LOW TEMPERATURE PHOTOLUMINESCENCE STUDY ON ZINC TRIS THIOUREA SULPHATE SINGLE CRYSTAL

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Singles crystals of semiorganic Zinc Tris Thiourea sulphate were grown by slow evaporation technique. The x-ray powder diffraction (XRD) pattern of ZTS crystal confirms the orthorhombic crystal structure. FTIR study assigns the presence of functional groups and confirms the co-ordination of zinc metal ions with thiourea. The UV-Vis spectrum studies the optical transparency of the crystal. Temperature dependent Luminescence study from 300K to 77K exhibits peaks of one violet, two blue and one green emission. The variation of energy gap with low temperature exhibit interesting hysteresis. The stokes shift has been determined as 133.93nm or 9.27eV.

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1.Introduction

Non-linear optics (NLO) receives greater attention due to the invention of new non-linear optical frequency conversion materials since, they have a significant impact on laser technology[1], optical communication[2] and data storage technology[3]. The frequency conversion technique is useful for extending the wavelength range of lasers which led to the various useful devices such as harmonic generators, optical parametric oscillators, electro optic modulators and amplifiers for high power lasers[4]. The quest for new frequency conversion materials is presently concentrated on semiorganic crystals, due to their large non-linearity, high resistance to laser induced damage, low angular sensitivity and good mechanical properties. Thiourea, a centrosymmetric molecule form non-centrosymmetric complexes by co-ordinating with different metal ions leading to nonlinear optical properties [1]. Thiourea molecule coordinates with several transition metal ions to form stable coordination complexes, which can be crystallized either by solution growth technique [2- 3] or by gel growth technique [4-6]. In these coordination complexes, thiourea is linked to the central metal through sulphur atom rather than nitrogen [7]. Thiourea possess a large dipole moment and it forms number of semiorganic materials such as Bis thiourea Cadmium Chloride [8], Zinc thiourea sulphate[9] and Zinc thiourea chloride[10]. The single crystals of these materials have very high laser damage threshold[3]. Motivated by these considerations, the Zinc thiourea sulphate has been crystallized for the present study and characterized by the XRD, FTIR, UV-Vis and Low temperature PL studies. The results have been discussed and reported in this paper.

2. Experimental details

The single crystals of ZTS were obtained by slow evaporation technique at room temperature. Photographs of ZTS as grown crystals are shown in Fig.1. The powder XRD was performed by using Richseifert diffractometer. The FTIR spectrum was recorded using Perkin

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Elmer spectrum BX model spectrophotometer by KBr pellet technique in the range 400 – 4000cm^{-1} at a resolution 2 cm^{-1}. The UV-Visible absorption spectrum was recorded using Perkin Elmer Lamda 35 spectrophotometer in the spectral range 200 to 1100nm using Perkin Elmer Lamda 35. The PL emission spectrum was recorded by VARIAN Cary Eclipse Fluorescence Spectrophotometer employing 150 Watts Xe arc discharge lamp as the excitation source.

3. Results and discussions

Powder XRD analysis The figure1 presents the photograph of TTCC crystals which are bright, transparent and colourless with well defined external faces. The figure 2a has shown the recorded powder XRD for the grown pure ZTS crystals at room temperature using a wavelength of 1.5418Å. The peaks are indexed by the method of least square fit using CELN program. The crystals are found to be crystallized in orthorhombic structure, The lattice parameters and the corresponding cell volume are presented in Table 1 and they are found to be in good agreement with the reported values [11-12]. The theoretical XRD pattern (figure 2b) for ZTS has been simulated by using Lazy Pulverix programme and it agrees with the experimental XRD pattern. The theoretical d-spacings obtained are found to be in good agreement with the experimental observed d-values in Table 1. But it is notable by comparing the figures 2a and 2b that there is a slight deviation between the observed and theoretical intensities. This deviation may be due to the preferred orientation. Generally in powder diffraction data, preferred orientation has a significant influence on the intensity distribution of the diffraction pattern which in turn causes the deviation of experimental diffractometer data from the ideal intensity pattern [13-15]. However it has been observed that the lattice parameters obtained from this theoretical study are in excellent agreement with the experimental values as given in Table 1. Moreover, the observed absences of h00 with h odd, 0k0 with k odd and 00l with l odd gives the hint that the lattice is of primitive type [14-15]. This theoretical study also confirms the space group of ZTS as Pca21.

