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STUDIES ON GROWTH AND VARIOUS PROPERTIES OF L-CYSTINE DOPED ZTS CRYSTALS

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Abstract:

Undoped and L-cystine doped Zinc Tris-thiourea Sulfate (ZTS) crystals were grown by aqueous solution method. 5 mole % of L-cystine was added as the dopant into aqueous solution of ZTS for growing the doped crystal. Colorless and non-hygroscopic crystals were grown after a growth period of 35 days. Solubility studies were carried out by gravimetrical method.The functional groups of the samples were identified by FTIR technique. XRD studies reveal that the grown crystals crystallize in orthorhombic structure. From the microhardness measurement, it is confirmed that L-cystine doped ZTS crystal is more harder than undoped ZTS crystal. Surface features of the samples were studied by SEM method. Dielectric constant and dielectric loss were measured for the samples at different frequencies. SHG studies were performed to measure the relative SHG efficiency to prove that the samples are the better candidates of NLO materials.

Key Words: ZTS, Doping, Solution Method, XRD, FTIR, Hardness, SEM, Dielectrics, NLO & SHG

1. Introduction:

The interaction of high intense light with the various materials to generate new light altered in phase, frequency and amplitude is known as nonlinear optics (NLO). The field of NLO and photonics are rapidly emerging as the technology for the 21st century. Photonics is the technology in which a photon instead of an electron is used to acquire, store, process and transmit information. NLO materials are necessary to manipulate the light and these are gaining importance in technologies such as electro-optics and lasers which includes industry, medicine, entertainment, remote sensing, optical data storage, optical communication, optical computing and dynamic image processing [1-3]. The complex of organic and inorganic materials gives semiorganic materials, which possesses higher mechanical strength and thermal stability compared to organic materials [4, 5]. Zinc tris-thiourea sulphate (ZTS) crystal is a semiorganic NLO material for second harmonic generation (SGH) from metal complexes of thiourea. High–damage threshold and wide transparency make it a better alternative for KDP crystals in frequency – doubling and laser fusion experiments [6-8]. ZTS crystal crystallizes in the non-centrosymmetric orthorhombic space group $Pca2_1$ [9, 10]. It is reported the many organic complex crystals like tris(thiourea) zinc chloride (TTZC), bis(thiourea) cadmium chloride (BTCC), bis(thiourea) cadmium acetate(BTCA) have been studied [11-13]. Balasundari et al. reported the growth and studies of picric acid doped ZTS crystals in the literature [14]. In the present work, the growth of undoped and L-cystine doped ZTS crystals were grown by slow evaporation technique. The effects of L-cystine doping on structural, spectral, mechanical, electrical, SEM studies and NLO properties of ZTS single crystals have been studied.

2. Experimental Method:

2.1 Synthesis of Undoped and L-Cystine Doped ZTS Salts: Undoped Zinc Tris-thiourea Sulphate (ZTS) was synthesized by stoichiometric incorporation of zinc sulphate heptahydrate in to thiourea. Analar grade zinc sulphate heptahydrate and thiourea were taken in the ratio 1:3 The amount of the reacting materials for the synthesis of ZTS salt were calculated according to the reaction given below.

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

The calculated reactants were dissolved in deionized water, saturated solution was prepared and stirred well for about 2 hours using a hot plate magnetic stirrer. Then solution was filtered to remove the unwanted and insoluble impurities if any present in the solution. For the reaction takes place between the reactants, the solution was heated at 50 ^{o}C and the synthesized salt of ZTS was obtained. For getting the L-cystine doped ZTS salt, 5 mole% of L-cystine was added into the solution of ZTS and the same procedure was followed as given for preparing the undoped ZTS salt.

