Research Article **ISSN: 2393 – 9532**

International Journal of Arts and Science Research

Journal home page: www.ijasrjournal.com

EFFECT OF A GROUP 10 BIVALENT METAL ION DOPING ON THE GROWTH, OPTICAL, THERMAL AND MECHANICAL PROPERTIES OF ZTS CRYSTALS

J. Thomas Joseph Prakash[*1], S. Ekadevasena[2], A. Kanagavalli[1], J. Martin Sam Gnanaraj[1], S. Shek Dhavud[3], M. Iyanar[4]

[1*]PG and Research Department of Physics, Government Arts College, Trichy, Tamilnadu, India.
[2]Department of Physics, Sri Subramaniya Swamy Arts College, Tiruttani, Tamilnadu, India.
[3]PG and Research Department of Physics, Jamal Mohammed College, Trichy, Tamilnadu, India.
[4]PG and Research Department of Physics, National College, Trichy, Tamilnadu, India.

ABSTRACT

Group 10 bivalent metal ion (Ni^{2+}) added ZTS crystals were obtained from its aqueous solution. The crystal structure was confirmed by single crystal X-Ray diffraction. Powder X-Ray diffraction pattern suggests that the grown crystals are in single phase. Optical examination ranged from 190 nm to 1100 nm suggests that the grown crystal is transparent in the entire visible region. The thermal analysis reveals the thermal stability of the crystal. The microstructural morphology and the elemental composition of the doped specimen was obtained from SEM and EDX analysis.

KEYWORDS

Crystal structure, Thermal analysis and Mechanical Properties of ZTS Crystals.

Author for Correspondence:

Thomas Joseph Prakash J,

PG and Research Department of Physics,

Government Arts College,

Trichy, Tamilnadu, India.

Email: armyjpr1@yahoo.co.in

INTRODUCTION

Nonlinear optical (NLO) frequency conversion materials have a significant impact on laser technology, optical communication and optical storage technology. The search for new frequency conversion materials over the past decade has led to the discovery of many organic.

Materials with SHG efficiency have significant impact on laser technology, optical communication and optical storage technology.

Many organic materials were discovered during the past few decades as a result for the search of novel frequency conversion materials. These materials were observed to possess NLO property with high nonlinear susceptibilities. Yet some disadvantages like inadequate transparency, poor optical quality, and lack of robustness, low laser damage threshold, and inability to grow to large size crystals made the researchers to begin the hunt for new materials with large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness. As a result a new class of materials were explored which were known as "Semiorganic materials"[1-3].

Zinc Tris Thiourea Sulphate is an efficient semiorganic NLO material. It is a type II SHG material having the SHG efficiency of nearly 1.2 times more than KDP crystal[2-5]. The high damage resistance[6] and the low cut off value favours the material for frequency conversion process in high power lasers. ZTS material is less hygroscopic, crystallizing in orthorhombic symmetry with the space group of $Pca2_1$. The frequency doubling phenomena, laser damage threshold and the thermal stability of ZTS crystals reported to be better than the other NLO crystals[5-7]. Rapid growth rate along the c direction than a and b direction was observed and reported by Marcy *et. al*,[5]. The variation of growth rate and the morphology with respect to pH of ZTS crystal was reported by Ushasree *et. al*,[8].

ZTS is a good engineering material finding its application in electro optic modulation. Metal ion doped materials are currently receiving a deal of attention due to rapid development of laser diodes. Adding transition metal as an additive in the crystalline matrix of ZTS crystals influences the physical properties greatly[9-17]. Some of the explored metal complexes of urea and urea analogues other than ZTS crystals are, zinc thiourea chloride (ZTC), bis thiourea chloride (BTCC) and copper thiourea chloride (CTC) and GCTS. These crystals have better nonlinear optical properties than KDP[18].

Synthesis of Zinc Tris Thiourea Sulphate salt

Analytical Reagent Grade Zinc Sulphate and Thiourea salts were used as precursors in the synthesis process. The starting materials used were highly pure (99%) and obtained from Merck Company. Thiourea and Zinc Sulphate were taken in the molar ratio of 3:1. The reactants were stirred well at room temperature for 4h. When the reactants are mixed together a white crystalline adduct was formed at the bottom of the beaker. This adduct is used for the growth of ZTS crystals. The adduct is filtered using a what man filter paper. The filtered salt is heated gently in order to remove moisture.

