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Growth and Characterization of Pure and Potassium Sulfate - Doped Zinc (tris) Thiourea Sulfate (ZTS) Single Crystals

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***Abstract*— Pure and potassium sulfate doped Zinc tris-Thiourea sulfate (ZTS) crystals were grown by single diffusion gel technique. The morphological alteration was occurred as a result of doping. An elemental confirmation was performed by using Energy Dispersive X - ray Analysis (EDAX). An orthorhombic structure of both crystals was confirmed and the value of lattice parameters was calculated by X- ray diffraction (XRD) analysis. The presence of functional groups was obtained by FT-TR analysis. Vickers micro hardness study was carried out for both crystals and it was founded that doped crystal was harder than pure crystal. Photoluminescence study gave confirmation of insulating nature of both crystals. Second harmonic Generation efficiency was confirmed by Kurtz-Perry powder method and it gave result of enhancement of SHG efficiency of doped ZTS crystal.**

***Keywords*— Gel technique, Characterization, Doping, ZTS crystal, Mechanical strength, SHG efficiency, NLO material**

I. INTRODUCTION

In recent years, organometalic non linear optical (NLO) materials have attained immense appeal form researchers due to a range of their technological applications in photonic field [1]. Zinc tris (thiourea) sulfate is one of the most important organometalic non linear optical crystals having applications in laser experiments and for second harmonic generation (SHG). ZTS possesses an orthorhombic crystal structure with lattice parameter as a= 11.126 A^o, b = 7.773 A^o and c = 15.491 A^o and space group Pca2$_1$ [2]. It possesses1.2 times more second harmonic generation efficiency that of KDP crystal [3], which makes it more important SHG application.

In the present work, elemental analysis (EDAX), structural analysis (XRD), FT-IR analysis, PL study, Micro hardness study and second harmonic generation study have been carried out. By controlling nucleation rate, pure and doped ZTS crystals were grown using single diffusion gel technique. The growth and characterization of doped with various dopants on ZTS crystals are reported in recent papers [4-8]. In order to understanding of the effect of potassium sulfate as a dopant on ZTS crystal, the doped crystals were grown and their characterization was carried out.

II. EXPERIMENTAL

The single diffusion gel growth technique was adopted to grow pure and potassium sulfate doped ZTS crystals. The gel was prepared by drop-wise addition of acetic acid to sodium metasilicate solution of specific gravity of 1.05gm/cc and its pH was adjusted to 4-5. AR grade of 3N thiourea solution was made using millipore water. The solution was stirred for one hour. To grow doped crystal, 1N measure of potassium sulfate was used to prepare its solution obtained through stirring for 3 hours. The solution so prepared was transferred to a set of test tubes as an inner solution.

The gel was found to be set in 8 days in the case of doped ZTS while for pure ZTS; it was 3-15 days. Once the gel set, zinc sulfate heptahydrate of 1N as the outer solution was poured over the gel. Crystallization period was found to be 1to 2 weeks for doped ZTS crystals while for pure ZTS it was 2-4 weeks. Highly transparent pure and doped ZTS crystals were successfully grown as shown in fig.1 and 2 respectively.