2.2 Determination of Solubility: In solution growth, the solubility of a material in a particular solvent is an essential criteria and the solubility was measured by gravimetrical method [15]. The solubility of the samples was determined for different temperatures at 30°C, 35, 40, 45, and 50 °C. The synthesized ZTS salt was added step by step to de-ionized water at a particular temperature taken in a beaker kept on the hot plate of magnetic stirrer and stirring was continued till a small precipitate was formed. This gave confirmation of supersaturated condition of the solution. Then, 5 ml of the solution was pipetted out in a petri dish and it was warmed up till the solvent was evaporated out. By measuring the amount of salt present in the petri dish, the solubility (in g/100 ml) of ZTS in de-ionized water was determined. The same procedure was followed to find the solubility of the L-cystine doped ZTS sample. The solubility curves for the samples are shown in Fig.1. From the graph it is

observed that the solubility of the samples in water increases linearly with temperature, showing a high solubility gradient and positive temperature coefficient, which ensures the slow evaporation technique is the appropriate method to grow single crystals of undoped and L-cystine doped ZTS samples. When L-cystine was doped into ZTS, the solubility is found to be more and the increase in solubility for the L-cystine doped crystal is responsible for morphological change and hence the undoped and doped crystals have the different morphology.

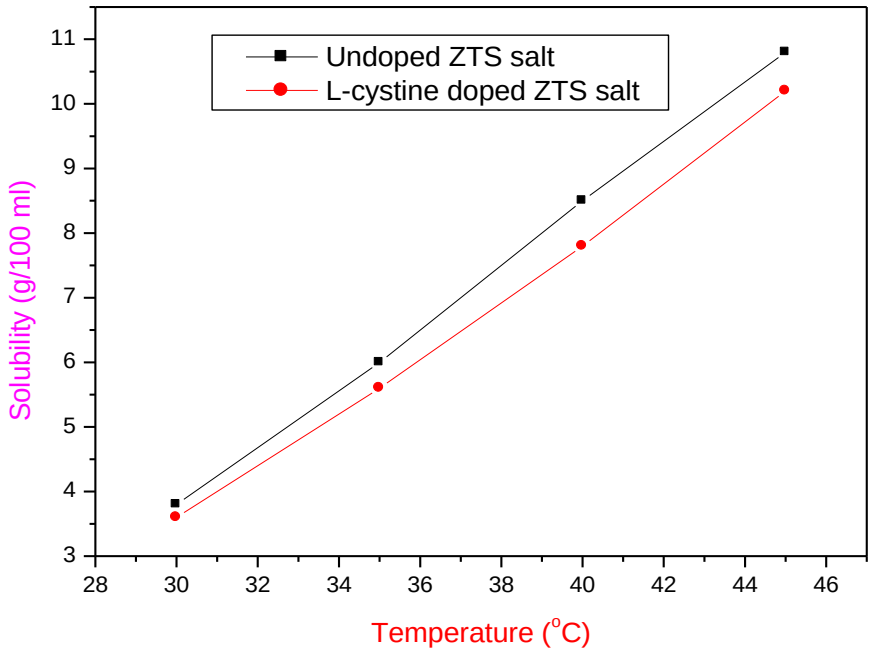
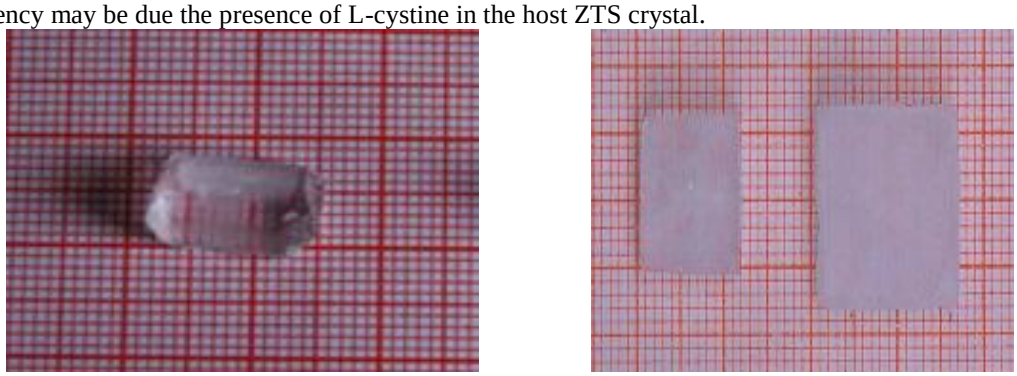


