Growth & Characterization of ZINC (Tris) Thiourea Sulphate (ZTS) Single Crystals

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Abstract-ZTS is a potential semiorganic nonlinear optical (NLO) material.Single crystal ZTS is grown by slow evaporation method but ZTS seed was grown by Gel technique. As seed is grown by Gel technique the quality of crystal is good, transparency is better and morphology is also differ from ZTS crystal completely grown by slow evaporation method. In the present study of Single crystals of pure zinc tris-thiourea sulfate (ZTS) were grown by the slow evaporation solution growth method at a constant temperature (~36^{0}C). The qualitative analysis is study from the Fourier transform infrared spectroscopy

Key words: Solution growth ZTS, second harmonic generation (SHG),nonlinear optical (NLO) crystal, Fourier transform IR spectroscopy (FTIR)

INTRODUCTION

Zinc tris-thiourea sulphate (ZTS) is a well-known nonlinear optical (NLO) crystal having 1.2 times more second harmonic generation (SHG) efficiency than that of potassium dihydrogen phosphate (KDP).

ZTS is prepared by reacting zinc sulfate and thiourea in a 1:3 molar ratio. It crystallizes in an orthorhombic crystal system with space group PCa21. It also has better optical nonlinearity, excellent transmission and good mechanical strength as compared to many NLO materials. Due to the demand for reasonable crystal size, better NLO, thermal, mechanical, and optical properties in optoelectronic and SHG applications, continuous efforts are being made to modify the properties of ZTS crystal by adding different impurities and/or modifying growth parameters.

Ushasree et al have studied the variation of growth rate with a wide range of pH values and the effect of pH on the different properties of ZTS. Moitra and Kar et al have tried to grow large-sized crystals by lowering the temperature at different rates. Iyanar et al have grown bulk ZTS single crystals unidirectionally along the [100] direction by the Sankaranarayanan–Ramasamy (SR) method.

Variation in the thermal stability and SHG efficiency of ZTS by adding KI, NaCl, KCl, and LiBr has been reported. These were grown from aqueous solution by the low temperature solution growth (LTSG) method and by adopting the slow evaporation of solvent technique. These crystals were subjected to Fourier transform infrared (FT-IR) spectroscopy for measurement.

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Method and preparation

Growth of ZTS from aqueous solution - The growth of Zinc (tris) thiourea sulphate crystals can be explained as follows

The crystal grown using 99% pure chemical of Zinc sulphate, Calcium sulphate and thiourea: for crystal growth, aqueous solutions of molecular proportion of thiourea and zinc sulphate and thiourea and calcium sulphate in the molar ratio of 3:1 were reacted under continuous stirring at room temperature (~36^{0}c) according to final reaction

$$ZnSO_4 + 3CS(NH_2)_2 = Zn[CS(NH_2)_2]_3SO_4$$

The ZTS compound so obtained was dissolved to saturation in distilled water at room temperature and the solution was left in beaker.

Here in the case of ZTS the seed is prepared by gel growth technique by "**Dr. Kiran Rathod**" PhD student under "**Dr I. B. Patel**" from "**VEER NARMAD SOUTH GUJRAT UNIVERSITY**". ZTS crystals were grown by slow evaporation at room temperature (~36^{0}C).

For the growth process, pure grade chemical were used. The aqueous solution of zinc sulphate and thiourea were prepared in distilled water in the molecular ratio of 1:3.

The obtained crystal is as shown in photograph below:

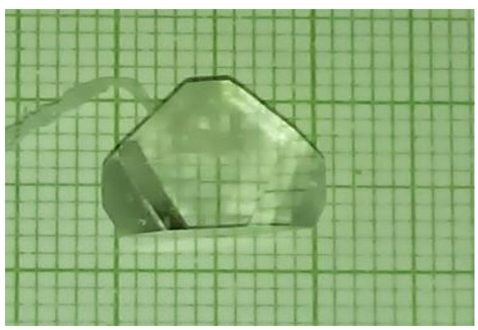

Figure -1 ZTS single crystal

FTIR

The thiourea crystal exhibits the bands in the region 400-750cm^{-1},1050-1150cm^{-1}and 1300-1650cm^{-1}.These bands are arises due to the strong coupling between C=S,C-N and partial (NH_2) vibrations, respectively. In the case of ZTS the very strong vibrational lines observed at 711 and 1397cm^{-1} in FTIR spectrum are due to the CS symmetric and asymmetric stretching vibration modes, respectively. The strong peak at 1021 and 1397cm^{-1} have been assigned to CN symmetric and asymmetric stretching vibrational modes. The intense peak at 1622cm^{-1} is due to N-H bending vibrations. The asymmetric NCN bending is observed at 471 cm^{-1}.

