CHAPTER 10

EXPERIMENT AND THEORETICAL INVESTIGATION OF SECOND ORDER OPTICAL SUSCEPTIBILITIES FOR $Bi_2ZnB_2O_7$ BORATE SINGLE CRYSTALS

We have synthesized and characterized single crystal of bismuth borates $Bi_2ZnB_2O_7$. The results of the experimental measurements and the ab initio theoretical study of the linear and non-linear optical susceptibilities are presented here. Theoretical calculations are based on a structural model built from our measured atomic parameters. The optical properties were measured by analyzing the diffuse reflectance data obtained with a Shimadzu UV-3101PC double-beam, double-monochromator spectrophotometer. This compound shows anabsorption edgeat about 360 nm corresponding to energy 3.44 eV. The theoretical calculations have been performed byusing the Full Potential Linearized Augmented Plane Wave (FP-LAPW) method. We have used the Generalized Gradient Approximation (GGA), using the exchange–correlation energy of Engel-Vosko. We present calculations of the frequency-dependent complex dielectric function $\varepsilon(\omega)$ and its zero-frequency limit $\varepsilon_1(0)$. The optical properties are analyzed and the origin of some of the spectral peaks is discussed in terms of the calculated electronic band energy structure. The linear optical properties show strong negative uniaxial anisotropy and birefringence which favors large second order susceptibility $\chi^{(2)}_{ijk}(\omega)$ Our calculations show that $\chi^{(2)}_{333}(\omega)$ is the dominant component possessing the largest total Re $\chi^{(2)}_{ijk}(0)$.

10.1 Historical Review

Binary bismuth borates have been of continuing interest for their optical properties [1-4]. These compounds display a large nonlinear optical efficiency [5-10]. The reinvestigation of the ZnO-Bi_2O_3-B_2O_3 system has now resulted in the discovery of yet another non centrosymmetric compound, $Bi_2ZnB_2O_7$, which is closely related to the melilite structural family based on the akermanite ($Ca_2MgSi_2O_7$) and gehlenite ($Ca_2Al_2SiO_7$) end-members. $Bi_2ZnB_2O_7$ and $Ca_2SiB_2O_7$ are the only borate representatives of the melilite family known to date. The bismuth borates $Bi_2ZnB_2O_7$ and $Ca_2SiB_2O_7$ have been synthesized by solid-state reactions at temperatures in the 650-825°C range at 1 atm pressure [11].

These compounds are the only synthetic diborate members of the melilite family, $A_2XZ_2O_7$, in which layers of A cations alternate with XZ_2O_7 tetrahedral layers. Except for $CdBiGaB_2O_7$, the synthesis of other substituted bismuth borate melilites has been unsuccessful. The crystal structures of $Bi_2ZnB_2O_7$ and $CaBiGaB_2O_7$ have been determined by powder X-ray diffraction and refined by the Rietveld method using powder neutron diffraction data. $CaBiGaB_2O_7$ adopts the regular tetragonal melilite structure ($P\bar{4}2_1m$ space group, Z=2) containing B_2O_7 tetrahedral dimers. The refinement of split eight-coordinated sites for the Ca^{2+} and Bi^{3+} interlayer cations suggests the presence of additional disorder. $Bi_2ZnB_2O_7$ adopts a unique orthorhombic melilite superstructure (*Pba*2 space group, Z = 4) containing both tetrahedral B_2O_7 and triangular B_2O_5 dimers. The Bi^{3+} cations occupy two distinct interlayer sites with strongly asymmetric 6-fold coordination environments.

The preliminary measurement of second harmonic generation efficiencies (d_{eff}) of powder samples has yielded values of 4.0 times ($Bi_2ZnB_2O_7$) and 1.6 times ($CaBiGaB_2O_7$) compared to a KH_2PO_4 standard. The present study is aimed to simulate the linear and nonlinear optical susceptibilities of bismuth borates $Bi_2ZnB_2O_7$ crystal by using the Full Potential Linear Augmented Plane Wave (FP-LAPW) method which has proven to be one of the most accurate methods [12, 13] for the computation of the electronic structure of solids within Density Functional Theory (DFT) approach. To our knowledge there is no experimental data and first principle calculations on the linear and