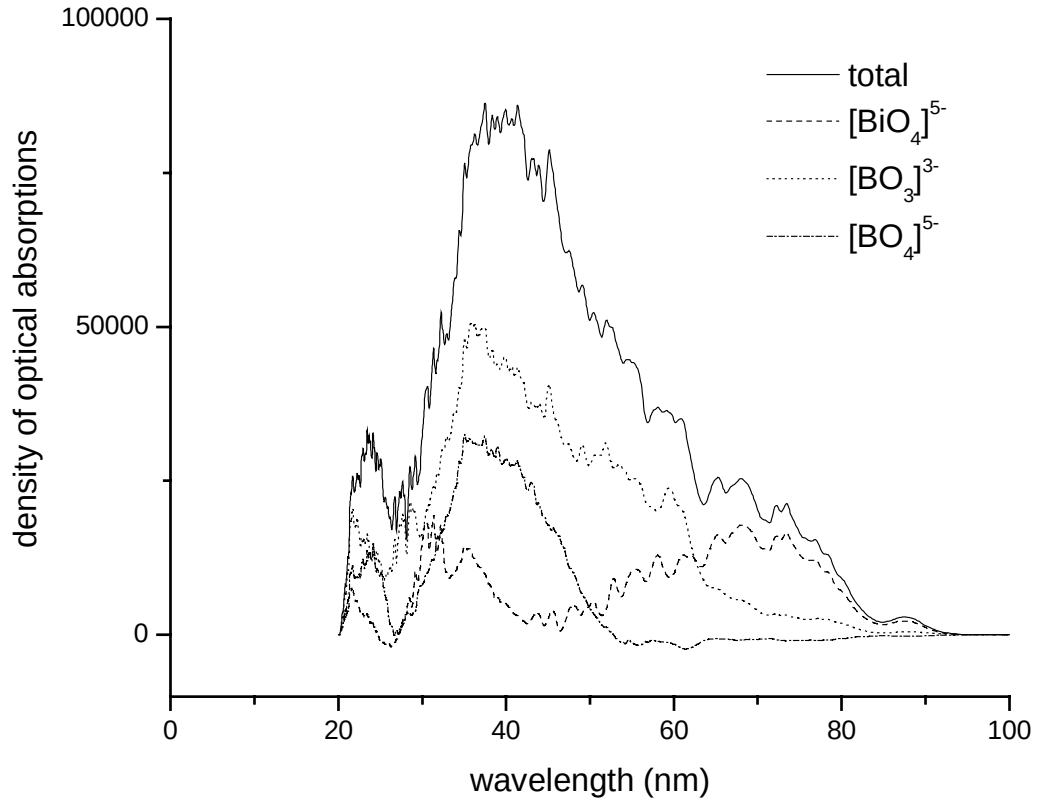

Figure 2 The density of optical absorptions for the total BiB_3O_6 (solid line), $[BiO_4]^{5-}$ (dash line), $[BO_3]^{3-}$ (dot line) and $[BO_4]^{5-}$ (dash-dot line) at scalar-relativistic HF level.