Wavenumber(cm^{-1})		Assignment
Thiourea	ZTS	
469	471	symmetric NCS bending
740	711	C=S symmetric stretching vibration mode, C-Cl stretching vibrations
	946	C-H bending (Alkene, disubstituted, trans)
1089	1021	C=N symmetric stretching vibration mode, S=O stretching vibrations(sulfoxides)
	1118	C=S stretching vibrations
1417	1397	C=S asymmetric stretching vibration mode, Sulfites
	1507	C-NO, Nitroso compounds,C-NO_2 , nitro compounds
1627	1622	N-H bending vibrations,-N=N- stretching vibrations
	3196	N-H stretching vibrations, secondary, bonded; one band
3100-3300	3396	Imines(=N-H); one band

Table-1

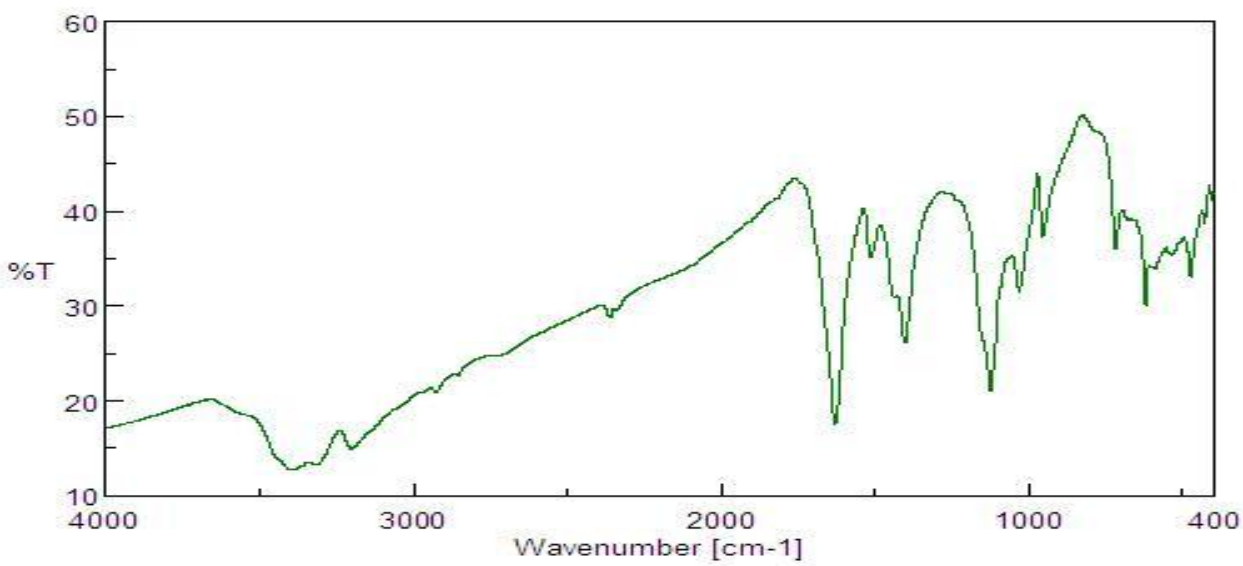

Figure 2 –FTIR of ZTS single crystal

RESULT

Single crystal ZTS is conveniently grown by employing slow evaporation technique. The transparency of the grown crystal is good enough in comparison with the crystal grown by the other technique. The measured density of ZTS crystal is 0.9918gm/cm^3.The FTIR studies revealed the shifting of CS stretching (1397cm^{-1}) of thiourea to lower values and thereby ascertains the coordination of sulphur with metals.

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