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Growth and Studies of Halides doped Zinc Tris-Thiourea Sulphate (HZTS) Crystals

P. Suveetha*, T. Sathya, S. Sudha, M.B. Jessie Raj

P.G. and Research Department of Physics, Bishop Heber College (Autonomous), Tiruchirappalli – 620 017. TN, India.

*Corresponding Author, E-mail: suveetha89@gmail.com

Abstract: Single crystals of Sodium chloride and Potassium iodide (Halides) doped Zinc tris-thiourea sulphate (ZTS) were grown from low temperature solution growth technique by slow evaporation method using water as solvent. The powder X-Ray diffraction pattern were recorded and indexed. The UV transmittance spectrum has been recorded. The optical band gap was estimated using Tauc's plot. The TGA/DTA studies show the thermal properties of the crystals.

Keywords: Crystal growth, powder XRD, UV, TGA-DTA.

1. Introduction

Zinc tris-thiourea sulphate (ZTS) is a promising semi-organic non-linear optic (NLO) material for second hormonic generation from metal complexes of thiourea. ZTS possesses 1.2 times more nonlinear efficiency than KDP [1], [2], [3]. The effect of several dopants on structural and physical properties of metal complexes of thiourea and potassium dihydrogen phosphate (KDP) has been reported [3], [4], [5]. ZTS is a novel metal organic crystal with potential application in electro-optic modulation. It belongs to the orthorhombic system with the space group Pca21 (point group mm2) [2], [3]. Although the crystal growth, kinetics and characterization of ZTS have been extensively investigated [6], [7], [8], a systematic investigation of the effect of halides in the growth medium of ZTS single crystals has not been reported. The present work, Sodium chloride and Potassium iodide added ZTS were synthesized and bulk crystals were grown by slow evaporation method. Also the grown crystals have subjected to various characterizations such as powder XRD, optical absorption study (UV) and thermal studies of TGA/DTA.

2. Experimental

2.1. Synthesis and crystal growth

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Undoped ZTS was synthesised according to the reaction

$$ZnSO_4+3CS(NH_2)_2 \rightarrow Zn\,[CS\,(NH_2)_2]_3SO_4$$

Analytical reagent (AR) grades thiourea and zinc sulphate in the molar ratio 3:1 were dissolved in triply deionised water and it was mixed using a magnetic stirrer.

To synthesis sodium chloride and potassium iodide doped ZTS, sodium chloride and potassium iodide was added to the solution of ZTS separately. These solutions were stirred thoroughly for 2 hours and filtered by Whatmann filter paper. The supersaturated solutions are prepared, then single crystals of NaCl and KI doped ZTS crystals were grown by slow evaporation techniques at room temperature. Single crystals of NaCl and KI doped ZTS were grow about 8-10 days and reach their optimum size in 20 days.

3. Material Characterization

The grown crystals are confirmed by Rigaku x-ray diffractrometer with cukα (λ=1.5418Aº) radiation. The optical property of the title compounds have been assessed by using LAMBDA-35 UV spectrometer. In order to estimate the thermal behaviour, thermo gravimetric analysis and differential thermal analysis of NaCl and KI doped ZTS.

4. Result and Discussions

4.1. Powder x-ray diffraction

The samples were scanned for 2Θ value from 0 to 80º at a rate of 2º /min. The crystal structure of ZTS was reported by [9], [10].

X-ray diffraction patterns of NaCl doped ZTS and KI doped ZTS crystals were shown in Fig.1&2. The appearance of sharp and strong peaks confirms the good crystallinity of the grown samples. The characteristic peaks have appeared at around 32º and 27.6º (2Θ) in NaCl doped crystals, and at around 25.5º (2Θ) in KI doped crystals, shift in the peak position (2Θ) may be due to change of dopant NaCl and KI in ZTS crystal lattice. The crystalline perfection of the ZTS-NaCl as well as ZTS-KI crystals are extremely good without having any internal structural grain boundaries and mosaic nature.

