Sciencia Acta Xaveriana
An International Science Journal
ISSN. 0976-1152

Volume 7
No. 2
pp. 69-80
September 2016

GROWTH AND CHARACTERIZATION STUDIES OF GLYCINE ZINC CHLORIDE A SEMI ORGANIC NLO SINGLE CRYSTAL

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Abstract: Non-linear optical materials find wide range of applications in the fields of optoelectronics, fiber optic communication, computer memory devices etc. Tris-Glycine Zinc Chloride (TGZC) is one of the NLO materials exhibiting more efficiency. In the present study Tris-Glycine Zinc Chloride was grown using slow evaporation technique. Single crystal X-ray diffraction analysis revealed that the crystal belongs to orthorhombic system with the space group Pbn21. The optical absorption study was showed that the crystal is transparent in the entire visible region with a cut off wavelength of 210 nm. The optical band gap was found to be 4.60 eV. Various functional groups present in the material were identified by FTIR analysis. The dielectric study was showed that the dielectric constant and dielectric loss decreases exponentially with frequency at different temperatures.

1. Introduction

Non linear optical materials are known as high level of signal processing, which are required for the applications of optical communication [1-2]. A common and often productive route to organic materials has been to utilize molecules with electron donating and accepting moieties attached to a conjugated system. The optical response of an SHG active material is influenced by both the chemical purity and structural composition of the bulk sample [3]. A variety of both organic and inorganic nonlinear crystals have been proposed in the past fifteen years some of them having even reached the level of development and industrialization [4-5]. Inorganics are highly resistant owing to their ionic or covalent nature of their intermolecular bonding, while their figure of merit reaches a plateau exemplified by KTP [6] which may well be a ceiling. In contrast while organic materials are often more fragile their nonlinearity may surpass by several orders of magnitude than that of inorganic materials owing to the possible involvement of highly polarizable π-electron system. Moreover, the structural flexibility of organic molecules and the possibility of precise and adequate organic syntheses assisted by predictive molecular engineering rules may well be a decisive fascinating asset of organics in contrast to the more rigid nature of minerals [7]. The thermal and mechanical stabilities of these organic crystals are not convenient for industrial applications as a frequency doubler of high mean power. In order to improve on these drawbacks, a new type of hybrid organic- inorganic crystal was proposed in 1991 [8]. This crystal engineering provides salts with large nonlinear responses and enhanced stabilities compared to the corresponding molecular organic crystals. Moreover, they exhibit a wider transparency range and bulky crystal morphologies [9- 10]. In this research article XRD, FTIR, optical and electrical properties of the grown single crystal of TGZC are reported and verified with reported work.

2. Experiment

2.1 Crystal growth

Glycine and zinc chloride were taken in the ratio of 3:1 and dissolved in distilled water using magnetic stirrer for six hours to get homogeneous solution. The reaction between glycine and zinc chloride is as given below,

$$3C_2H_5NO_2 + ZnCl_2 \rightarrow (C_2H_5NO_2)_3ZnCl_2$$

The as prepared saturated solution was filtered and kept in a constant temperature bath maintained at 45 °C for slow evaporation of solvent. The single crystal of tris-glycine zinc chloride was grown in a period of 30 days of dimension (13mm x 7mm x 3.3mm). The as grown crystal of tris glycine zinc chloride crystal is shown in Fig.1.

Fig.1. TGZC single crystal from slow evaporation method

3. Results and discussion

3.1 XRD analysis

The well grown tris glycine zinc chloride single crystal was subjected to single crystal X-ray diffraction analysis in order to determine the lattice parameters. It was found that the crystal has the lattice parameters a=11.189 Å, b=15.192 Å, c=15.496 Å with volume about 2634.1 $Å^3$. The crystal is belongs to orthorhombic primitive system. The obtained lattice parameters are given in Table-1.