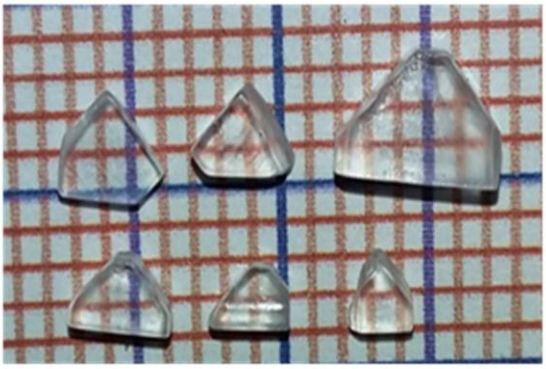

Figure 1: Grown Pure ZTS crystal

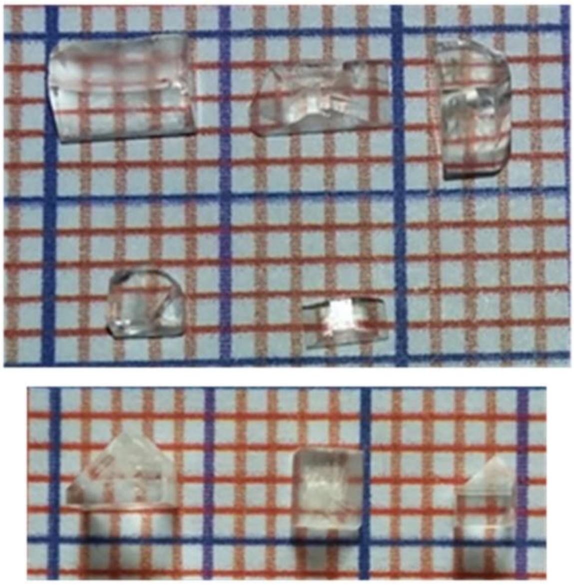

Figure 2: Potassium sulfate doped ZTS crystals

III. RESULTS & DISCUSSION

EDAX Test

Energy Dispersive X-ray Analysis (EDAX) test was accomplished using Geon 5610 LV Model at 15 kV - 20 kV and Oxford Olympus software.

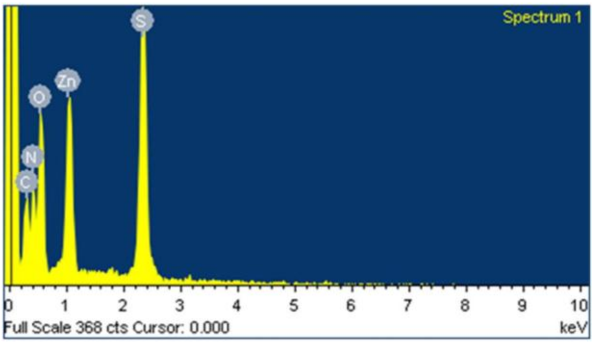

Figure 3: EDAX spectra of pure ZTS crystal

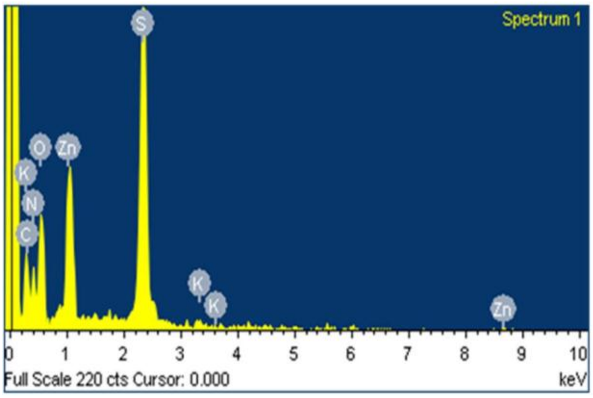

Figure 4: EDAX spectra of Potassium sulfate doped ZTS crystal

Table 1: Stchiomatric ratio of element of Potassium sulfate doped ZTS crystal

Element	Weight%	Atomic%	Compd%
C	9.14	13.17	33.49
N	8.40	10.38	32.38
S	8.73	4.72	21.81
K	0.19	0.09	0.23
Zn	9.71	2.57	12.09
O	63.82	69.07	
Totals	100.0		

The elemental confirmation of the two crystals was completed by using Energy Dispersive X-ray Analysis (EDAX); in order to confirming the presence of elements N, O, C, S and Zn in the pure ZTS crystal and N, O, C, S, Zn and K in the doped crystal, as observed in the spectrum shown in Fig. 3 and Fig. 4. It is also observed the absence of any inpuriry in both samples. The Stchiomatric ratio of every element of Potassium sulfate doped ZTS crystal are given in Table 1.

