Synthesis, Thermal,Dielectric and Non-Linear Optical Studies of SemiOrganic Pottasium Thiourea Chloride Single Crystal

S.Raju[1*],V.Santhanakrishnan[1],C.Murugesan[2]

[1]Department of Physics,Jaya Engineering College,Chennai,Tamilnadu,India.

[2]Department of Chemistry,Jaya Engineering College,Chennai,Tamilnadu,India.

Abstract

The Semi-organicPottasium Thiourea Chloride (KTC) was grown by slow evaporation method. The structural studiesofKTC single crystal was carried out by using powder X-ray.Thermal Analysis was carried out by Perkin-Elmer thermal analyzer (STA 409 PC) and the DTA trace indicates a strong endothermic peak at 210 °Cdue to the melting of the crystal. Dielectric studies and Complex Impedance analysis made by E4990A impedance analyzer.Kurtz Perry method was employed to find Second harmonic Efficiency of grown KTC single crystals.Good transparency, thermal stability and NLO test suggests Pottasium Thiourea Chloride single crystals can be used for optical applications.

Key words: Crystal Growth, X-ray diffraction,Impedance Analysis, SHG efficiency.

INTRODUCTION

NLO Materials plays a significant role in the emerging era of Photonics. Photonics involves the application of photons for information and image processing. Nonlinear optical processes have applications in vital functions such as frequency conversion and optical switching .The quest for new frequency translation resources over the previous decade has directed to the unearthing of numerous organic NLO materials with high nonlinear susceptibilities. Conversely, their exists insufficient transparency, poor optical quality, lack of robustness, low laser damage threshold and inability to grow to larger size have hampered the use of single crystals of organic materials in real-world presentations in devices.

Hence materials researchers engrossed their consideration on innovative constituents in order to placate the contemporary day technical requirements. In the modern preceding a new group of materials have been urbanised i.e. semi organic crystals. Semi organic crystals have large nonlinearity, high resistance, too large induced damage, low angular sensitivity and good mechanical hardness.

Semi organic NLO crystals are anticipated to own the assistances of both organic and inorganic materials. Current reports have established that organic crystals, can have very huge nonlinear susceptibilities comparative to inorganic crystals and their use is hindered by their low optical transparencies, poor mechanical properties, low laser damage thresholds and poor processibility. In dissimilarity, purely inorganic NLO materials characteristically have exceptional mechanical and thermal properties but often own moderately diffident optical nonlinearities due to their absence of protracted delocalization.

In Semiorganics, polarisable organic molecules are stoichiometrically inevitable within an inorganic host; e.g. an organic ion-inorganic counter ion salt, such as L-arginine phosphate or an organic ligand-metal ion complex, such as zinc tris (thiourea) sulfate (ZTS)[1]. Divulging ionic character to large NLO-response organic molecules via complexation and or salt formation augments the mechanical and optical properties of these materials additional and more renders them fairly flexible for NLO effects. A further advantage of this approach is that Semiorganics are prepared by crystallization from near-ambient temperature solvents. These types of semiorganic NLO crystals are categorised by various polyhedrals with a central metal ion bounded by a number of organic and / or inorganic ligands. They can be expressed as MM'LnL'm, where M, M' stand for different metal ions and L, L' for organic and / or inorganic ligands. The organic ligand (L) is usually more dominant in the NLO effect.

The non-linear optical properties of some complexes of thiourea have fascinated momentous attention in the last few years, because both organic and inorganic components in it donate specifically to the procedure of second harmonic generation. The thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment and its ability to form a widespread network of hydrogen bonds. Some of the potential thiourea complexes are zinc thiourea chloride (ZTC) bis thiourea cadmium chloride (BTCC) and zinc thiourea sulphate (ZTS)[2.]
These crystals have better nonlinear optical property than standard potassium dihydrogen phosphate (KDP).

Organic crystals can have huge nonlinear susceptibilities when compared to inorganic crystals, but exhibit low damage threshold and poor stability [3,4,5,6]. In contrast, pure inorganic NLO materials typically have excellent mechanical and thermal properties, but often possess relatively very low nonlinearities due to their lack of extended electron delocalization.

Inorganic crystals grown from slow evaporation methods may typically have lower laser damage thresholds, and more optical in homogeneities throughout the bulk, due to impurities and defects resulting from the extremely non-equilibrium growth conditions. In order to retain the merits and overcome the shortcomings, some new classes of NLO crystals such as semi organic crystals have been developed. Semi organic crystal is one in which the typically high-optical nonlinearity of a purely organic ion is combined with the favourable mechanical property and thermal properties of an inorganic counter ion[7]. Semi-organic materials possess large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness compared to organic and inorganic materials[8,9]. Hence, much attention has been paid to grow new semi-organic nonlinear optical materials, in view of their potential applications in the field of telecommunications, optical information storing devices and second harmonic generation. The thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment and ability to form extensive network of hydrogen bonds [10].