Fig.1 Photograph of grown TTCC crystal.

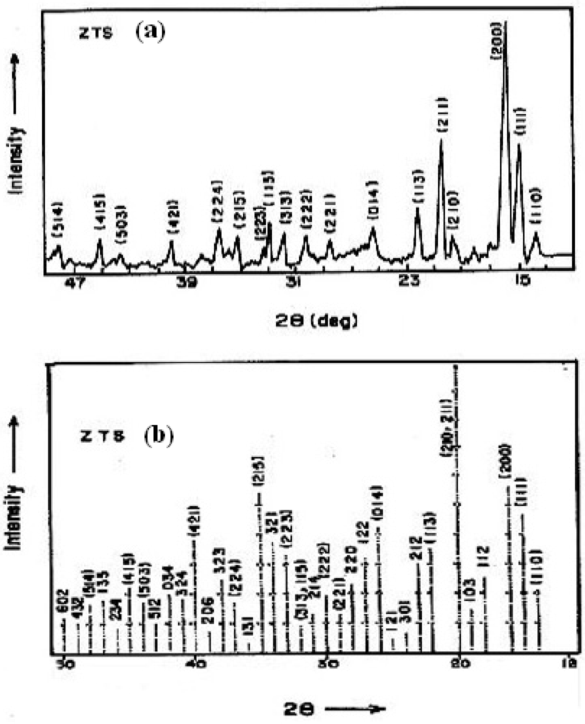

Fig.2 X-ray powder diffraction pattern of TTCC crystal

Table 1 The comparison of experimental and theoretical d-values and lattice parameters for ZTS.

Sl.No.	$d_{exp.}$(Å)	$d_{theo.}$(Å)	hkl	Sl. No.	$d_{exp.}$(Å)	d_{theo}(Å).	hkl
1.	6.51	6.454	110	20.	2.69	2.696	223
2.	5.92	5.870	111	21.	–	2.648	321
3.	5.54	5.545	200	22.	2.55	2.539	215
4.	–	4.888	112	23.	–	2.466	131
5.	–	4.647	103	24.	2.46	2.444	224
6.	4.52	4.550	210	25.	–	2.379	323
7.	4.37	4.361	211	26.	–	2.324	206
8.	4.02	3.977	113	27.	2.25	2.250	421
9.	–	3.910	212	28.	–	2.200	324
10.	–	3.654	301	29.	–	2.129	034
11.	–	3.540	121	30.	–	2.084	512
12.	3.41	3.424	014	31.	2.06	2.065	503
13.	–	3.286	122	32.	2.01	2.003	415

Sl.No.	$d_{exp.}$(Å)	$d_{theo.}$(Å)	hkl	Sl. No.	$d_{exp.}$(Å)	d_{theo}(Å).	hkl
14.	–	3.177	220	33.	–	1.992	234
15.	3.13	3.111	221	34.	–	1.935	135
16.	2.95	2.934	222	35.	1.89	1.885	514
17.	–	2.928	214	36.	–	1.842	432
18.	2.81	2.817	313	37.	–	1.827	602
19.	2.72	2.757	115	–	–	–	–
$a_{exp.}$ (Å)	$a_{theo.}$ (Å)	$b_{exp.}$ (Å)	$b_{theo.}$ (Å)	$c_{exp.}$ (Å)	$c_{theo.}$ (Å)	Cell Volume ($Å^3$)	
11.290±0.03	11.290	7.687±0.02	7.687	15.297±0.03	15.297	1327.6	

FTIR analysis The Fig. 3 shows the FTIR spectrum of the ZTS crystal and table2 presents the observed absorption frequencies and their assignments in relation to their characteristic vibrational modes. The broad envelope positioned in between 2750-3500 cm^{-1} corresponds to symmetric and asymmetric stretching modes of NH_2 grouping of zinc coordinated thiourea. The bond of thiourea was not shifted to lower frequency on formation of metal thiourea complexes indicating that the nitrogen to zinc bonds are not present and that the bonding must be between sulphur of thiourea and zinc. If the bonding is through sulphur, there will be a decrease in the C=S stretching frequency and an increase in the C-N stretching frequency. It is observed from the spectrum that the symmetric and asymmetric C=S stretching vibrations at 740 cm^{-1} and 1417 cm^{-1} of thiourea are shifted to lower frequency 714 cm^{-1} and 1396 cm^{-1} in ZTS. The C-N stretching vibration at 1089 cm^{-1} and 1470 cm^{-1} are shifted to 1120 cm^{-1} and 1502 cm^{-1} in ZTS. These observations confirm the coordination of

