Synthesis, growth and optical characterisation of nickel added Boro Formate single crystal for optical applications

Malliga P1*, Dharshan V2 and Deepika V2
1Department of Physics, Sathyabama Institute of Science and Technology, Chennai-600 119, India
2Department of Information Technology, Sri Venkateswara College of Engineering, Chennai-602 117, India

E-mail: *calltomp@gmail.com

Abstract: A nonlinear optical crystal Boro formate added with nickel (NBF) was produced by chemical synthesis. Slow Evaporation method was adopted to produce such a crystal from an aqueous solution. To understand phase identification and information on unit cell dimensions XRD technique was undertaken. The FT-IR spectroscopy measures the light absorbed by the various bond making the vibrating molecule. The functional group present in NBF was thus found. The UV-Visible absorption of light by NBF crystal has produced a distinct spectrum which aids in the identification of the compound and to ascertain the optical property of the compound. The crystal is transparent from a wavelength of 330mm. The frequency doubling property of NLO crystals was verified through SHG studies. The elements present in NBF crystal was confirmed by EDAX studies.

Keywords: Crystal growth; FTIR; UV-Vis; Nonlinear material; X-ray Diffraction.

1. INTRODUCTION

Materials with nonlinear optical properties find an important place in telecommunication devices, remote sensors, digital electronics, geophysics, multistage frequency converters, space research and medical surgical tools [1], [2], [3], [4]. Earlier inorganic crystals were considered to have extreme hardness, transmission and thermal stability. Later organic crystals with enhanced characteristic properties were sought after. However organic materials were not suitable for design due to the lack of their mechanical and thermal stabilities. These combined properties were observed in semi organic materials. This is due to the fact that polarised organic molecules easily bind with organic molecules. Moreover semi organic crystals have better optical and mechanical properties enabling good design flexibility. Such crystals can be grown from aqueous solutions by slow evaporation techniques with good crystalline features.

Nowadays novel materials with higher order second harmonic generation (SHG), better transmittance and prominent mechanical stability is aimed at. Metal substituted semi organic crystal find their way in this class of novel crystals. They are most suitable to meet the challenge sand have established themselves among the researchers prominently in view of their magnificent thermal, optical and mechanical properties.

Also recently metal added organic boric acid crystals have proved their competence with other novel materials in possessing higher nonlinear optical properties. Keeping this in mind nickel added boro formate was developed by our team. It seems to be a healthy candidate as a NLO material. Thus interest is shown to synthesise and develop such a Metal added boric formate crystal and study its crystalline properties using various characterisation techniques such as X ray diffraction, FT-IR, UV-
Visible spectroscopy and SHG test. It is of interest to present our results to prove NBF to be a suitable contestant for optical design instruments.

2. EXPERIMENTAL PROCEDURE

2.1. Crystal Growth

Synthesis of NBF crystal was initiated by making a mixture containing Merck and analytic grade Nickel nitrate, Boric acid and Formic acid. The solution was made with millipore water. This solution was taken in a Borosil beaker and placed in a magnetic stirrer to get an even solution and later filtered using Whatann filter paper. This well mixed solution was tightly covered with transparent plastic sheets with pores to enable steady evaporation. The mixture was left undisturbed for 40 days at room temperature or constant temperature bath until small crystalline samples were visible. Perfect seed crystals were isolated among them and recrystallized to get larger transparent crystal with perfect shape and free from impurities. The size of the crystals so obtained as in Fig. 1 was 10x2x2 mm$^3$ which grew in a period of 30 days.

2.2 Characterization

To study the growth parameters of NBF crystal and its crystalline nature X-ray diffraction instrument (XRD) was used. The presence of various vibrational bonds between molecules was determined using Fourier Transform Infrared (FT-IR) in the finger print region 400–4000cm$^{-1}$. The transparency region of NBF crystal was verified using UV–Vis spectrophotometer (UV VIS NIR). The inclusion of elements in NBF crystal and its basic composition was determined by energy dispersive analyser (EDAX). Second harmonic generation (SHG) was used to ensure NLO property of NBF crystal.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction Analysis

Phase identification of a grown crystal and information on its unit cell dimensions can be obtained through X-ray diffraction. Here a beam of known wavelength X ray is impinged on the grown crystal. The scattered beam defines the crystal structure by producing pattern of peaks. By studying the peak pattern at specified angle the unit cell parameters can be determined. The values of the cell parameters
such as a, b, c are listed in Table 1. The values are a = 3.33 Å, b = 4.67 Å, c = 5.56 Å and α= 70.33˚ β = 88.43˚, γ = 67.63˚ with volume = 469 Å. This confirms that the single crystal belongs to triclinic system.

