

AN INVESTIGATION OF SEM, DIELECTRIC AND NLO PROPERTIES OF THIOUREA POTASSIUM IODIDE (TPI) SINGLE CRYSTALS

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ABSTRACT

Single crystals of thiourea potassium iodide (abbreviated as TPI) $K [CS (NH_2)_2] I$ were successfully grown by slow evaporation method at room temperature from its aqueous solution. The harvested crystals were of average dimensions $13 \times 3 \times 3 \text{ mm}^3$. Powder X-ray Diffraction studies were carried out and the lattice parameters of the grown crystals have been evaluated. Surface morphology of the TPI was studied by scanning electron microscope (SEM). The dielectric response of the sample was studied in the frequency region 100 Hz to 10 kHz. From the second harmonic generation (SHG) efficiency test it is evident that the sample has the efficiency 1.1 times that of potassium dihydrogen phosphate (KDP).

Keywords: Crystal growth, Slow Evaporation, SEM, Dielectric, Second Harmonic Generation

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INTRODUCTION

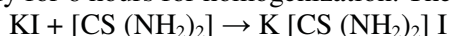
Nonlinear optical (NLO) materials are capable of generating the second harmonic frequency and play an important role in the development of photonics applications¹⁻⁴. The origin of nonlinearity in NLO materials arises due to the presence of delocalized π -electrons system, connecting donor and acceptor groups and responsible for enhancing their asymmetric polarizability⁵. Semi organic nonlinear optical (NLO) crystals have been attracting much attention due to high nonlinearity, chemical flexibility, high mechanical and thermal stability, and good transmittance⁶⁻⁸. Materials with large second order optical nonlinearities, transparency at all wavelengths involved and stable physiochemical performance are needed in order to realize many applications^{9,10}. In the case of metal organic coordination complexes, the organic ligand is usually more dominant in the NLO effect. Regarding the organic ligands, small π -electron systems such as thiourea $[CS (NH_2)_2]$, thiocyanate (SCN) and urea have been used with remarkable success. The centro symmetric thiourea molecule, when combined with inorganic salt yields noncentro symmetric complexes, which have the NLO properties¹¹. Thiourea crystals also exhibit pyroelectric effect, which is utilized in infrared (IR), ultraviolet (UV), scanning electron microscopy

(SEM) detection and infrared imaging¹². In the present investigation, an alkali metal halide has been added to thiourea in the ratio 1:1 and from the obtained product, single crystals of thiourea potassium iodide (TPI) were grown. The grown crystal was subjected to various characterization techniques.

EXPERIMENTAL

Synthesis and crystal growth

Thiourea and potassium iodide (E. Merck) were mixed in a stoichiometric ratio of 1:1 in doubly distilled water and then stirred continuously for 6 hours for homogenization. The chemical reaction is as follows-



The obtained product was purified by the repeated recrystallization process. The complete dissolved solution was filtered using micro filter paper and taken in a Petri dish. It was optimally closed using a perforated polythene paper and kept in undisturbed conditions. The solution was allowed to evaporate at room temperature. After a growth period of 40 days, a well developed TPI single crystal of dimension $13 \times 3 \times 3 \text{ mm}^3$ was harvested and the photograph of as grown single crystal is presented in Fig.1.

