CHAPTER 7

INVESTIGATION OF THE ELECTRONIC BAND STRUCTURE, DENSITY OF STATES AND X-RAY PHOTOELECTRON SPECTRA OF NONCENTROSYMMETRIC YTTRIUM ALUMINIUM BORATE SINGLE CRYSTALS

The band structure and density of states are calculated for Yttrium Aluminium Borate $YAl_3(BO_3)_4$, a nonlinear optical crystal, using the full-potential linear augmented plane wave method. Our calculations show that this crystal possesses a direct energy gap (Γ) of 5.1 eV in reasonable agreement with experimental value 5.70 eV. The small discrepancy between the experimental and the calculated value of the energy gap is typical for the local density approximation. Our calculations show strong and weak hybridization between the states. The calculated density of states was compared reasonably well with our own experimental density of states measured by X-ray photoelectron spectroscopy with respect to peak positions but not with respect to peak heights. This could be attributed to the presence of defect states.

7.1 Historical Review

Yttrium Aluminium Borate $YAl_3(BO_3)_4$ (YAB) belongs to a family of double borates which crystallise in the trigonal structure of the mineral huntite $CaMg_3(CO_3)_4$ and belongs to the space group R32 [1]. The general formula of these compounds is $RX_3(BO_3)_4$, where R=Y^{3+}, Gd^{3+} and other lanthanides, and X=Al^{3+}, Sc^{3+} Ga^{3+}, Cr^{3+}, Fe^{3+} [2]. YAB is a non-centrosymmetric crystal and as early as in 1974 it was reported as a very effective second-harmonic generating material [3]. Furthermore, owing to its good chemical stability and the possibility of substituting Y^{3+} ions with other lanthanide ions, namely Nd^{3+}, Yb^{3+}, and Er^{3+}, it is a good material for laser applications.

The nonlinear optical properties of this material along with lasing properties led to the fabrication of numerous systems generating red, green and blue light due to self-frequency doubling effect [4]. They also possess relatively large two-photon absorption [5], which makes them promising second and third order optical materials. At the same time they are good matrices for different rare earth ions [6, 7].The further use of the YAB crystals is restrained by absence of reliable band structure parameters. It may give information about the dispersion of the bands in the k-space, which is directly connected with the effective masses. However, more important is the calculation of the transitions dipole moments determining linear and non-linear optical properties.

This information will be useful for technologists to obtain crystalline materials with the desirable parameters. We are not aware of any first principle band energy calculations for this compound. In the present work we have performed first principles band energy and density of states calculations for YAB crystals using the full potential linear augmented plane wave method which has proven to be one of the most accurate methods [19, 20] for the computation of the electronic structure of solids within Density Functional Theory (DFT). Simultaneously X-Ray Photoelectron Spectroscopy (XPS) measurement has been performed and compared with the theoretical density of states.

7.2 STRUCTURAL ASPECTS AND COMPUTATIONAL DETAILS

7.2.1 Crystal Growth

YAB melts in congruently at 1280°C and decomposes into YBO_3 and $AlBO_3$ [8] therefore high-temperature solution growth method is used to obtain the crystals. $K_2Mo_3O_{10}$ flux with 3wt% of B_2O_3 was used by us to lower the temperature of YAB crystallization below the temperature of the peritectic transformation. The crystals were grown from a 200g starting solution containing 20 wt% of YAB in $K_2Mo_3O_7$-B_2O_3 solvent by means