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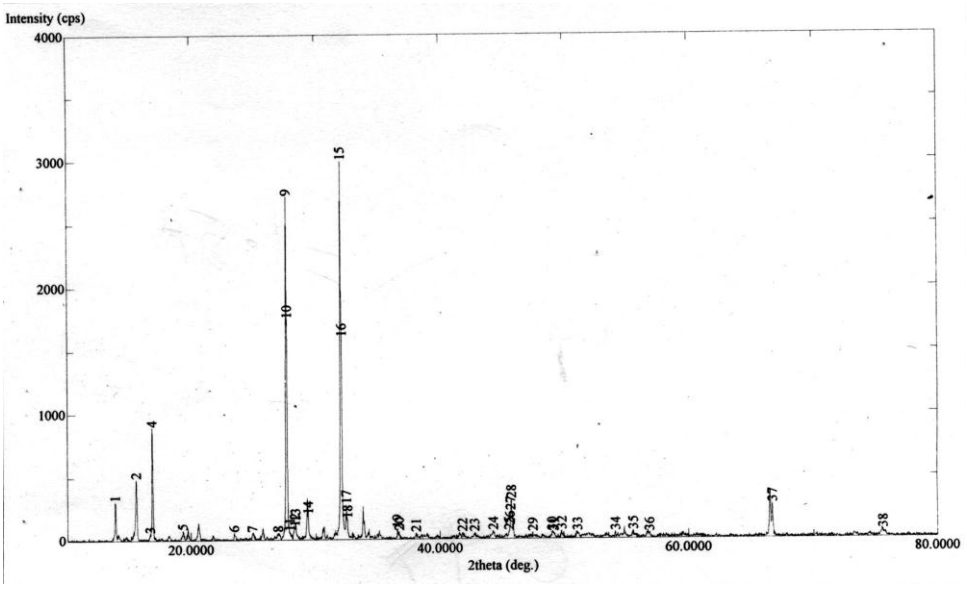

Fig.1. XRD Pattern of ZTS doped with NaCl

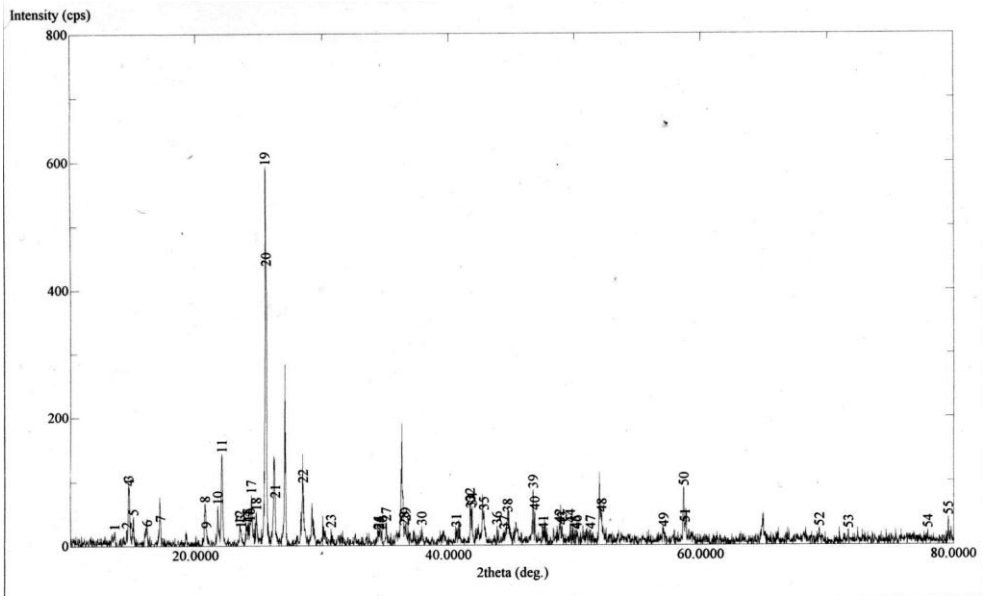

Fig.2. XRD Pattern of ZTS doped with KI

4.2. UV-Visible Spectrum

The UV- Vis range from 200 to 400nm is very important for the realization of SHG output and this range is useful for diode and solid state lasers [11].

The UV transmission spectra of NaCl and KI doped ZTS are shown in Fig.4&5**.** The optically clear single crystals of thickness about 1mm were used for this study. There is no appreciable absorption of light in the entire visible range [2]. It can be seen from the transmission curve that lower cut off wavelength lies nearly 225nm

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and 233nm in NaCl and KI respectively, which implies the grown crystals are potential material for frequency doubling [2], [3].