Growth of Ni^{2+} doped ZTS crystals

The dried salt is now taken in a separate beaker after choosing a suitable solvent for growth of crystals. Saturated solution is prepared using the synthesized salt. The mixture is now stirred well thoroughly to get a clear solution. 0.2 mol% Nickel nitrate (98%, Loba, AR grade) was added to the solution. The homogenized solution is now stirred well for 2 hours. After 2 hours the clear solution is filtered in a clear beaker and kept covered using a perforated foil sheet to facilitate slow evaporation process. Ni^{2+} doped ZTS crystals were obtained after a time span of 35 days. The grown crystal is shown in Figure No.1.

Single crystal XRD

The structure of the grown crystal was confirmed using BRUKER KAPPA APEX II single crystal X-Ray diffractometer. Ni^{2+} doped ZTS crystals were observed to crystallize in orthorhombic symmetry with a space group of $Pca2_1$. The obtained cell parameter values are shown in Table No.1. On comparing the obtained cell parameter values with the reported literature, slight variations were observed in the cell values which may be due to the incorporation of the dopant. No changes were observed in the morphology of the grown crystal due to the addition of the dopant which confirms the crystal structure remains unaltered on the incorporation of the dopant. The diffraction pattern obtained for Ni^{2+} doped ZTS crystal is shown in Figure No.2.

Powder X-Ray diffraction analysis

JEOL JDX powder x-ray diffractometer was employed for tracing the powder XRD pattern. The obtained powder XRD pattern is shown in the Figure No.3. The well-defined Bragg's peak indicates that the Ni^{2+} doped ZTS crystal is highly crystalline. The prominent peak at a specific 2θ angle suggests the crystallinity of the sample. A set of prominent peaks were obtained from the powder

XRD data. Powder XRD pattern suggests the single phase formation of Ni^{2+} doped ZTS crystal.

Linear Optical property

The UV-Vis-NIR spectrum of Ni^{2+} doped ZTS crystals was recorded within the range of 190 nm to 1100 nm using PERKIN ELMER LAMBDA 35 double beam UV-Vis spectrophotometer. Transparency in the entire visible region ranging from 300 nm to 700 nm without any strong absorptions is key property of a material to possess nonlinear optical property. A sample of 1 mm thickness was used for this measurement. From the Figure No.4(a) it is observed that the lower cut-off wavelength of undoped and Ni^{2+} doped ZTS crystals is 300 nm. The material is found to be transparent in the entire visible region without any absorptions. Hence Ni^{2+} incorporated ZTS crystals are potential candidates in optical device fabrications.

Estimation of Optical Band Gap and Optical constants

Optical band gap and the optical constants viz., extinction coefficient, reflectance and refractive index of Ni^{2+} doped ZTS crystals were estimated from the UV- Visible spectral analysis.

Absorption coefficient (α) was calculated from the optical absorption spectrum and it is given by the formula,

$$\alpha = \frac{2.303\log\left(\frac{1}{T}\right)}{t}$$

Where T is the transmittance obtained from the UV spectrum and t is the thickness of the crystal.

The optical band gap (E_g) has been evaluated from the transmission spectra and the optical absorption coefficient (α) near the absorption edge is given by

$h\nu\alpha = A(h\nu - E_g)^{1/2}$.

Where A is a constant, Eg is the optical band gap, h the Planck's constant and ν frequency of the incident photons. The band gap of Ni^{2+} doped ZTS crystals were obtained by plotting $(\alpha h\nu)^2$ versus hν and extrapolating the linear region near the onset of the absorption edge to the energy axis which is shown in Figure No.4(b).

It could be observed from the Figure No.4 that Ni^{2+} doped ZTS crystals possess a large transmittance in the visible region by possessing a band gap of 4 eV. The optical band gap of ZTS crystals was observed to be Incorporation of a metallic impurity decreases the band gap making it an eligible candidate for optoelectronic applications. Near the UV region, absorption arises from electronic transition associated within the thiourea units of ZTS. The orbital P electron delocalization in thiourea arises from the mesomeric effect. This P electron dislocation is responsible for its nonlinear optical response and absorption in near UV region. The wide range of transparency in UV, visible and IR regions enables good transmission of the second harmonic frequency of Nd: YAG laser. This is an added advantage in the field of optoelectronic applications[19].