XRD Analysis

Pure and doped ZTS crystals were subjected to powder X-ray diffraction analysis using Regaku Miniflex diffractometer and at a wavelength of 1.540 Å with step size 0.008^0. Both the samples were examined with CuKα radiation in the 2θ range from 10^0 to 80^0 for ZTS crystal and from 20^0 ^{to} 80^0 for Potassium sulfate doped ZTS crystal. PXRD analysis reveals that both crystals have an orthorhombic structure with space group $Pca2_1$. The experimental values of lattice parameters of pure and doped ZTS crystals are in good agreement with those reported (ZCPDS - 760778) as shown in table 2[9]. XRD pattern of pure and doped ZTS crystals are shown in Fig. 5 and Fig.6. XRD experimental data of Potassium sulfate doped ZTS crystal are shown in table 3.

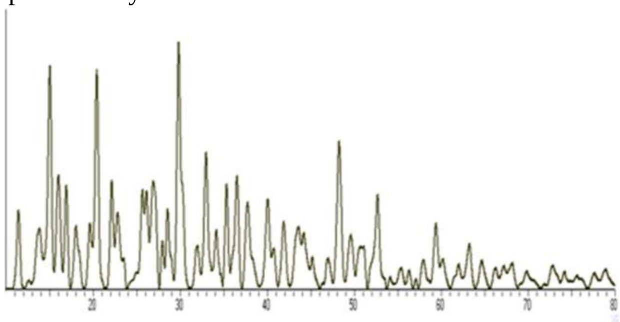

Figure 5: XRD pattern of pure ZTS crystal

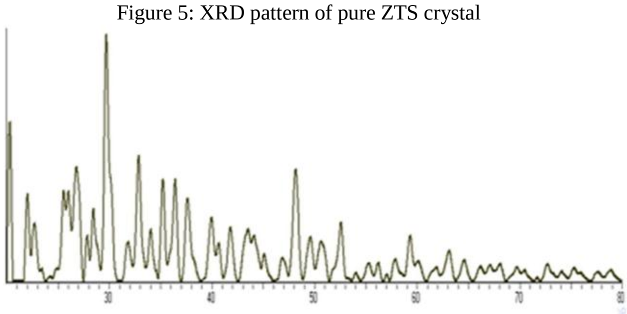

Figure 6: XRD pattern of Potassium sulfate doped ZTS crystal

Table 2: Comparison of lattice parameters of pure and doped ZTS crystals

Parameters	Pure ZTS crystal	doped ZTS crystal	ZCPDS (760778) Data
a (Å)	11.13	11.12	11.12
b (Å)	7.76	7.71	7.77
c (Å)	15.56	15.58	15.49
V $(Å)^3$	1343.8	1335.7	1338.4
Space Group	$Pca2_1$	$Pca2_1$	$Pca2_1$
Structure	Orthorhombic	Orthorhombic	Orthorhombic

Table 3: XRD data of Potassium sulfate doped ZTS crystal

d_{theo} A^0	d_{exp} A^0	hkl	d_{theo} A^0	d_{exp} A^0	Hkl
3.29	3.30	1 1 4	2.09	2.09	1 1 7
3.12	3.12	2 2 1	2.06	2.06	5 1 2
2.80	2.81	3 1 3	2.04	2.04	3 1 6
2.74	2.74	4 0 1	1.92	1.92	5 2 1
2.68	2.68	3 2 0	1.92	1.92	1 4 0
2.63	2.64	3 2 1	1.89	1,89	4 3 0
2.54	2.54	3 2 2	1.89	1,89	1 2 7
2.54	2.54	3 1 4	1.88	1.88	4 3 1
2.46	2.46	0 3 2	1.85	1.85	6 0 0
2.39	2.39	1 1 6	1.85	1.85	1 1 8
2.38	2.38	3 2 3	1.83	1.83	2 4 0
2.27	2.27	3 1 5	1.80	1.80	6 1 0
2.25	2.25	4 0 1	1.80	1.80	6 0 2
2.22	2.22	2 2 5	1.79	1.79	1 4 3
2.17	2.17	4 2 2	1.79	1.79	6 1 1
2.17	2.17	4 1 4	1.75	1.74	6 0 3
2.15	2.15	0 3 4	1.70	1.70	6 1 3
2.15	2.15	0 2 6	1.70	1.70	4 3 4
2.10	2.10	3 3 1	1.64	1.64	3 3 6