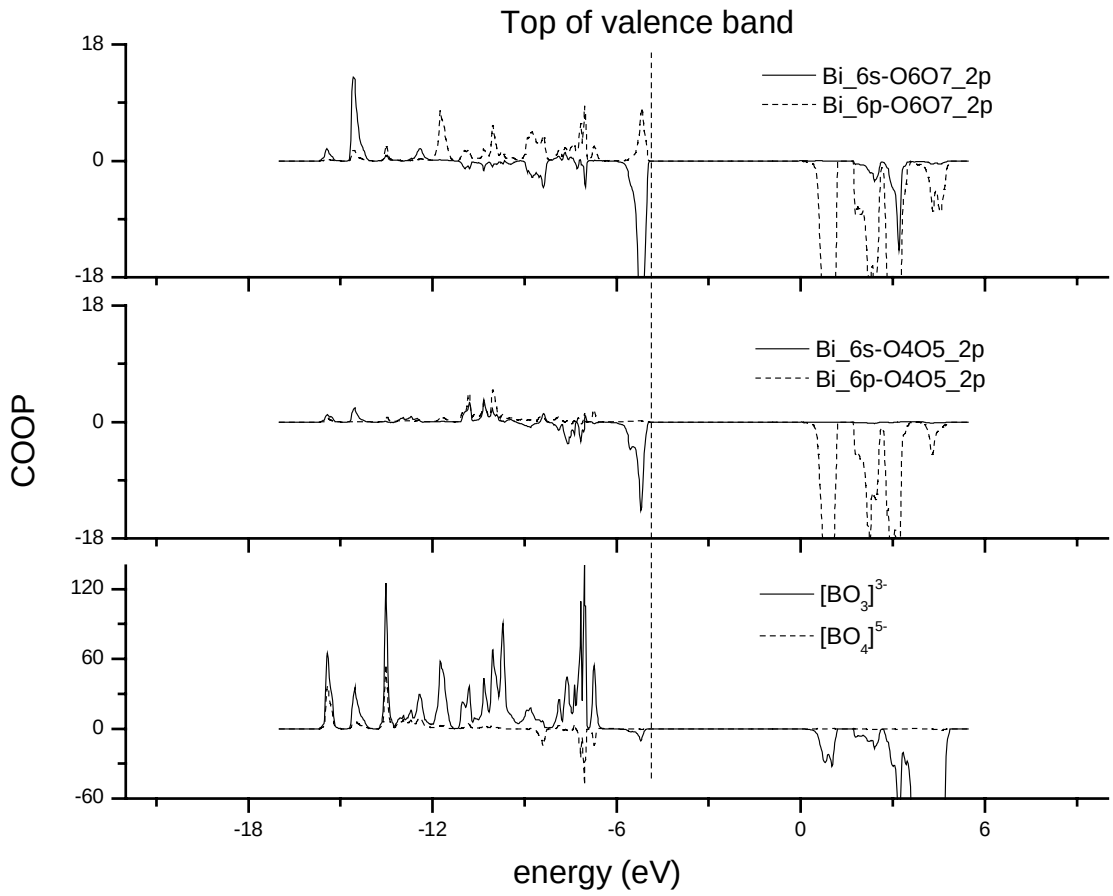

Figure 3 Crystal orbital overlap population (COOP) plots for the interactions of Bi-O in $[BiO_4]^{5-}$ units (top), B-O in $[BO_3]^{3-}$ (middle) and $[BO_4]^{5-}$ (bottom) for the non-relativistic B3PW calculation.

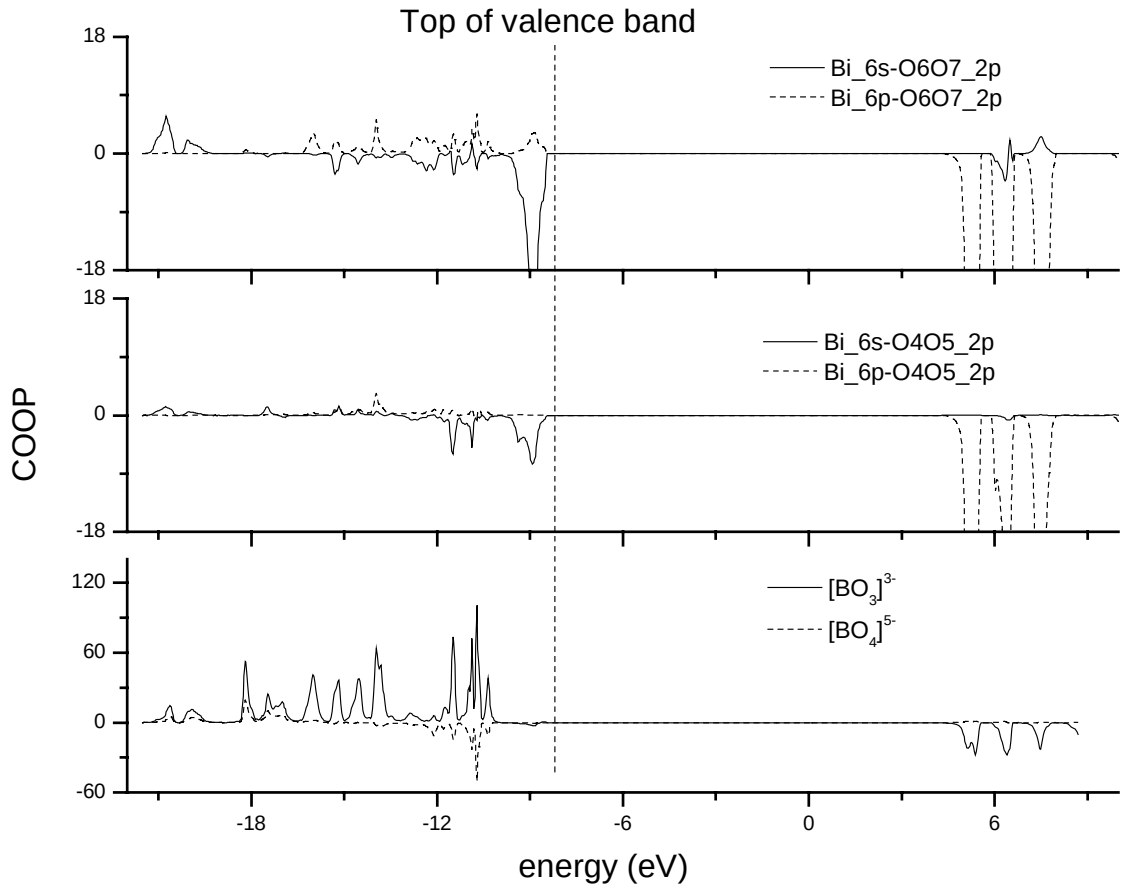

Figure 4 Crystal orbital overlap population (COOP) plots for the interactions of Bi-O in $[BiO_4]^{5-}$ units (top), B-O in $[BO_3]^{3-}$ (middle) and $[BO_4]^{5-}$ (bottom) for the scalar-relativistic HF calculation.