Extinction coefficient (K) can be obtained from the following equation

$$K = \frac{\lambda\alpha}{4\pi}$$

The reflectance (R) in terms of the absorption coefficient and refractive index (η) is given by the expressions

$$R = \frac{1 \pm \sqrt{1 - \exp(-\alpha t) + \exp(\alpha t)}}{(1 + \exp(-\alpha t))}$$

$$\eta = \frac{-(R+1) \pm \sqrt{(-3R^2 + 10R - 3)}}{2(R-1)}$$

The variation of extinction coefficient with photon energy and reflectance with wavelength are shown in Figure No. 4(c) and 4(d) respectively. The refractive index (η) was found to be 1.25 at 1100 nm for undoped and Ni^{2+} doped ZTS crystal which was estimated from the plot of wavelength vs refractive index plot (Figure No.4(e)).

Surface Morphology and Compositional Analysis

The SEM micrographs were obtained in various resolutions and magnifications using HITACHI model SEM equipped with EDX. The SEM micrographs of Ni^{2+} doped ZTS crystals are shown in Figure No.5 (a)-(d). From the SEM micrographs it is evident that the particles are evenly distributed. Ni^{2+} doping does not alter the surface morphology of the ZTS crystal. The presence certain microstructural defects can also be seen clearly in Figure No.5(d). Since the particles are closely packed in the SEM micrograph it is evident that the title material possesses good electrical conductivity. The presence of Ni^{2+} in the crystal lattice of ZTS crystal is confirmed by EDX analysis. The EDX pattern is shown in Figure No.6 which confirms the doping of Ni^{2+} in ZTS crystal. The compositional ratio of Ni^{2+} doped ZTS crystal is shown in Table No.1.

Thermal analysis

The TGA and DTA curves were recorded simultaneously for Ni^{2+} doped ZTS crystals are displayed in Figure No.7. The percentage of weight loss of the material as a function of temperature is measured in TGA. The absence of water of crystallization in the molecular structure is indicated by the absence of weight loss around 100 °C[20]. Since there is no weight loss in the temperature ranges 0-230 °C Ni^{2+} doped ZTS are thermally stable till 230 °C. The TGA curve also shows the difference stages of decomposition. The first stage of weight loss begins at 223.86°C for Ni^{2+} doped ZTS which is attributed to the evaporation of water molecules as well as the decomposition loosely bonded molecules in the crystal lattice of ZTS crystals. The second stage of weight loss at 310.31 °C for Ni^{2+} doped ZTS. The TGA curve shows that maximum weight loss occurs in the temperature range 232 °C -310 °C due to the liberation of volatile substance like sulphur oxide in the compound and this appeared to be the major stage of decomposition[21].

DTA curve for Ni^{2+} doped ZTS shows the endothermic transition at 250 °C and 370 °C. The first endothermic peak coincides with the melting point of the crystals. The melting point of undoped ZTS is 239 °C[22] and for Ni^{2+} doped ZTS is 250 °C. The sharpness of the endothermic peaks in DTA curve suggests good degree of crystallinity of the materials. It can be noted that the undoped sample has less melting point than the Ni^{2+} doped ZTS crystal. The absence of other peaks before the melting point of the sample confirms that there is no other transition taking place in the material and this insures the thermal stability of the material for possible applications in lasers.

Spectral properties of Ni^{2+} incorporated ZTS crystals

The FTIR spectra of Ni^{2+} doped ZTS were carried out to study the functional groups present in the grown crystals. The observed FTIR spectrum is depicted in Figure No.3. The FTIR spectrum shows a broad envelope positioned between 2713 and 3305 cm^{-1} arising out of the symmetric and asymmetric modes of the NH_2 group zinc coordinated thiourea[23]. The absorption band observed at 1621 cm^{-1} Ni^{2+} doped ZTS is assigned to NH_2 bending mode vibrations. The symmetric and asymmetric C=S stretching vibrations are observed in the bands 1400 cm^{-1} and 714 cm^{-1}. The absorption at 1510 cm^{-1} is due to N–C–N stretching vibration for Ni^{2+} doped ZTS. The presence of sulphate ion is confirmed by the absorption band at 471 cm^{-1}. The vibration frequencies of the Ni^{2+} doped ZTS crystals are presented in the Table No.2.