FTIR Analysis

FTIR analysis was carried out on both the crystals with Bruker Alpha T FTIR spectrometer using KBr based pellets of the sample powders the crystals. The spectra were obtained in the range of 500 - 4000 cm^{-1} at room temperature and are shown in Fig. 7 and Fig. 8. The functional groups in both the crystals are compared in table 4.

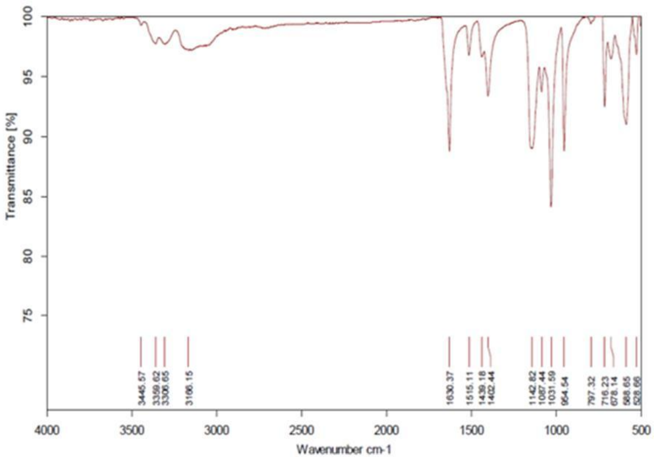

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Figure 7: FT IR spectra of pure ZTS crystal

As shown in Fig. 7 and Fig. 8 of FT IR spectra, There are small shifts observed as a result of dopant as well as one more C-N stretch was observed due to effect of dopant. The peaks as 3306.65 cm^{-1} and 3359.62 cm^{-1} of pure ZTS crystal as well as the peaks as 3358.33 cm^{-1}, 3358.33 cm^{-1} and 3374.03 cm^{-1} for doped ZTS crystal are obtained due to N-H stretching. The C-O stretching vibrations ware occurred at 1142.82 cm^{-1} and at 1153.08 cm^{-1}. The one more peck at 604.70 cm^{-1} are added in doped ZTS crystal.

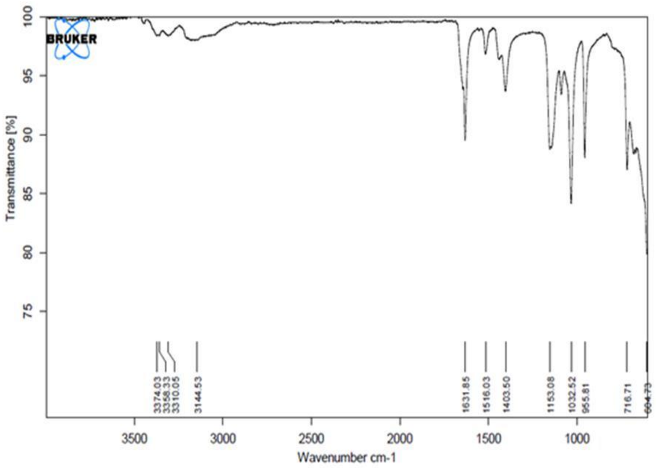

Figure 8: FT IR spectra of Potassium sulfate doped ZTS crystal

Table 4: Comparison of FT IR data of pure and Doped ZTS crystals

Pure ZTS crystal (wave no. in cm^{-1})	Potassium sulfate doped ZTS (wave no. in cm^{-1})	Assignments
588.65	-	C-Cl stretch
-	604.70	C-Cl stretch
678.14	-	-C=C-H:C-H bend
716.23	716.71	C-H rock
797.32	-	=C-H bend
954.54	955.81	=C-H bend
1031.59	1032.52	C-N stretch
1087.44	-	C-N stretch
1142.82	1153.08	C-O stretch
1402.44	1403.50	C-C stretch
1439.18	-	C-C stretch
1515.11	1516.03	N-O asymmetric stretch
1630.37	1631.85	N-H bend
3166.15	3144.53	O-H stretch
3306.65	3310.05	N-H stretch
3359.62	3358.33	N-H stretch
-	3374.03	N-H stretch
3445.57	-	O-H stretch

