Characteristic Studies of Tris (thiourea) Zinc (II) Sulphate on 'S' Block Metals

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Abstract

The influence of alkali metals (Na, K and Rb) doping on the properties and crystal growth of tris(thiourea)zinc(II)sulphate crystals by slow evaporation solution growth technique at 30°C has been investigated. Each metals as dopant incorporate into the crystal lattice even at its low concentrations is well confirmed by energy dispersive X – ray spectroscopy (EDS). In the powder X –ray diffraction (XRD), high intense peaks are observed for all doped specimens due to stress developed in the crystal because of doping when compared to pure one. Single crystal XRD reveals a nominal increase in the cell parameter values of the doped samples compared to pure. Presence of each alkali metal quantitatively is confirmed by inductively coupled plasma (ICP) technique. It is interesting to observe the enhancement of fluorescence intensity of pure ZTS by the dopant in the photoluminescence (PL) spectra. The grown crystals are also characterized by FT-IR, UV-V is and TG/DSC methods. The second harmonic generation (SHG) efficiency, an essential character required for the single crystals to identify the non-linear optical (NLO) property, was performed by kurtz powder technique.

Keyword: 'S' block metals, Rubidium sulphate, TGDSC, ICP, ZTS.

Introduction

Recent fact reveals that doping influences the electrical, mechanical, electro-optical properties, also the nature of host material and the dopant is influenced by their surface morphology [1-13]. A promising senmiorganic NLO material is suitable for Nd:YAG laser with high SHG efficiency laser damage threshold. Its SHG and laser damage threshold values are 1.2 [14] times that of KDP [15]. Being a good engineering materials for SHG device application and laser fusion experiments, with a novel metal organic crystal with potential application in electro-optic modulation, ZTS belongs to orthorhombic system with the space group Pca2, (point group mm2) though the crystal growth, kinetics and characterization of ZTS are reported [16-20], the effect of alkali metals doping (1 mol%) in the growth medium of ZTS single crystals systematically has not been reported. This made me an interest in this area. This paper explains the doping effect of S block metals like sodium, potassium and rubidium (1mol%) to Tristhioureazincsulphate through FTIR, UV-VISIBLE SPECTRA, POWER XRD, SEM-EDS, SINGLE CRYSTAL XRD, ICP, PL SPECTRA, TGDSC AND SHG.

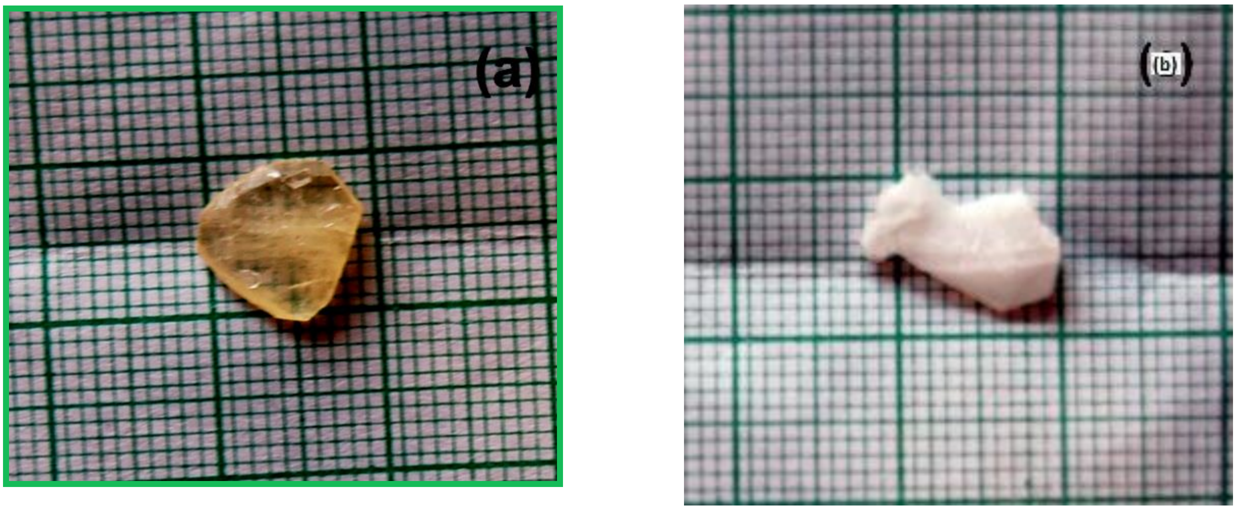
Experimental

Synthesis and crystal growth

Zincsulphateheptahydrate(EM) and thiourea (SQ) are mixed in 1:3 stoichiometric ratio to synthesise tris(thiourea)zinc(II)sulphate (ZTS) as given in the chemical reaction. During preparation in the deionized water, (<70^{o}C) temperature was maintained.