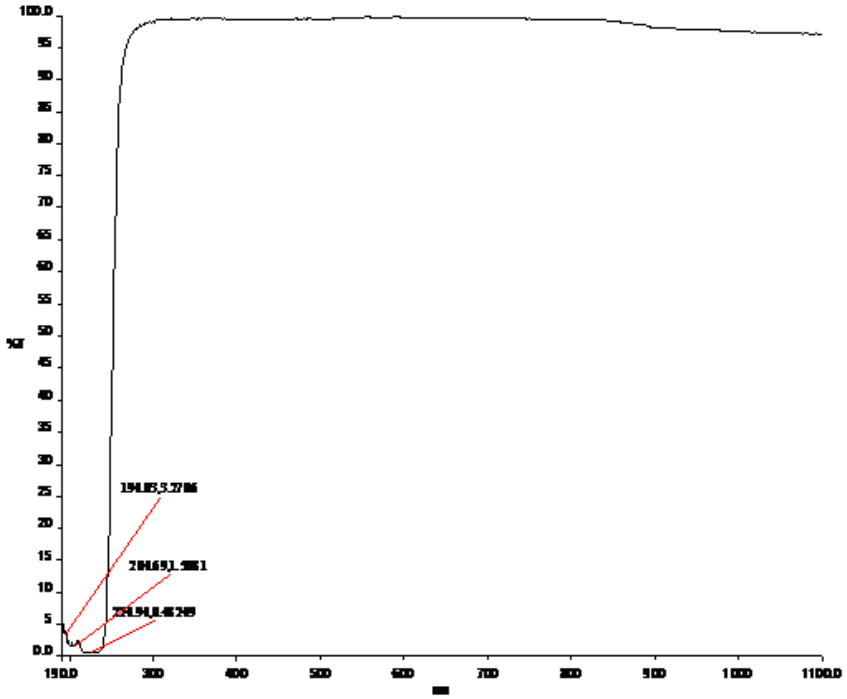

Fig.3. UV Transmission Spectrum of ZTS doped with NaCl

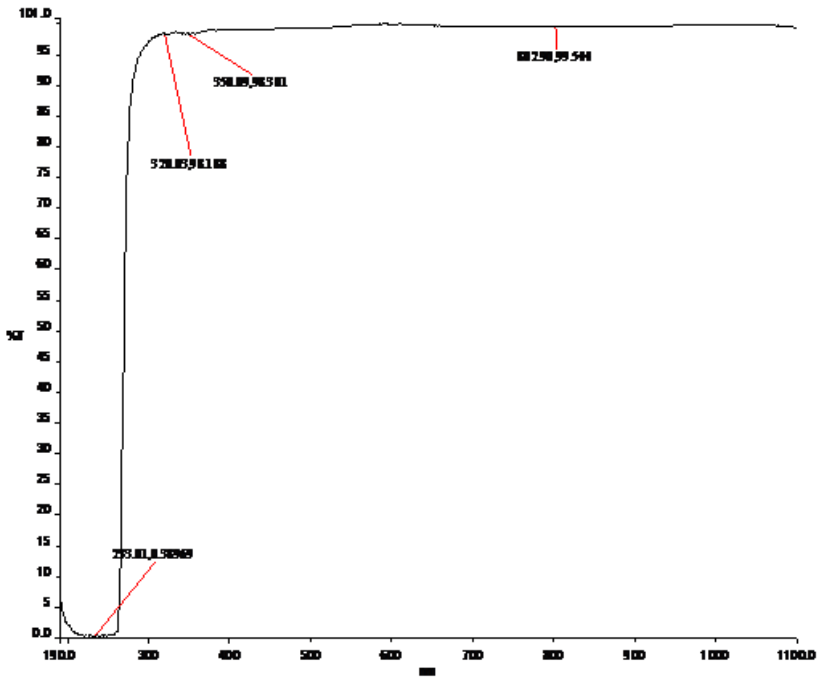

Fig.4. UV Transmission Spectrum of ZTS doped with KI

4.3. Thermal analysis

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The chemical decomposition, phase transition temperature, melting point and the weight loss of the grown crystals were determined by TGA. TGA/DTA was carried out NETZSCH proteus thermal analyser. Thermal analyser in the temperature range from 0 to 500ºC for NaCl doped ZTS crystals. There is no weight loss up to 225ºC, so the crystals are thermally stable up to 225ºC .It is observed a weight loss about 20% occurs only around at 280ºC. A total weight loss of about 60% occurs at 500ºC.

DTA curve of ZTS-NaCl crystals shows that a solid-solid phase transition peaks occurs at 100ºC and 160ºC. Above 225ºC the weight loss observed in TGA curve is compensated by DTA curve. This insures the thermal stability of NaCl doped ZTS material used up to 290ºC for possible application in optoelectronic devices.

For KI doped ZTS crystals, TGA curve is observed that there is small weight loss in the temperature range 300-310ºC. A total weight loss of around 70% occurs only at 500ºC with subsequent stages. The resulting thermogram is shown in fig. 5&6. Since, these crystal shows no phase transition, when the temperature is slowly increased from room temperature up to 500ºC. Geometry of KI doped ZTS crystal molecular layer are retained its relative position, with their neighbours [12].

