



# Growth and Electrical Studies on Pure and L-Alanine Mixed TTCC Single Crystals

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## ABSTRACT

Single crystals of pure and L-alanine mixed Tetra thiourea copper chloride (LATTCC) crystals were grown successfully by slow evaporation method at ambient temperature. The electrical properties of the grown crystals have been analysed by studying the variation of dielectric constant and dielectric loss with frequency and temperature. It was found that both the dielectric constant and dielectric loss increases with increase in temperature and decrease with increase in frequency. The a.c conductivity increases with increase in temperature and frequency.

**Keywords:** AC conductivity; Crystal growth; Dielectric constant; Dielectric loss; Solubility; TTCC.

## 1. INTRODUCTION

Over past two decades, there has been remarkable interest in growth and characterization of nonlinear optical material crystals (Selvakumar *et al.* 2006a; Revathi and Rajendran, 2012; Ruby and Raj, 2013; Sagadevan and Priya, 2014; Jeyakumari *et al.* 2004). The demand for crystals in developing technology, factories, electronic industry, in the field of Optics, etc. stimulated many advances in crystal growth. Integrated microelectronics and optoelectronics necessities improved crystal growth technology (Barr, 1961).

Among semi-organic NLO materials, the metal complexes of thiourea were identified as potential candidates to replace the conventional NLO crystals in the field of nonlinear optics owing to their superior nonlinear optical properties and low  $\epsilon_r$  values. Thiourea being a naturally centro-symmetric molecule doesn't exhibit NLO properties, however when it forms complexes with metal ions, it exhibit NLO characteristics (Anie Roshan *et al.* 2001). Several interesting results have already been reported on several properties of impurity added thiourea complexes (Sivakala *et al.* 2014; Sivakala *et al.* 2015).

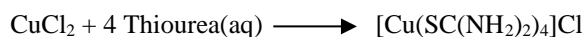
Tetra thiourea copper chloride (TTCC) is one such material. TTCC crystallises in the tetragonal lattice and the unit cell parameters are  $a = b = 13.4082 \text{ \AA}$ ,  $c = 13.8074 \text{ \AA}$ ,  $V = 2482.29 \text{ \AA}^3$ ,  $\alpha = \beta = \gamma = 90^\circ$ . Space group and the number of molecules per unit cell ( $Z$ ) are found to be  $P4_12_12$  and 8 respectively. Most of the amino acids individually exhibit the NLO property. In recent past, the

NLO efficiency of these semi organic crystals were further improved by aminoacid doping.

In the present study, we have grown pure Tetra thiourea copper chloride (TTCC) crystals by slow evaporation technique and mixed L-alanine, the simple amino acid as an impurity in different molar ratios. The electrical properties of the grown crystals are reported herein.

## 2 EXPERIMENTAL METHOD

Tetra thiourea Copper chloride (TTCC) compound was synthesized by the reaction of GR (99 % pure Merck) grade thiourea with Copper (II) chloride dihydrate in stoichiometric ratio 1:4. The calculated quantities of thiourea and Copper (II) chloride salts were dissolved in the mixed solvent of water-ethanol taken in the ratio of 1:1. The synthesized salt was purified by recrystallization process.



Different concentration of L-alanine mixed TTCC single crystals were grown by slow evaporation technique at room temperature by preparing supersaturated solution. The super saturated solution was prepared with the help of solubility curve shown in Fig. 1.

And, the good quality small crystals were obtained by slow evaporation technique. The photograph of the grown crystals are shown in Figure 2.

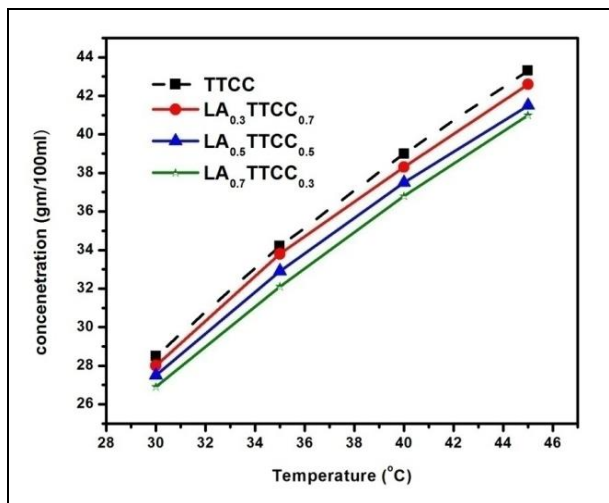


Fig. 1: Solubility curve for pure and L-alanine mixed TTCC.

