# CHAPTER 3

## ELECTRONIC BAND STRUCTURE, ELECTRONIC PROPERTIES AND CHARGE DENSITY DISTRIBUTION OF THE NONCENTROSYMMETRIC $LiNaB_4O_7$ BORATE SINGLE CRYSTALS

*$LiNaB_4O_7$ 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) Å, b=14.072(3) Å, c=10.238(2) Å, Z=16, and V=1919.9(7) Å$^3$. It has two independent and interpenetrating 3D frameworks consisting of $[B_4O_9]^{6-}$ groups bridged by Oatoms, 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.*

## 3.1 HISTORICAL REVIEW

Borates have been extensively investigated because of their potential applications in Nonlinear Optics (NLO) and laser engineering. It has excellent properties such as short growth period, large effective nonlinear coefficient, high damage threshold, and good mechanical properties. As a result of their complicated crystal structures borates are among the most interesting and therefore the most extensively studied materials. Since 1962, when the binary phase diagram $Bi_2O_3$–$B_2O_3$ were investigated, many methods of obtaining the borate crystals were found and described in detail [1–6]. It was also established that, borate crystals, in particular $BiB_3O_6$, exhibit high NLO susceptibilities [7–10], particularly for Second Harmonic Generation (SHG) and Third Harmonic Generation (THG) applications. Theoretical examinations have shown that, anionic groups and chemical bonding structures of boron atoms have a major influence on the nonlinear properties of these crystals [11, 12].For example, $BaB_2O_4$, $LiB_3O_5$, $CsB_3O_5$, and $YCa_4(BO_3)_3O$ are all well-known NLO crystals [13]. The binary $Bi_2O_3$–$B_2O_3$ phase diagram has been investigated by Levin and McDaniel [14], and at least five compounds, $Bi_{24}B_2O_{39}$ [15], $Bi_4B_2O_9$ [16], $Bi_3B_5O_{12}$ [17], $BiB_3O_6$ [18], and $Bi_2B_8O_{15}$ [19], have been proposed and structurally characterized.

Among these, $Bi_4B_2O_9$ was reported to have high double refraction [20], $Bi_3B_5O_{12}$ displays stimulated Raman scattering and luminescence properties [21,22] and $BiB_3O_6$ is the most extensively studied because it has been established as a NLO material with promising physical properties and has furthermore been characterized in detail with respect to their piezoelectric, pyroelectric, dielectric, elastic, and thermoelastic properties [23]. Theoretical studies have shown that, the presence of irregular Bi–O coordination polyhedra and their structural arrangement lead to the extraordinarily large optical SHG effect on $BiB_3O_6$. It is reasonable to emphasize that other interesting materials may also be found in more complex borates incorporating bismuth together with other cationic elements. Based on this idea, several ternary (quaternary) bismuth-containing borates that crystallize in the noncentrosymmetric space groups have been recently synthesized, including $BaBiBO_4$, $Bi_2ZnB_2O_7$, $CaBiGaB_2O_7$, $Bi_2CaB_2O_7$, and $Bi_2SrB_2O_7$ [24-26].