CHAPTER 9

INVESTIGATION OF THE ELECTRONIC BAND STRUCTURE AND X-RAY PHOTOELECTRON SPECTRA FOR NON-CENTROSYMMETRIC $Bi_2ZnB_2O_7$ NONLINEAR SINGLE CRYSTAL

We have synthesized and characterized the bismuth borate $Bi_2ZnB_2O_7$ single crystals. The results of the experimental measurements of the X-Ray Diffraction (XRD) and X-Ray Photoelectron Spectrum (XPS) along with an ab initio theoretical study of the electronic band structure, and density of states, are reported. The theoretical calculations are based on crystal structure built from our experimentally determined atomic parameters. The theoretical calculations have been done by using the Full Potential Linearized Augmented Plane Wave (FP-LAPW) method. We applied the Perdew-Burke-Ernzerhof Generalized Gradient Approximation (GGA) and the Engel-Vosko GGA formalism. The observed XPS pattern is in good agreement with the theoretical one, confirming the pure phaseof $Bi_2ZnB_2O_7$. The purity and composition of the as-prepared sample are studied by XPS analysis. XPS measurements show that the bismuth possesses +3 valence state, and Zn and B species exist only in the traditional valence states of Zn^{2+} and B^{3+}. The O 1s spectra are broad and asymmetric and can be deconvoluted into two peaks. The lower and higher binding energy peaks (around 530.1 eV and 531.5 eV) are assigned to originate from O 1s(1) and O 1s(2) terms, respectively, which are attributed to non-bridging oxygen (B-O⁻ bonds) and bridging oxygen (B-O-B bonds), respectively. Our calculations show that$Bi_2ZnB_2O_7$hasan indirect energy gap and that Bi-O bonds are of strong covalent character.

of crystal parameters as well as the atomic coordinates and the equivalent isotropicdisplacement parameters have been presented in our recent work [18]. Although the $Bi_2ZnB_2O_7$ structure was previously refinedon the basis of powder diffraction data by the Rietveld method [12], our single crystal data are more accurate due to the use of relatively large reflection/ parameter ratio. Therefore, theoretical calculations in this work are based on the model built from our measured atomic parameters.

Polycrystalline sample of $Bi_2ZnB_2O_7$ was prepared by heating a stoichiometric mixture of Bi_2O_3, ZnO, and H_3BO_3 at 600°C during two weeks with several intermediate re-mixings. X-ray powder diffraction data were collected by using the monochromatized Cu Kα radiation of a Bruker D8 ADVANCE diffract to meter. Optical diffuse reflectance spectra were measured at room temperature with a Shimadzu UV-3101PC double-beam, double-monochromator spectrophotometer. $BaSO_4$ powder was used as a standard (100% reflectance). The X-Ray Photoelectron Spectroscopy (XPS) measurements were performed by using the LHS-10 hemispherical electron analyser at constant Pass Energy Ep=97 eV giving a FWHM of 0.9 eV to the Ag $3d_{5/2}$ line. Non-monochromatised Al Kα x-ray line was used with characteristic energy 1486.6 eV. The calibration of the kinetic energy scale was done according to the ASTM-E 902-88 standard.

The spectra recorded were a wide scan and the detailed spectra of each one of the observed lines (C1s, O1s, B1s, Bi4f, Zn2p). All the samples had a binding energy shift (+4.7 eV) due to electrostatic charging. The estimation of this shift was done by considering that the C1s component (attributed to the sample contamination) with the lower binding energy should appear at 284.6 eV. The spectra presented here are shifted by this value apart from that of C1s. All the spectra were fitted after a Shirley background subtraction to one (or more) components with a mixed Gaussian-Lorenzian character. From the BE values of Zn2p, Bi4f and B1s the chemical state of these elements appears to be ZnO, B_2O_3 and Bi_2O_3.