$ZnSO_4.7H_2O + 3[CS\ (NH_2)_2] \rightarrow Zn\ [CS\ (NH_2)_2]_3\ SO_4$

Re-crystallization was repeated in order to puritfy the product. Crystal growth was performed by a slow evaporation solution growth technique (SEST). A saturated aqueous solution of ZTS was prepared. The S block metals Na (I) in the form of Na_2CO_3, K(I) in the form of KCl and Rb(I) in the form of RbSO4 are mixed as impurity in 1 mol% concentrations to the aqueous growth medium. The seed crystals floats on the saturated solution and left for slow evaporation at room temperature (30oC). Solvent used is triply distilled water. Within 20-25 days the crystallization took place and when they attained an optimal size and shape they were harvested. High quality transparent crystals were harvested from the growth medium at low concentration (1 mol%) of dopants. Photographs of the as-grown doped and undoped crystals are shown in fig. 1.



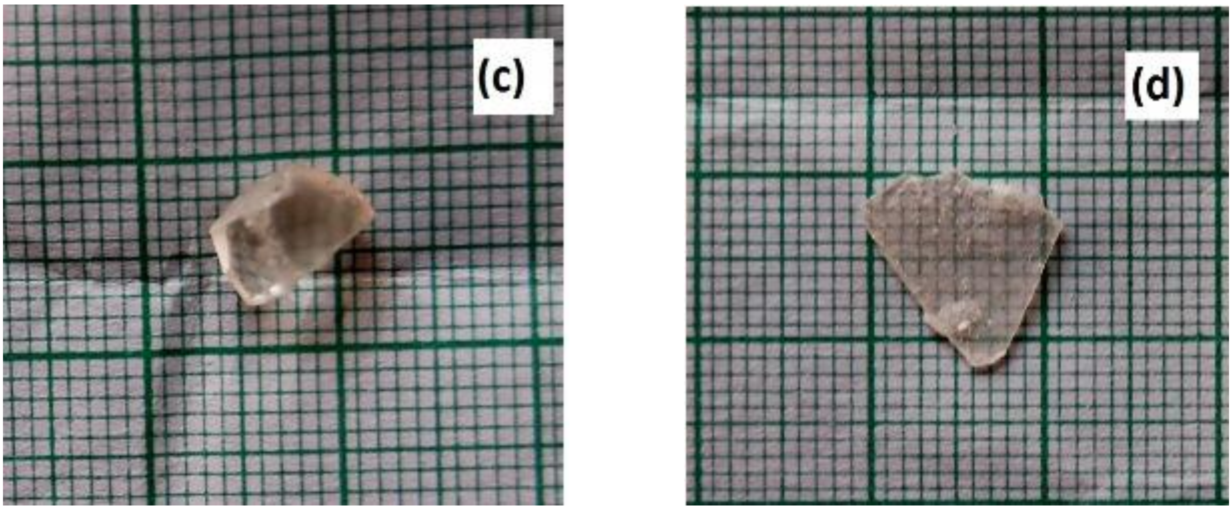


Figure 1 Images of (a) Pure ZTS, (b) ZTS/Na, (c) ZTS/K and (d) ZTS/Rb crystals.

Materials and Methods

FT-IR:

A comparison of FT-IR spectra of pure and doped ZTS specimens reveals that the doping results in small shifts in some of the characteristic vibrational frequencies, which could be due to lattice strain developed as a result of doping. An absorption band in the region 2750 to 3400cm^{-1} corresponds to the symmetric and asymmetric stretching frequencies of NH_2 group. The absorption bands observed in the spectra of pure (1624 cm-1) and doped specimens Na(I)-doped (1402 and 717 cm), K(I)-doped (1412 and 730 cm), Rb(I) doped (1402.29 and 715.7 cm) from the above observation we can suggest that the S block metals co-ordinate with thiourea through sulfur only. FT-IR spectra of pure and alkali metals doped ZTS are show in fig. 2

