

Ocular suitability of Fertilizer (Urea) doped Semiorganic NLO single Crystal: Tri-Glycine potassium chloride

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ABSTRACT

Urea of different percentage in molecular ratios was added to synthesized Tri-Glycine Potassium Chloride (TGPC) and assent to grow for some months to study the behavioral changes of Tri-glycine potassium chloride by the effect of Urea. The grown crystal was first characterized by UV [1] studies and it was analyzed that the transparency was reduced by a blow of fertilizer and a small change occurred in its wavelength and the absorbance range. This research is trying to be authenticating the causes by an impact of Urea on TGPC through the SEM and FTIR studies.

Keywords

Semiorganic, Nonlinear optical, Slow Evaporation, UV, SEM and FTIR.

1. INTRODUCTION

In modern year organic – inorganic mixture materials have attracted huge consideration. In particular, the present fascinating field of research is to synthesize, grow and characterize semi organic NLO crystals. There are so many attempt has been made to synthesize and grow number of NLO semi organic crystals, the discussion from that shows semi organic crystal posses both the good qualities of host organic materials and additive-inorganic material [2].The research with Single crystals of urea thiourea with mercuric chloride, sulphate, semi-organic nonlinear optical materials, having good second harmonic generation. Its UV-Vis spectra showed that the crystals had a wide optical window, no absorbance and good optical transmittance in the entire visible region. The FTIR analysis confirms the presence of functional groups in the grown crystals [3].The research related with amino acid single crystal like glycine with zinc chloride having good application in the field of NLO. [4]

A Single crystal of L-Glycine was grown from aqueous solution by slow evaporation method. The optical properties of the grown crystals were studied using UV-Vis spectral analysis. Optical absorption study reveals the transparency of the crystal in the entire visible region. This shows it has good transparency and the powder X-ray diffraction analysis confirms the crystalline nature [5]. Similarly, the Effect of amino acid (proline) doped on triglycine sulphate has good dielectric properties and also its Curie temperature increases when we doped with inorganic materials [6]. Good, and optical high qualities single crystal of GLO has been grown by slow evaporation techniques, its XRD result confirm that it is a monoclinic crystal and the optical absorption studies infer that the crystal possess very low absorption in the entire visible and IR region. Due to the presence of high transference range, high damage threshold values and high second harmonic efficiency crystal may be used for NLO

application [7]. A research from pure triglycine sulphate (TGS) and LiSO₄-doped TGS crystals were investigated with the help of slow evaporation method. It has good NLO property and electrical conductivity property. It has a good dielectric, microhardness, and thermal characters. And this crystal was found highly transparent and full faced. The direct current conductivity is found to increase with temperature as well as dopants concentrations. Curie temperature remains the same for pure and doped crystals, but dielectric constant and dielectric loss increases with dopants concentration. The experimental result shows the suitability of the grown crystal for optoelectronic applications [8].

Above form the literature review implies that, the commercial use of glycine is, for nuclear magnetic resonance (NMR) spectroscopists, glycine can serve as a standard for checking and calibrating spectrometer performance or utilizing the various isotopic enrichments commercially available for quick implementing and demonstrating a variety of techniques like rotational resonance. In general, the doped tri-glycine potassium chloride has some greater advantage when compared with single TGPC because it overcomes the disadvantage of single TGPC. Such as, ferroelectric domains possess high mobility at room temperature, depolarization by electrical and thermal means and microbial contamination with time during the growth and low Curie point and so on .These are done by adding Suitable impurities to TGPC crystals .This research is trying to enrich the changes in general properties of TGPC by adding Urea fertilizer of different molecular ratios and examined the changes through SEM and FTIR studies. In this investigation the urea acts as an impurity and it influences some changes in the general properties on tri-glycine potassium chloride. Generally triglycine potassium chloride finds some applications in the fabrication of capacitors, transducers and sensors.