Second Harmonic Generation Efficiency test

The second harmonic generation (SHG) efficiency of the grown crystals was checked by using Kurtz and Perry Power method[24]. Powder SHG measurement was carried out using Nd: YAG laser of 1064 nm wave length. The grown crystals were finely powdered and filled in a micro capillary tube. After sealing the capillary tube, the grown crystals was subjected to Nd: YAG laser radiation and the SHG efficiency of the title material was confirmed by an emission of green radiation. The input laser energy incident on the sample was of 0.68 J. The measured outputs for Ni^{2+} doped ZTS crystal was 3.9 mJ. This indicates that the efficiency of SHG of Ni^{2+} doped ZTS is 1.3 times greater than KDP crystal which was used as a standard reference material.

Table No.1: Compositional analysis of Ni^{2+} doped ZTS crystal

S.No	Elements	Wt %	At %	K-Ratio
1	S	66.40	80.03	0.6010
2	Zn	32.09	18.97	0.2847
3	Ni	1.51	1.00	0.0152

Table No.2: FTIR assignments of Ni^{2+} doped ZTS crystal

S.No	Ni^{2+} dopedZTS	Bond Assignments
1	3305	ν_s (NH_2)
2	2358, 2713	Hydrogen bonding interaction of COOH in Crystal lattice
3	1621	δ (NH_2)
4	1510	ν_s (N–C–N)
5	1400	ν_{as} (C=S)
6	1125	ν_s (C–N)
7	1030	ν_s (C–N)
8	714	ν_s (C=S)
9	615	ν_{as} (N–C–S)
10	471	δ_s (N–C–S)

ν_s – Symmetric stretching, ν_{as} – Asymmetric stretching, δ - bending, δ_s–Symmetric bending, ν – Stretching

Figure No.1: As grown Ni^{2+} doped ZTS crystal

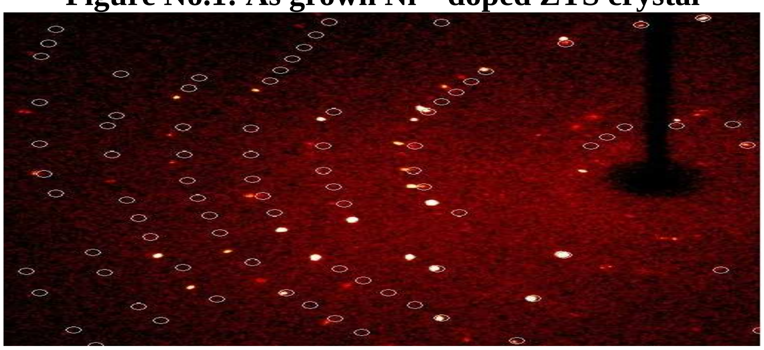

Figure No.2: Single Crystal X-Ray diffraction pattern of Ni^{2+} doped ZTS crystal

