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AN INVESTIGATION OF SEM, DIELECTRIC AND NLO PROPERTIES OF THIOUREA POTASSIUM CHLORIIDE (TPC) SINGLE CRYSTALS

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ABSTRACT

Single crystals of thiourea potassium chloride (abbreviated as TPC) K [CS $(NH_2)_2$] Cl were successfully grown by slow evaporation method at room temperature from its aqueous solution. The harvested crystals were of average dimensions 19×10×6 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 TPC 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

INTRODUCTION

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 polarizability[1]. The search for new frequency conversion materials primarily concentrated on organic compounds and many organic NLO materials with high nonlinear susceptibilities have been discovered[2,3]. However, the implementation of organic single crystal in practical device applications has been impeded by their often inadequate transparency, poor optical quality and low laser damage threshold. Semi organic nonlinear optical (NLO) crystals have been attracting much attention due to high nonlinearity, chemical flexibility, high mechanical and thermal stability, and good transmittance[4-6]. 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. Thiourea forms number of NLO active metal coordination compounds[7-11]. The thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment and ability to form extensive network hydrogen bonds. Further, thiourea is one of the few simple

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organic compounds with high crystallographic symmetry. It crystallizes in the rhombic bipyramidal division of rhombic system and acts as a good ligand. The centro symmetric thiourea molecule, when combined with inorganic salt yields noncentro symmetric complexes, which have the NLO properties[12]. In the present investigation, an alkali metal halide potassium chloride has been added to thioura in the ratio 1:1 and from the obtained product, single crystals of thiourea potassium chloride (TPC) were grown. The grown crystal was subjected to various characterization techniques.

EXPERIMENTAL

Synthesis and crystal growth

Thiourea and potassium chloride (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-

$$KCl + [CS\ (NH_2)_2] \rightarrow K\ [CS\ (NH_2)_2]\ Cl$$

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 35 days, a well developed TPC single crystal of dimension 19×10×6 mm^3 was harvested and the photograph of as grown single crystal is presented in Fig.-1.

RESULTS AND DISCUSSION

Powder XRD Analysis

Powder X ray diffraction studies of the TPC were carried out using PANalytical, XPert PRO powder X-ray diffractometer employing CuKα radiation (λ = 1.5418 Å) radiation at room temperature with a scanning speed of 1^o/ min and a scanning range of 10 degree to 60 degree. The lattice parameter values of TPC were calculated as a=5.214 Å, b=7.342 Å, c=8.401 Å and α= β= γ= 90º. From the lattice parameters it is clear that the TPC crystal belongs to orthorhombic structure. The powder X-ray diffraction pattern of TPC is shown in Figure-1. Well-defined Bragg peaks obtained at specific 2θ angles indicating that the crystals are ordered.