Figure 1: Solubility curves for undoped and L-cystine doped ZTS salts

2.3 Growth of Crystals: In the present investigation, the undoped and L-cystine doped zinc tris-thiourea sulphate crystals were crystallized separately at 30°C by slow evaporation method. 200 ml of saturated solutions of the undoped and L-cystine doped zinc thiourea sulphate were prepared separately using the solubility data at 30°C and these solutions were stirred using a magnetic stirrer for 2 hours and filtered. The filtered solutions were taken in the growth vessels. The growth vessels were covered by means of perforated polythene papers and kept in a vibration free platform and solutions were allowed to evaporate slowly at 30°C. By slow evaporation, the solution gets supersaturated and nucleation starts. Within a period of 35 days, the grown crystals were harvested from the growth vessels and the harvested crystals of unodped and L-cystine doped zinc tris-thiourea sulphate are shown in the figure 2. The crystals are found to be transparent and well faceted. The morphology of L-cystine doped zinc thiourea sulphate is found to be square shaped with less transparency. The poor transparency may be due the presence of L-cystine in the host ZTS crystal.



(a) (b)

Figure 2: Undoped (a) and L-cystine doped ZTS crystals

3. Results and Discussions:

3.1 ICP and CHN Analyses for the Grown Crystals: The samples were separately dissolved in HNO_3 and make up into 100 ml using HPLC grade water and ICP analysis was carried out and also CHNS analysis was carried out. The elements present in the samples like Zn, C, N, O, S etc were detected.

3.2 FTIR Studies: The Fourier Transform infrared spectrum of L-cystine doped ZTS crystal was recorded using JASCO FTIR 460 spectrometer by KBr pellet technique in the range 450-4500 cm^{-1} and is shown in Fig. 3. The broad envelop present in the range 2750 and 3500 cm^{-1} corresponds to the symmetric and asymmetric stretching modes of NH_2 grouping of zinc coordinated thiourea. The presence of sulphate ions is clearly evident by its peaks around 715 and 1401 cm^{-1} .in the sample. The absorption band observed at 1630 cm^{-1} in the spectrum may be assigned to the NH_2 bending vibration. The absorption at 1500 and 1112 cm^{-1} are assigned to the N-C-N mode. The absorption band at 715 cm^{-1} corresponds to the C=S stretching vibration. Table 1 represents the vibrational frequencies for L-cystine doped zinc thiourea sulphate crystals. The frequency assignments are given in accordance with the data reported in the literature [16].