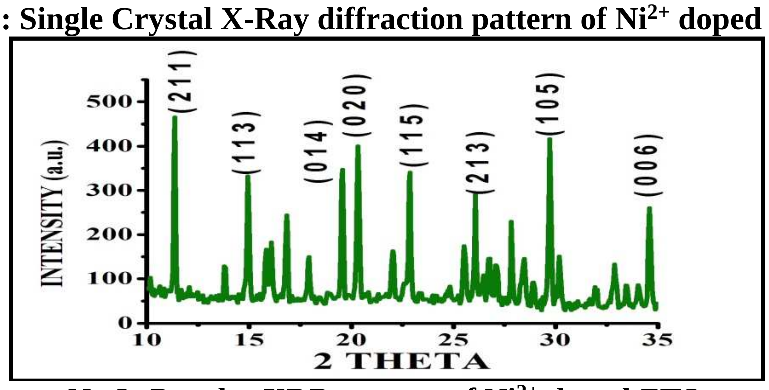

Figure No.3: Powder XRD pattern of Ni^{2+} doped ZTS crystal

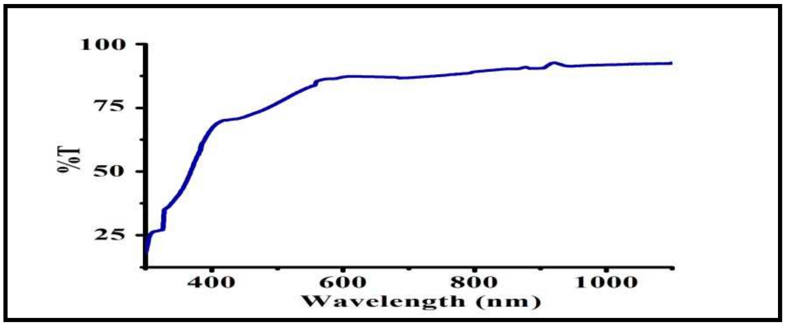

Figure No.4(a) UV Transmission spectrum of Ni^{2+} doped ZTS crystals

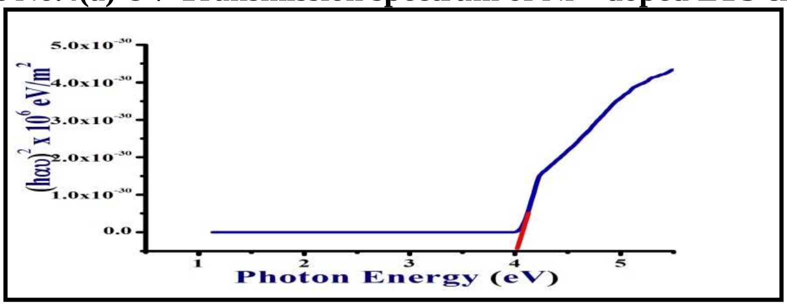

Figure No.4(b) Tauc's plot of Ni^{2+} doped ZTS crystal

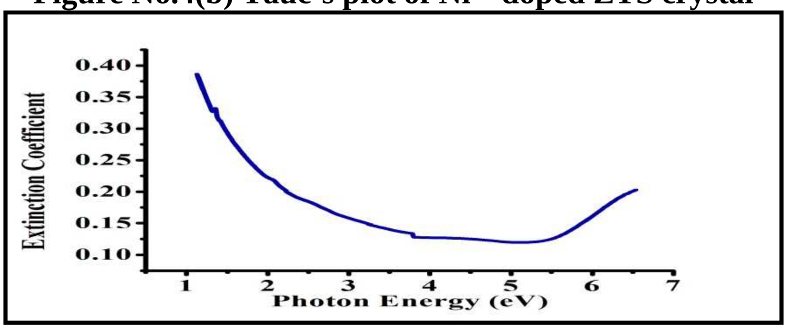

Figure No.4(c) Photon Energy vs Extinction coefficient of Ni^{2+} doped ZTS crystal