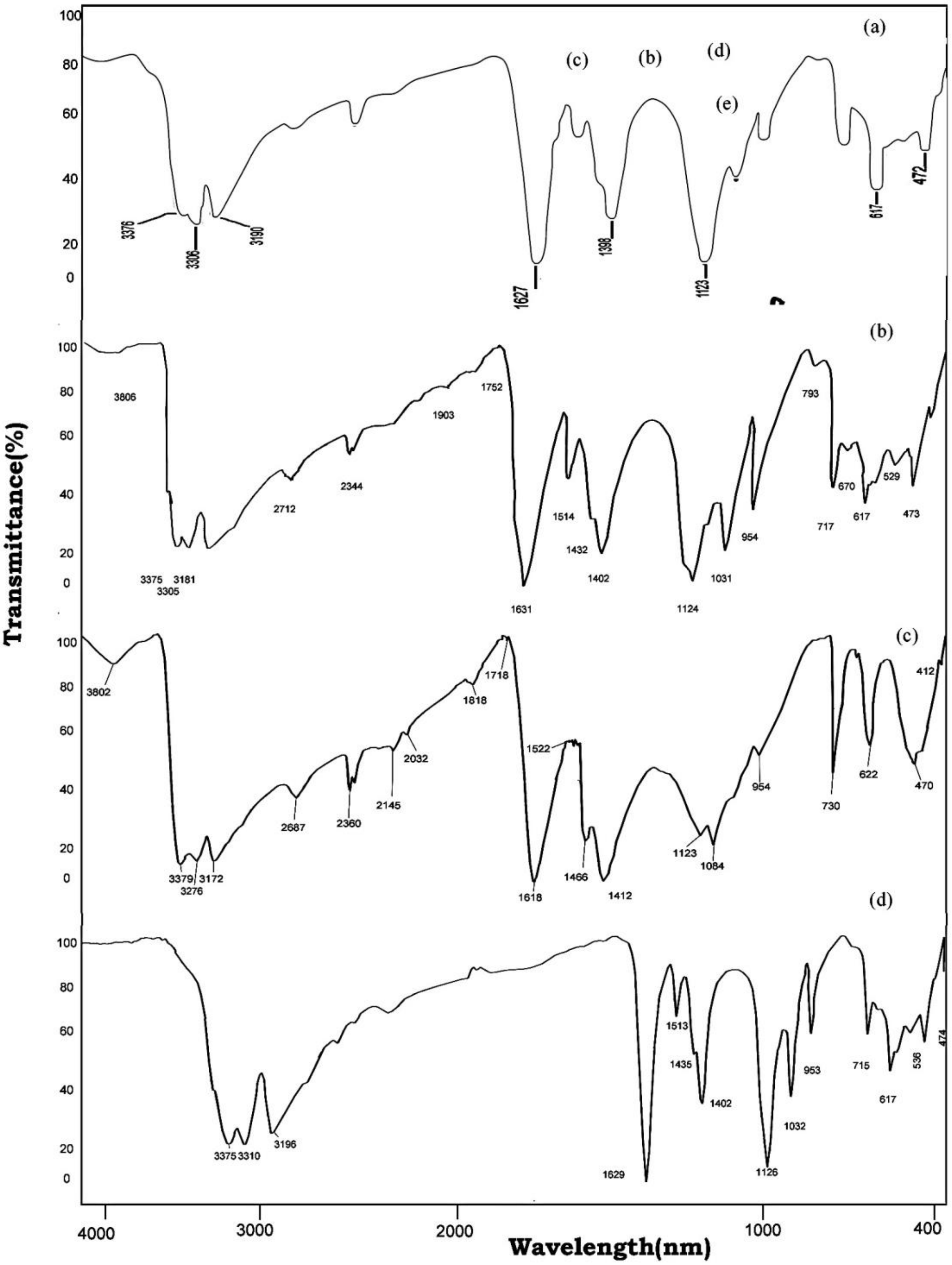


Figure 2 FTIR of (a) Pure ZTS, (b) ZTS/Na, (c) ZTS/K and (d) ZTS/Rb doped crystals.

Powder and single crystal XRD analyses:

The powder XRD patterns of pure and alkali metals doped-ZTS specimens are shown in fig.3

