International Journal for Research in Engineering Application & Management (IJREAM)
ISSN : 2454-9150 Vol-05, Issue-01, April 2019

Synthesis, Growth and Characterization of Tetrathiourea Pottasium Bromide Doped KCL Crystal

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Abstract - Single crystals of tetrathiourea pottasium bromide (TTPB) be developed by slow evaporation technique. The grown crystal was clear by Fourier Transform Infrared (FT-IR), spectral studies and single crystal X-ray diffraction. Single crystal X-ray analysis investigation demonstrates that TTPB takes shape in orthorhombic crystal system framework with space group Pbca. The title compound was further portrayed by UV-Vis-NIR examine demonstrates that the single crystal is straightforward in the specific wavelength range and TG/DTA examination. The microhardness test was completed for developed grown crystals. Dielectric examines on the developed grown crystal gauge the dielectric steady and dielectric misfortune as for frequency.

Key Words: Crystal growth, Photo Luminescence, Solution growth and Dielectric properties.

I. INTRODUCTION

Crystal growth assumes an imperative job in present day innovation. Crystals are the solids in which the fundamental structure obstructs; the particles are masterminded routinely in a space lattice with express geometrical symmetry. Single crystal find a wide extent of uses in laser technology, optoelectronics, light emitting diodes, thermography, etc, as such improvement of single crystals are at most criticalness for further headway in materials investigate.

Non linear optical crystal are generally utilized in present day optical science and innovation for frequency change of laser light , i.e., to generate laser radiation at a particular wavelength in obvious. [David and Nikosgosyan, 2005].

Thiourea in combination with metal complexes forms semi-organic compound gives a low cutoff wavelength and it is applicable for high frequency conversion. A segment of the reported promising NLO crystals of thiourea complex are potassium thiourea bromide (Roshan et al., 2001), bis thiourea cadmium chloride (Selvakumar et al., 2005) and zinc thiourea chloride (Rajasekaran et al., 2001). In the present examination, thiourea is united with potassium bromide to shape an entrancing semi-regular jewel tetra thiourea potassium bromide; K (N2H4CS)4 Br (TTPB).

In the present investigation, thiourea is joined with potassium bromide to shape a fascinating semi-natural mass size single crystal of tetra thiourea potassium bromide (TTPB) doped kcl crystal. The development of mass size crystal by slow solvent evaporation technique and its characterization studies, for example, FT-IR, TG-DTA and powder XRD were accounted for. The spectral, optical and thermal studies of title crystal contrasted and the comparable thiourea crystal and announced.

II. EXPERIMENTAL ANALYSIS

Single crystal of Tetra Thiourea Potassium Bromide Doped KCl was synthesised by dissolving thiourea and potassium bromide in double refined water in a molar proportion 4:1. Potassium chloride (KCl) as an added substance is included into thiourea potassium bromide arrangement in a sum amount of (1M%) by the strategy by slow evaporation solution growth technique at room temperature to get another new crystal. All the crude materials utilized in the development procedure were Analytical reagent grade (E MERCK). Since thiourea has the coordination ability to frame distinctive periods of metal-thiourea complexs, the blend of the reactants must be mixed well to dodge co-precipitation of various stages.

The solution was altogether mixed for 8hrs using magnetic stirrer. The solution was later sifted by whatman filter paper in a flushed container. The beaker was secured with trasnparent paper to avoid dust inclusion and kept at room temperature. The purity of TTPBr doped KCl crystals were accomplished by recrystallization process. Great optically transparent KCl doped TTKBr crystals have been crystallized with very much characterized faces in a time of 35 days. Because of the doping of the polluting influences on the crystals, striking changes in the physical properties were gotten (Fig. 1). The magnificence behind the crystals lies with its inside and out characterized morphology, which isn't represented elsewhere.

III. RESULTS AND DISCUSSION

3.3.1. Powder X-ray Diffraction analysis

The grown single crystal of TTPBr was complete by single crystal X-ray diffraction examination using ENRAF NONIUS CAD4 diffractometer (Enraf-Nonius, 1992).. The recorded spectrum of the sample was taken at room

 DOI : 10.18231/2454-9150.2019.0346

temperature in a 2θ range of 10 to 80° using Cu-Kα radiation of wavelength 1.5418 Å. X-ray diffraction pattern (Fig. 2) shows the strong and sharp peaks definite the crystalline nature of the crystals grown. The TTPB doped KCL crystal were analyzed by single crystal X-ray diffraction, it belongs to orthorhombic space group Pbca, the unit cell parameters were originate to be a = 15.429Å, b = 7.127Å and c = 8.340Å. There are slight variations in the lattice parameters and cell volume of the TTPB doped KCL crystal.

