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# Hydrothermal Synthesis, Growth, Optical, Thermal and Dielectric studies of Zinc boro oxalate (ZnBO)

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## Abstract

*A new semi organic non linear optical (NLO) zinc boro oxalate single crystals were grown by Hydrothermal synthesis. The title compound has been subjected. UV-Visible characterization to analyse optical properties.TGA/DSC to analyse thermal stability. Dielectric studies to explore electro optical property.*

**Keywords:** Zinc boro oxalate, Hydrothermal synthesis, UV-Visible; Dielectric studies.

## Introduction

Nowadays crystal growth and categorization of semiorganic materials has become passion for many researchers due to their budding significance in conversion of laser frequency, optical parameter oscillators(OPO) for coherent light sources, Q-switch signal operation and data ware house[1-3]. Last decade various types of organic NLO substances like organic polymers[4-7] and organic crystals[8-11] have been divulged. But some organic NLO crystals have some imperfections. Now so many crystal growth experts, have interest in synthesis of semiorganic NLO materials. These crystals have nature of excellent properties like optical, high damage threshold, low liquefaction. The high co-efficient of non-linear property make this material for SHG.

The synthesis of ZnBO scope includes, based on the excellent properties of semiorganic NLO materials such as potassium boro oxalate[12], Lithium bis L-malato borate[13], potassium bromalate[14] and potassium boro succinate[15].

## Materials and Methods

**Crystal growth and Synthesis:** ZnBO crystals are synthesized by Hydrothermal method. The apparatus called autoclave or hydrothermal bomb used in this process. We used the autoclave with the capacity of 25ml to grow the crystal. The starting materials $Zn(NO_3)_2.6H_2O$, $H_3BO_3$ and oxalic acid taken in 0.5:1:2 ratio. The whole material transferred in to autoclave (Hydrothermal bomb). After that 10 ml distilled water added and stirred well until a homogeneous solution was obtained, then the hydrothermal bomb tightly closed with a lid. After that it is placed in a crystallization reactor. Then we slowly increase the temperature of the reactor. First half an hour the nutrient material (starting materials) maintained in room temperature. Then 90$^o$C maintained for 10hours. After that 50$^o$C maintained for 10 hours. Then it is cooled at room temperature for 3 hours. The autoclave opened after 24 hours. Then the solution mixture is poured in to beaker and it is covered with perforated paper. The time taken to grow crystal is 15 days. Recrystallization done by using 1:1 ethanol: water to get good quality of crystals.

## Results and Discussion

**UV-Visible Spectral studies:** To analyse optical property, UV-Visible spectrum was taken in the wavelength range from 190nm to 790nm. The instrument that used in the analysis was lambda 25 spectrophotometer. During this analysis the speed and data interval maintained at 120nm/min and 1,0000nm. To use a material in optical device, that material should have some important parameters such as optical transmittance and transparancy cutoff wavelength. The graph shown in fig.1.It is observed that the spectrum exhibits low absorbance in the whole visible region. So it has enough transparancy nearly82% with the lower cut off wavelength 230nm. This attractive property of the crystal indicates that it can be used in optical devices. The energy of optical band gap can be calculated from the formula Eg= 1240/λ(nm) in ev. where λ is the lower cut off wavelength(230 nm). The band gap of ZnBO crystal is found to be 5.39 ev. As per the graph the crystal shows large transmission range from 230nm. Based on above studies we are concluding this crystal can used in optical devices cum frequency doubling.

**Thermal analysis:** Thermal consistency of ZnBO was measured by thermo gravimetric analysis and differential scanning calorimetry studies concurrently. The equipment used in the analysis is SDT Q600 V20.9 Build 20 analyzer in atmosphere of nitrogen. The temperature measured between 50 $^o$C to 1000 $^o$C with 10 $^o$C/minute rate. The weight of the sample taken to carry out the experiment was 5.8330 mg. TGA-DSC graphs are shown in fig.2. Thermo gravimetric analysis shows that the material thermally stable up to 150 $^o$C. In this graph weight loss takes place in three stages. First stage decomposition starts at 150 $^oC$ and it is completed at 200 $^oC$. Second decomposition starts at 250 $^oC$ and it is completed at 500 $^oC$. Last stage decomposition starts at 550 $^oC$ and completed at 750 $^oC$. During this decomposition 70.38% of material eliminate in to gaseous products. $CO_2$, OH, and hydrocarbon gases are the eliminating products. The unconsumed mass of 29.62%, which is discarded in crucible possibly carbon mass at hand after all of the decomposition function, it is further observed that the DSC curves shows that the peak at 190 $^oC$ is the melting point of the curve and the peak at 250 $^oC$ and 550 $^oC$ are due to the elimination hydroxyl and borate groups removed from the material[16,17].

