SYNTHESIS, OPTICAL AND THERMAL PROPERTIES OF SEMIORGANIC NONLINEAR OPTICAL CRYSTALS GROWN BY SOLUTION GROWTH SLOW EVAPORATION TECHNIQUE

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ABSTRACT

Bisthiourea potassium chloride, 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 recording the powder X – ray diffraction and it verified by using single XRD. 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 260 nm. Thermal analysis was carried out to determine the thermal stability and the melting point of the grown crystal using TG/DTA. Second - Harmonic generation were investigated to explore nonlinear optical characteristics of the materials using Kurtz powder technique.

KEYWORDS: Optical Materials, Crystal Growth from Solution, Nonlinear Optics

INTRODUCTION

In recent years, second order nonlinear optical materials have attracted many researchers because of their potential applications in various emerging technological fields [1 - 7]. Today, crystal growth technology has advanced rapidly for the development of novel nonlinear optical materials (NLO) for various applications such as optical switching, frequency conversion and electro-optical modulation [8-13]. The organic NLO materials have large nonlinear optical coefficients compared to inorganic material, but their use is impeded by their poor mechanical and thermal properties and low laser damage threshold [14].

The inorganic NLO materials have excellent mechanical and thermal properties but possess relatively modest optical nonlinearities due to lack of extended π-electron delocalization [15]. In view of these problems, a new class of materials have been developed from organic and inorganic complexes called semi organic [14, 16]. In these materials, high optical nonlinearity of pure organic compound is combined with the favourable mechanical and thermal properties of inorganic materials [14-18]. Semi organic crystals have large damage threshold, wide transparency range, less deliquescence, excellent nonlinear optical coefficient, low angular sensitivity and exceptional mechanical properties [19, 20].

In the present work, Bisthiourea Potassium Chloride (BTPC), 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 studies and nonlinear optical studies and were discussed in detail.
SYNTHESIS AND CRYSTAL GROWTH

By mixing aqueous solutions of Potassium Chloride and Thiourea in the stoichiometric ratio 1:2 the BTPC salt has been synthesized. The following reaction estimates the required quantity of Potassium Chloride and Thiourea.

\[ \text{KCl} + 2 \text{CS} (\text{NH}_2)_2 \rightarrow \text{K} [\text{CS} (\text{NH}_2)_2]_2 \text{ Cl}_2 \]

The calculated amount of KCl and thiourea were dissolved in deionised water and stirred well using a magnetic stirrer for about 8 hours. The product was purified by repeated recrystallization before it is used for crystal growth. BTPC crystals were grown from aqueous solution by slow evaporation technique. After continuous recrystallisation and filtration, optically good quality single crystal having dimensions 16 × 14 ×8 mm³ were obtained within a period of 5 weeks. The photograph of as grown crystal of BTPC is shown in the fig.1

RESULTS AND DISCUSSIONS

Single Crystal X-Ray Diffraction

Single crystal X-ray diffraction analysis has been carried out to confirm the crystallinity and to find the lattice parameters of the grown crystals. The grown crystals were subjected to single X-ray diffraction studies using BRUKER NONIUS CAD4 Single crystal X-ray diffractometer.

The obtained results show that the diffractometer to obtain unit cell parameter grown crystals belong to Orthorombic system with space group I. The determined lattice parameters are \( a = 5.48^\circ \text{A} \quad b = 7.65^\circ \text{A} \quad c = 8.55^\circ \text{A} \), \( V=359^\circ \text{A} \cdot \text{A}^2 \) And \( \alpha = 90^\circ \).

Powder X-Ray Diffraction Analysis

X-ray diffraction technique is used to investigate the inner arrangement of atoms in a crystalline material.
The grown BTPC Crystals were subjected to powder X-ray diffraction studies. The X-ray powder diffraction pattern of the grown crystals was obtained using XPERT-PRO Diffractometer with copper (K-alpha 1) radiation of wavelength 1.54056 Å operating at a voltage of 40 KV and a current of 20mA. The indexed powder XRD diffractogram of BTPC crystals is shown in fig 2. The sharp peaks with maximum intensity characterize the XRD pattern, indicating the formation of well defined crystallites. From the powder XRD analysis it is observed that the lattice parameters are exactly matches with the single XRD data.

