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Synthesis, Optical, Mechanical and Thermal Studies on Novel Nonlinear Optical Bisthiourea Potassium Nitrate Crystal By Solution Growth Technique

M. Radha Ramanan [1], R. Radhakrishnan [2], S. Krishnan [3] V. Chithambaram [4]*

[1] Department of Physics, Arasu Engineering College, Kumbakonam

[2] PG & Research, Department of Physics, Jamal Mohamed College, Tiruchirappalli

[3] Department of Physics, B.S Abdur Rahman University, Vandaloor, Chennai

[4]* Research Centre Physics, Dhanalakshmi College of engineering, Tambaram, Chennai,

*Corresponding author's email: chithambaramv@gmail.com

Abstract— Bisthiourea Potassium nitrate, a new semiorganic nonlinear optical crystal, has been grown by solution growth slow evaporation technique for the first time. The grown crystal were characterised by single XRD to conform lattice parameter. The presence of functional groups was confirmed by using fourier transform infrared (FTIR) analysis. Optical behaviour such as UV – Vis – NIR absorption spectrum was carried and the UV cut-off wavelength for the grown crystal is at 270 nm. Thermal analysis was carried out to determine the thermal stability and the melting point of the grown crystal using TG/DTA. The mechanical properties of the grown crystals have been studied using Vickers micro hardness tester for different loads. Second - Harmonic generation were investigated to explore nonlinear optical characteristics of the materials using Kurtz powder technique.

Keywords : FTIR, XRD, NIR, BTPN

I. INTRODUCTION

In recent years, most of the NLO Researchers are working with the idea of combining such high optical non linearity of organic compound with the favorable mechanical and thermal properties of inorganic materials [1]. Today, nonlinear optical (NLO) materials have been studied extensively for their possible applications in various technologies such as telecommunication, optical computing, optical data storage and optical information processing [2 – 9]. NLO crystals with high conversion efficiencies for second harmonic generation (SHG) and transparent in visible, ultraviolet ranges are required for various devices in the field of optoelectronics and photonics [10-12]. To be useful in this technology, the materials should possess large second order optical nonlinearities, short transparency cutoff wavelength and good thermal stability. Organic materials possess good optical non-linearity compared with inorganic crystals but they are thermally unstable and exhibits low laser damage threshold [13]. Semi organic crystals have large damage threshold, wide transparency range, less deliquescence, excellent nonlinear optical coefficient, low angular sensitivity and exceptional mechanical properties [14, 15].

In the present work, Bisthiourea Potassium nitrate (BTPN), a desirable semi organic nonlinear optical crystal, has been grown from aqueous solution using slow evaporation technique. The grown crystals were subjected to various characterizations such as Single crystal X-ray diffraction analysis, Fourier Transform Infrared (FTIR) analysis, optical absorption studies, Thermal, mechanical studies and nonlinear optical studies and were discussed in detail.

2. EXPERIMENTAL

2.1 Materials and Crystal Growth

The materials were synthesized by taking thiourea (AR grade) and potassium nitrate (AR grade) in a ratio of 2:1. The calculated amount of thiourea was first dissolved in deionized water. Potassium nitrate was then added to the solution. The solution was agitated with a magnetic stirring device for 24h continuously and filtered after complete dissolution of the starting materials. The prepared solution was allowed to dry at room temperature and the crystals were obtained by slow evaporation technique. Optically good quality single crystals having dimensions 22x12x6 mm^3 were grown within the period of 40-45 days. The photograph of as grown crystal of BTPN is shown in the fig. 1.

Fig.1.As grown BTPN crystals

3. RESULTS AND DISCUSSION

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3.1. Single crystal X-ray diffraction

The grown crystals were subjected to single crystal X- Ray diffraction analysis using ENRAF NONIUS CAD4 X-ray diffractometer to determine the cell parameters. The grown crystal belongs to monoclinic system having space group P and the lattice parameters are a=5.34 Å, b=7.35 Å, c = 8.73 Å.