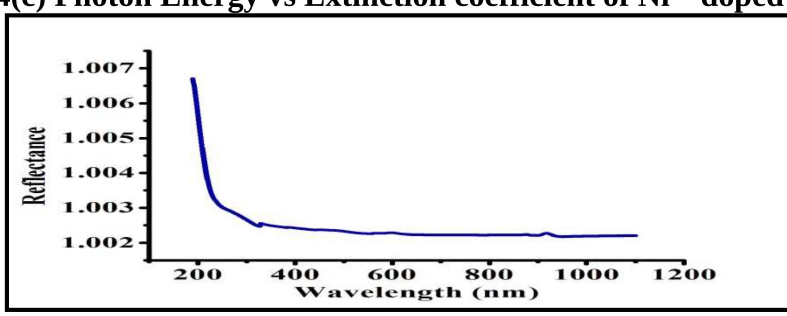

Figure No.4(d) Wavelength vs Reflectance plot of Ni^{2+} doped ZTS crystal

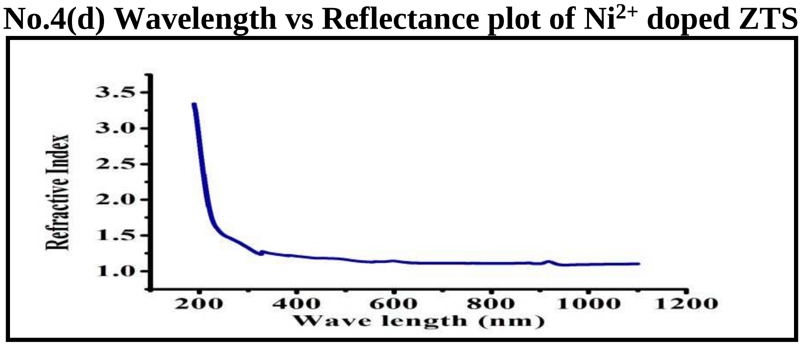

Figure No.4(e) Wavelength vs Refractive Index of Ni^{2+} doped ZTS crystal

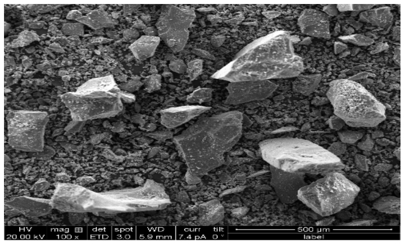
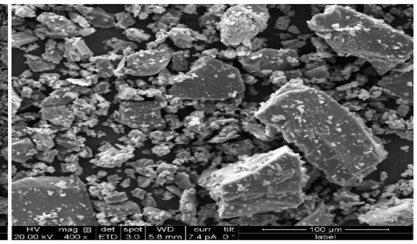

Figure No.5(a)Figure No.5(b)

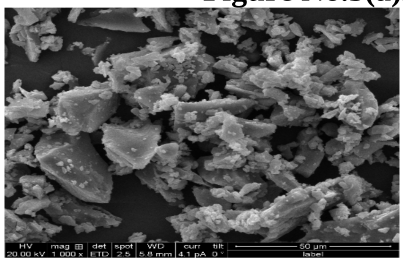
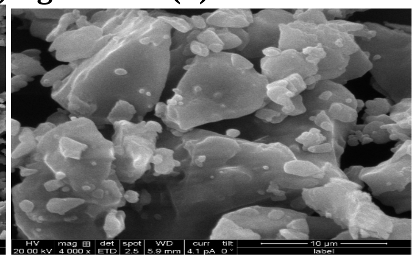

Figure No.5(c)Figure No. 5(d)