3.3.2. FT- IR Analysis

The functional groups were recognized by using PERKIN ELMER RXl Fourier Transform Infrared spectrophotometer in the range of 400-4000 cm". From Fig. 3 shows FT-IR spectrum of TTPB doped KCL crystal. In the FT-IR spectrum, the peak at 3608 cm^{-1} is assign to OH stretch of water. It is supported by its bending mode at 1614 cm^{-1}. The OH stretch of maleate should also occur close to 3423 cm^{-1}. But it is not clearly resolved. The peak at 3088 is due to N-H vibration of NH_3^+. The aromatic C-H vibration gives its peak at 3046 cm^{-1}. The C=O vibration occurs at 1723 cm^{-1}. The asymmetric and symmetric vibrations of CO_2 occur at 1515 and 1383 cm^{-1}. The bending mode of CH_2 gives peaks at 1369 and 1418 cm^{-1}. The C-C vibration gives peaks at 1244 cm^{-1}. The aromatic C-H bend modes are due to peaks at 737 and 778 cm^{-1}. The peaks at 577 cm^{-1} are due to torsional oscillation of NH_3^+. Hence from the IR spectral analysis presence kcl in association with tetrathiourea potassium bromide is clearly evident. The FT-IR frequency assignment of TTPB doped KCL crystal is presented in Table 1.

3.3.3. FT- Raman Analysis

The polarized Fourier Transform Raman (FT-Raman) spectra were recorded for the pure and doped mNA in order to qualitatively analyze the occurrence of functional groups in the range 4000 – 50 cm^{-1}. The recorded spectra of TTPB doped KCL crystal as shown in Fig. 4. The NH stretching bands are observed at 3020 cm^{-1} for TTPB doped KCL crystal.

3.3.4. Optical Study

2.3.4.1. UV-Visible Analysis

The optical absorption plays an important role in identifying the potential of the NLO material. The optical absorption spectra of TTPB doped KCL crystal have been recorded in the region 200-800 nm using LAMBDA-35 UV-Vis spectrometer (Lefur et al., 1995). In this study, the lower cut-off wavelength of TTPB doped KCL crystal is 322 nm. The low absorption in the visible and NIR regions down with low cut off wavelengths validate the suitability of the grown crystals for NLO applications. The UV-Vis spectrum of TTPB doped KCL crystal as shown in Fig. 5.

3.3.4.2. PL Study

The PL spectra is a powerful tool for characterizing the optical and photochemical properties of semiconductor materials and the PL peak intensity correlates directly with the defect densities (surface oxygen vacancies) in materials (Sun et al., 2012). Fig. 6 shows PL spectra of title crystal corresponding to 400–700 nm excitations. A peak at 415 nm was observed with small peaks at 525 and 695 nm when excited at 220 nm. The peak observed at 415 nm may be due to Near Band Edge (NBE) emission.

3.3.4.3. Micro-Hardness Studies

Hardness of a material is calculated of its resistance to local deformation. It is associated with other mechanical properties like elastic constants and yield stress of materials. In this case the indentations were conceded out using a Vickers pyramidal indenter (Metatech Microhardness Tester) for various loads ranging from 10 to 80 g for a constant time of indentation (10s). The hardness number (Hv) of the crystal was calculated using the relation

$$H_v = 1.8544P/d^2 \text{ (kg/mm}^2\text{)}$$

where Hv is the Vickers micro hardness number, P the practical load in kilograms, and d the mean diagonal length of the groove in mm. The nature of variation of hardness with load was determined by plotting micro hardness number (Hv) against load (P). From the results, it is experimental that hardness number increases as load increases (Fig. 3.7). This is in agreement with normal indentation size effect. The work hardending coefficient ‘n’ was found to be less than 2, which in turn supports the concept of Onitsch.

3.3.4.4. TGA analysis

The thermal activity of the single crystal was experienced by Perkin-Elmer thermal analyzer (STA 409 PC). TGA analysis of TTPB doped KCL crystal was carried out between 30ºC to 800ºC. The heating rate was maintained at 10ºC/min in air to determine the thermal stability of the compound (Fig. 3.8). The endothermic transition around 220°C followed by an added endothermic peak at 310° C. There is no endothermic or exothermic peak up to 800° C in the DTA curve while TGA shows almost complete weight loss and the residual weight obtained at 800° C. Further, it is seen that there is no entrapped water in the crystal as there is no weight loss below 220ºC.