Fourier Transform Infra Red (FTIR) Analysis

FTIR analysis is a technique that provides information about the functional groups of bis thiourea potassium chloride single crystal. The FTIR Spectrum of the grown crystals was recorded in the wave number range 400-4000 cm$^{-1}$ using a Perkin Elmer FTIR, using KBR Pellet technique and is shown in fig.3. In the FTIR spectrum (Fig. 3) of BTPC, the NH stretching vibrational bands of NH$_2$ observed at 3385, 3275 and 3174 cm$^{-1}$ were found shifted to different wavenumber region when compared to that of the free ligand. The peak observed at 2682 cm$^{-1}$ is due to N=CH$_2$ stretching. The intense sharp peak at 1616 cm$^{-1}$ is due to C=C stretching. The absorption peak observed at 1083 P=O stretching.
UV-Visible-NIR Spectral Studies

The UV-Visible-NIR Spectrum for the grown crystal was carried out between 200-800 nm using VARIAN CARY 5E Spectrophotometer and is shown in Fig. 3. From the absorption spectra it is noticed that the crystals have high transmittance in the entire visible NIR region of the spectrum and this facilitates the grown crystals to be potential nonlinear optical materials for second harmonic of Nd: YAG LASER. The crystal is highly transparent in the region between 260 nm to 800 nm. The cut off wavelength is around 260 nm.

![Figure 4: UV-Vis-NIR Spectrum of Bisthiourea Potassium Chloride](image)

Thermo Gravimetric Analysis

Figure 4 shows the Simultaneous TG/DTA Thermogram. TGA measurements were used at a heating rate 20°C/min in Nitrogen atmosphere over the temperature range in between 50° C and 300° C. In the lower temperature range from 50° C to 176.2 ° C there is no weight loss observed, that is due to withstanding the thermal stability of the sample. The major weight (2.211 mg) loss was observed in the temperature range in between 176° C and 258.5° C, that is due to decomposes of Thiourea. DTA spectrum shows the endothermic peak was observed at 178.9°C, which is due to the melting point of Thiourea. The other endothermic peak was observed at 231.8 °C, is due to decomposition of Thiourea. The TGA major decomposing temperature at 231.8 °C is exactly matching of DTA results.

![Figure 5: TG/DTA Spectrum of BTPC](image)
Second Harmonic Generation Test (SHG)

The NLO property of the grown BTPC crystals was confirmed by Kurtz-Perry powder technique. The SHG measurement was carried out using Q-Switched mode locked Nd: YAG LASER with first harmonic output at 1064nm, with an input power of 3.5 mJ and a pulse width of 10 ns at a repetition rate of 10 HZ. The SHG behaviour was confirmed by the output of intense green light emission from the crystal. The sample converts the 1064 nm radiation into green (532nm) while passing the Nd:YAG LASER output into the samples which confirms the SHG. The NLO efficiency of the grown crystals is found to be greater than that of KDP crystal.

CONCLUSIONS

Optically transparent good single crystals of BTPA were grown from aqueous solution using slow evaporation technique. Single crystal X-ray diffraction analysis confirms the grown crystals crystallize in Orthorhombic system having space group I. The various functional groups present in BTPC crystals have been confirmed by FTIR analysis. The transparency nature of the crystal in the UV – Vis-NIR in the region was 200 nm to 800 nm. It has a lower UV cut off wavelength of 270 nm. From the TG and DTA curves, the sample is highly stable up to 176°C which indicates that the material is thermally stable. The NLO efficiency of the grown crystals is found to be greater than that of KDP crystal. Because of all the above properties the crystals BTPC is suitable for optoelectronics device applications.

REFERENCES