Hardness Measurement

Vickers hardness tests were carried out on the crystals. The hardness H_V is calculated using the formula as given

$$H_v = 1.854\ P/d^2 \ \ Kg/mm^2 \qquad (1)$$

where, H_v is hardness, P is the load applied in Kg and d is mean diagonal length of the indentation impression in mm. Good surfaces of both crystals were mounted one after one on the platform of the Vickers micro hardness tester for various applied loads from 10 gm to 60 gm. The dwell time was 5 second and the average diagonal was used to calculate

micro hardness number. A plot of hardness versus the applied load, for ZTS crystals, is -shown in Fig. 9.
As can be seen, hardness is found to increase with load increasing form 10 gm to 60 gm. It is also observed that hardness of doped crystal is higher than that of pure ZTS crystal, a desirable result from the device fabrication view point.

The energy band gap of both ZTS crystals were calculated using formula

$$E=hc/\lambda \qquad (2)$$

where, λ = wavelength of the band gap luminescence,
h = Planck's constant
Energy band gap of doped ZTS crystals was calculated to be 3.1 eV whereas for pure ZTS crystal, the band gap was calculated to be 3.4 eV. Usually, the energy band gap of an insulator is above 3 eV.

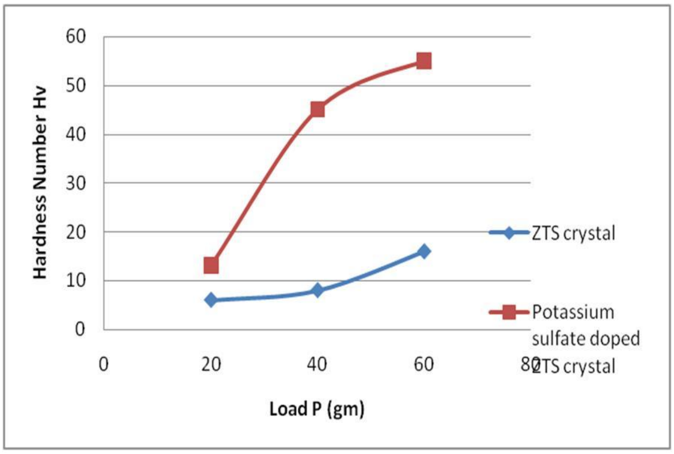

Figure 9: Plot of Load Vs Hardness of pure and Potassium sulfate doped ZTS crystals

Photoluminescence Study
Pure and Potassium sulfate ZTS crystals ware subjected to photoluminescence study as reported [10]. ZTS crystals are also reported with PL study with different parameters [11-12]. The excitation and emission spectra of pure and doped ZTS crystals are shown in Fig.10 and Fig.11. The excitation spectra were obtained in the range of 220nm-350nm and emission spectra were obtained in the range 350-650nm. An excitation peak of pure ZTS was recorded at 248 nm while for doped ZTS crystal it was at 249nm accompanied by a minor shift in the peak frequency. Whereas an emission peak of pure ZTS was recorded at 369nm, for doped ZTS crystal it was at 395nm, also exhibiting difference in the peak intensities. Compared to pure ZTS crystal, however, it doesn't bear any practical effect on the result.