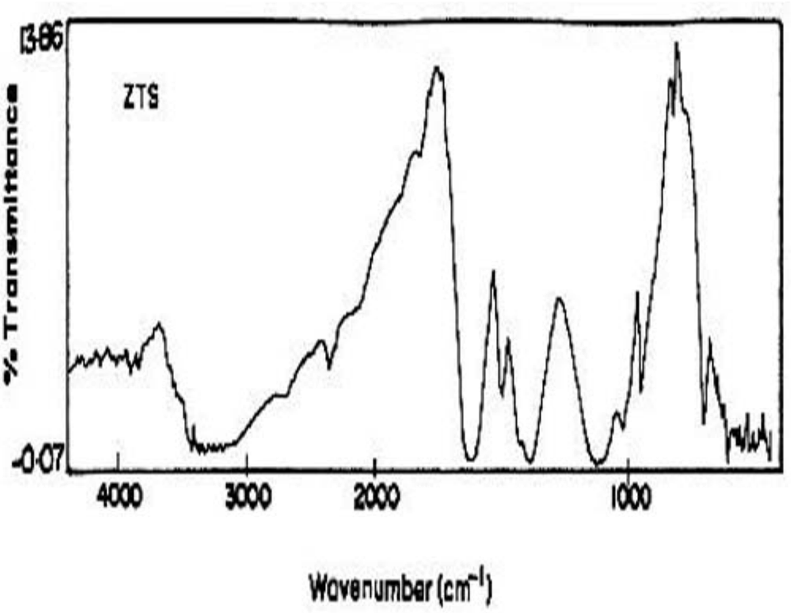

Fig.3 FTIR spectrum of TTCC crystal.

Table 2 The comparison and assignment of FTIR bands of ZTS with Thiourea

Sl. No.	Thiourea $CS(NH_2)_2$	ZTS $Zn[CS(NH_2)_2]_3SO_4$	Assignment
1.	–	620	S-O stretching
2.	740	714	C=S symmetric stretching
3.	1089	1120	N-C-N stretching
4.	–	1136	SO_2 symmetric stretching
5.	1417	1396	C=S asymmetric stretching
6.	1470	1502	N-C-N stretching
7.	1625	1608	NH_2 (or) NH bending
8.	-	1734	N-H stretching
9.	1778	–	N-H stretching
10.	1819	–	N-H stretching
11.	3376	3410	NH_2 stretching

metals with thiourea through sulphur. The formation of sulphur- zinc bond is expected to increase the contribution to the highly polar character of the structure of thiourea molecule which is shown in figure 4, resulting in a stronger double bond character for the nitrogen to carbon bond and a stronger single bond character for the carbon to sulphur bond. The observed increase in N-C-N stretching vibrational frequency may also be attributed to a stronger double bond character of the carbon to nitrogen bond on complex formation. The bands 620 cm^{-1} and 1136 cm^{-1} observed in ZTS corresponds to S-O stretching vibration which confirms the presence of sulphate ion. All other peaks can be assigned to NH_2 bending and stretching vibrations[16-17]

UV-Vis Spectrum The transmission spectrum of ZTS recorded in the UV-Vis region is shown in figure 5. It reveals the transparent wavelength region in the visible region which gives hints for insulating nature of the crystal[18]. The low cutoff wavelength is at about 275 nm. The absorption in the near ultra violet region (200 – 400 nm) arises from the electronic transitions associated within the thiourea units of ZTS. In this spectra, there is a peak in the region of 1037 nm which is nearer to 1040 nm which is the fundamental wavelength of Nd : YAG lasers[19]. They are overtones of N-H vibrations. The absorption in this region can result in optical damage at high power levels. This reduction in absorption has significant contribution towards an improvement in the laser damage resistance of the crystal. The lower cut off of these crystals below 300 nm is an advantage in semiorganic NLO materials over organic materials. The extended wide transparency will enable higher harmonic generation and wavelength extension by cascaded frequency conversion processes. The wide transmission in the