DTA curve of ZTS-KI crystals shows the thermal stability. It concludes that the thermal stability of ZTS is increasing with doping of KI. KI is the better alternative than NaCl for device fabrication.

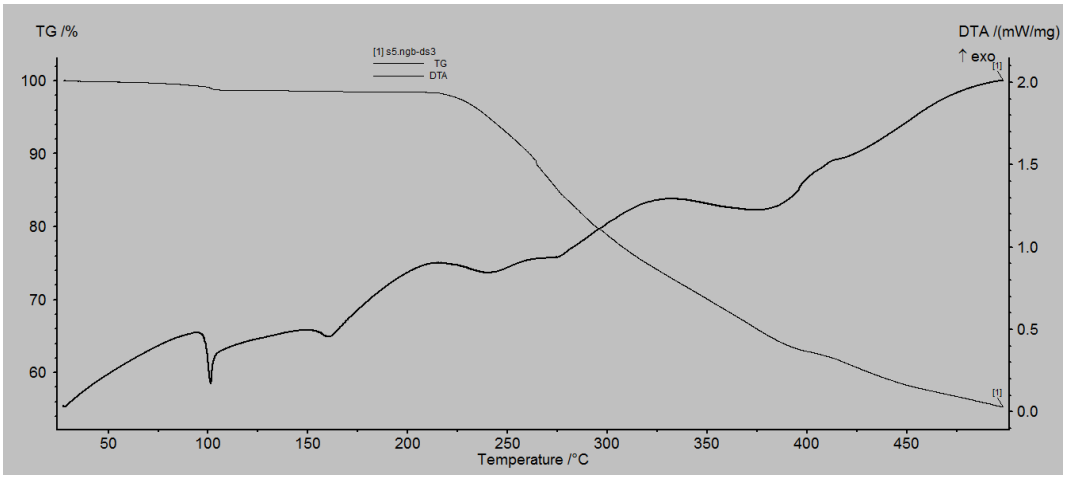

Fig.5. TGA/DTA of ZTS doped with NaCl

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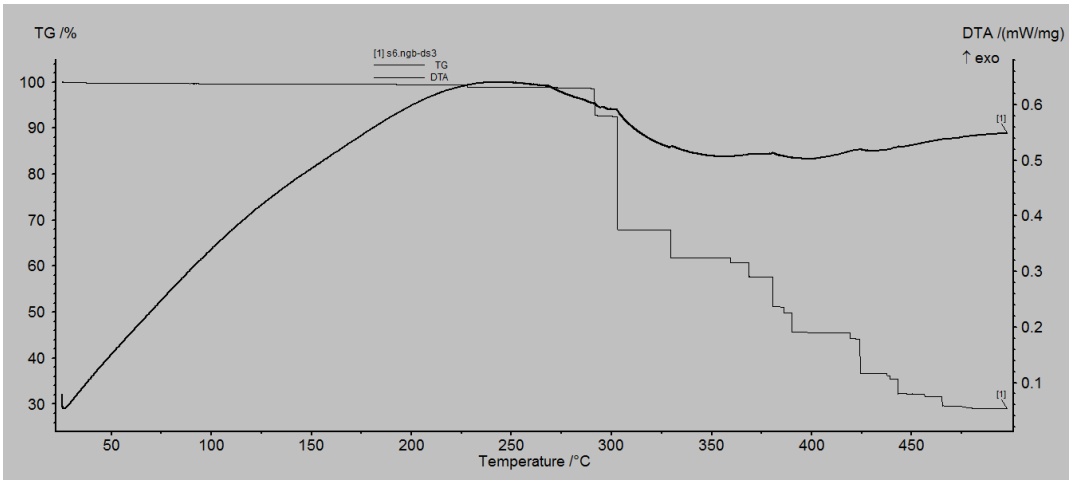

Fig.6. TGA/DTA of ZTS doped with KI

5. Conclusion

Optical quality single crystals of sodium chloride and potassium iodide doped ZTS were grown from aqueous solution by slow evaporation method at room temperature. Crystalline nature of the grown crystals such as sodium chloride and potassium iodide doped ZTS are confirmed by powder X-ray diffraction (XRD) pattern. The optical transmission spectra (UV) reveal that both the crystals are having cut off wavelength lies nearly 225nm and 233nm in NaCl and KI crystals respectively. The increase in thermal stability due to the presence of NaCl and KI is observed from TGA/DTA.

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