2. EXPERIMENTAL

2.1. Synthesis and crystal growth

The Glycine (AR Grade) and Potassium Chloride (AR Grade) were re-crystallized for the needs of purity and good result. After that, the titled Single Crystal was synthesized by taking a molecular ratio of 3 percent of Glycine (Merck) added with 1% of Potassium Chloride (Merck) and it was dissolved in triple distilled water. The pH value of the super-saturated solution is kept at 6.0. The solution was filtered and transferred to a Petri dish for the seed preparation [7]. The fertilizer component named urea is added by considerable molecular ratio (3:1:1) (0.62589g: 0.20718g: 0.1669g) with TGPC and once again it is dissolved with triple distilled water and transferred into a Petri dish for crystallization. The sample of seeds is suspended in the 500ml beaker that contains same supersaturated solution and placed lonely for some days for

the growth process. The harvested grown crystal was taken and grained finely for Character studies.

3. CHARACTERIZATION

The grown crystals were harvested and grained finely for studying its characterizations. The optical activity of urea doped tri-glycine potassium chloride was investigated by UV-Vis spectrometer and its functional groups analysis were taken by FT-IR investigation and also the grain size of titled crystal was taken by SEM studies.

4. RESULT AND DISCUSSION

4.1. UV-Vis Studies

The optical activity of titled crystal was studied by UV-Vis spectrometer. UV absorption, Reflection and transmission studies were carried out by the spectrometer. The comparison graphs were plotted for each recorded value by the use of Origin 6 software [1]. The investigation result implies that, the transmission wave length appears from 195 nm to 200nm and absorption wave length lies at zero line. This is the basic qualification of NLO materials and therefore it may be used for optical applications. The comparison graphs[Fig-1,2] of UV absorption, Reflection, transmission shows that, there is a change in intensity by doping Tri-glycine potassium chloride with Urea but there is no modulations in the wave lengths.

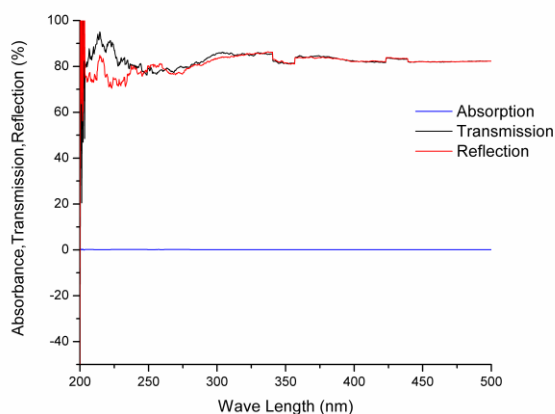


Fig. 1. UV-Vis graph of Tri-Glycine Potassium chloride without Urea doped

4.2. FTIR studies:

The grown crystals were subjected to FT-IR analysis. The sample prepared with KBr in the form of pellets. The FT-IR spectrum of tri-glycine potassium chloride was recorded in the region 4000-400 cm^{-1} employing Shimadzu IFS 66V spectrometer [Fig-3, 4].

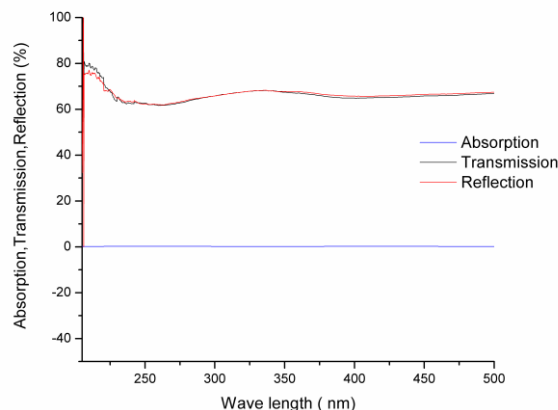


Fig.2. UV-Vis graph of Tri-Glycine Potassium chloride doped with Urea

4.2.1. FTIR studies for TGPC without Urea doped

4.2.1.1. O-H Bonding

Carboxylic acids can bond intermolecularly with solvent that are proton accepter, then the FT-IR spectra falls in such solvent band near 3100 cm^{-1} . This is due to O-H bonding. Similarly, in the FT-IR spectral line of TGPC single crystal, a line appears at 3105 cm^{-1} . Therefore, a carboxylic acid in amino acid group intermolecularly bond with proton accepter solvent, which is potassium chloride.