The optical limiting behavior in thiourea metal complexes was discussed [11]. Some of the reported promising NLO crystals of thiourea complex are zinc tris thiourea sulfate[12], bis thiourea cadmium chloride[13], zinc thiourea chloride [14] and bis thiourea zinc chloride[15].Zinc tris (thiourea) sulfate is a desirable semi-organic nonlinear optical material, which exhibits low angular sensitivity, and is useful for type-II second-harmonic generation[16]. A study on the nucleation kinetics of tris thiourea zinc cadmium sulphate was reported[17]. The thermal and mechanical properties of tris thiourea zinc cadmium sulphate was studied[18] This chapter reports the synthesis and the growth of semi organic nonlinear optical crystal potassium thiourea chlorides by the slow evaporation technique. The grown crystals have been subjected to thermal, dielectric, and second harmonic generation (SHG) efficiency studies.

EXPERIMENTAL

Synthesis

In our present work, potassium thiourea chloride crystals have been grown by the slow evaporation method. Saturated solutions of thiourea with potassium chloride is mixed with thiourea in triple distilled water in the molar ratio of 1:1 as per the equation below for KCl

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

By repeated re-crystallization process the purity of the salts were further increased and the super saturated solutions were kept undisturbed at room temperature. Optically transparent defect free seed crystal was obtained within the period of 15days. Large size single crystals were grown by slow cooling method using a homemade constant temperature bath. The structure of the grown crystals was estimated by the XRD studies which confirm there is a small change in the lattice parameter values of the grown crystals.

Fig.1 Pottasium Thiourea Chloride Crystal

RESULTS AND DISCUSSION

Thermo Gravimetric Analysis

The Thermo Gravimetric Analysis (TGA) of KTC was carried out between room temperature 27 °C and 800 °C at a heating rate of 20 °C per minute and the recorded spectrum is shown in the Fig.2 using Perkin-Elmer thermal analyzer (STA 409 PC). The experiment was performed in nitrogen atmosphere although the TG trace appears nearly straight up to 188.3 °C. The differential thermal analysis (DTA) was also carried out in the same atmospheric conditions (at a heating rate of 20 °C per minute). A careful examination of the DTA curve revealed that, a minor endothermic peak around 210 ºC. A steady decrease in weight (40.76%) up to 245°C can be observed which may be due to the decomposition of the sample.

The DTA trace indicates a strong endothermic peak at 210 °Cdue to the melting of the crystal. Hence from the thermal studies it was inferred that the crystal could retain its texture up to 183.3 °C. It's application can be restricted up to 183.3°C only, which is higher than that of other semiorganic materials like cadmium mercury thiocyanate dimethyl-sulphate CMTD (150 °C), cadmium mercury thiocyanate monomethyl ether CMTG (100 °C), L-alanine cadmium chloride (LACC) (110 °C), triallyl thiourea cadmium chloride (ATCC) (101 °C), triallyl thiourea mercury chloride (ATCB) (133 °C) and allyl thiourea mercury bromide (ATMB) (125 °C). Good thermal stability and high melting point are much desirable for device applications.

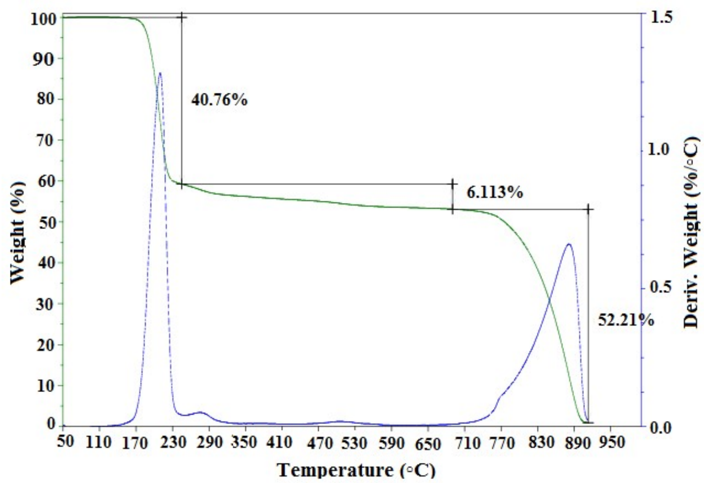

Fig. 2 TGT- DTA Analysis of KTC

Dielectric Studies

The capacitance and conductivity of a material is defined by its dielectric properties. The variation of the dielectric constant against frequency at room temperature for the crystal is shown in Fig. In general, the dielectric constant is higher at the lower frequencies and then decreases with increasing frequency, and remains constant at a higher frequency region. The grown crystals were very thin and in the form of needle so making a parallel plate capacitor structure type is difficult. Hence, for doing dielectric studies the samples were powdered and the capacitor structure was taken in the form of pellet. Measurements were made on the pellet by varying the frequency from 50 Hz to 5 MHz at different temperatures.