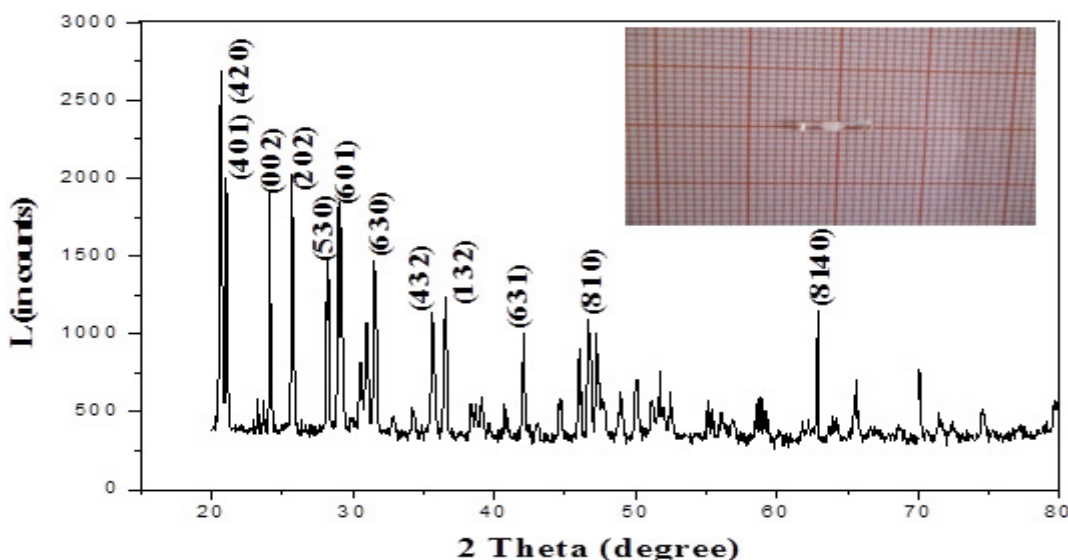


Fig-1: Photograph and XRD spectra of TPI

RESULTS AND DISCUSSION

Powder XRD Analysis

Powder X ray diffraction studies of the TPI were carried out using PANalytical, XPert PRO powder X-ray diffractometer employing $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) radiation at room temperature with a scanning speed of $1^\circ/\text{min}$ and a scanning range of 20 degree to 80 degree. The lattice parameter values of TPI were calculated as $a=b=20.1264 \text{ \AA}$, $c= 7.2145 \text{ \AA}$ and $\alpha= \beta= \gamma= 90^\circ$ and it is clear that the TPI crystal belongs to tetragonal structure. The powder X-ray diffraction pattern is shown in Fig-1. Well-defined Bragg peaks obtained at specific 2θ angles indicating that the crystals are ordered.

SEM Analysis

In order to analyze the nature and surface morphology of the grown crystal, SEM analysis was employed. Scanning Electron Microscope studies for TPI single crystals were carried out using FEI Quanta 200 SEM. Since the organic materials are non-conducting in nature, carbon coating should be done for 10 s before subjecting the TPI crystal surface to electron beam. The SEM images of TPI crystal were taken

into different magnifications and are shown in Fig-2 and it depicts the surfaces of as grown crystal. It is observed that the surface of the TPI crystals appears as smooth.

Dielectric Studies

The dielectric constant for TPI was measured using Agilent 4284-A LCR meter. The dimensions of the samples used were 5x2x3 mm³. Two opposite surfaces across the breadth of the sample were treated with good quality silver paste in order to obtain good ohmic contact. By using the LCR meter, the capacitance of these crystals was measured for the frequencies 100 Hz, 1 kHz and 10 kHz at various temperatures ranging from 40 to 150 °C. The dielectric constant of the grown crystals was calculated by using the relation-

$$\epsilon_r = C_c / C_a$$

Where C_c is the capacitance of the crystal and C_a is the capacitance of the air of same dimension as that of the crystal. Figure-3 shows the temperature dependence of dielectric constant for TPI crystals at the frequencies 100 Hz, 1 kHz and 10 kHz. It may be observed from the figures that the dielectric constant increases with increase in temperature. The dielectric constant of the materials is due to the contribution of electronic, ionic, dipolar and space charge polarizations, which depend on the frequencies. At low frequency all these polarizations are active. The space charge polarization is generally active at low frequencies and high temperature.