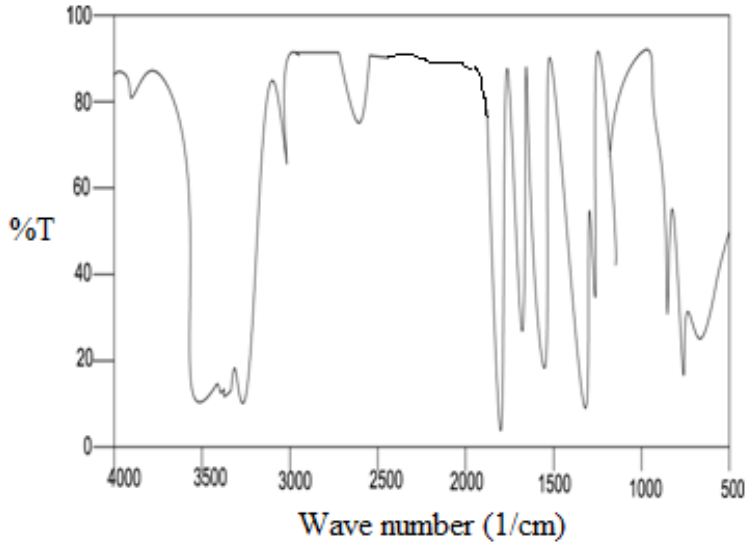


Figure 3: FTIR spectrum of L-cystine doped ZTS crystal

Table 1: FTIR vibrational frequencies for L-cystine added ZTS crystal

Vibrational frequencies (cm^{-1})	FTIR assignments
2750-3500	NH_2 symmetric and asymmetric Stretching
1630	NH_2 bending
1500	N-C -N Stretching
1401	C=S Stretching
1112	N-C-N Stretching
715	C=S Stretching

3.3 X-Ray Diffraction (XRD) Studies:

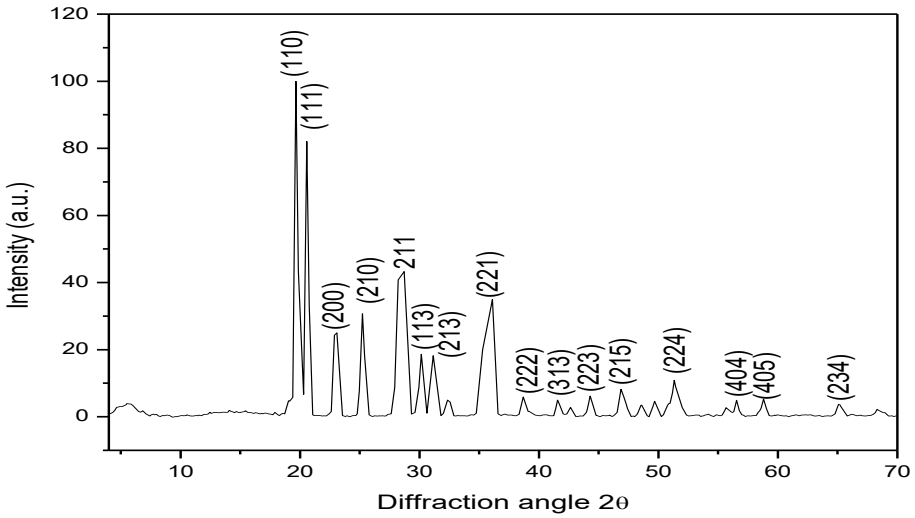


Figure 4: Powder X-ray diffraction pattern of L-cystine doped ZTS crystal

Powder X-ray diffraction analysis using an X-ray diffractometer (Model Ritz-170) with CuK_α radiation of wavelength 1.54056 Å was carried out and CELN software package was used to index the various peaks. The X-ray diffraction pattern for L-cystine doped zinc thiouera sulphate in presented in figure 4. The samples are observed to be crystallizing in orthorhombic structure and volume of the unit cell is found using the relation V = abc where a, b, c are the unit cell parameters. For finding the unit cell parameters, UNITCELL software package was used. The obtained crystallographic data for the samples are provided in the table 2. The crystallographic data for undoped ZTS crystal are found to be comparable with those of L-cystine doped ZTS crystal [10].

Table 2: Lattice parameters and unit cell volume of L-cystine doped ZTS single crystals
$\alpha = 90^o$, $\beta = 90^o$ and $\gamma = 90^o$

Lattice parameters	Pure ZTS [10]	L-Cystine Doped Zinc Thiourea Sulphate
a (Å)	11.165	11.162
b (Å)	7.790	7.793
c (Å)	15.525	15.526
Cell Volume $(Å)^3$	1350.292	1350.536