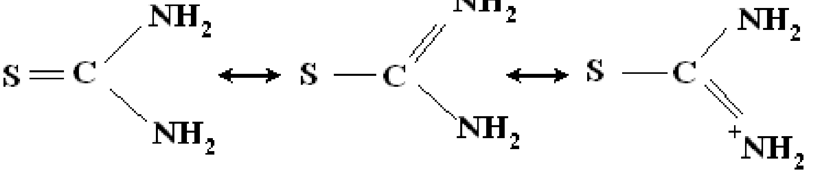

Fig.4 The resonance structure of thiourea molecule

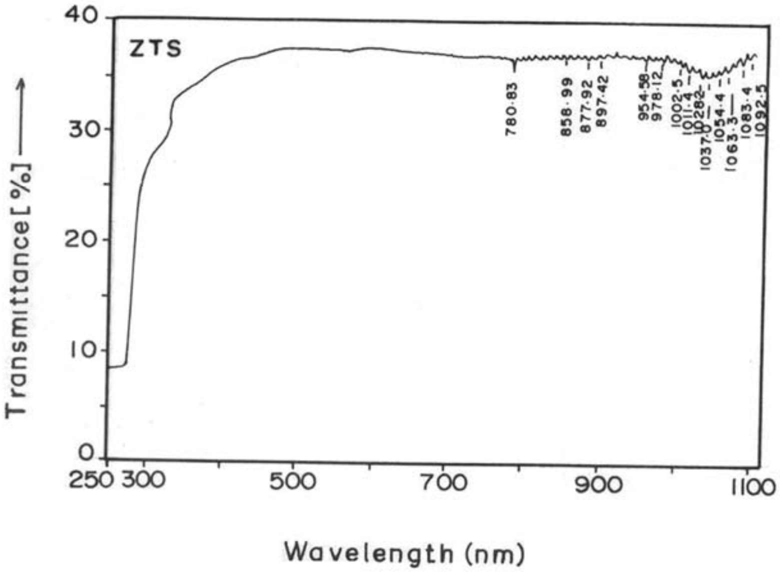

Fig.5 UV-Vis spectrum of TTCC crystal.

entire visible region (300 to 1100 nm) enables it to be a potential candidate for optoelectronic applications**.**

PL Spectrum The PL spectra of ZTS crystals were recorded with an excitation wavelength of 385nm for temperature ranging from 300K to 77K during cooling and heating process and shown in figure 6 and figure 7 respectively. Zn is a transition metal impurity. It is fast diffuser even at low temperatures and gives rise to both radiative and nonradiative centres [20]. The room temperature PL spectrum at 300K comprises prominent violet emission peak at 408.93nm, strong blue emission at 422.87nm and one very weak blue shoulder peak at 484.92nm. Besides these, one green emission peak is identified at 526.86nm. Becker and Bard have attributed the blue emission band at 428nm to S^{-2} vacancies [21- 23]. Bhattacharjee et al have ascribed 418nm peaks to S^{2-} vacancy [22, 24-25]. Murase et al [26] ascribed the blue emission band at 470nm to Zn^{2+} acceptor. Yanagida et al [27] have observed defect related longer wavelength luminescence at about 420nm, in addition to the band gap luminescence. Denzler et al [28] identified four types of point defects which can be present in ZnS, generating four trap levels inside the energy gap. Vacancies of Zn and S could be treated as localized acceptor and donor states whereas the interstitial atoms of S and Zn led to acceptor and donor states respectively. The emission occurring at longer wavelengths were made associated with the vacancy sites.

The prominent band gap violet luminescence at 408.93nm has shown small red shift with decrease of temperature from 408.93nm at 300K to 409.84nm at 77K whereas the position of all other peaks remains almost constant with respect to temperature. This red shift with decreasing temperature indicates that this band also undergoes the temperature induced