Figure No. 5(a)-5(d) SEM micrograph of Ni^{2+} doped ZTS crystal

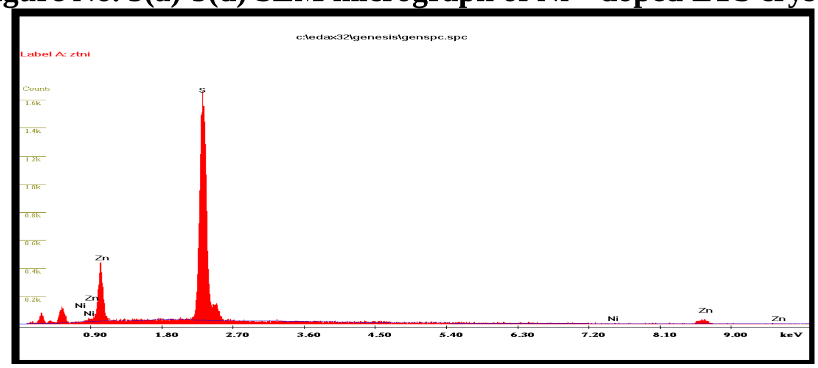

Figure No.6: EDX spectrum of Ni^{2+} doped ZTS crystal

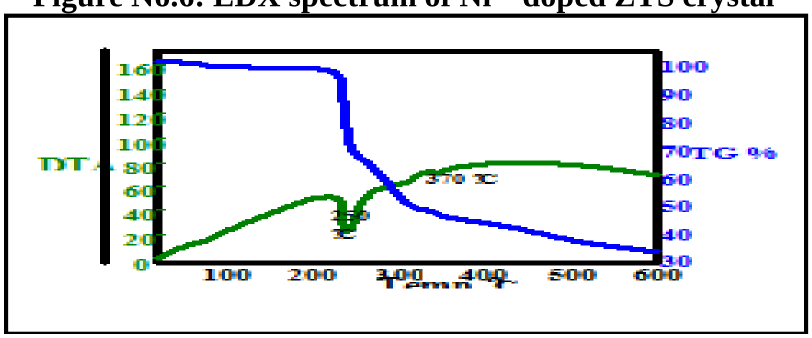

Figure No.7: TG/DTA Thermogram of Ni^{2+} doped ZTS crystal

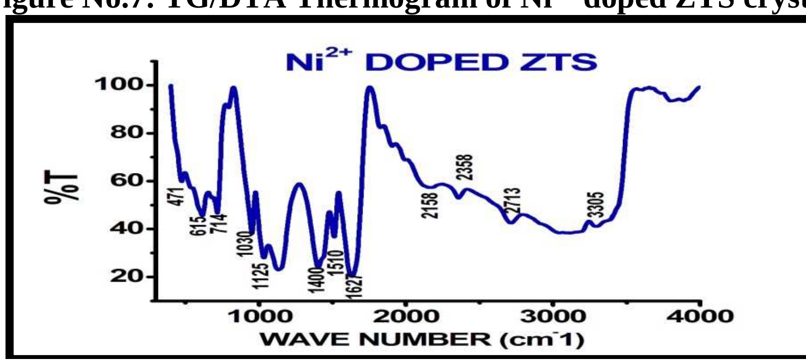

Figure No.8: FTIR spectrum of Ni^{2+} doped ZTS crystal

CONCLUSION

Ni^{2+} doped ZTS crystals were grown by conventional slow evaporation solution growth technique. The structure and the cell parameters of the grown crystal was confirmed by single crystal x-ray diffraction analysis. Incorporation of Group 10 metal ion enhances the optical property of the material. The refractive index of Ni^{2+} doped ZTS crystal was observed to be 1.25 which makes it a significant material for antireflection coating in solar thermal devices. SEM micrographs show the uniform distribution of particles on the crystalline surface. The substitution of Nickel ion in the crystal lattice of ZTS crystal was confirmed by EDX analysis. The enhancement of the thermal decomposition temperature to 250 °C makes the material an eligible candidate for laser applications. Nonlinear optical test provides information regarding the second harmonic generation efficiency of Ni^{2+} doped ZTS crystal. The results suggest that the title material can be used in the fabrication of optoelectronic and nonlinear optical devices.

ACKNOWLEDGEMENT

The authors wish to express their sincere gratitude to PG and Research Department of Physics, Government Arts College, Trichy, Tamilnadu, India for providing necessary facilities to carry out this research work.

CONFLICT OF INTEREST

We declare that we have no conflict of interest.

BIBLIOGRAPHY

1. Xing G, Jiang M, Shao Z and Xu D. Bis thiourea cadmium chloride- a novel NLO crystal, Chin, *Journal of Lasers*, 14, 1987, 357-364.
2. Velsko S. Laser Program Annual Report, Lawrence UCRL-JC 105000, Lawrence Livermore National Laboratory, *Livermore, CA*, 1990.
3. Warren L F. Electronic materials our future, in: Allred R E, Martinez R J, Wischmann K B (Eds.), Proceedings of the Fourth International Sample Electronics Conference, *Society for the Advancement of Material and Process Engineering, Covina, CA*, 4, 1990, 388.
4. Newman P R, Warren L F, Cunningham P, Chang T Y, Copper D E, Burdge G L, Polak Dingels P, Lowe- Ma C K, in: Chiang C Y, Chaikin P M, Cowan (Eds.) D O. *Advanced Organic Solid State Materials, Materials Research Society Symp. Proc., Materials Research Society, Pittsburgh, PA*, 173, 1990, 557.
5. Marcy H O, Warren L F, Webb M S, Ebbers C A, Velsko S P, Kennedy G C, Catella G C. Second harmonic generation in zinc tris (thiourea) sulfate, *Applied Optics*, 31(24), 1992, 5051-5060.
6. Venkataramanan V, Subramanian C K, Bhat H L. Laser induced damage in zinc tris(thiourea) sulfate and bis(thiourea) cadmium chloride, *Journal of Applied Physics*, 77(11), 1995, 6049.
7. Kerkoc P, Venkataramanan V, Lochran S, Bailey R T, Cruickshank F R, Pugh D, Sherwood J N, Moseley R, Goeta A E, Lehmann C W, Howard J A K. Thermal properties of the nonlinear optical crystal zinc tris (thiourea) sulphate, *Journal of Applied Physics*, 80(12), 1996, 6666.
8. Ushasree P M, Jayavel R, Subramanian C, Ramasamy P. Growth of zinc thiourea sulfate (ZTS) single crystals: a potential semiorganic NLO material, *Journal of Crystal Growth*, 197(1-2), 1999, 216-220.
9. Rockwell International Corporation Seal beach, CA, Patent-US5581010.
10. Xifa Long, Guofu Wang, Han T P J. Growth and spectroscopic properties of Cr^{3+}-doped $LaSc_3(BO_3)_4$, *Journal of Crystal Growth*, 249(1-2), 2003, 191-194.
11. Jayaraman, Ramajothi, Sivasubramanian, Dhanuskodi. Optical and microhardness studies of semiorganic nonlinear optical material: L- histidine tetrafluoroborate, *Crystal Research and Technology*, 38(11), 2003, 986-991.