3.4 SHG Studies: The second Harmonic Generation (SHG) test for the grown crystals were performed by the powder technique of Kurtz and Perry [17] using Nd:YAG laser with first harmonics output of 1064 nm, width 8 ns and repetition rate 10 Hz. Thiourea is an organic molecular compound which crystallizes in non-centrosymmetric space group and this gives SHG. This phenomenon is connected with the influence of crystal symmetry on the optimum contribution of the macroscopic nonlinearity susceptibility of the crystals. The second harmonic signal generated from the grown samples was confirmed from the emission of green radiation and it proves that the samples are second harmonic generators. The energy outputs of the fundamental and the second harmonic intensity were determined using the power meter from which the SHG conversion efficiency of the grown crystals were determined. The energy output of fundamental beam was measured to be 80 mJ and the SHG energy output was measured and the energy conversion efficiency is calculated and and the relevant data are presented in table 3. Here KDP was used as the reference material. The results show that the SHG efficiency gets increased when ZTS crystals are doped with L-cystine.

Table 3: Values of relative SHG efficiency

Sample	**Energy conversion efficiency**
Undoped Zinc thiourea sulphate	2.20
L-cystine doped zinc thiourea sulphate (5 mole %)	2.62

3.5 SEM Studies: Surface features of a crystal is a key factor to understand the mechanism and history of crystal growth. The surface studies also provides information about the nature and distribution of imperfections in a crystal. Structural and geometrical investigaton of the surface is the most fundamental step in a crystal. To understand the surface features of the grown crystals, SEM image was recorded using a scanning electron microscope (SEM) and it is shown in the figure 5. Observations revealed that the faces of the crystal contains some growth patterns and well defined growth layers with large step growth was observed in the sample. The growth layers observed on the surface is produced by secondary nucleations and spreading of layers from its growth centers.The thick growth layers maybe due to the presence of impurities. Also straight parallel growth patterns such as striations are observed. In between the two striations the surface is found to be smooth.

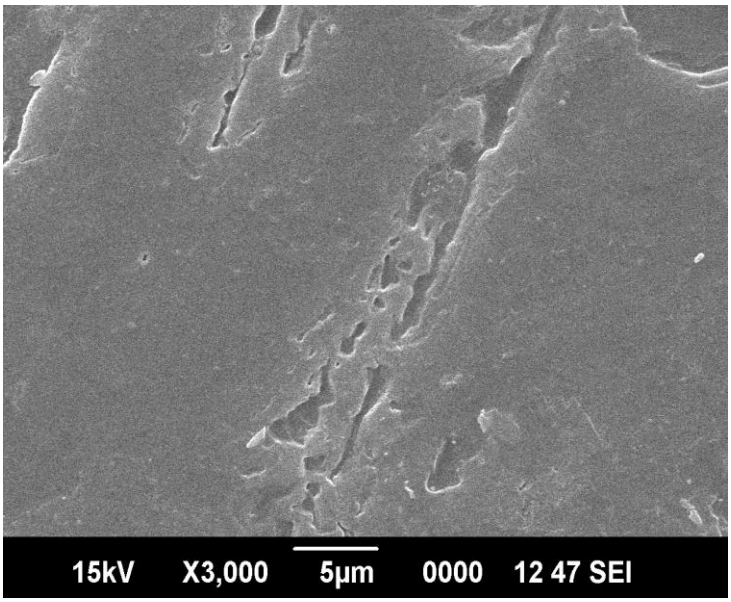


Figure 5: **SEM image of L-cystine doped ZTS cystal**

3.6 Vickers Hardness Studies:

The hardness of a material is a measure of its resistance to plastic deformation. The permanent deformation can be achieved by indentation, bending, scratching or cutting. Various mechanical characterstics of a material such as toughness, brittleness, etc, can be investigated by hardness measurements. Most hardness tests produce plastic deformation in materials and all variables affect the plastic deformation. The variation of microhardness (H_v) with increasing load may be classified into four groups viz., H_v remains unaffected, H_v decreases, H_v increases, H_v shows complex variation[18,19]. In an ideal crystal the hardness value should be independent of applied load. But in a real crystal, the load dependence is observed. Microhardness measurements were carried out using a Vickers microhardness indenter (Leitz Weitzier harness tester). In the present investigation, various loads such as 10, 20, 30, 40, 50, 60 g were applied on the sample to find average indentation length. Microhardness number 'H_v' is determined using the relation,

