AN INVESTIGATION OF SEM, DIELECTRIC AND NLO PROPERTIES OF THIOUREA MONO POTASSIUM PHOSPHATE (TMPP) SINGLE CRYSTALS

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ABSTRACT

Single crystals of thiourea mono potassium phosphate (abbreviated as TMPP) were successfully grown by slow evaporation method at room temperature from its aqueous solution. The harvested crystals were of average dimensions 12x10x4 mm³. Powder X-ray Diffraction studies were carried out and the lattice parameters of the grown crystals have been evaluated. Surface morphology of the TMPP 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 0.8 times that of potassium dihydrogen phosphate (KDP).

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

INTRODUCTION

In the recent past semi organic nonlinear optical single crystals are getting more attention due to its inherent physical and chemical properties. The search for new frequency conversion materials primarily concentrated on organic compounds and many organic NLO materials with high nonlinear susceptibilities have been discovered¹ ². 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. Recently, noticeable research has been focused on semi organic material, which is an organic material mixed with inorganic materials. They have been attracting much attention due to high nonlinearity, chemical flexibility, high mechanical and thermal stability, and good transmittance³⁴. 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(NH2)2], thiocynate (SCN) and urea have been used with remarkable success. The thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment and ability to form extensive network hydrogen
bonds\textsuperscript{6}. Further, thiourea is one of the few simple organic compounds with high crystallographic symmetry. It crystallizes in the rhombic bipyramidal division of rhombic system and acts as a good ligand\textsuperscript{7}. The centro symmetric thiourea molecule, when combined with inorganic salt yields noncentro symmetric complexes, which have the NLO properties\textsuperscript{8}. Thiourea forms number of NLO active metal coordination compounds\textsuperscript{9-13}. In the present investigation, mono potassium phosphate has been added to thiourea in the ratio 1:1 and from the obtained product, single crystals of thiourea mono potassium phosphate (TMPP) were grown. The grown crystal was subjected to various characterization techniques.

**EXPERIMENTAL**

**Synthesis and crystal growth**

Thiourea and mono potassium phosphate (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 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 30 days, single crystal of TMPP of dimension 12x10x4 mm\textsuperscript{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 TMPP were carried out using PANalytical, Xpert PRO powder X-ray diffractometer employing CuK\textalpha{} radiation ($\lambda = 1.5418 \; \text{Å}$) radiation at room temperature with a scanning speed of 1\textdegree{} min and a scanning range of 10 degree to 60 degree. The grown crystals of TMPP were crushed into fine powder and were subjected to powder X-ray diffraction analysis. The lattice parameters were calculated as $a=14.7333 \; \text{Å}$, $b=7.6282 \; \text{Å}$, $c=5.4311 \; \text{Å}$ and $\alpha=\gamma=90^\circ$, $\beta=102.4^\circ$. From this it is clear that TMPP belongs to monoclinic system. The powder X-ray diffraction pattern is shown in Fig-1. Well-defined Bragg peaks obtained at specific 20 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 TMPP 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 TMPP crystal surface to electron beam. The SEM images of TMPP 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 TMPP crystals appears as smooth.

![Fig-2: SEM Images of TMPP](image)

Dielectric Studies
The dielectric constant ($\varepsilon_r$) of a material is generally composed of four types of contribution namely electronic polarization, ionic polarization, orientation polarization and space charge polarizations. At low frequencies, four types of polarizations occur and the total polarization becomes maximum and hence $\varepsilon_r$ is high, and the total polarization value decreases with increase in frequency and become minimum at optical frequency range. As the frequency increases the polarization mechanism one after another is frozen out. The dielectric constant and dielectric loss for TMPP were measured using Agilent 4284-A LCR meter. The dimensions of the samples used were 6x3x4 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 frequencies 100 Hz, 1 kHz and 10 kHz at various temperatures ranging from 40 to 150 $^\circ$C. The dielectric constant of the grown crystals was calculated using the relation-

$$\varepsilon_r = \frac{C_c}{C_a}$$

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 TMPP 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.

SHG Analysis
The Second harmonic generation efficiency of TMPP 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 TMPP. A second harmonic output signal of 64 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 TMPP crystal is 0.8 times that of standard potassium dihydrogen phosphate (KDP). From this it is evident that the TMPP is a good NLO crystal.

CONCLUSION

Single crystals of TMPP have been successfully grown by the slow evaporation technique from aqueous solution. The X-ray diffraction analysis confirmed the monoclinic 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 TMPP crystal is 0.8 times that of standard potassium dihydrogen phosphate (KDP).

REFERENCES