3.4. Dielectric Studies

Dielectric studies have been performed on tetra thiourea potassium bromide doped KCL crystal could be calculated dimensions of 14×6×1 mm^3. The dielectric constant and dielectric loss has been intended using the following equation (1) and (2).

$$\varepsilon = Cd/A\varepsilon 0 \quad \text{--- (1)}$$

$$\varepsilon = \varepsilon \tan\delta \quad \text{--- (2)}$$

 DOI : 10.18231/2454-9150.2019.0346

where, **C**, is a capacitance of pellet in farad (F), d is the thickness of the crystal, A is the area of the crystal, and ε_o, is the permittivity of free space ($\varepsilon_o = 8.86 \text{ X} 10^{-12}$ F/m).

Low value of dielectric loss indicates that the grown undoped and sodium sulfate doped TTPB crystals are good quality dielectric materials with less number defects. From the results, it is observed that TTPB crystals are doped with sodium sulfate, the dielectric constant and loss factor are found to be increasing. The increase in dielectric constant with temperature is generally attributed to the crystal expansion, the electronic and ionic polarizations and the presence of impurities and crystal defects.

The increase at higher temperatures is mainly recognized to the thermally generated charge carriers and impurity dipoles. The nature of variations of dielectric constant with frequency and temperature indicate the type of assistance that are present in them (Selvarajan *et al*.,1994).

The measurements of temperature dependent dielectric properties of the Tetra thiourea Potassium bromide doped KCL crystal in the temperature 40°C to 400°C range at the frequency 50Hz-5MHz. Figure 9 showed that the dielectric constant and its response to temperature of Tetra thiourea Potassium bromide doped KCL crystal.

From the plotted graph, it is depicted that the dielectric constant of Tetra thiourea Potassium bromide doped KCL crystal different temperature, such as 40 °C, 100 °C, 200 °C, 300 °C and 400 °C which is increasing with increase in temperature. Thus, lower dielectric properties of tetra thiourea Potassium bromide doped KCL crystal depict its suitability for production of electro-optical application.

IV. CONCLUSION

Synthesized crystal of TTPB doped KCL with dimensions of 14×6×1 mm^3 was grown by slow evaporation method using acetone as a solvent. Powder X-ray diffraction studies were carried out using to calculate the lattice parameters of the grown crystals. FT-IR spectrum confirms the occurrence of functional groups and their vibrational modes in TTPB doped KCL crystal. The highest percentage of optical transmission makes the material suitable for second harmonic generation.

There is no endothermic or exothermic peak up to 800° C in the DTA curve whereas TGA shows almost complete weight loss and the residual weight obtained at 800° C. The sharpness of the endothermic peak shows good degree of crystallinity of the grown crystal. The work hardending coefficient ‘n’ was found to be less than 2, which in turn supports the concept of Onitsch. Thus, the promising crystal growth characteristics and good optical properties make TTPB doped KCL a potential material for photonics device applications.

Finally in dielectric studies the variation of dielectric loss as a function of temperature and experimental that dielectric loss increases with increase in temperature. Therefore, lower dielectric properties of tetra thiourea Potassium bromide doped KCL crystal depict its suitability for production of electro-optical application.

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Figure 1 Photograph of the grown single crystal of TTPB