Formula	System	Space Group	a (Å)	b (Å)	c (Å)	V(Å3)	α = β = γ
$(C_2H_5NO_2)_3ZnCl_2$	Orthorhombic	Pbn21	11.189	15.192	15.496	2634.1	90°

Table-1 Unit cell parameters of tris glycine zinc chloride single crystal

3.2 FTIR

The FTIR Spectra of the as grown TGZC crystals were recorded in the KBR phase in the frequency region 400-4000 cm^{-1}. The recorded FTIR spectrum is shown in Fig.2 and was compared with the standard spectra of the functional groups. The characteristic peak at 1520 cm^{-1} is due to COO stretching. The very broad peak at 3199 cm^{-1} is due to O-H stretching. The strong band at 1134 cm^{-1} established the presence of C-N stretching. The band 2694 cm^{-1} represents the existence of CH_2 stretching and the peak at 1637 cm^{-1} represents C=O stretching and 1610 cm^{-1} represents NH_2 deformation. The wave number assignment for the functional groups present in TGZC is tabulated in Table 2.

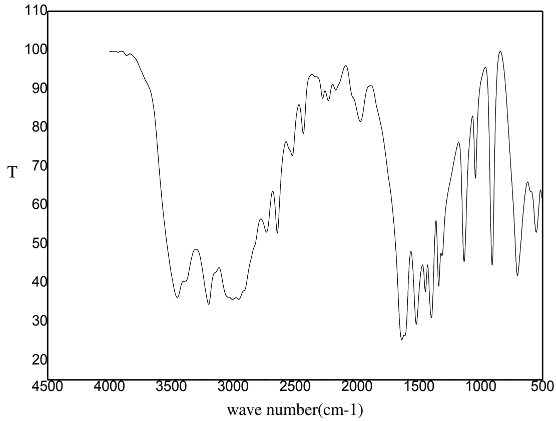

Fig.2 FTIR Spectrum of TGZC NLO single crystal

WAVE NUMBER	ASSIGNMENTS
1520	COO^{-} Stretch
1610	NH_2 deformation
1637	C=O Stretch
2694	CH_2 Stretch
3199	O-H Stretch
1134	C-N Stretch

Table-2 FTIR Spectral data of NLO single TGZC

3.3 ULTRA VIOLET TRANSMISSION STUDIES

A good optical transmission is desirable for NLO crystal. To determine the optical transmittance range and hence to find the suitability for the application of optical device, the grown crystal was analyzed by UV-Visible spectral analyses. The absorption spectrum is recorded in the wavelength range of 190-1100 nm using SHIMADZU MODEL UV 1650 PC Spectrophotometer. It is clear from the spectrum, that the crystal is highly transparent in entire visible region, confirmed by very low absorbance. UV cut off of the crystal is found to be 210 nm which is one of the desirable properties of the materials possessing NLO activity [14, 15] The plot of variation of $(\alpha h\nu)^2$ versus hv is shown in the Fig.4 and the band gap of tris-glycine zinc chloride crystal is found out to be 4.6. As a consequence of wide band gap, the grown crystal has large transmittance in the visible region [16].