$$H_v = 1.8544\ P/d^2\ kg\ mm^{-2}$$

Where P is the applied load in kg and d is the diagonal length of the indented impression in mm. The variations of microhardness number with the applied load for undoped and L-cystine doped ZTS crystals are presented in the figure 6. It is observed from the results that the hardness increases with increase of the applied load for both the samples and this indicates that the samples have reverse indentation size effect. This can be explained on the basis of depth of penetration of the indenter. When the load increases, a few surface layers are penetrated initially and then inner surface layers are penetrated by the indenter with increase in the load. The measured hardness is the characteristics of these layers and the increase in the hardness number is due to the overall effect on the surface and inner layers of the sample. The hardness values are found to be increasing when ZTS crystals are doped with L-cystine and this confirms that ZTS crystals are hardened due to doping of L-cystine.

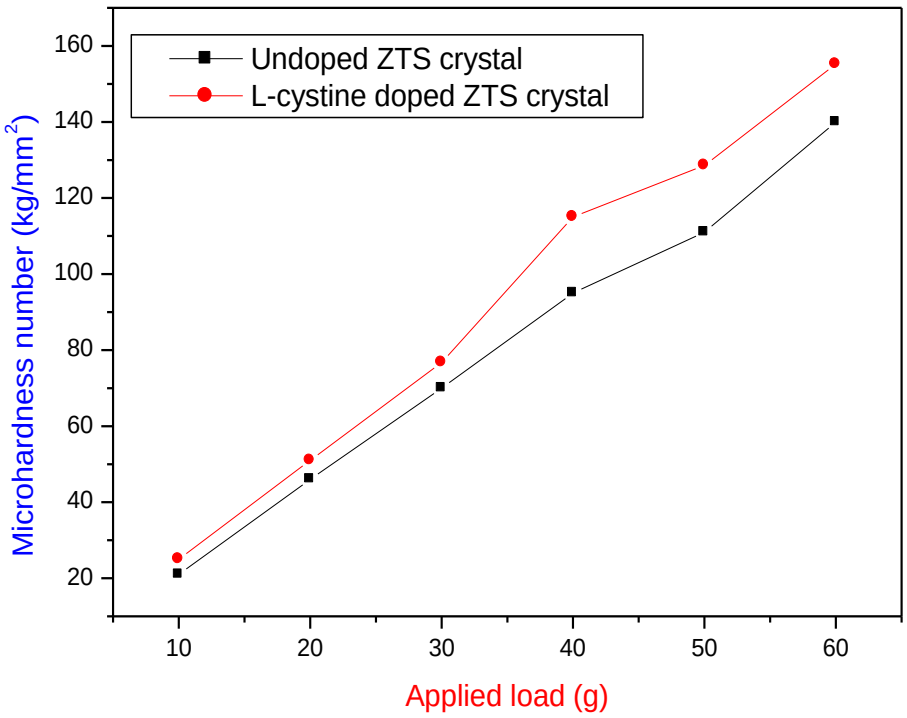


Figure 6: Plots of hardness number versus applied load for undoped and L-cystine doped ZTS crystals