**Dielectric studies:** To study the electrical properties of the solids, dielectric constant can be used. The CPPC method can be used to study, measure the capacitance and dielectric loss with the frequency between 50 Hz to 5 MHz with HIOKI-LCR HITESTER 3535 at different temperature 343k and 353k. The interpretations were studied during the sample was cooling, the dielectric constant was analyzed and found by taking the average capacitance (Ccrys). Figure-3. depicts the difference of the dielectric constant using the process of frequency. To study the ZnBO crystals, high clearness rectangular pattern crystals with dimensions 4.75mm X 2.5mm X 1.5mm were used. To achieve the best conductive exterior layer, each sample was layered with best quality of graphite. During the study it was identified through the graph that the dielectric constant value was more at lesser frequency and almost stable during the greater frequencies. Based on the measure of divergence and charge dislocation the dielectric stability value may vary. Differences in dielectric stability at greater frequencies is ascribed to the lack of space charge divergence near the grain boundary interface[18,19].

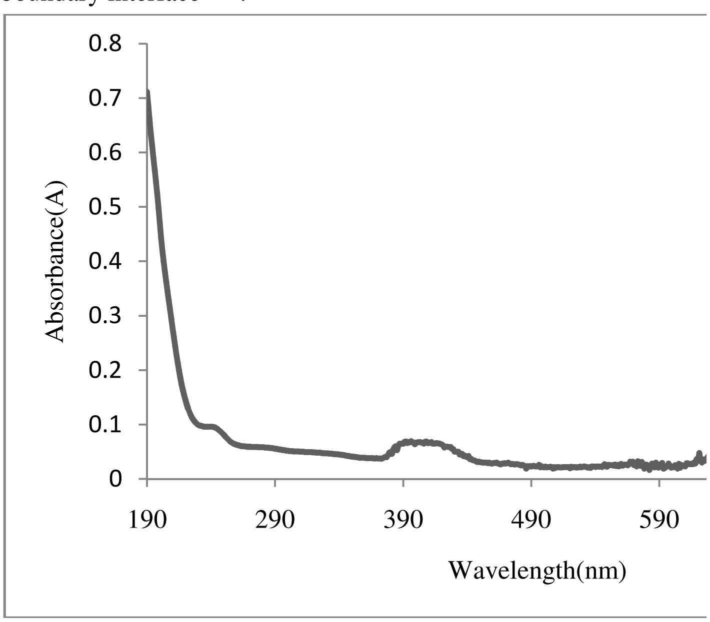


**Figure-1**
**UV-Visible spectrum of ZnBO**

Dielectric loss (tan δ) should be maintain as low as possible, for the material probable applicant of NLO application. To use the NLO applications at best, greater frequencies should be used which can reveal very low dielectric loss[20]. This can be find in the graph Fig 4. This crystal was focused with an separate electric field, after commonly a redistribution of charges founds and currents are triggered. By the use of formula[21] $\sigma ac = \varepsilon_0 \varepsilon r \omega \tan\delta$, the calculation was done for ac conductivity, in this ω is the angular frequency ($\omega = 2\pi\nu$). The ZnBO crystals ac conductivity changes was showed in Fig 5. with frequency variations. The higher the frequency the conductivity too get increases but its zero until 10KHz. The reason for the lesser effect in the mobility and the charge carriers ionic size is because of the less electric conductivity. This also tends to variation in the structure of electronic bonds. Notable ac conductivity variation will be seen at greater frequencies. It proofs the well found relation $\sigma = n_d e \mu e$, that electrical conductivity is relative to carrier concentrations and mobility. In this $n_d$ is the number solidity of electron and μe is the mobility of electron. This shows the ZnBO crystals optical conductivity will grows by increase in the energy which applies.

**NLO Test:** Non-linear optical property of ZnBO was executed by Kurtz powder technique. In this technique an output of NdYAG laser having a wavelength of 1064 nm with 35ps duration of the pulse and the repetition rate of 10Hz is falls on the powdered sample. The second harmonic generation signal in visible region at 532 nm(green light) is measured at different points on the powder material using a detector photomultiplier tube and gated integrator. The efficacy of frequency doubling is found to be 1.2 times more than that of KDP. This property make use of ZnBO can be used in communication systems.

