CHAPTER 5

SPECIFIC FEATURES, GROWTH AND CHARACTERIZATION OF NONCENTROSYMMETRIC BORATE SINGLE CRYSTAL $CaBiGaB_2O_7$

Anon-centrosymmetric borate, $CaBiGaB_2O_7$, has been grown by solid-state reaction method at temperature below 700°C. The single-crystal X-ray structural analysis has shown that itcrystallizes in the tetragonal space group $P-42_1m$ with $a = 0.7457(1)$ nm, $c = 0.4834(1)$ nm, $Z = 2$. It has a three Dimensional (3D) structure in which $[B_2O_7]^{8-}$ groups are bridged by $[GaO_4]^{5-}$ tetrahedra through sharing O atoms to form $2D^2_\infty [GaB_2O_7]^{5-}$ layers that are further linked by Bi^{3+}/ Ca^{2+} cations giving rise to the final 3D framework. The IR spectrum confirms the presence of $[BO_4]^{5-}$ groups and the UV-VIS diffuse reflectance spectrum shows that the optical band gapis about2.9 eV. This value is compared with our band structure calculations using the full potential linearized augmented plane wave approach within a framework of the Engel-Vosko GGA formalism.

5.1 HISTORICAL REVIEW

Borates have attracted considerable attention because they have important practicalapplications as materials for Nonlinear Optical (NLO) effects, in particular optical Second Harmonic Generation (SHG) and linear Electro-Optics Effects (EOE). For example, b-BaB_2O_4,LiB_3O_5, CsB_3O_5, and $YCa_4(BO_3)_3O$ are all well-known NLOmaterials [1].The binary Bi_2O_3-B_2O_3 phase diagram was investigated by Levin and McDaniel[2], and at least five compounds were structurally characterized including $Bi_{24}B_2O_{39}$ [3], $Bi_4B_2O_9$ [4], $Bi_3B_5O_{12}$ [5], BiB_3O_6[6], and $Bi_2B_8O_{15}$ [7]. Among them, $Bi_4B_2O_9$ was reported to have a high birefringence [8], $Bi_3B_5O_{12}$ displays

stimulated Raman scattering and luminescence properties [9,10], and BiB_3O_6 is the most extensively studied because it has been established as a NLO material with outstanding physical properties. Measurements ofthepiezoelectric, pyroelectric, dielectric, elastic, and thermoelastic properties have been reported [11].

Theoretical studies have shown that, the presence of irregular Bi-O coordination polyhedra and their structural arrangement lead to the extraordinarily large SHG effect in BiB_3O_6. It is reasonable to believe that, other interesting materials may also be found in more complex borates incorporating bismuth together with other metal elements. Based on this idea, several ternary (quaternary) bismuth-containing borates that crystallize in the non-centrosymmetric space group shave been recently synthesized, including $BaBiBO_4$, $Bi_2ZnB_2O_7$, $CaBiGaB_2O_7$, $Bi_2CaB_2O_7$, and $Bi_2SrB_2O_7$ [12-14]. Among these, $CaBiGaB_2O_7$ was prepared in powder form, its crystal structure was determined from powder diffraction data using the Rietveld method [13].

The present study is aimed to synthesize and characterize the non-centrosymmetric borate, $CaBiGaB_2O_7$ and to present calculations of the band structure and density of states using the Full Potential Linear Augmented Plane Wave (FP-LAPW) method. In the course of our systematic investigation of novel borate NLO materials, we have successfully isolated single crystals of $CaBiGaB_2O_7$ and re-determined its crystal structure using the single crystal XRD technique. This structural information is used for the theoretical calculations. The FP-LAPW method has been proven to be one of the most accurate methods [15, 16] for the computation of the electronic structure of solids within Density Functional Theory (DFT) approach. This method has been applied for the calculations of many borates [17]. In addition, we have also measured the IR and UV-VIS diffuse reflectance spectrum of this compound. To the best of our knowledge there are no experimental measurements of XRD, IR and UV-VIS and no first principles calculations on the non-centrosymmetric borate, $CaBiGaB_2O_7$. Therefore a combined experimental and theoretical study of the non-centrosymmetric borate, $CaBiGaB_2O_7$ is timely and would help in understanding the origin of the electronic properties.