3.2. FTIR analysis

The FTIR spectrum was recorded using Bruker IFS 66V spectrophotometer by KBr pellet technique in the region 4500 – 400 cm^{-1} and is shown in Fig 2

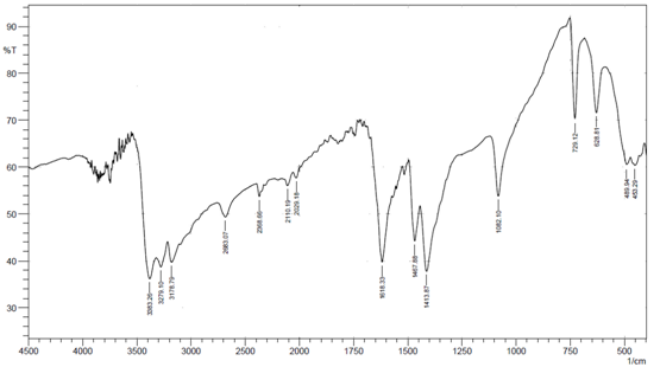

Fig. 2.FTIR Spectrum of BTPN crystals

Vibrational spectroscopy is useful in the identification of functional groups. Molecular vibrational information can be obtained from the absorption or emission of infrared radiation and also from the inelastic scattering of light. Infrared radiation, when incident upon matter is capable of giving indirect but very valuable information on molecular structure. The frequency assignments are presented in Table 1.

FTIR frequency(cm-1)	Band Assignment
3383	NH stretching
3279	NH2 asymmetric stretching
2683	$NH3^+$ symmetric stretching
1618	C=N stretching
3178	NH2 symmetric stretching
1467	N=C=N stretching
1413	–COO– symmetric stretching / – NO_3
729	NO group bending
628	N–H bending

Table 1. FTIR Functional groups

3.3. Optical absorption studies:

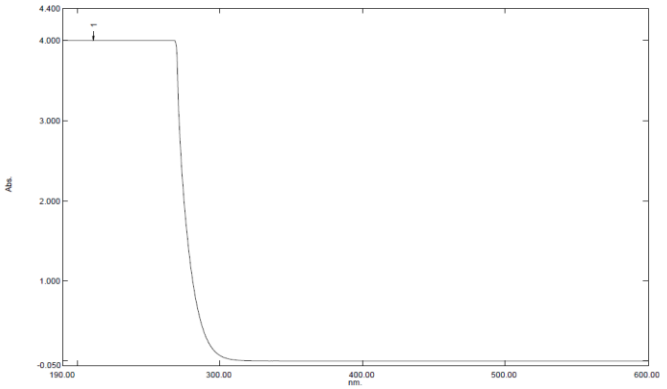

Fig. 3.UV-Vis spectrum of BTPN crystals

The optical absorption spectral analysis of the grown crystal was carried out between 200-600 nm using VARIAN CARY 5E spectrometer and is shown in the fig.3. It is observed from the spectrum that there is very low absorbance in the entire visible region and shows maximum absorption at UV region. This is one of the most desirable properties of the crystals for the fabrication of optical devices. The UV cutoff wavelength was found to be at 270 nm

3.4. Thermal analysis

The thermo gravimetric analysis of bisthiourea potassium nitrate crystals was carried out for the sample weight of 8.820 mg between 50 to 550˚ C at a heating rate of 20 K min^{-1} in nitrogen atmosphere using NETZSCH STA 409 C/CD thermal analyzer and the resultant spectrum is shown in the fig. 4.