| Sl.No | Cell Parameters in Angstrom Units | Volume in Å | System α=β=γ= 90˚ |
|-------|----------------------------------|-------------|-------------------|
| 1     | a = 3.33 Å                       | 469 Å       | α= 70.33˚         |
| 2     | b = 4.67 Å                       |             | β = 88.43˚        |
| 3     | c = 5.56 Å                       |             | γ = 67.63˚        |

3.2. FTIR Analysis

FTIR method makes use of a beam of IR light through a sample. Once the light is absorbed by the sample the molecules undergo vibration of specific frequencies which can be recorded as peaks called spectrum. Here the developed crystal NBF was tested using FTIR analysis and the outcomes obtained from the spectral peaks were compared. In the middle IR region between 400 and 4000 cm\(^{-1}\), the FTIR spectrum was studied and is shown in Fig. 2. The hydrogen bonding present in N–H stretching can be observed through absorption peaks at 3500 and 2500 cm\(^{-1}\). A stretch at 1675 cm\(^{-1}\) confirms the bonding between C and O having a stretching vibration. Bending oscillation due to C and OH ensures the presence of carboxylic acid. A carboxylic stretch O-H is visible at 3000 cm\(^{-1}\) [5]. The aromatic band due to in plane and out of plane bending is obviously visible at 698 cm\(^{-1}\), 943 cm\(^{-1}\) and 1029 cm\(^{-1}\). The presence of boric acid due to B-OH stretch is visible at 3371 cm\(^{-1}\). Likewise the asymmetric stretch denotes B-O stretch at 1411 cm\(^{-1}\) and 1506 cm\(^{-1}\) whereas symmetric stretch of B-O is explicit at 943 cm\(^{-1}\) [6]. The above observations justify the presence of basic functional groups present in the experimental crystal sample [7]. FTIR studies thus provide an insight about the light absorbed by the bonds of vibrating molecules in NBF crystal to provide a molecular fingerprint.

![Figure 2. FTIR spectrum of NBF Crystal](image-url)
3.3. UV-Vis-NIR spectral Analysis

The electrons are excited from the lower energy to upper energy states when they absorb light of ultra-violet region (200–400 nm) which is termed as UV–Vis NIR spectral analysis. Such a spectrum for the NBF crystal is shown in Fig. 3 and was recorded in the range of 200–1200 nm. A transparency range from 300 to 1200 nm is obviously visible. There seems to be minimum absorption in this range, which enhances the usage of NBF crystal for SHG applications. The figure below depicts the entire absorbance range with a marked transparency lower cut off wavelength at 330 nm. This region is essential for using the crystal for optoelectronic switches [8]. This sufficient transparency condition can be tapped useful for remote sensing and related usage too [9].

![Image](image_url)

**Figure 3.** UV–Vis–NIR spectrum of NBF crystal

3.4. Kurtz and Perry SHG test

Non-centrosymmetric crystals needs to possess NLO efficiency which can be tested Kurtz powder technique. When the output frequency is doubled in the grown powdered sample after passing a beam 1064 nm from Q-switched Nd: YAG laser the NLO efficiency is tested. This is preliminary study for nonlinear property of any crystal. The NBF crystal emit bright green light (λ=532 nm) proving that it possess NLO efficiency.

3.5. EDAX Analysis

Energy dispersive X-ray analysis (EDAX) gives a true picture of the elements present in NBF crystal [11]. In the present study, the EDAX analysis was carried out for NBF crystals using FEI QUANTA 200F energy dispersive X-ray micro analyzer. The results observed in the elemental analysis of the grown crystals are shown in Fig. 4. The EDAX spectrum confirms the presence of carbon, nickel, borate and oxygen.
4. CONCLUSION

An excellent crystal Nickel added boro formate which forms a metallo organic single crystal is grown with enhanced optical properties. The synthesis technique followed by slow solvent evaporation has produced an unique crystal whose UV lower cut off region is at 330 nm. A defined crystallographic structure is confirmed by XRD method. FTIR study depicts the various vibrational odes present in NBF crystal. The powder SHG measurement shows that the grown Nickel added Boro Formate crystal has better higher NLO efficiency.

References

[1] K.Selvaraju et al 2007 Optics Communications 269 230–234
[2] H. O. Marcy et al 1992 Applied Optics 31 24
[3] P.Veluchamy et al 2017 IOSR Journal of Applied Physics 9 69-75
[4] N.Vijayan et al 2006 Crystal Growth & Design 6
[5] X.T. Liu et al 2012 Appl Phys 107 949–957
[6] R.Bairava Ganesh et al 2005 Journal of Crystal Growth 282 429–433
[7] Stuart B 2004 Infrared Spectroscopy: Fundamentals and Applications
[8] Azhar S M et al 2017 Opt Laser Technol 87 11-16
[9] ChidambaramVet al 2010 Physica B 405 2605-2609.
[10] R.Mohan Kumar et al 2005 Journal of Crystal Growth 275 1935–1939
[11] Bhuvaneswari Arvind, Ret al NCRTAM ISSN-2319-7560