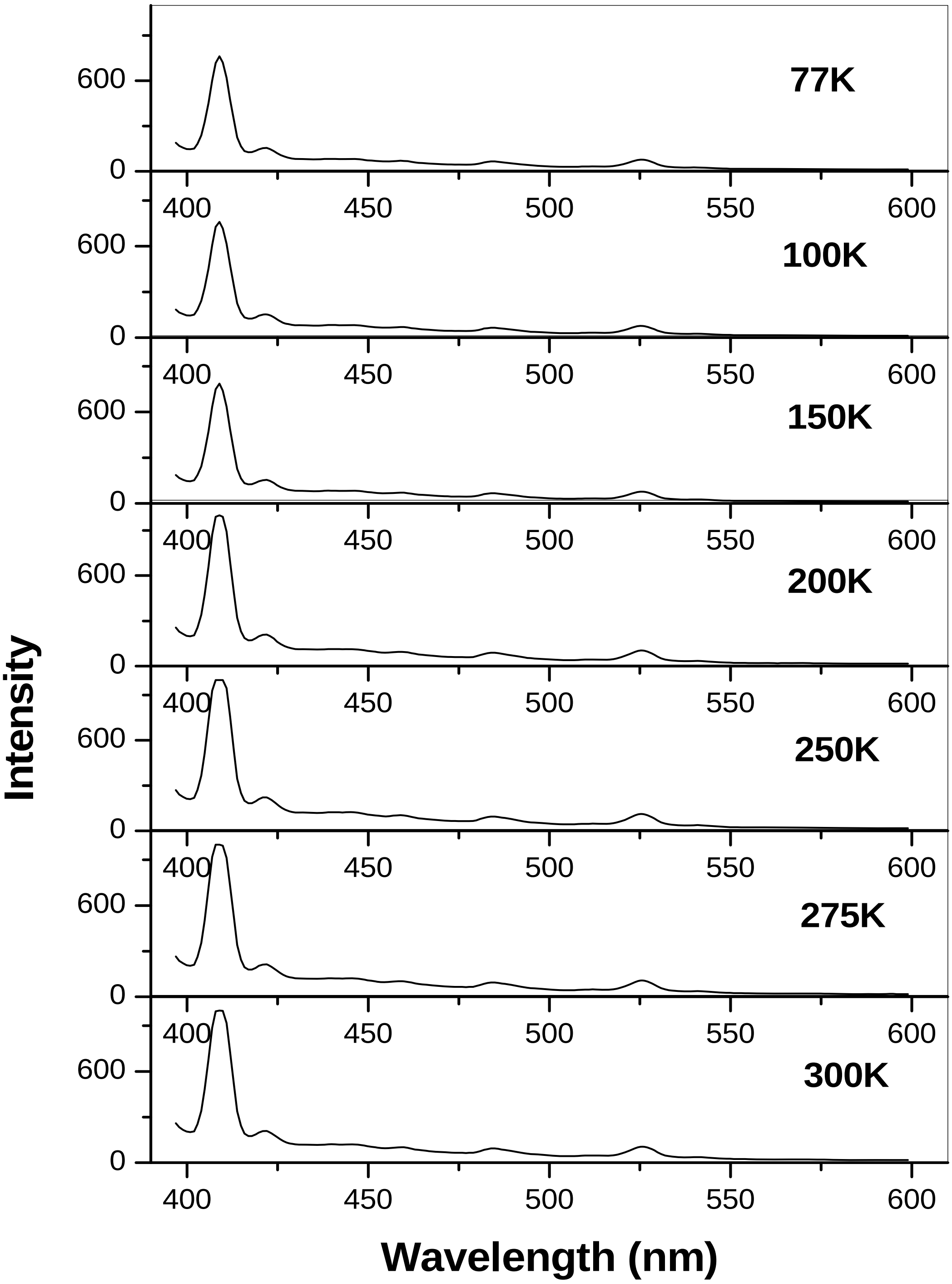

Fig.6 Temperature dependent PL spectra of TTCC crystal during cooling process.