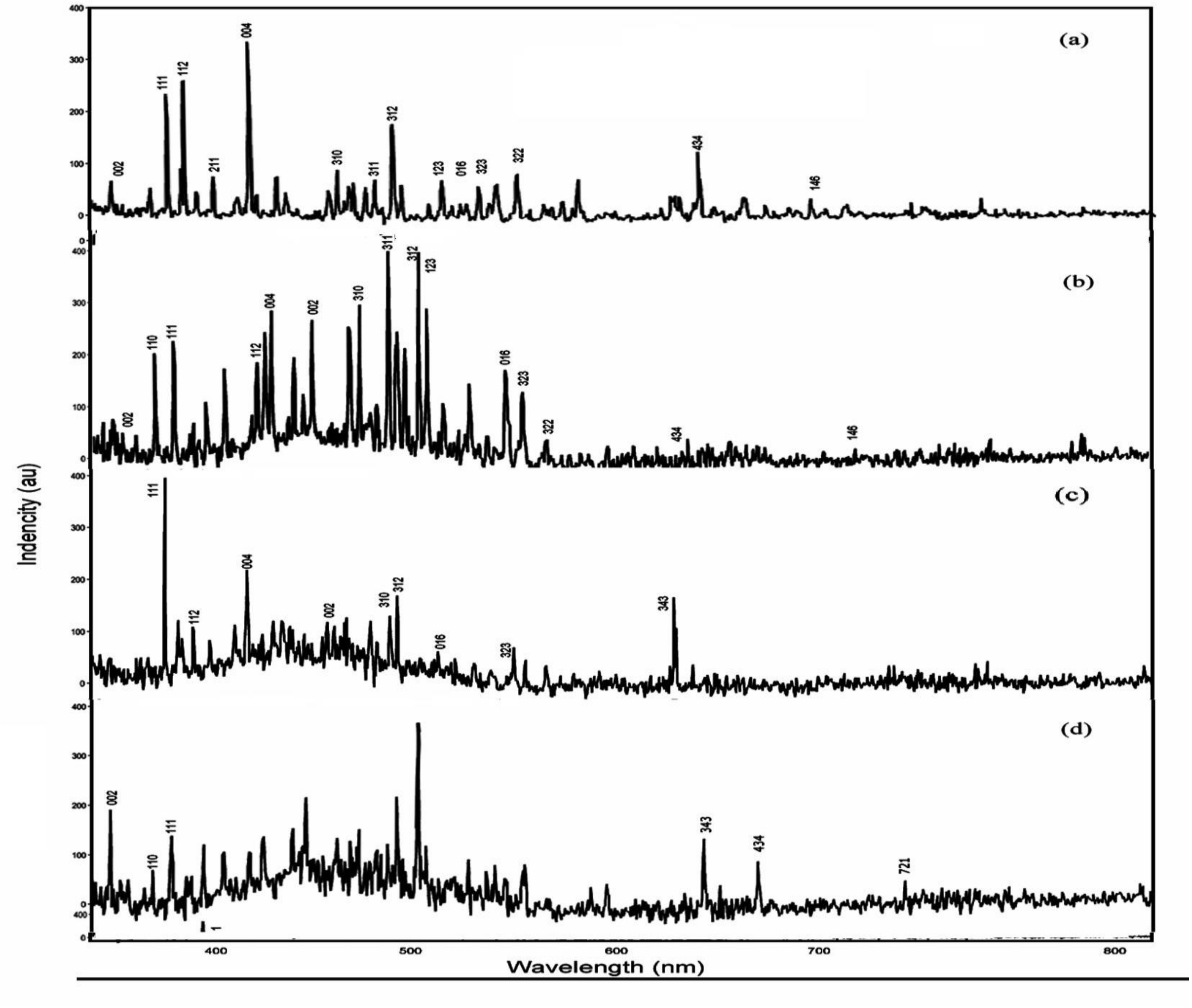
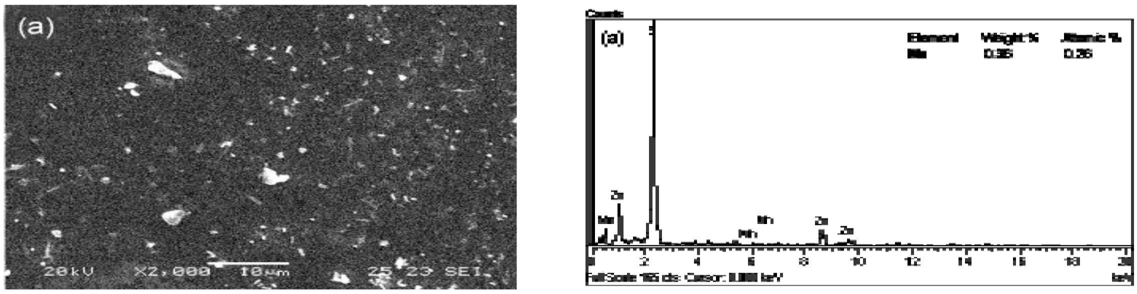


Figure.3 Powder XRD (a) Pure ZTS, (b) ZTS/Na, (c) ZTS/K (d) ZTS/Rb doped crystals

SEM-EDS Analysis Figure 4 SEM – EDS of (a) Pure ZTS, (b) ZTS/Na, (c) ZTS/K (d) ZTS/Rb doped crystals