4.2.1.2. NH_3^+ Stretching Vibrations:

The broad envelope in the high energy region between 3100 cm^{-1} and 2600 cm^{-1} occurs in FT-IT spectrum indicates that, there is NH_3^+ stretching vibrations presented in the sample and also the region of absorption bands extends to about 2000 cm^{-1} due to multiple combination and overtone bands. The FT-IR spectrum of Tri-Glycine potassium chloride sample having spectral strong band between 3105 cm^{-1} and 2608 cm^{-1} . Hence, these lines prove that NH_3^+ stretching vibrations are presented in the sample. And this region also extent up to 2169 this is due to the prominent band near 2000 cm^{-1} and 2200 cm^{-1} may be assigned to a combination of the asymmetrical NH_3^+ bending vibrations and torsional oscillation of the NH_3^+ group. The NH_3^+ stretching region shows broad bands characteristics of hydrogen bonding^[11].

4.2.1.3. Torsional Motion of NH_3^+ :

In amino acid group the torsional motion of NH_3^+ groups appears near 500 cm^{-1} . This is due to N-H stretching vibration. Here, the spectrum of TGPC having a normal spectral line exactly at the wave number of 505 cm^{-1} . Therefore, the specimen TGPC having NH_3^+ torsional motions. This is due to NH_3^+ stretching vibration.

4.2.1.4. C-N stretching vibration:

Weak to medium intensity bands for un conjugated C-N bond in primary, secondary and tertiary aliphatic amines occurs in the region of 1000 cm^{-1} to 1250 cm^{-1} . They are due to coupled C-N stretching mode. This depend the nature of the amine and substitution on the alpha carbon atom. Therefore the spectral line for C-N stretching vibration occurs at the wave number of

1075 cm^{-1} . Similarly, The TGPC having a Normal peak wave number at 1043 cm^{-1} .

4.2.1.5. NH_2 Wagging:

Theoretically NH_2 wagging occurs at a broad absorption at approximately 800 cm^{-1} . Here the small broad band occurs near 890 cm^{-1} . This is due to NH_2 stretching vibrations. The above discussions, observed, calculated FTIR frequencies and its assignments are given in table 1.

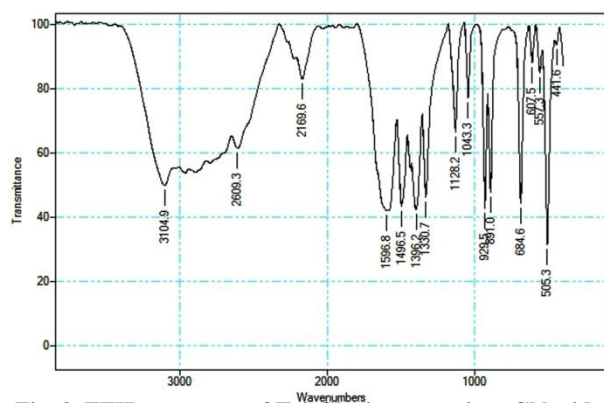


Fig. 3. FTIR spectrum of Tri-Glycine potassium Chloride without Urea doped

Table 1. Observed [9] and calculated FTIR frequencies (cm^{-1}) and assignments for Tri-glycine potassium chloride without Urea doped.