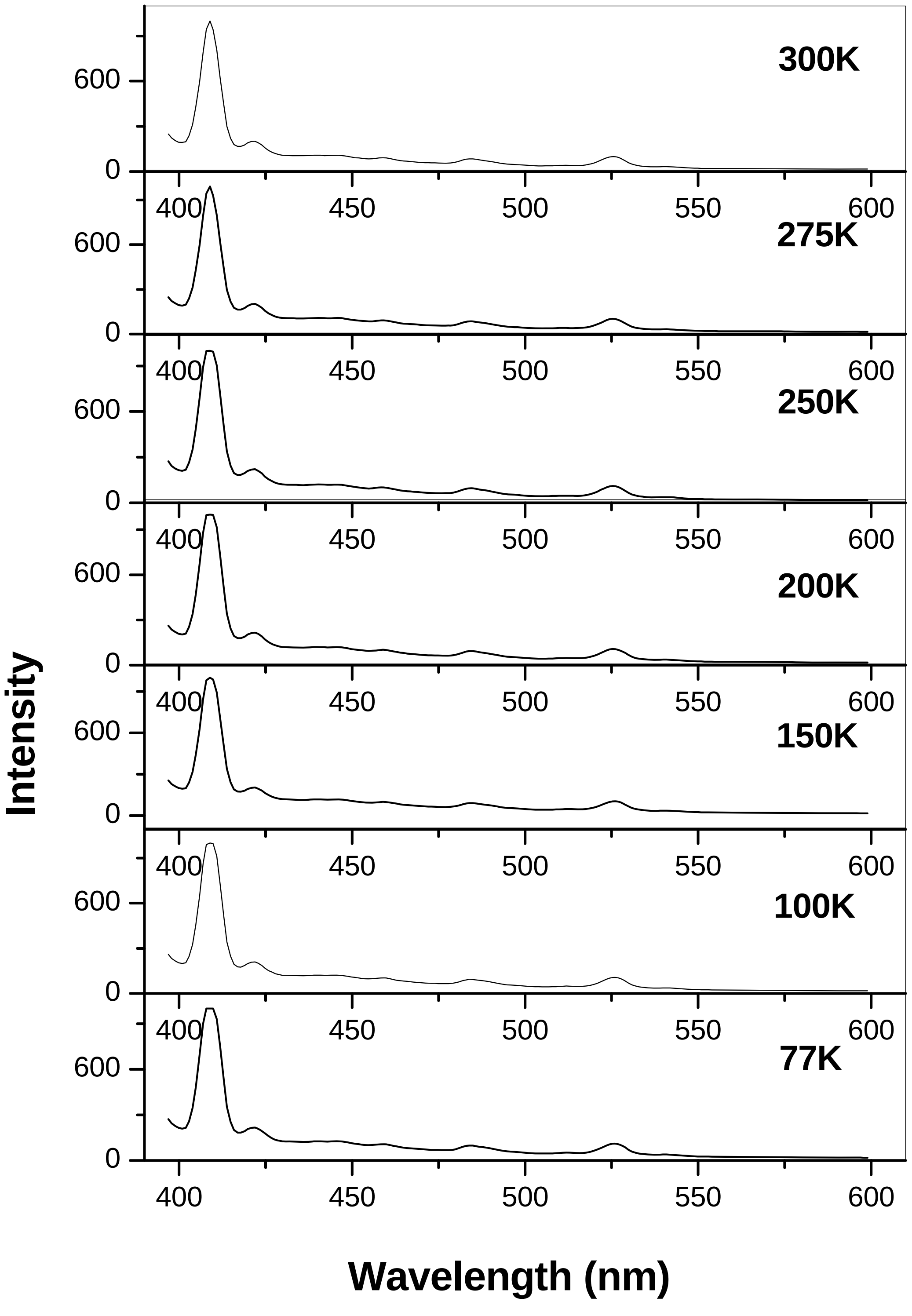

Fig.7 Temperature dependent PL spectra of TTCC crystal during heating process.

band gap shrinkage. Therefore it is reasonable to suggest that the violet emission from ZTS crystal is originated from Zn vacancy related defects or their complexes. This attributes the transition between the conduction band and Zn vacancy acceptor level which could give rise to luminescence at 408.93nm [29, 30]. The band gap has been deduced as 3.03 eV at room temperature from the band gap luminescence by using the formula

$$E=hc/\lambda$$

where λ is the wavelength of the band gap luminescence. It shows the insulating nature of the crystal nearer to the semiconducting region. It is interesting to note that the temperature dependence of the energy gap during cooling and heating process exhibits interesting hysteresis loop as shown in figure 8.

The strong blue emission at 420nm lies in the spectral region is associated with the luminescence from self activated centre. These centers have been attributed to crystal lattice vacancies [21, 23]. It has been reported that 422.87nm peak has been classically termed as self activated luminescence and known to be due to the recombination of carriers between S vacancy related donor and valance band [31]. The weak shoulder blue peak observed at 484.92nm may arise due to native point defects e.g. recombination of conduction band to Zn valence. The weak green peak at 526.86nm is thought to be due to recombination between S vacancy and Zn related acceptor centre [31].

The PL and UV-Vis spectra have shown maximum emission at 408.93nm and maximum absorption at 275nm respectively. The difference between the position of the band maxima of the absorption and emission spectra of the same electronic transition known as Stokes shift [32-33], is determined as 133.93nm or 9.27eV.