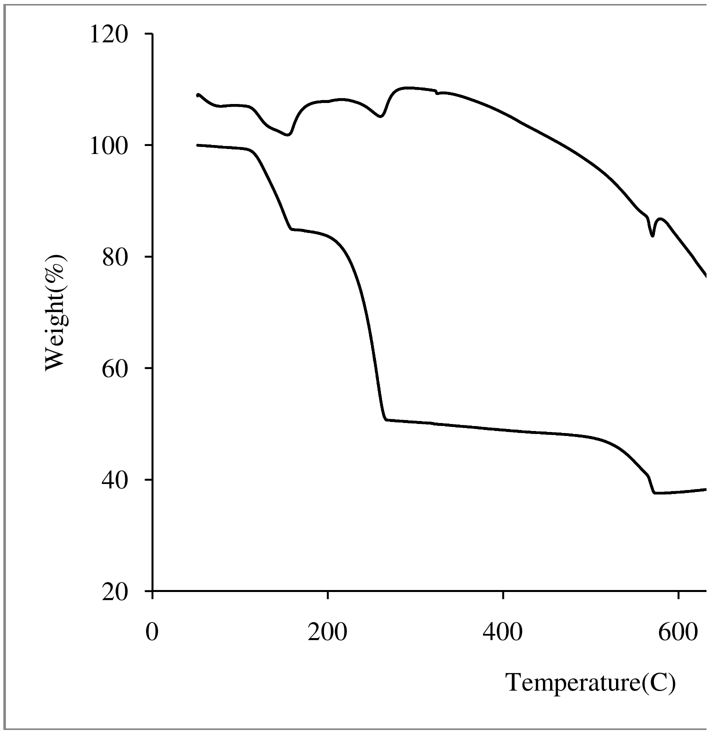


**Figure-2**
**TGA/DSC graph for ZnBO**

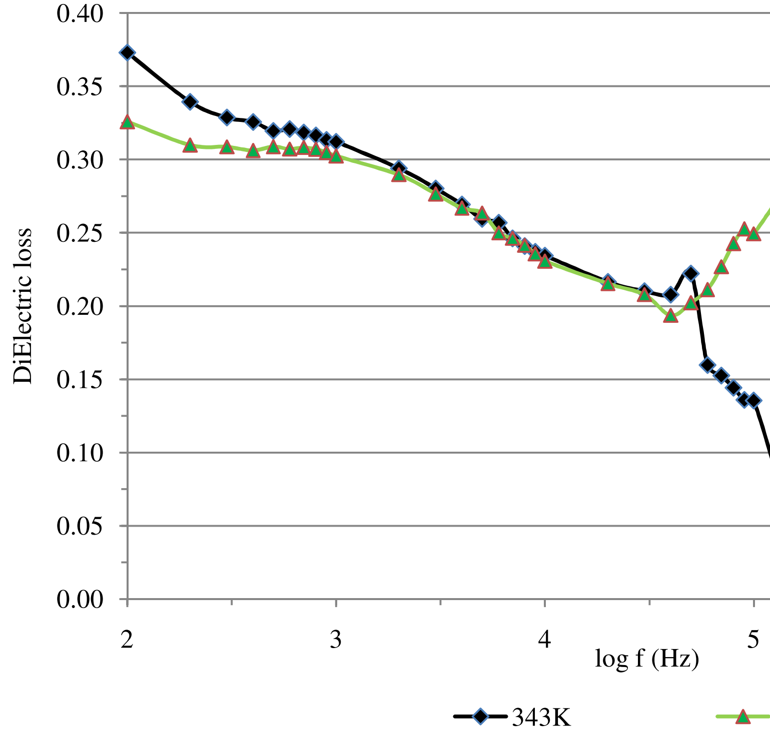


**Figure-4**
**Dielectric loss (vs) log f graph for ZnBO**

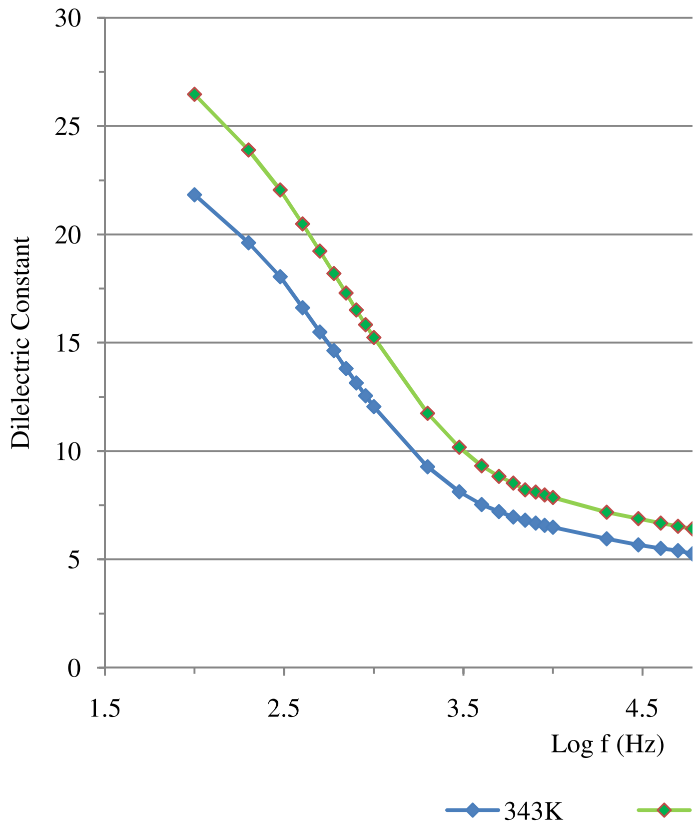


**Figure-3**
**Dielectric constant (vs) Log f graph for ZnBO**

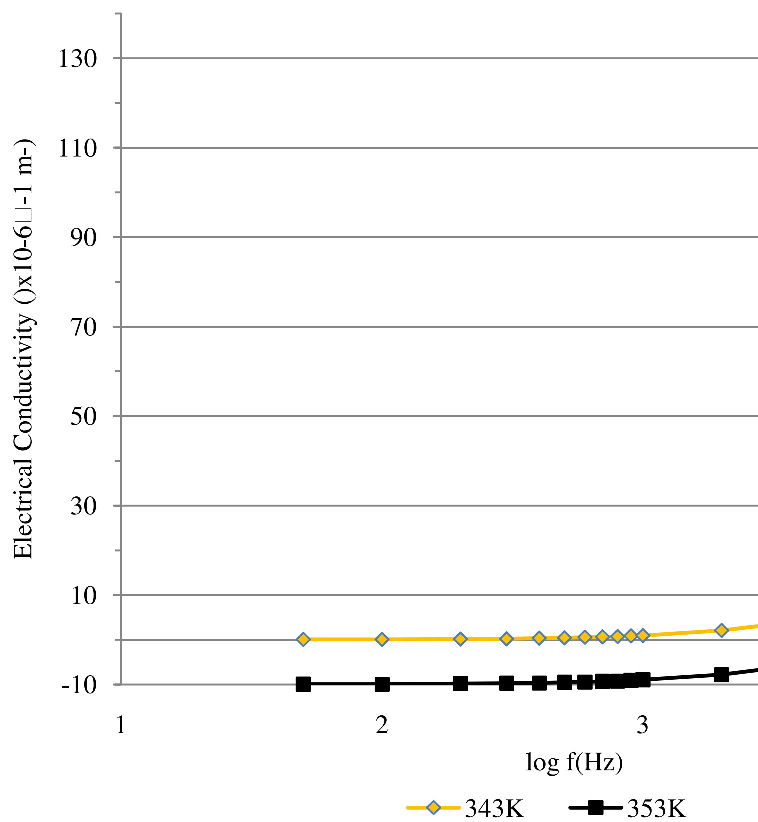


**Figure-5**
**Electrical conductivity(vs) log f graph for ZnBO**

## Conclusion

A new nonlinear (NLO) material Zinc boro oxalate(ZnBO) has been synthesized by hydrothermal method. Optical absorption studies shows that the crystal shows lucid property and the UV cut off wavelength is identified at 230 nm. The lower cut off value of the optical transmittance shows that ZnBO can be used for the propagation of lower wavelength lasers. These studies emphasize that ZnBO can be considered for the tailoring of optoelectronic devices. TGA and DTA shows that the material is thermally stable up to 150$^oC$. From Kurtz powder technique, the powder SHG efficacy of ZnBO is comparable to that of KDP. Its efficacy is 1.2 times greater than that of KDP crystals.

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