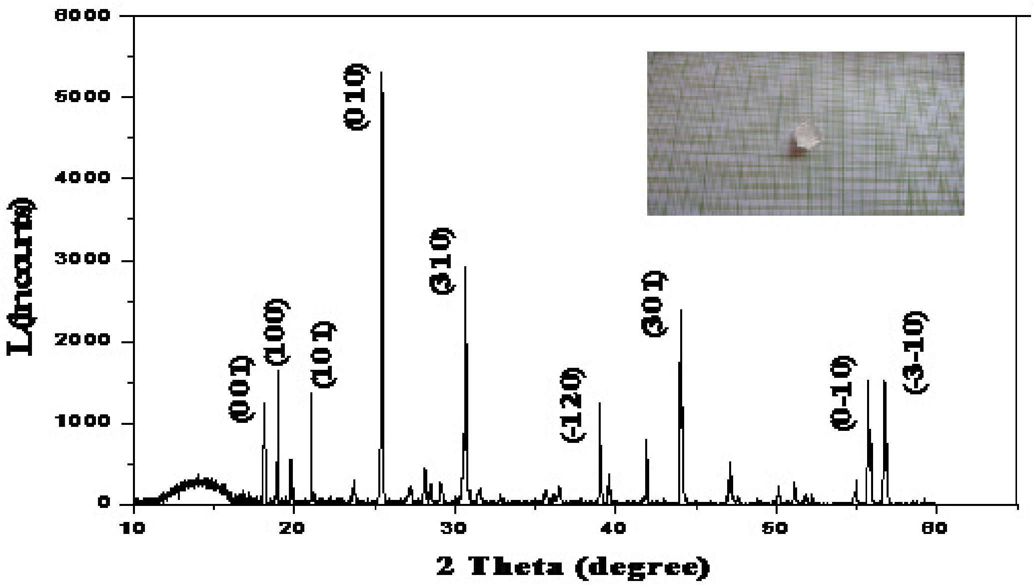

Fig-1: Photograph and XRD spectra of TPC

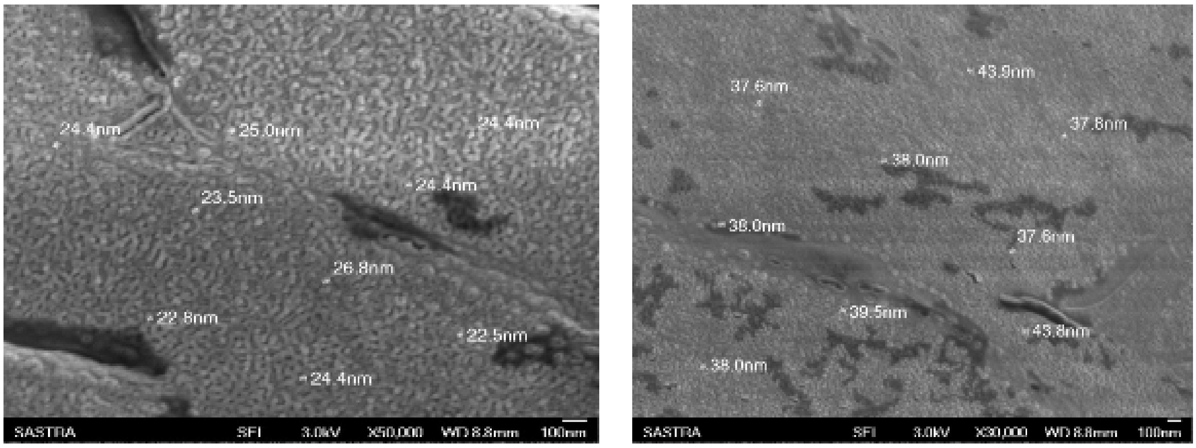

Fig-2: SEM Images of TPC

SEM Analysis

In order to analyse the nature and surface morphology of the grown crystal, SEM analysis was employed. Scanning Electron Microscope studies for TPC 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 TPC crystal surface to electron beam. The SEM images of TPC 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 TPC crystals appears as smooth.

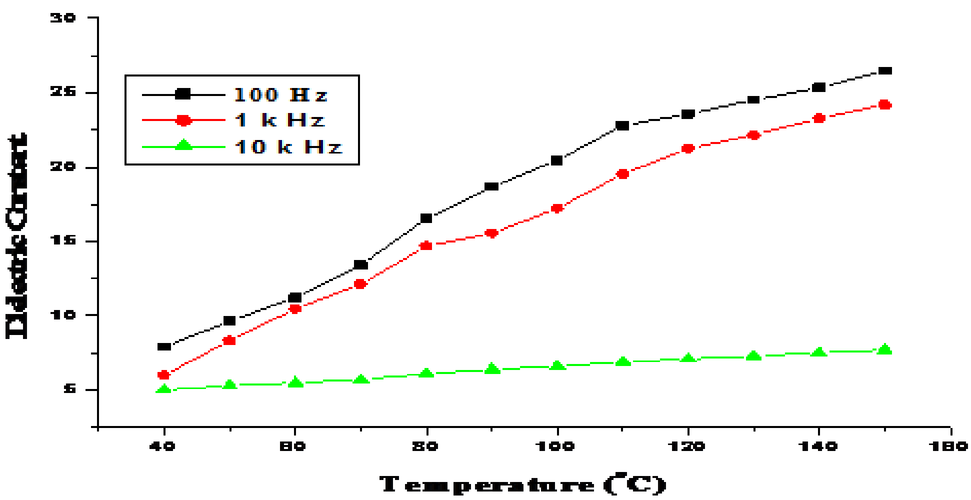

Fig-3: Temperature dependence of dielectric constant

Dielectric Studies

The dielectric constant for TPC was measured using Agilent 4284-A LCR meter. The dimensions of the samples used were 5x4x3 mm^3. 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 frequencies100 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

$$\varepsilon_r = C_c / C_a$$

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 TPC crystals at the frequencies 100 Hz, 1 kHz and10 kHz. It may be observed from the figure 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.

SHG Analysis

The Second harmonic generation efficiency of TPC 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 TPC. 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 TPC crystal is 1.1 times that of standard potassium dihydrogen phosphate (KDP). From this it is evident that the TPC is a good NLO crystal.

CONCLUSION

Single crystals of TPC have been successfully grown by the slow evaporation technique from aqueous solution. The X-ray diffraction analysis confirmed the orthorhombic 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 TPC crystal is 1.1 times that of standard potassium dihydrogen phosphate (KDP).

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