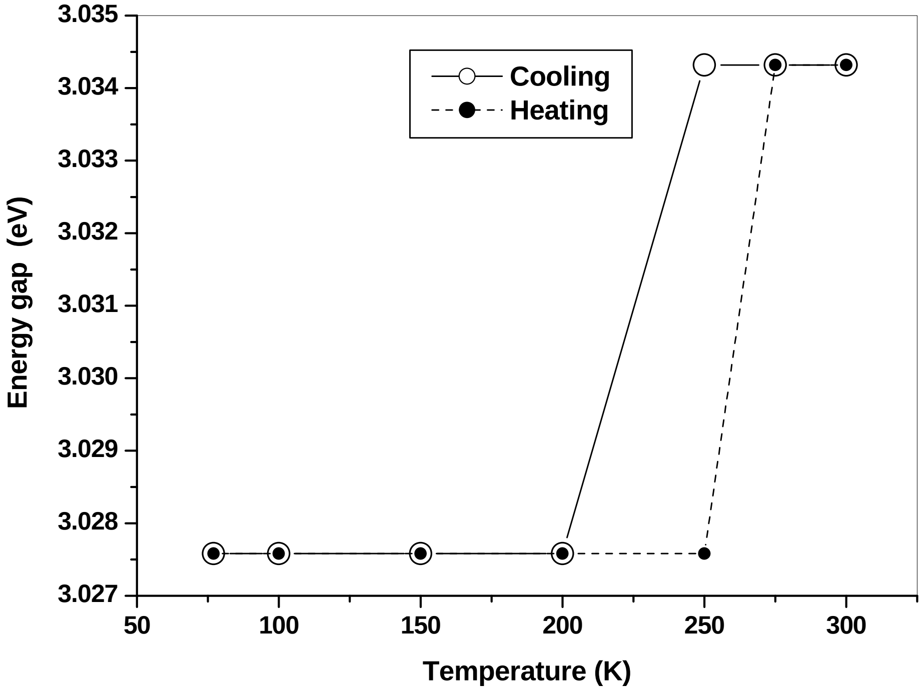

Fig.8 Plot of energy gap versus temperature for TTCC crystal

4. Conclusions

Pure ZTS crystals having reasonably good crystalline quality have been grown by slow evaporation technique. The crystals are bright, transparent and colorless with well defined external appearance. The XRD study indexed the Braggs reflections and the lattice parameters obtained are a=11.290Å, b=7.687Å, c=15.297Å, V=1327.6Å^3 and α=β=γ=90° with orthorhombic crystal structure of space group Pca21. The FTIR study assigns vibrational frequencies and tabulated in table 2. The UV-Vis study deduces the cut off wavelength as 275nm. The crystal has shown wide transmission in the entire visible region. These enables the crystal to be a potential candidate for optoelectronic applications. The PL spectrum shows maximum emission at 408.92nm which confirms the energy gap as 3.03eV. Generally the energy gap of the insulator lies above 3eV[18].

These confirm that the ZTS crystal is an insulator nearer to the semiconductor region. The nature of the crystal gives the hint whether the crystals are insulator or semiconductors. Semiconductor crystals are mostly coloured crystals and insulator crystals are transparent. To be very clear, a crystal can have no strong electronic and vibronic transitions in the visible spectral region of 740nm to 360nm or 1.7eV to 3.5eV. It is notable that the present grown crystals are found to be colourless, transparent and clear. It exhibits no strong electronic or vibronic transitions in the visible spectral region between 740 and 360nm. This confirms the nature of the ZTS crystal as an electrical insulator. The PL spectra collected from room temperature to 77K by cooling have shown one violet prominent emission at 408.93nm, one blue prominent emissions at 422.87nm and one very weak shoulder peak at 484.92nm and green emission peak at 526.86nm. The violet emission at 408.93nm is originated from Zn vacancy related defects or their complexes. The band gap luminescence have shown red shift from 408.93 nm to 409.84nm with decrease of temperature and exhibits interesting hysteresis loop with respect to temperature. The blue emission at 422.8nm corresponds to S^{-2} vacancies. The blue emission at 484.92 nm is due to native point defects. The stokes shift has been determined as 133.93nm or 9.27eV. Thus the characteristics of ZTS crystal has been studied and reported.

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