 DOI : 10.18231/2454-9150.2019.0346

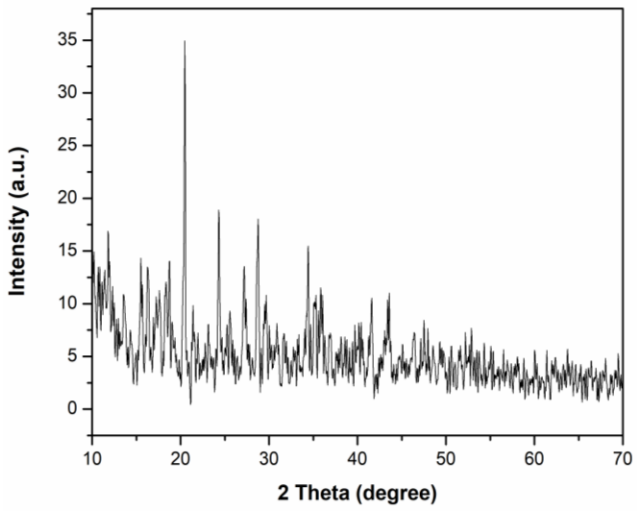

Figure 2. The XRD pattern of TTPB doped KCL crystal

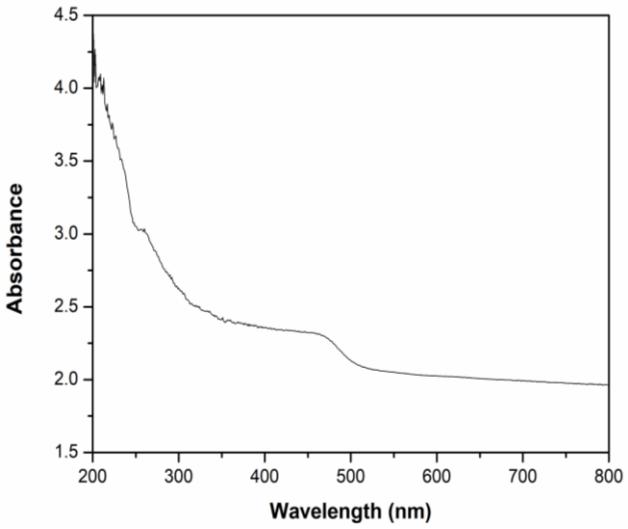

Figure 5. The UV-Visible spectrum of TTPB doped KCL crystal

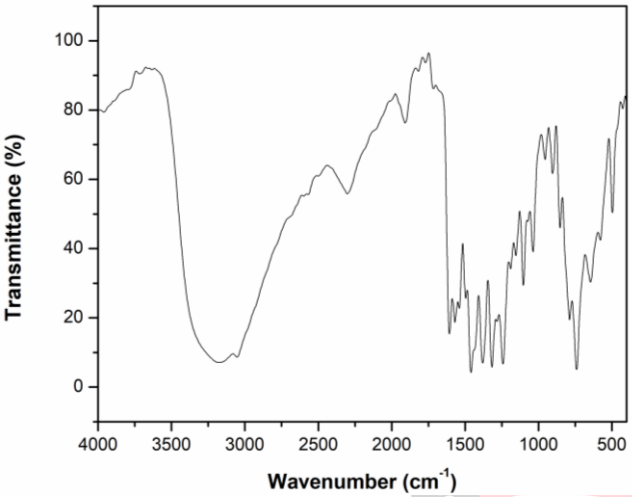

Figure 3. The FT-IR spectrum of TTPB doped KCL crystal

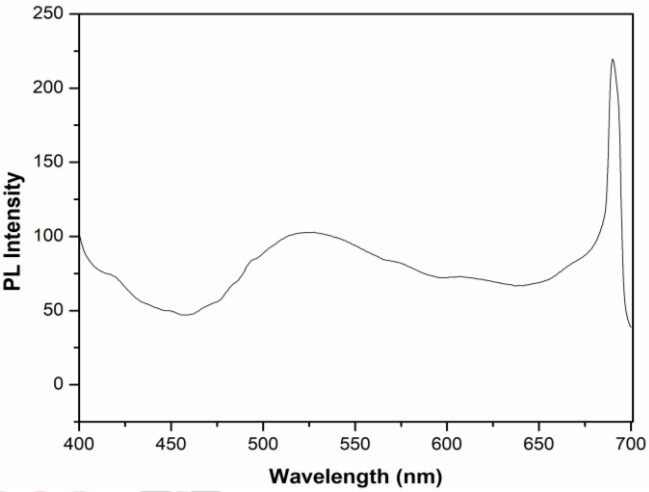

Figure 6. The PL spectrum of TTPB doped KCL crystal

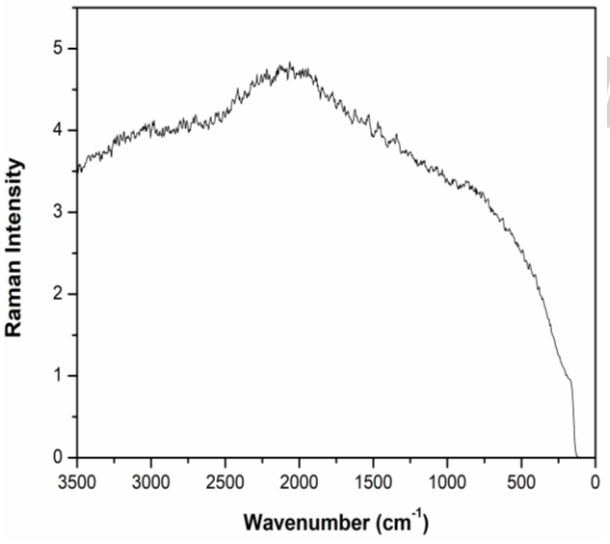

Figure 4. The FT-Raman spectrum of TTPB doped KCL crystal

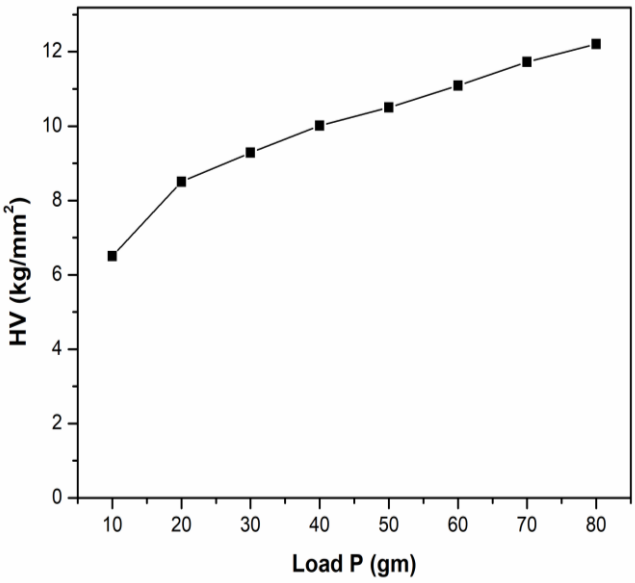

Figure 7. The hardness test of TTPB doped KCL crystal

 DOI : 10.18231/2454-9150.2019.0346