(a)
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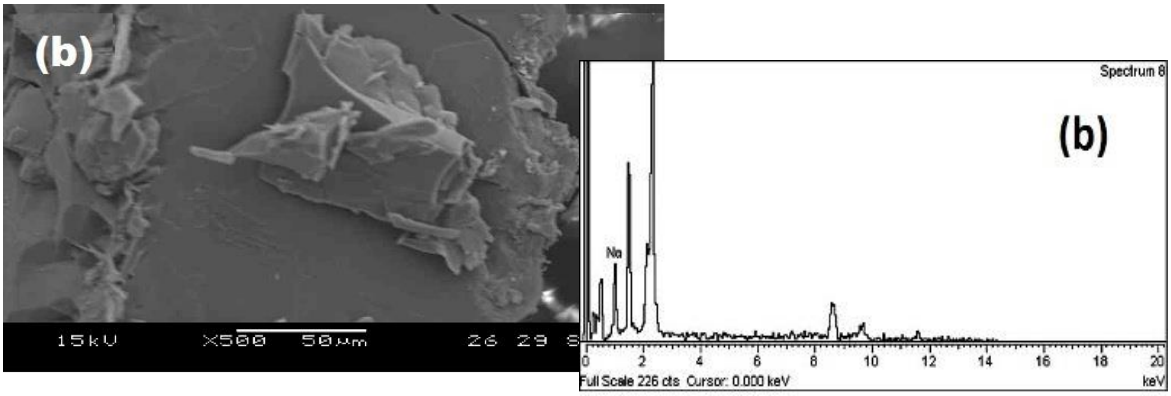
(b)
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(b)
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Full Scale 226 cts Cursor: 0.000 keV
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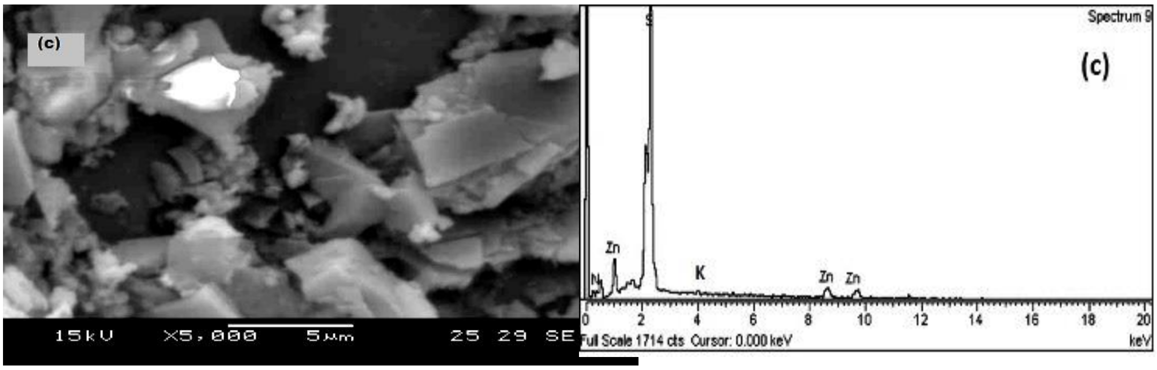
(c)
15kV X5,000 5µm 25 29 SE
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(c)
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K
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0 2 4 6 8 10 12 14 16 18 20
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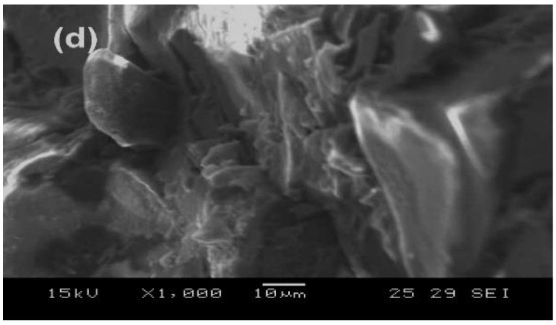

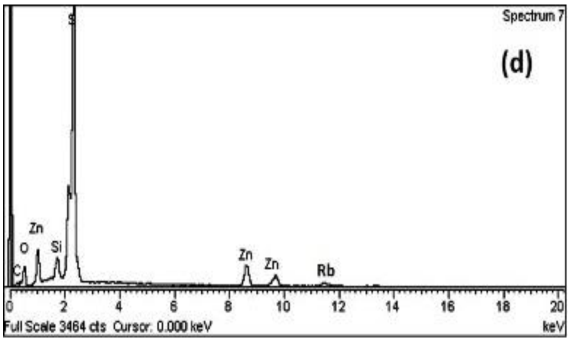

It reveals that the no new phases were observed by doping, however there are changes in the intensities of some characteristic peaks. In the case of Na(I) and Rb (I)-doped ZTS multi peaks are obtained with high intensity, than K(I) doped ZTS specimens when compared to pure ZTS. The most prominent peaks with maximum intensity of the XRD patterns of pure and doped specimens are quite different. The undoped and doped specimens belong to orthorhombic system with $P_{ca}2_1$ space group. These attributed to strains in the lattice. From the schereer equation the particle size of samples is calculated as Na(I) doped-15.06nm, K(I) doped 12.98nm, Rb(I) 13.8nm. The single crystal XRD reveals values that for S block metals doped ZTS crystals vary only slightly from that of pure ZTS, which is given in the Table 1. **JCPDS value of ZTS**

Table 1. JCPDS value of ZTS

System	**a A^o**	**b A^o**	**c A^o**	**v A^{o3}**	**Space Group and System**
ZTS	**7.794**	**11.152**	**15.494**	**1348**	**orthorhombic system with $P_{ca}2_1$**
ZTS-Na	**7.778**	**11.142**	**15.505**	**1341**	**orthorhombic system with $P_{ca}2_1$**
ZTS-K	**7.776**	**11.121**	**15.471**	**1339**	**orthorhombic system with $P_{ca}2_1$**

ZTS-Rb	**7.766**	**11.126**	**15.477**	**1338**	**orthorhombic system with $P_{ca}2_1$**

The information about the surface nature and its suitability for device fabrilation is given by SEM study. Also the presence of the influence of S block metals doping on the surface morphology of ZTS crystal reveals the formation of structure defect centers. In the case of Na(I) and K(I) doped ZTS, larger scatter centers are observed. Rb(I) doped ZTS shows cauliflower like appearance as shown in fig. 4.