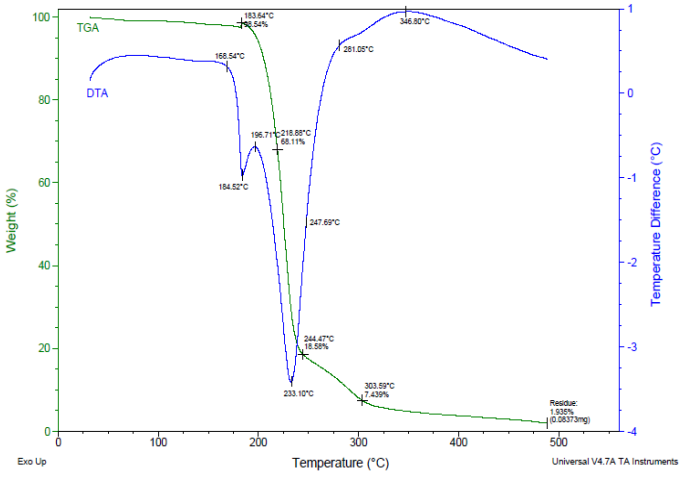

Fig. 4. TG/DTA Spectrum of BTPN crystals

The TGA illustrates that there is no loss below 200º C illustrating the absence of water in the crystal lattice and the sharp weight loss at 183º C, without any intermediate stages, is assigned as melting point of the crystal. After that above 183º C the crystal slightly starts to decompose from 215º C, 244º C, and 303º C. The sharpness of this peak shows the good degree of crystallinity and purity of the sample. Thus from the thermal

studies, the crystal can retain its texture up to 183º C.

3.5. Micro hardness study

The micro hardness studies were carried out to determine the mechanical strength of the grown BTPN single crystal using HMT 2 T, Vicker's micro hardness tester. The indentation marks were made on the surface of BTPN single crystal at room temperature by applying load of 25, 50 g. The Hv is found to increase with increase in the load from 25 to 50 g and crack occurs at higher loads. A graph has been plotted between Hv and applied load P. The Vicker's micro hardness number Hv of the crystal was calculated using the relation Hv=1.8544 P/d2 kg/mm^2; here, Hv is the Vicker's hardness number in kg/mm^2, P is the applied load in kg and d is the average diagonal length of the indentation in mm . From the graph the hardness value increased before 50g and decreased with increase of applied load, which may be due to the release of internal stresses generated with indentation. The grown crystal could withstand a mechanical strength (hardness) of 29.45 kg/mm^2.

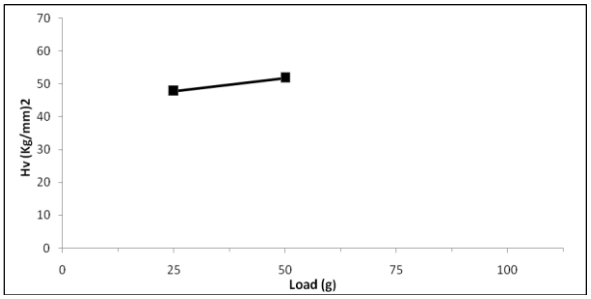

Fig. 5. Plot of load (vs.) H_v for BTPN crystal

3.6. NLO test

The second harmonic generation efficiency measurement was carried out on the grown crystal using the Kurtz Perry powder technique. The crystal was grounded into a homogenous powder of particles and densely packed between two transparent glass slides. The powder sample with average particle size 100-115µ were illuminated using Q-switched Nd : YAG laser emitting a fundamental wavelength of 1064 nm with the pulse width of 8ns. The second harmonic generations were confirmed by the emission of green radiation (532nm).The output power is found to be greater than that of KDP.

4. Conclusions

Optically good quality crystals of BTPN were grown by slow evaporation solution growth technique at room temperature. The functional groups were confirmed from FTIR analysis. The thermal stability of the materials was established by TG/DTA and it is observed that the material is stable up to 183º C. Vickers microhardness was calculated in order to understand the mechanical stability of the grown crystals. The NLO property of the crystal was examined by performing Kurtz powder test using Nd:Yag laser. Thus BTPN crystal can be used as an effective material for nonlinear optical applications.

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