Obs. frequency (cm^{-1})	Cal. frequency (cm^{-1})	Assignment of vibration
3200	3105(W)	O-H –Stretching
3100-2600	3105 - 2608(W)	NH_3^+ - Stretching
2200-2000	2169(S)	NH_3^+ asymmetric bending and torsional
1550 – 1480	1583 – 1495(W)	NH_3^+ Symmetric bending
1300-1500	1495,1396,1330, (W)	Carboxylate anion stretching
1075	1043(N)	C-N stretching ^[10]
Above 800	890(W)	NH_2 wagging
800-650	890-685(W)	N-H bending
775	685(W)	C-Cl stretching
500	505(W)	Torsional mode

*W-weak: S-strong: N-normal

4.2.2. FTIR study of TGPC doped with Urea

4.2.2.1. Hydrogen stretching vibration

Carboxylic acids can bond intermolecularly with solvent that are proton acceptor, then the FT-IR spectra measured in such solvent band falls near 3600 cm^{-1} . This is due to Hydrogen bonding. Similarly, in the FT-IR spectral line of Urea doped TGPC single crystal, a line appears at 3606 cm^{-1} . Therefore, a carboxylic acid in amino acid group intermolecularly bond with proton acceptor solvent, which is potassium chloride.

4.2.2.2. N-H Stretching vibration

The spectrum of urea complex interprets very similar to those of the amino complexes. If bonding of urea to a metal occurs through oxygen, this may result in decrease of the C=O stretching frequency due to higher contribution, but no appreciable change in the N-H stretching mode. This may be due to the fact that in free urea, the N-H bond is involved in intermolecular hydrogen bonding in the solid state. C-N stretching frequency increases considerably. In general N-H stretching occurs at 3400 cm^{-1} to 3600 cm^{-1} . Here, the spectral lines of urea doped TGPC appears at 3417 cm^{-1} is of very high intensity.

4.2.2.3. C-C Ring stretching vibration

Generally the skeletal vibration involving in C-C ring Stretching observed in the range of 1400 cm^{-1} to 1500 cm^{-1} . When we doping urea with tri-glycine potassium chloride, there are two peaks appears very near to each other in the region of 1405 cm^{-1} and 1494 cm^{-1} . This confirms that there is a strong C-C ring stretching invoked in these ratios.

4.2.2.4. C-H out of plane bending vibration

The C-H out of plane bending vibration of Tri-glycine potassium chloride occurs due to the isolated hydrogen atoms existing in that sample. Generally the spectrum occurs in the region between 650 cm^{-1} and 1000 cm^{-1} . This FTIR spectrum of TGPC having two spectral line in this region such as 687 cm^{-1} and 859 cm^{-1} . This shows that it has C-H out of plane bending vibration one has near 1000 cm^{-1} having high intensity and other having medium intensity which is near to 650 cm^{-1} region.

4.2.2.5. N-H bending vibration

The N-H bending band of medium intensity occurs very near to 650 cm^{-1} to 800 cm^{-1} . The urea doped Triglycine potassium chloride spectrum occurs at 687 cm^{-1} . This is because of N-H bending vibration and also the impact of urea on TGPC.

4.2.2.6. C-O stretching vibration

If the compounds contain polar groups then the peaks appear very near in the region at 1000 cm^{-1} to 1300 cm^{-1} . TGPC doped with urea has the spectral line at 1025 cm^{-1} . It shows that there is a C-O stretching vibration presented in this sample. The above discussions, observed, calculated FTIR frequencies and its assignments are given in table 2.

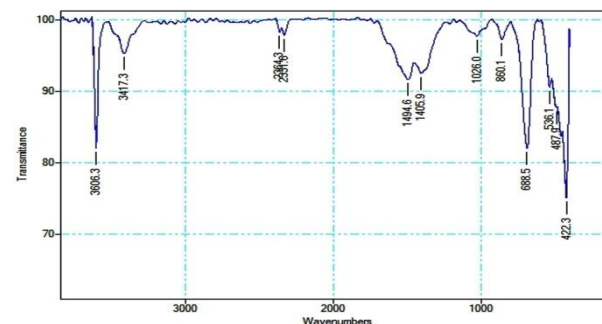


Fig.4. FTIR spectrum of Tri-Glycine potassium Chloride doped with Urea

Table: 2. Observed and calculated FTIR frequencies (cm^{-1}) and assignments for Tri-glycine potassium chloride doped with urea.