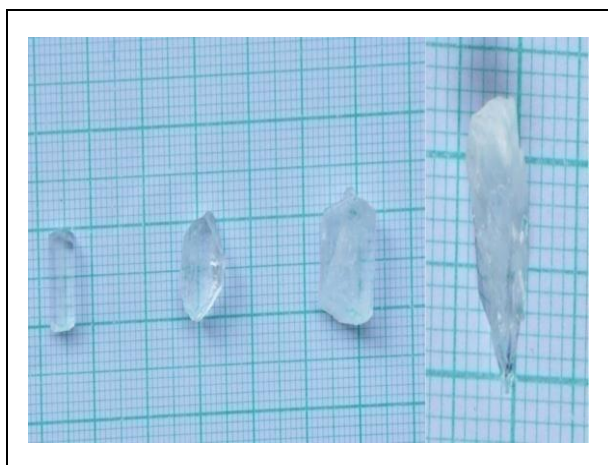


Fig. 2: Photograph of Grown crystals [From Left: TTCC; LA<sub>0.3</sub>TTCC<sub>0.7</sub>; LA<sub>0.5</sub>TTCC<sub>0.5</sub> and LA<sub>0.7</sub>TTCC<sub>0.3</sub>].

### 3. CHARACTERIZATION

Dielectric studies furnish a great deal of information regarding the dielectric constant that arises from the contribution of different polarizations, namely electronic, ionic, atomic, space charge, etc., developed in the material subjected to the electric field variations. All these four polarizations are active at low frequencies. The dielectric characteristics of the material are important to know the transport phenomena and the lattice dynamics in the crystal. It also gives the information about the nature of atoms, ions, bonding and their polarization mechanism in the material. The dielectric analysis is an important characteristics to fetch knowledge based on the electrical properties of the material as the function of frequency and temperature. Based on this analysis the capability of storing electric charges by the material and capability by transferring the electric charge can be assessed. Dielectric properties are correlated with the electro optic properties of the crystal. Dielectric measurements were made following the methods adopted

by Mahadevan and his co-workers (Joseph John and Mahadevan, 2008; Joseph John and Mahadevan, 2007) at various temperatures ranging from 35-150°C with fixed frequency 1 kHz using a Agilent 4284 A LCR meter. The observations were made while cooling the sample. The dimensions of the crystals were measured using a travelling microscope. Air capacitance ( $C_{air}$ ) was also measured. The crystals were shaped and polished and the opposite faces were coated with graphite to form a good ohmic contact. As the crystal area was smaller than the plate area of the cell, the real part of the dielectric constant was estimated using Mahadevan’s relation  $n$  (Joseph John and Mahadevan, 2008).

$$\epsilon' = [A_{air}/A_{cry}][C_{cry} - (C_{air} (1-A_{cry}/A_{air}))/C_{air}]$$

where  $C_{cry}$  is the capacitance with crystal (including air),  $C_{air}$  is the capacitance of air,  $A_{cry}$ , is the area of the crystal touching the electrode and  $A_{air}$  is the area of the electrode. The imaginary part of the dielectric constant ( $\epsilon''$ ) was calculated with the measured dielectric loss factor ( $\tan \delta$ ) using the relation

$$\epsilon'' = \epsilon' \tan \delta$$

The AC electrical conductivity ( $\sigma_{ac}$ ) was calculated using the relation

$$\sigma_{ac} = \epsilon_0 \epsilon \omega \tan \delta$$

Where  $\epsilon_0$  is the permittivity of free space ( $8.85 \times 10^{-12} \text{ C}^2\text{N}^{-1}\text{m}^{-2}$ ) and  $\omega$  is the angular frequency ( $\omega = 2\pi f$ ;  $f$  is the frequency of the applied electric field).

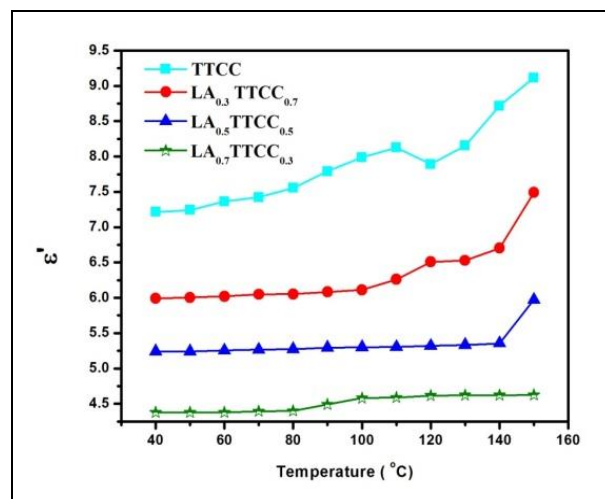


Fig. 3: Variation of  $\epsilon'$  with temperature for pure and L-alanine mixed TTCC single crystals at 1 kHz.

### 4. RESULTS & DISCUSSION

The variations of dielectric constant, dielectric loss factor ( $\tan \delta$ ) and AC and DC electrical conductivity of pure TTCC and different concentration of L-alanine

mixed TTCC crystals at different temperatures ranging from 40 to 150 °C at frequency 1 kHz are shown in Fig. 3-6.