The ZTS crystalline matrix which is very clear from fig. 5 Shows Analysis of the surface at different sites. The EDS graph confirms the presence of the alkali metals and the incorporation of the S block metals reveals that the incorporation of metals is non-uniform over the whole crystal surface.

ICP:

The amount of dopant in alkali metals doped specimens are estimated using ICP and the foreign metal ion entering into the ZTS crystal matrix is much smaller but significant. The actual dopant concentration in the crystalline matrix is given in Table 2. Doping and actual concentration of S block metals.

Sample	**Actual dopant concentration in the crystalline matrix/ ppm**
ZTS-Na	**34.4**
ZTS-K	**5.4**
ZTS-Rb	**5.6**

Optical studies:

UV-visible spectrometer in the spectral range 400-700nm for pure and doped samples are shown in fig. 5. It appears that the doping of alkali metals does not destroy the optical transmission. The cut off wavelength is nearly 350-500nm in the case of all specimens, and there is high is percentage of transmittance in the entire visible region for pure and alkali metal doped ZTS crystals. No significant λ_{max} shift is observed but the absorbance is reduced drastically by doping, except for ZTS-Na doped specimen (Table-3), where there is a slight increase in absorbance value. Due to its high transparency, these doped crystals are quite useful for optical device applications. The band gap energy can be calculated using equation $\mathbf{Eg = hc/\lambda_{max}}$

Where: h – plank constant, C – Velocity of light, Eg – 1.243 x 10^3/ λ_{max}

For pure and doped specimens bond gap energy is calculated and due to doping it is interesting to see an increase in band gap.

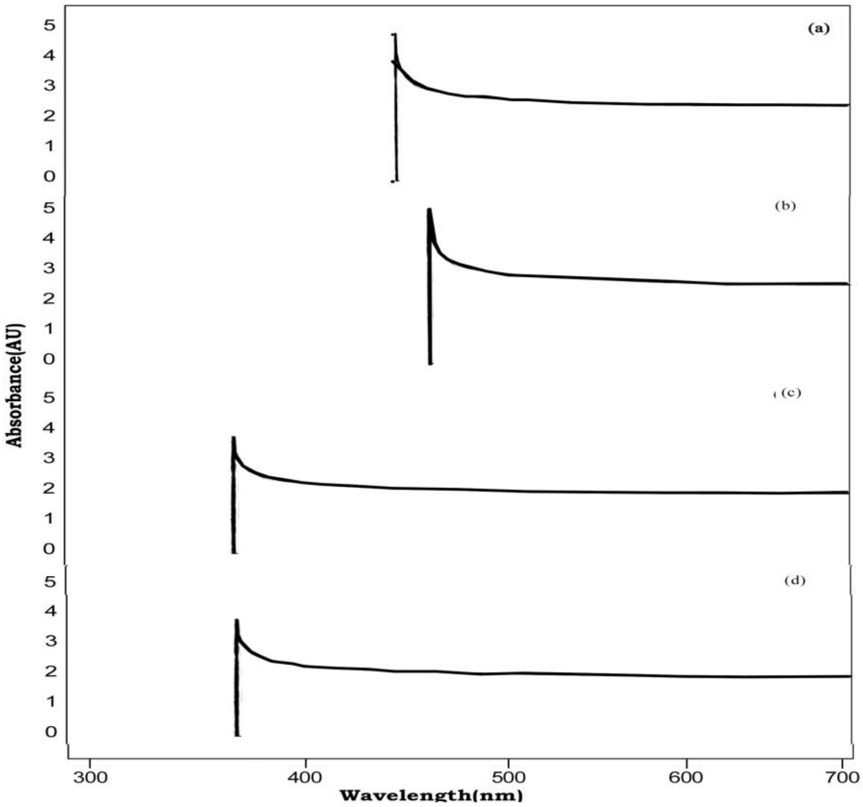

Figure 5 UV-visible of (a) Pure ZTS, (b) ZTS/Na,(c) ZTS/K and (d) ZTS/Rb doped crystal

SHG

The influence of doping alkali metals on the NLO properties of the as grown ZTS and alkali metal doped ZTS crystals were subjected to SHG test with 2.5 mj/pulse as input radiation. The Table - 4 gives the output SHG intensities of pure and doped specimens from the SHG values it is clear that in the case of doped Na(I) and K(I) specimens the value is reduced than the undoped which could be due to ineffective facilitation of charge transfer by the dopant in the ZTS crystal. SHG output for Rb(I) doped specimens is greater (~1.5 times) than ZTS crystals.