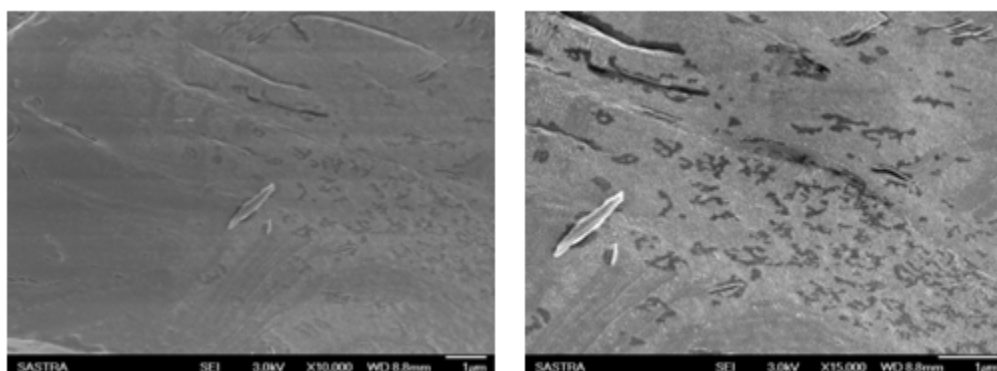


Fig-2: SEM Images of TPI

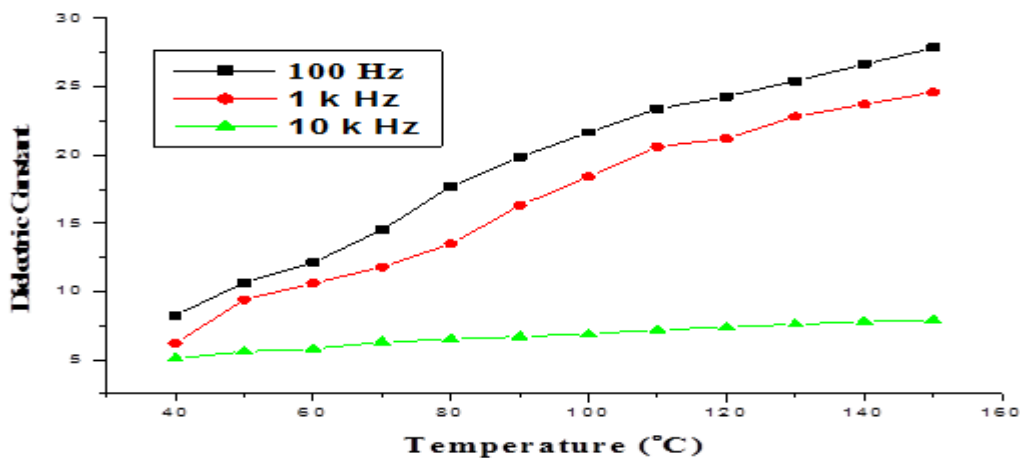


Fig-3: Temperature dependence of dielectric constant

SHG Analysis

The Second harmonic generation efficiency of TPI was examined by Kurtz and Perry powder technique. A Q- switched mode locked Nd: YAG laser of wavelength 1064 nm with a pulse width of 8 ns and a repetition rate of 10 Hz was allowed to pass through the powdered sample which is kept in a capillary tube. The emission of green light with a wavelength of 532 nm confirms the second harmonic generation efficiency of TPI. A second harmonic out signal of 87 mV was obtained for an input beam of energy 2.149 mJ /pulse. For the same incident radiation the output signal was observed as 79 mV for KDP. Hence it is found that the SHG efficiency of TPI crystal is 1.1 times that of standard potassium dihydrogen phosphate (KDP). From this it is evident that the TPI is a good NLO crystal.

CONCLUSION

Single crystals of TPI have been successfully grown by the slow evaporation technique from aqueous solution. The X-ray diffraction analysis confirmed the tetragonal structure of the crystal. The SEM analysis reveals the existence of the surface and growth morphology of the grown crystal and it shows that the presence of few cracks and visible inclusions on the surface of the crystal. The dielectric test reveals that the total polarization value of the titled sample decreases with the increase in the frequency and become minimum at optical frequency range. From the SHG efficiency test it is evident that the efficiency of TPI crystal is 1.1 times that of standard potassium dihydrogen phosphate (KDP).

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