Structural, electronic properties and charge densitydistribution of the $LiNaB_4O_7$: Theory and experiment

Abstract

The title compound was synthesized by employing high-temperature solution reaction methods at 840 °C. Single-crystal XRD analysis showed that it crystallizes in the orthorhombic noncentrosymmetric space group Fdd2, with unit cell parameters a = 13.326(3) , b = 14.072(3) , c = 10.238(2) , Z = 16, and V = 1919.9(7) ^{3}. It has two independent and interpenetrating 3D frameworks consisting of $[B_4O_9]^{6-}$ groups bridged by O atoms, with intersecting channels occupied by Na^+ and Li^+ cations. The IR spectrum further confirmed the presence of both $BO_3$and BO_4 groups. UV-vis diffuse reflectance spectrum showed a band gap of about 3.88 eV. Solid-state fluorescence spectrum exhibited the maximum emission peak at around 337.8 nm. Furthermore we have performed theoretical calculations by employing the state-of-the-art all-electron full potential linearized augmented plane wave (FP-LAPW) method to solve the Kohn Sham equations. We have optimized the atomic positions taken from our XRD data by minimizing the forces. The optimized atomic positions are used to calculate the electronic band structure, the atomic site-decomposed density of states, electron charge density and the chemical bonding features. The calculated electronic band structure and densities of states suggested that this single crystal possesses a wide energy band gap of about 2.80 eV using the local density approximation, 2.91 eV by generalized gradient approximation, 3.21 eV for the Engel-Vosko generalized gradient approximation and 3.81 eV using modified Becke-Johnson potential (mBJ). This compares well with our experimentally measured energy band gap of 3.88 eV. From our calculated electron charge density distribution, we obtain an image of the electron clouds that surround the molecules in the average unit cell of the crystal. The chemical bonding features were analyzed and the substantial covalent interactions were observed between O and O, B and O, Li and O as well as Na and O atoms.