12. Marly B, Camargo, Robert D, Stultz, Milton Birnbaum, Milan Kokta. Co^{2+}: YSGG saturable absorber *Q* switch for infrared erbium lasers, *Optics Letters,* 20(3), 1995, 339-341.
13. Denisov I A, Demchuk M I, Kuleshov N V, Yumashev K V. Co2+:LiGa5O8Co2+:LiGa5O8 saturable absorber passive *Q* switch for 1.34 µm Nd3+:YAlO3Nd3+:YAlO3 and 1.54µm Er3+:glassEr3+:glass lasers, *Applied Physics Letters,* 77(16), 2000, 2455.
14. Duan X L, Yuan D R, Wang L H, Yu F P, Cheng X F, Liu Z Q, Yan S S. Synthesis and optical properties of Co^{2+}-doped $ZnGa_2O_4$ nanocrystals, *Journal of Crystal Growth,* 296(2), 2006, 234-238.
15. Kuleshov N V, Mikhailov V P, Scherbitsky V G, Prokoshin P V, YumashevK V. Absorption and luminescence of tetrahedral Co^{2+} ion in $MgAl_2O_4$, *Journal of Luminescence,* 55(5-6), 1993, 265-269.
16. Xingyu Mao, Feng Xu, Jianchen Tang, Wenli Gao, Shandong Li, Youwei Du. Effects of Co-doping on the crystallization and magnetic properties of Cu-free nanocrystalline Fe–Nb–B alloys, *Journal of Magnetism and Magnetic Materials,* 288(2), 2005, 106-110.
17. Konstantin V, Yumashev. Saturable absorber Co^{2+}: $MgAl_2O_4$ crystal for *Q*switching of 1.34-µm Nd^{3+}: $YAlO_3$ and 1.54-µm Er^{3+}: glasslasers, *Applied optics,* 38(30), 1999, 6343-6346.
18. Lawrence M, Thomas Joseph Prakash J. Growth and characterization of pure and glycine doped cadmium thiourea sulphate (GCTS) crystals , *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,* 91(1), 2012, 30-34.
19. Bairava Ganesh R, Kannan V, Sathyalakshmi R, Ramasamy P. The growth of L-Glutamic acid hydrochloride crystals by Sankaranarayanan-Ramasamy (SR) method, *Materials Letters,* 61(3), 2007, 706-708.
20. Ramajothi J, Dhanuskodi S, Nagarajan K. Crystal growth, thermal, optical and microhardness studies of tris (thiourea) zinc sulphate - a semiorganic NLO material, *Crystal Research and Technology,* 39(5), 2004, 414-420.
21. Meenakshisundaram S, Parthiban S, Bhagavannarayana G, Madhurambal G. Influence of organic solvent on tristhioureazinc (II) sulphate crystals, *Journal of Thermal Analysis and Calorimetry,* 96(1), 2009, 125-129.
22. Ushasree P M, Jayavel R, Ramasamy P. Growth and characterisation of phosphate mixed ZTS single crystals , *Materials Science and Engineering:* B, 65(3), 1999, 153-158.
23. Rajasekaran R, Mohan Kumar R, Jayavel R, Ramasamy P. Influence of pH on the growth and characteristics of nonlinear optical zinc thiourea chloride (ZTC) single crystals, *Journal of Crystal Growth,* 252(1-3), 2003, 317-327.
24. Kurtz S K, Perry T T. A Powder Technique for the Evaluation of Nonlinear Optical Materials, *Journal of Applied Physics,* 39(8), 1968, 3798.

Please cite this article in press as: Thomas Joseph Prakash J *et al*. Effect of a group 10 bivalent metal ion doping on the growth, optical, thermal and mechanical properties of ZTS crystals, *International Journal of Arts and Science Research,* 3(1), 2016, 16 - 24.