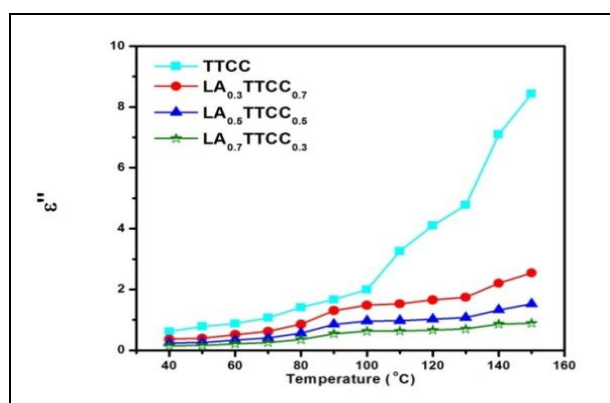


Fig. 4: Variation of  $\epsilon''$  with temperature for pure and L-alanine mixed TTCC single crystals at 1 kHz.

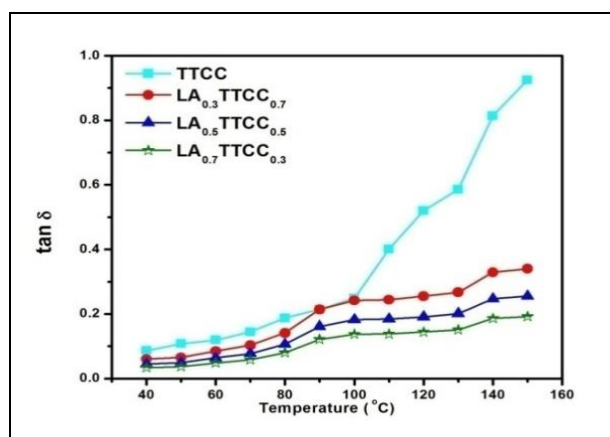


Fig. 5: Dielectric loss measurements at 1 kHz frequency for pure and L-alanine mixed TTCC single crystals.

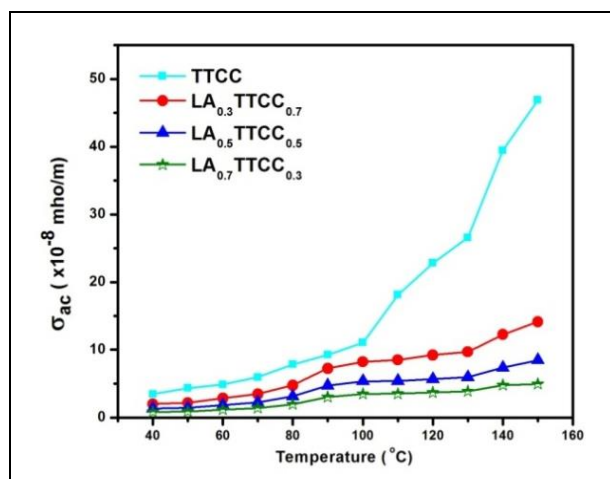


Fig. 6: AC conductivity of pure and L-alanine mixed TTCC mixed crystals at 1 kHz.

The electrical parameters, viz, dielectric constant, dielectric loss and AC electrical conductivities

observed in the present study are increased with the increase in temperature for all the grown crystals. The  $\epsilon_r$  and  $\tan\delta$  values were decreased whereas the  $\sigma_{ac}$  value increased with the increase in frequency of the AC applied for all the crystals considered in the present study. The nature of decrease in  $\epsilon_r$  and  $\tan\delta$  with frequency suggests that the crystals of this work seem to contain dipoles of continuously varying relaxation times. Since the dipoles of larger relaxation times are not able to respond to the higher frequencies, the dielectric constant and dielectric loss are low at higher frequencies. The characteristics of low dielectric loss with high frequency for the sample suggest that it possesses enhanced optical quality with lesser defects and this parameter is imperative for nonlinear optical applications (Balarew and Duhlew, 1984).

From the dielectric studies, it can be noted that in these samples there is a decrease in dielectric constant with increase in frequency and decrease in temperature indicating a normal dielectric behaviour (Anderson, 1964). Variation of  $\epsilon_r$  with temperature is generally attributed to the crystal expansion, the electronic and ionic polarizations and the presence of impurities and crystal defects. The slow variation of  $\epsilon_r$  of at low temperature is mainly due to the expansion of electronic and ionic polarizations. At higher temperatures, the increase is mainly attributed to the thermally generated charge carriers and impurity dipole.

#### 4. CONCLUSION

Single crystals of pure and L-alanine mixed Tetra thiourea copper chloride (LATTCC) were grown by slow evaporation method at ambient temperature. The electrical properties of the grown crystals have been analysed. The dielectric constant and dielectric loss values are directly proportional to temperature and inversely proportional to frequency. Out of four crystals,  $LA_{0.7}TTCC_{0.3}$  has lower  $\epsilon_r$  values. The low  $\epsilon_r$  values observed indicate that these crystals are not only good NLO materials but also promising low  $\epsilon_r$ -value materials finding much importance in the microelectronics industry. The AC conductivity of TTCC crystals are directly proportional to temperature and frequency. Also, L-alanine addition decreases AC conductivity of TTCC crystals.

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#### CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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