Fig.3 shows the variations of dielectric constant and dielectric loss with log frequency. It is found that the dielectric constant of KTC is high at low frequencies and it decreases with increasing frequency and dielectric constant increase with temperature and a similar trend is observed in the dielectric loss as shown in Fig.4. In KTC, at 50 Hz, the value of dielectric constant is found to be around 55 (308 K) and above 10 kHz, the value of dielectric constant remaining unchanged upto 5 MHz. At low frequencies, all the four contributions are active hence higher dielectric constant.

The decrease in dielectric constant with increase in frequency may be attributed to the dependence on the electronic, ionic, orientation and space charge polarizations. In the lower frequency region, dielectric loss is more due to the loss associated with ionic mobility. The low dielectric loss with high frequency implies that the sample possesses good optical quality with lesser defects.

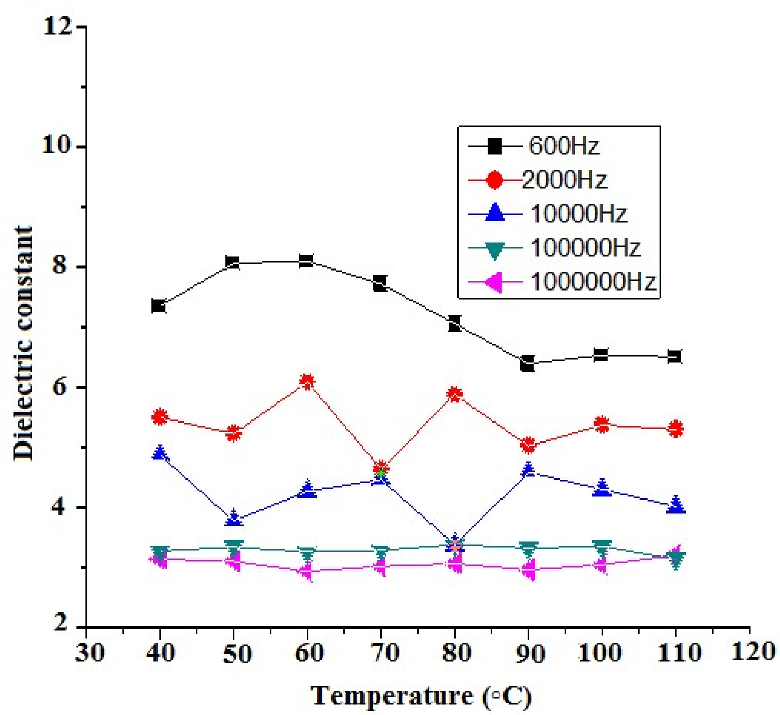

Fig. 3 Dielectric Constant Vs Temperature of KTC

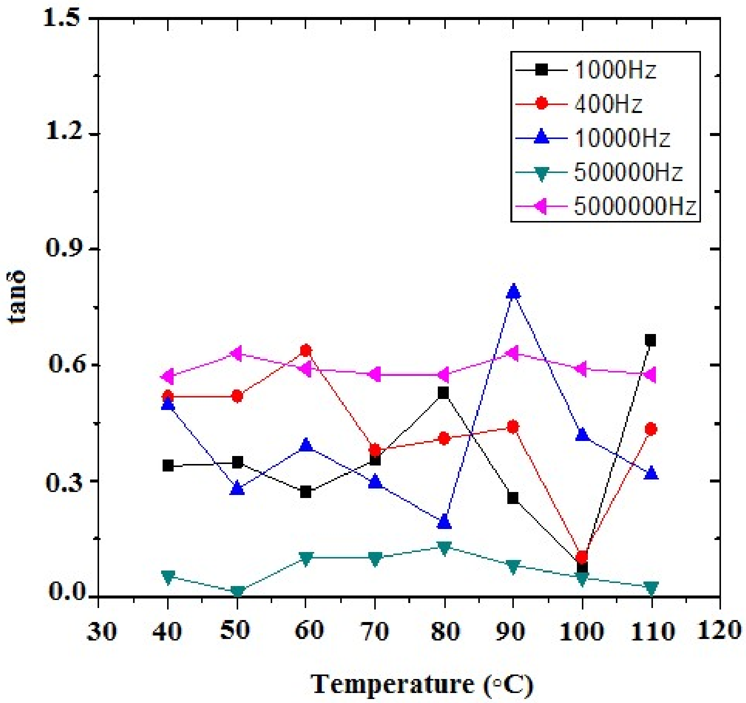

Fig.4 Dielectric Loss Vs Temperature of KTC

Impedance Analysis

For the impedance spectral analysis the grown KTC samples were grounded, as the grown samples were needle shaped and extremely difficult to make that as a parallel plate capacitor, and made into dense pellets and annealed at 60 ºC for 3 hours to remove the moisture and increase the density of the pellet. Silver paste was coated on both sides of the pellet and measurements were made in an impedance analyzer. The measurement was performed for various temperatures and selected data are given in the Fig. 5. In the Fig. 5 the real part of the impedance was plotted against the imaginary part of the impedance value. An ideal Nyquist or Cole-Cole plot might show three semicircles with the contributions from the (1) bulk of the grain (2) grain boundary contribution and (3) Electrode contributions. The experimental spectra clearly show two different semicircles for the KTC sample which might be due to the contributions from grain and grain boundary.