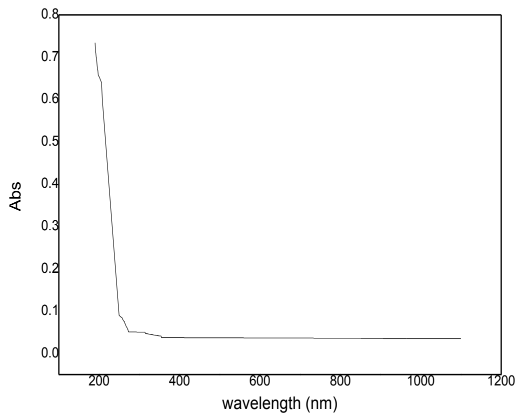

Fig.3 UV-vis-NIR Absorption spectrum of NLO single crystal

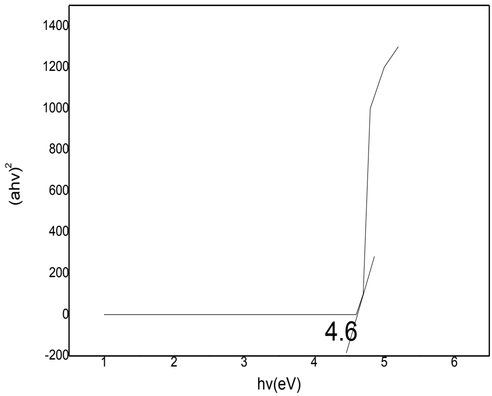

Fig.4 Tauc's plot of TGZC NLO single crystal

3.4 DIELECTRIC STUDIES

Dielectric constant and loss measurements with respect to frequency were measured and are shown in Fig.5 and 6 respectively. From the graph, it is observed that the dielectric constant and dielectric loss decreases slowly with frequency and attains saturation at higher frequencies. The dielectric constant of material is due to the electronic, ionic, dipolar and space charge polarization [17]. The lower value of dielectric constant at higher frequencies is a suitable parameter for the enhancement of SHG. The variation of dielectric constant is due to incorporation of metal ions inside tris-glycine zinc chloride crystal lattices and also, the characteristic of low dielectric loss with high frequency for the sample suggests that the crystal possesses enhanced optical quality with lesser defects and this parameter plays a vital role for the construction of devices for non-linear optical materials.

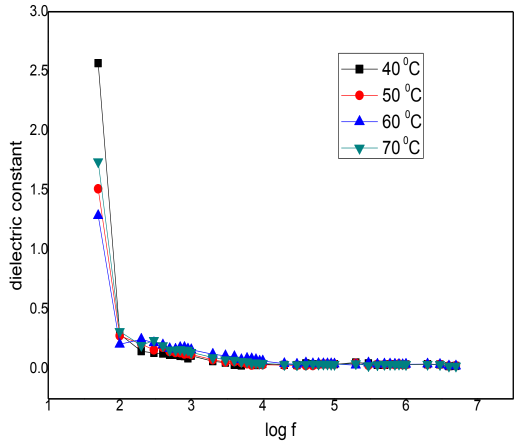

Fig.5 Dielectric constant TGZC NLO single crystal

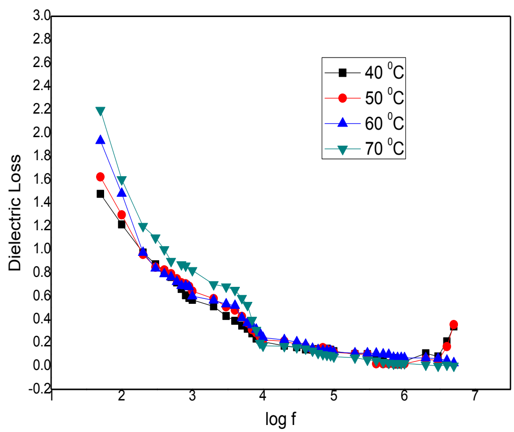

Fig.6 Dielectric loss TGZC NLO single crystal

CONCLUSION

The Tris-glycine zinc chloride $(C_2H_5NO_2)_3ZnCl_2$ is one of the semiorganic NLO materials. Good quality single crystal of TGZC was successfully grown from aqueous solution by slow evaporation technique at a constant temperature of 45 °C. The grown crystals were subjected to single crystal XRD studies which confirm the crystalline nature and crystal structure. FTIR spectral analyses confirms the presence of functional groups of the crystal. UV-visible study determines the optical absorption of the TGZC single crystal. The optical band gap is found to be 4.60 eV. Dielectric studies on the grown crystal shows that the dielectric constant and dielectric loss decreases with frequency and attains saturation at higher frequencies. In future, attempts will be made to grow bulk single crystals of TGZC and also the inclusion of suitable dopants will be identified. Characterization such as SEM and Etching will be carried out to study the perfection of the crystal.

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