Table- 4 SHG output

System	I_2 w/mv
Pure 2TS	6.7
2TS- Na	4.1
2TS- K	4.6
2TS- Rb	9.0

PL spectral studies

The fluorescence spectra of ZTS and alkali metals doped ZTS crystals are given in the figure – 6. In the case of pure ZTS there is no fluorescence intensity but Rb(I) (740.97) which are slightly higher. Na(I) and K(I) doped ZTS crystals there is no fluorescence intensity, which is similar to pure one itself.

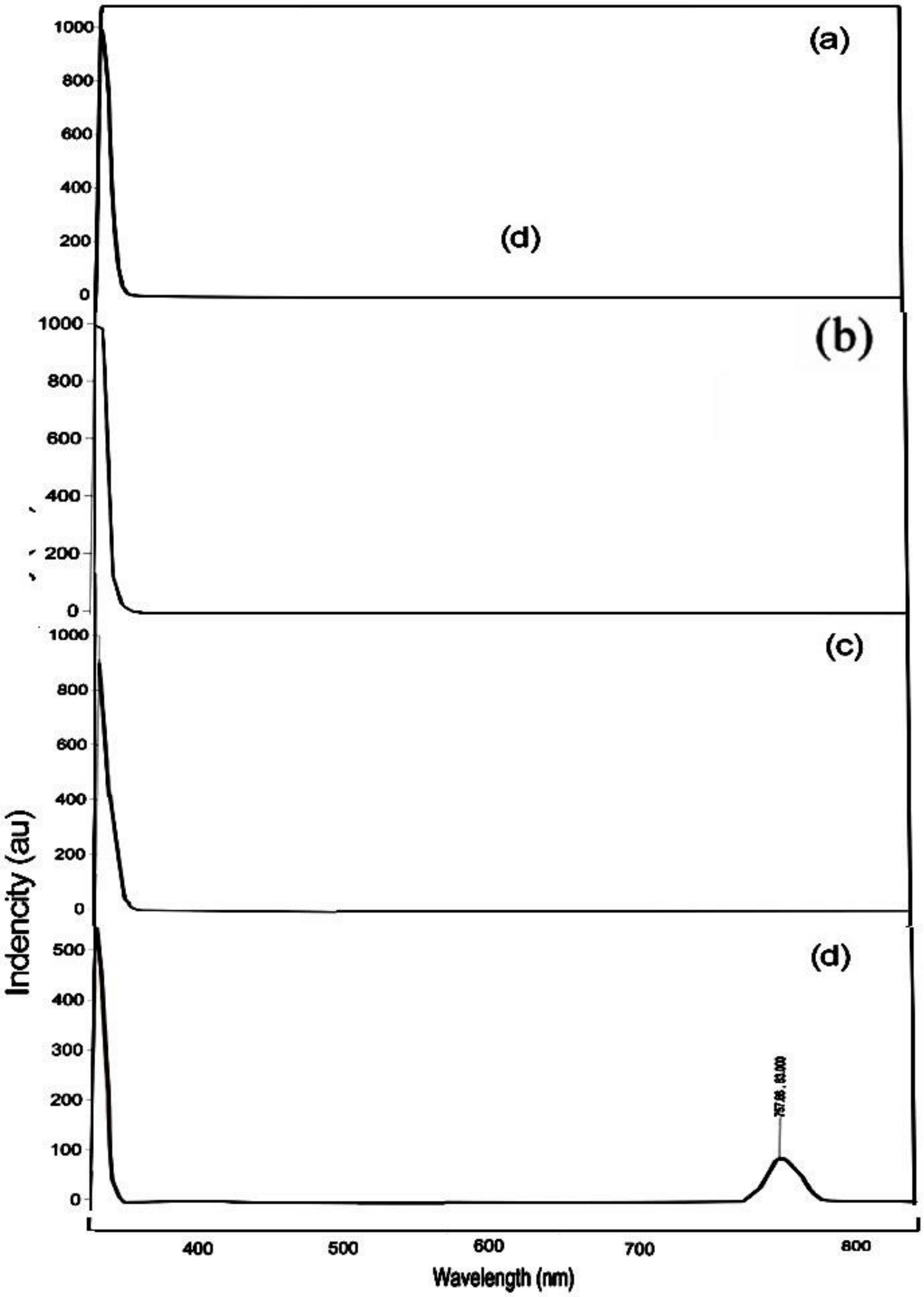

Figure 6 PL-Spectra of (a) Pure ZTS, (b) ZTS/Na, (c) ZTS/K (d) ZTS/Rb doped crystals

TG – DSC studies :-

The TG – DSC curve is recorded for pure and alkali metals (1 mole %) doped ZTS crystal and shown in figure – 7. The absence of weight loss around 100˚C shows that there is no water of hydration in the molecular structure. In the case of doped specimens the melting point is changed slightly which implies the incorporation of dopants in ZTS crystal. The suitability of the material for application in lasers is due to no de-composition up to the melting point, this implies that the materials are required for with standing high temperatures.