3.7 Dielectric Studies: Dielectrics are insulating materials with no free charges. But in the presence of an electric field, the material gets polarized. The dielectric constant, dielectric loss (tan δ) and electrical conductivity are the basic electrical properties of solid. The dielectric constant is a physical measure of the electric polarizability of a material. Polarization is due to atomic mechanisms like electronic, ionic, orientation and space charge polarizations. The amount of power loss in a dielectric material when subjected to an electric field is known as dielectric loss. A low value of dielectric loss is desired for a dielectric material for device applications. Determination of dielectric constant as a function of frequency and temperature provides insight into the polarization mechanisms within the dielectric under the influence of an electric field [20-22]. In the present investigation an LCR meter was used to measure the capacitance and dielectric loss factor of the samples. The frequency dependence of dielectric constant and dielectric loss for undoped and L-cystine doped ZTS crystals are presented in the figures 7 and 8. The high values of observed at low frequencies in pure and

doped `ZTS crystals may be due to the dominant presence of various polarizations arising as a consequence of the charge transfer complex nature of ZTS crystal. Low values of dielectric constant at high frequency are due to the decay of the dominant polarization. The grown crystals exist as a change transfer complex which contribution mostly for polarization in the direction of the applied field. As frequency increases, a situation will be reached where space charges cannot sustain and comply with the external field and hence polarization decreases. The low values of dielectric loss of the samples are an indication of the good quality of the grown crystals. From the results it is observed that the dielectric constant and dielectric loss are increased when ZTS crystals are doped with L-cystine.

Figure 7: Variations of dielectric constant with frequency for undoped and L-cystine doped ZTS crystals

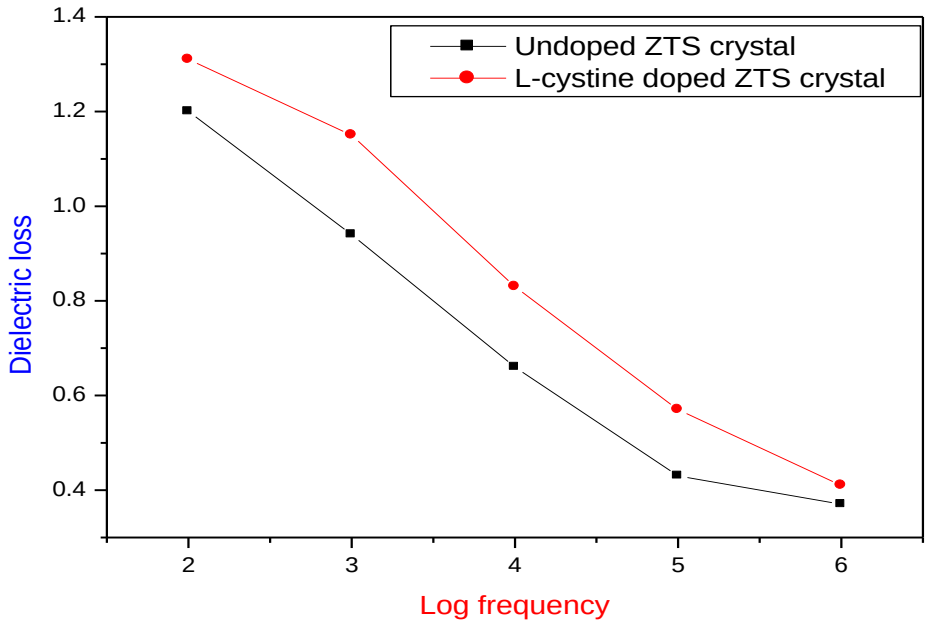


Figure 8: Variations of dielectric loss with frequency for undoped and L-cystine doped ZTS crystals

4. Conclusion:

Aqueous solution method was used to carry out the growth of undoped and L-cysine doped ZTS crystals. Solubility was found to be increasing with increase of temperature and hence the samples have the positive temperature coefficient of solubility. The crystal sturucture of ZTS crystal is not changed when it was doped with L-cystine. Low values of dielectric constant and dielectic loss indicate that the samples are the good electro-optic NLO materials. The stuides like SEM studies, FTIR studies, microhardness studies of undoped and L-cystine doped ZTS crystals were carried out and the results were analyzed.

5. Acknowledgement:

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