Observed frequency (cm^{-1})	Calculated frequency (cm^{-1})	Assignment of vibration
3600	3606 (W)	Hydrogen bonding
3400-3600	3417(S)	N-H Stretching ^[10]
1494-2331	1494-2331(S)	Can not identify
1400-1500	1405-1494(N)	C-C Stretching
1000-1300	1025(S)	C-O stretching
1000-650	859(S)	C-H out of plane bending
1000-650	687(N)	C-H out of plane bending
800-650	687(N)	N-H bending
775	536-400(N)	Can not Identify

*W-weak: S-strong: N-normal

4.3. SEM Analysis

The SEM images for urea doped and without doped triglycine potassium chloride was investigated by scanning electron microscope. For undoped urea with potassium chloride the grain size appears between 2 micro meters and 5 micro meters [Fig.5], but when it is doped with Urea the grain size may start to reduce nano meter range. This is visible in the SEM photographs [Fig.6].

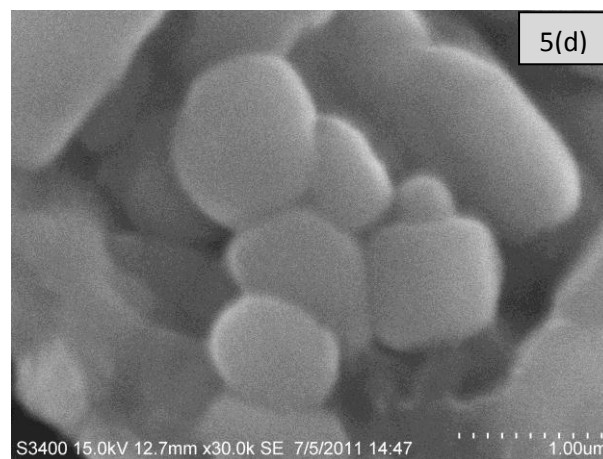
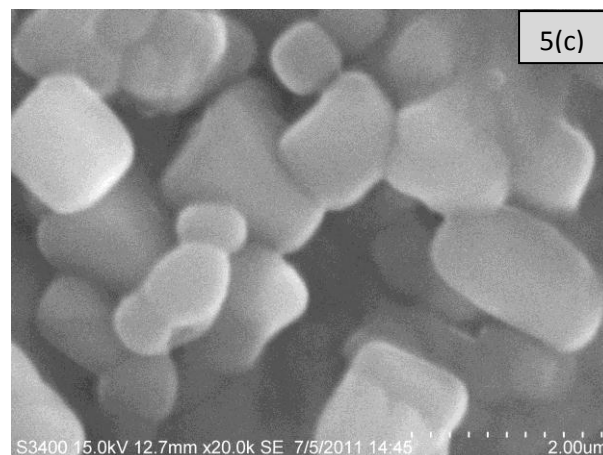
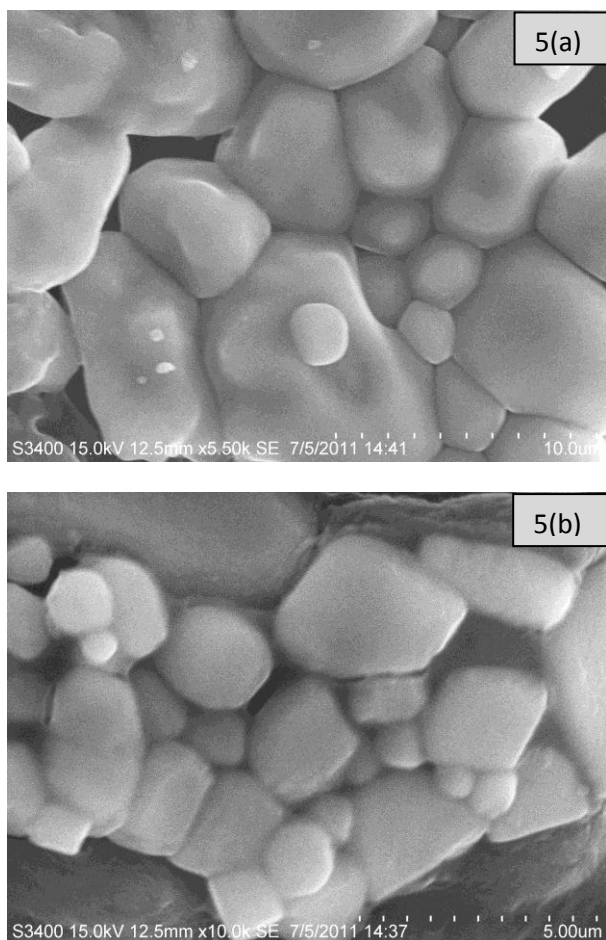