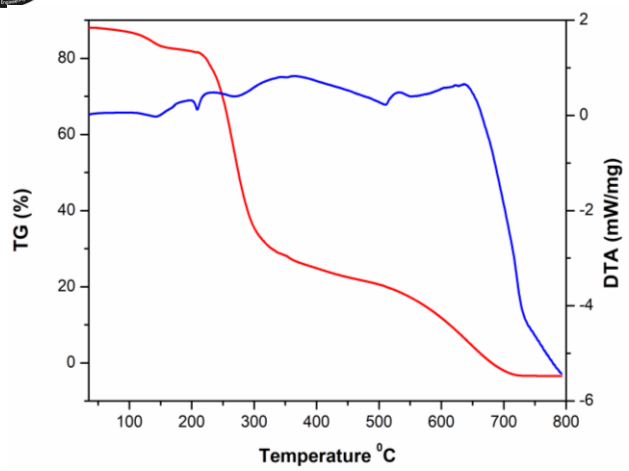

Figure 8. The TG-DTA analysis of TTPB doped KCL crystal

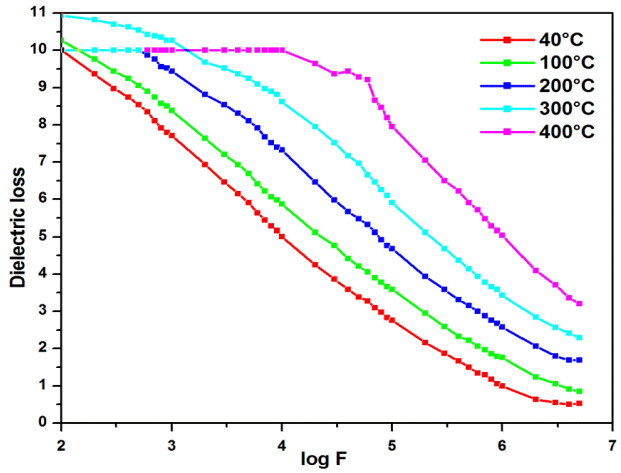

Figure 9. Dielectric Loss with Log F of Tetra thiourea Potassium bromide Doped Kcl Crystals for Different Temperature

Table 1. FT-IR spectral assignments of TTPB doped KCL

Wavenumbers (cm^{-1})	Assignments
3608	O-H stretching
3088	NH vibration of NH_3^+
3046	aromatic C-H vibration
1723	C=O vibration
1515	asymmetric CO_2 vibration
1383	symmetric CO_2 vibration
1369, 1418	CH_2 bending
1244	C-C vibration
737, 778	C–H bending vibration
577	Torsional oscillation of NH_3^+

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