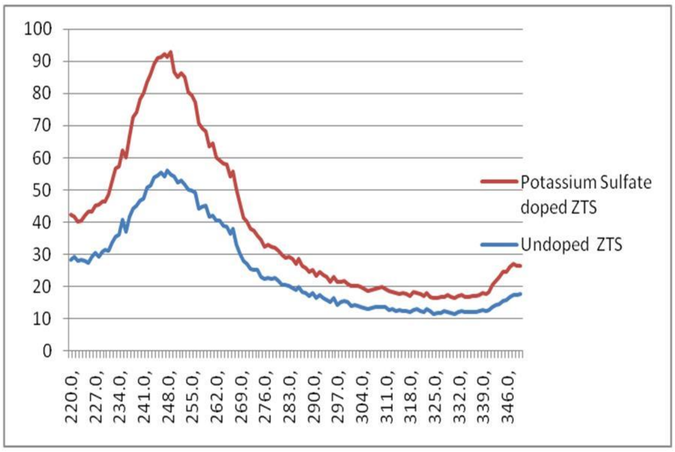

Figure 10: PL Excitation spectra of Pure and Potassium sulfate doped ZTS crystals

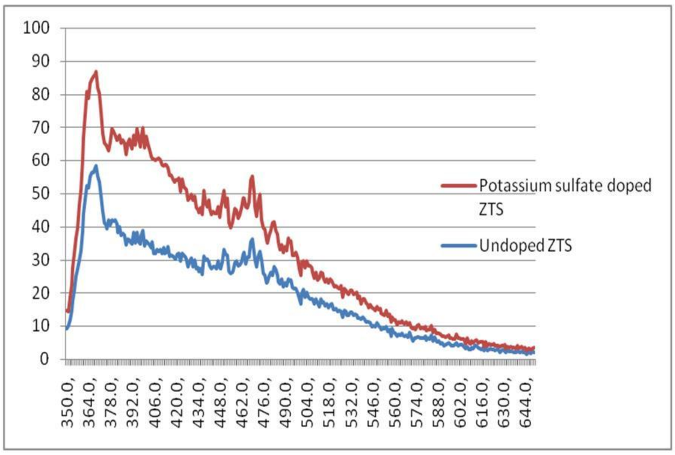

Figure 11: PL Emission spectra of Pure and Potassium sulfate doped ZTS crystals

SHG Efficiency Measurement
Kurtz- Perry powder experiments were carried out to measure second harmonic generation efficiency of pure and potassium sulfate doped ZTS crystals. SHG efficiency of both ZTS crystals was confirmed by this powder technique. The sample was made in powder form and filled into capillary. The sample was illuminated using fundamental high intensity beam of 1064nmfrom Nd:YAG laser with pulse width of 10 ns, repetition rate was 10 Hz and input energy was 0.5mJ/Pulse. This test yielded second harmonic efficiencies of the samples. The SHG efficiency of pure ZTS crystal was 48 mV while for doped ZTS crystals it was 52 mV. The SHG efficiency of potassium sulfate doped crystal is fairly increased, namely, 1.1 times that of the pure ZTS crystal a positive result of the doping.

IV. CONCLUSION

Pure and Potassium sulfate doped ZTS crystals were successfully grown by gel growth technique at the room temperature. The effect of dopant was observed as a change in morphology of doped ZTS crystals. As a result of doping of Potassium sulfate, gel setting time and crystal growth time were significantly decreased. The presence of all elements and the doping of Potassium sulfate were confirmed by EDAX test. The lattice parameters are founded to be fairly matched with reported value and an orthorhombic structure was confirmed of both crystals by powder XRD analysis. The functional group for both crystals was determined from FT IR spectra. PL study was stated that both crystals have insulating nature.The mechanical property of both crystals was evaluated by Vickers micro hardness test and it is concluded that doped crystal is harder than pure one. SHG test was performed by Kurtz-Perry powder and as a result of this test the efficiency of Second Harmonic generation was enhanced due to doping.

Thus, enhancement of SHG efficiency as well as increment in mechanical strength due to doping are the main findings of the present study that make Potassium sulfate doped crystal as a better candidate for NLO device fabrication.

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