In DSC curve the decomposition is recorded from 10˚C to 500˚C. In the DSC curve, the endothermic peak at ~ 180˚C in the figure for all doped specimens which could be due to liberation of water molecules. The three sharp endothermic peaks at ~240˚C - 360˚C in all specimens may be due to the decomposition of S block metals doped ZTS crystal into fragments and their subsequent volatilization.

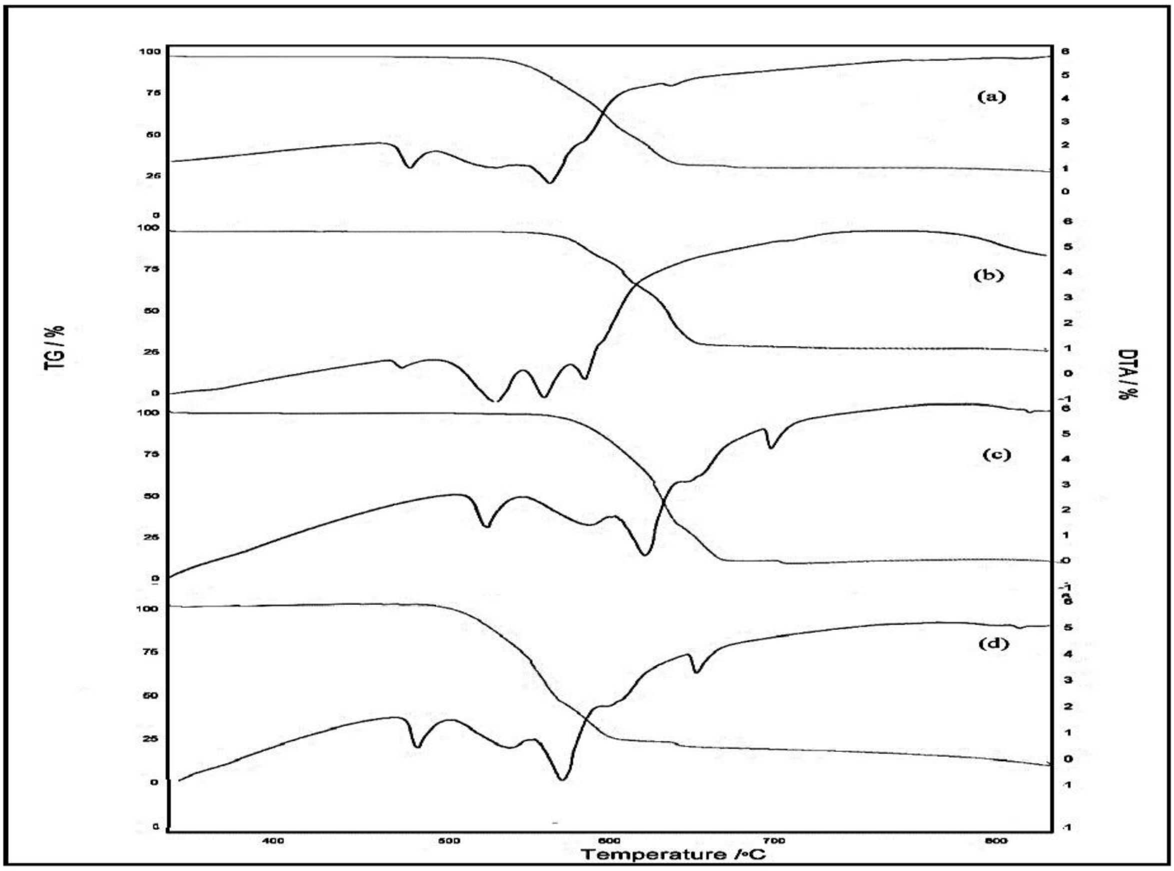

Figure 7 TG-DSC of (a) Pure ZTS, (b) ZTS/Na, (c) ZTS/K (d) ZTS/Rb doped crystals

Conclusion

Transparent crystals of pure and S block metals (Na(I), K(I) and Rb(I)) doped ZTS crystals are grown by slow evaporation solution grown technique. The single crystal XRD analysis gives the slight changes in all parameter value than the parent which tells that S block metals are incorporated as dopant only in crystal matrix is evidenced by energy dispersive X – ray spectroscopy. Some minor structural variations in FT – IR and XRD is observed due to doping changes in the external morphology of metal thiourea crystal is observed due to doping in SEM images. Thermal studies reveals the purity of the material and no decomposition is observed up to the melting point. SHG reveals that there is slight decrease in the case of Na, K and increased enhancement in Rb compared to pure ZTS values. There is reduction in the wavelength in the case of S block metals doped specimens compared to ZTS where there is a slight increased value. PL spectra shows that there is an increased flouresence intensity for all three S block metals.

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