

CHAPTER 2

INVESTIGATION OF THE ELECTRONIC BAND STRUCTURE, DENSITY OF STATES AND OPTICAL SUSCEPTIBILITIES OF $\text{Li}_3\text{InB}_2\text{O}_6$ ORTHOBORATE CRYSTALS

Using the structural parameters of the single crystal lithium indium orthoborate obtained by Penin et al. [Solid State Science 3 (2001) 461-468], from X-ray diffraction data, we present a first-principle's study of the electronic structure and the linear optical properties for the novel lithium indium orthoborate $\text{Li}_3\text{InB}_2\text{O}_6$. A full-potential linear augmented plane wave method within density-functional theory with the Engel-Vosko exchange correlation was used. This compound has a wide direct energy band gap of about 3.8 eV with both the Valence Band Maximum (VBM) and Conduction Band Minimum (CBM) located at the centre of the Brillouin zone. Our calculations of the partial density of states shows that, the upper valence band originates predominantly from the O-p, B-p and In-p states and the lower conduction band is dominated by the O-s/p, In-p and B-p states. Thus, the O-p states in the upper valence band and lower conduction band has a significant effect on the energy band gap dispersion. The uniaxial anisotropy $[\delta\epsilon = (\epsilon_0^{zz} - \epsilon_0^{xx}) / \epsilon_0^{tot}]$ is about -0.041.

2.1 HISTORICAL REVIEW

Borate compounds are currently very attractive to the scientific community owing to their wide range of applications [1-3]. They exhibit a high transparency in the Ultra-Violet (UV) and near Infra-Red (IR) region, good chemical stability, and high optical quality. The cationic subsystem influences the transparency and mechanical properties. Borates are among the most interesting and therefore the most extensively studied materials with interesting properties ranging from phosphorescence [4] ferroelectric, semiconducting behavior, and Nonlinear Optical (NLO) susceptibilities [2,5,6]. They have a high Second Harmonic Generation (SHG) coefficient, high optical damage threshold, high hardness, and can be used in laser frequency conversion. [7,8]. In addition, a boron atom may adopt triangular or tetrahedral oxygen coordination, the BO_3 and BO_4 groups may be further linked via common oxygen atoms to form isolated rings and cages or polymerize into infinite chains, sheets and networks, leading to a rich structural chemistry [2,9].

The oxoborates $\text{K}_2\text{R}_2\text{OB}_2\text{O}_6$ with $\text{R} = \text{Al}$ [6], Ga [6] or $\text{Cs}_2\text{Ga}_2\text{OB}_2\text{O}_6$ [10], have structures that contain triangular BO_3 and tetrahedral RO_4 ($\text{R} = \text{Al}, \text{Ga}$). With the view of finding new optical materials, similar to non rare-earth trivalent cations [11], it might seem interesting to investigate the properties of lithium borates such as $\text{Li}_6\text{R}_2\text{B}_4\text{O}_{12}$ with $\text{R} = \text{Al}$ [12] and Ga [13], which contain $[\text{R}_2(\text{BO}_3)_4]$ chains with two different BO_3 groups. In the system $\text{Li}_2\text{O}-\text{In}_2\text{O}_3-\text{B}_2\text{O}_3$ only $\text{Li}_3\text{In}_2\text{B}_3\text{O}_9$ has been synthesized and its structure characterized by Penin *et al.* [11]. Theoretical exploration has shown that, anionic groups and chemical bonding structures and coordination of boron atoms have an important influence on the nonlinear optical properties of these crystals [14, 15].

The theoretical investigation of the band structure may play a crucial role in understanding of the physical properties and give predictions of the nonlinear optical susceptibilities. First-principle's band structure calculations have been successfully used to obtain fundamental parameters of semiconductors and dielectrics. The structural parameters and dynamical properties of crystals determine a wide range of microscopic and macroscopic features; diffraction, sound velocity, elastic constants, Raman and infrared absorption, inelastic neutron scattering and specific