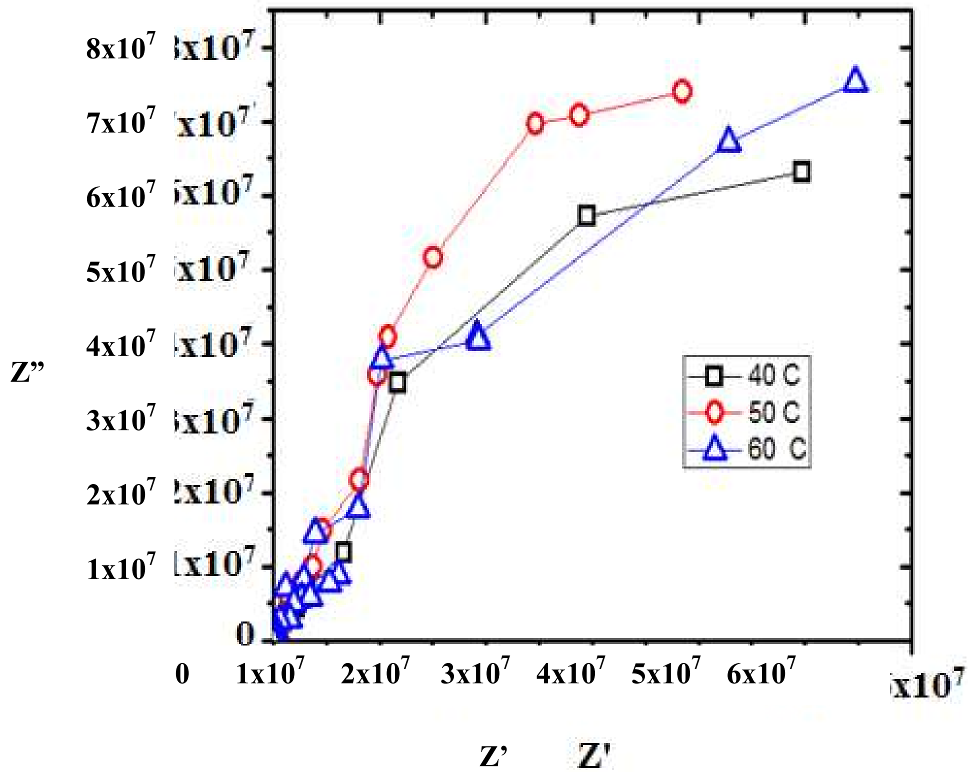

Fig.5 Cole-Cole Diagram of KTC

Nonlinear Optical Test

In order to check the suitability of the grown samples for NLO applications Kurtz Perry method was employed. The wavelength of the fundamental 1064 nm with a spot radius of 1 mm emitted from the Q–switched laser was converted to 532 nm by the KTC powders and switched between quartz plates. It is observed that the powder efficiency of KTC is around 1.9 times as that of the KDP sample which is used as a reference. A Q switched Nd:YAG laser of energy 2.0 mJ/pulse at 1064 nm with a repetition rate of 10 Hz and pulse width of 9 ns was used as a fundamental source of light. The input laser beam was passed through an IR reflector and then directed on the microcrystalline powdered sample packed in a capillary tube of diameter 0.154 mm (Table 1).

Table.1 SHG Studies of KTC

Sl. No.	Name of the Sample	Output power (milli joule)	Input power (Joule)
1	KCl + Thiourea	13.4	0.68
2	KDP (Reference)	8.8	0.68
3	Urea (Reference)	8.9	0.68

The power of the incident beam was measured using a power meter. The transmitted fundamental wave was passed over a monochromator, which separates 532 nm (SHG signal) from 1064 nm and is absorbed by a $CuSO_4$ solution. The green light was detected by a photo multiplier tube and displayed on a storage oscilloscope. The KDP and Urea were used as a reference materials and the SHG relative efficiency of the Pottasium thiourea chloride was found to be 1.9 times higher than that of KDP. The NLO efficiencies of some similar reported compounds were tabulated in table 4.8 of which KTC shows high NLO efficiency.

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