Fig.5. SEM images of TGPC without Urea doped

5. CONCLUSION

The Non Linear Optical Semiorganic urea doped, undoped Triglycine potassium chloride single crystal was grown by slow evaporation techniques. Its optical application was investigated by UV, FTIR, SEM studies. This investigation confirms that the crystal having good transparency when compared with urea doped crystal. Though it has slight variation in transparency, it can be used in NLO applications. Because there is no absorption peaks appears in its UV studies. This is the basic principle to study NLO properties. The functional groups were analyzed by its FT-IR Spectrums. It shows that, without urea doped titled crystal having no potassium chloride frequencies. Cause is that may be triglycine acting as a capping agent. But doping with urea glycine releases the KCl and absorbed Urea with in it. This result is having good agreement with and confirms by the investigation of SEM studies. And also adding Fertilizer in to titled crystal, its character gets some changes and also the grain size may be converted in to nano size.

6. ACKNOWLEDGEMENT

Author would like to thank Dr.A.Ravichandran, the Principal, Christ college of Engineering and Technology, Puducherry, for providing lab facilities and also additional bear and guidance. The author wish to thank Dr.Thilak Kumar, Professor of physics, Periyar Arts and Science, Cuddalore and

Dr.A.Christy Ferdinand, Professor of physics, St.Joseph's college of Arts and Science, Cuddalore for the writing up of FTIR characterization. And finally would like to express his sincere thanks to A.S.Manikandan, T. Thirumazhisai and A. Martin Joseph, the professor of physics, Christ college of engineering and technology, Puducherry for giving more encouragement and done the first review in this research.

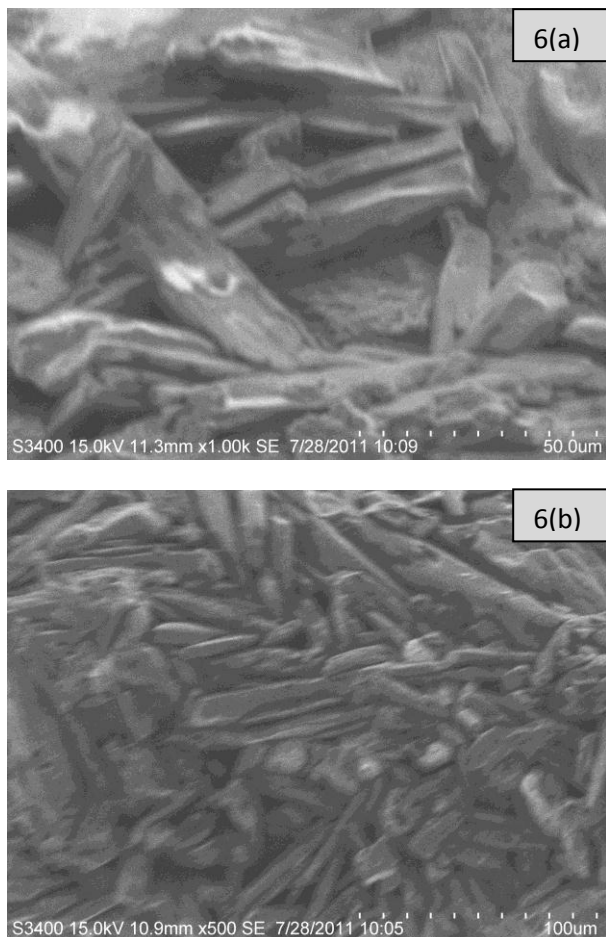


Fig.6. SEM images of TGPC doped with Urea

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