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Crystal Growth, Structural, Spectral, Optical and Mechanical Properties of Pure and Potassium Chloride Doped Zinc (tris) Thiourea Sulphate Single Crystals

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ABSTRACT

Single crystals of pure and potassium chloride (KCl) doped zinc (tris) thiourea sulphate (ZTS) were grown from aqueous solution by slow evaporation method. The unit cell parameters and crystal structure were determined by powder X – ray diffraction. The chemical compositions of the crystals were determined by Fourier transform infrared (FTIR) analysis. The cut off wavelength of the grown crystals was determined by UV-visible absorption spectra. The second harmonic generation of crystals was confirmed by Kurtz powder method using Nd: YAG laser. The dielectric response of the grown crystal was varied with varying frequencies. Microhardness test was also carried out on the samples to study the mechanical stability of the grown crystals.

Introduction

Over past two decades, nonlinear optical (NLO) materials are attracting a great deal of attention due to their potential applications in optic devices such as optical switches, optical modulator and electro optical devices [1, 2]. Recently high nonlinear optical properties of metal complexes of thiourea have been explored due to the centro symmetric thiourea molecule incorporated into respective inorganic salt yield non-centro symmetric material. Some of the potential thiourea complexes are Zinc thiourea chloride (ZTC), Cadmium thiourea chloride (CTC), Copper thiourea chloride (CTC), Bis thiourea zinc acetate (BTZA) and Zinc thiourea sulphate (ZTS). The second harmonic efficiency of ZTS single crystals have 1.2 times greater than KDP [3-5]. Zinc tris thiourea sulphate (ZTS) is a perfect semiorganic material for second harmonic generation (SHG) device application and laser tuned experiments [6]. Bhagavannarayana et al. have reported the influence of Mn-doping on the nonlinear optical properties and crystalline perfection of tris (thiourea) zinc (II) sulphate crystals: concentration effects [7]. The effect of sodium chloride on the properties of ZTS single crystals [8] and Influence of $MgSO_4$ doping on the properties of Zinc tris thiourea sulphate (ZTS) single crystals have been reported recently in our earlier communication [9]. Motivated by these considerations Zinc tris thiourea sulphate was synthesized and it is then doped with KCl as it is known that the properties of a crystal can be improved through doping process [10]. In the present investigation, we report ZTS has been doped with KCl to improve the SHG efficiency to find its better alternative to other NLO materials. The grown crystals were characterized by various characterization techniques, such as powder X-ray diffraction, FTIR studies, UV visible absorbance studies, SHG test, dielectric studies and microhardness studies.

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Experimental procedure

Synthesis and crystal growth

Pure crystal of Zinc tris thiourea sulphate (ZTS) was synthesized [11] by reacting stoichiometric amount of zinc sulphate and thiourea i.e., 1:3 in deionized water at room temperature. ZTS was synthesized according to the following reaction

$$ZnSO_4 . 10H_2O + 3[CS(NH_2)_2] \longrightarrow Zn[CS(NH_2)_2]_3$$

The mixed solution was continuously stirred using magnetic stirrer. After 4 hours the saturated homogeneous solution was prepared at room temperature and then filtered by Whatmann filter paper to increase the purity of the solution. The prepared saturated ZTS solution was kept in a glass vessel covered with perforated paper for slow evaporation in dust free atmosphere. The good quality transparent colourless ZTS crystal of size 6 x 5 x 4 mm^3 was harvested in 20 days [12].

The saturated homogeneous solution of pure ZTS was taken in a clean beaker and then 1 mol % of KCl solution was added to the ZTS solution for doping and the same procedure was followed as in the case of pure ZTS crystal. After 25 days, optical quality transparent colourless crystals of size 5 x 4 x 3 mm^3 were harvested. The photograph of the grown crystals of pure and KCl doped ZTS are shown in figures 1, 2.

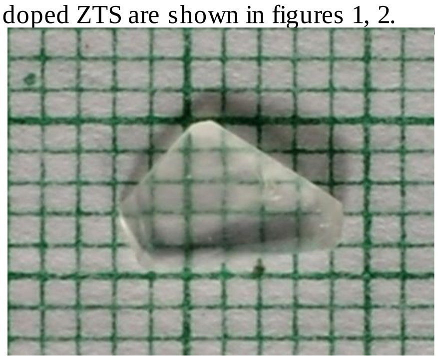

Figure 1. As grown crystal of pure ZTS

Figure 2. As grown crystal of KCl doped ZTS

Results and discussion

Powder X-ray diffraction studies

The single crystals of pure and KCl doped ZTS crystals were subjected to powder X ray diffraction studies using Rigaku diffractometer with CuKα radiation of wavelength of λ=1.5406 Å to determine the lattice parameters and crystal structure. The powder X- ray diffraction pattern of grown pure and KCl doped ZTS crystals are shown in figures 3, 4.

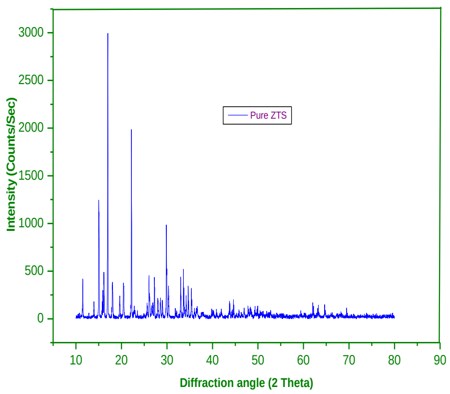

Figure 3. Powder XRD pattern of pure ZTS

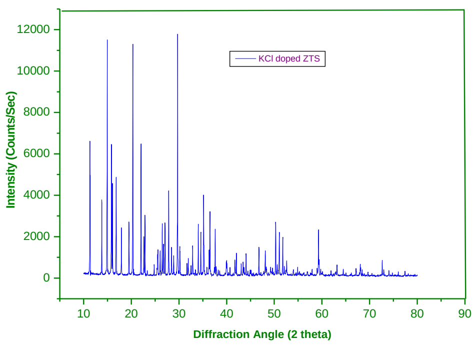

Figure 4. Powder XRD pattern of KCl doped ZTS

In XRD pattern the number of good intensity peaks were observed, these peaks shown that the high crystallinity of the grown crystals. The calculated lattice parameters of grown crystals were tabulated in table 1 and these values are good agreement with reportedvalues [13-14]. The grown crystals belong to the structure of orthorhombic system. There is a slight variation in the lattice parameters due to addition of KCl but the crystal structure was not altered from the original orthorhombic system.

Fourier transforms infrared spectroscopy analysis

Fourier transform infrared (FTIR) spectroscopy was used to identify the functional groups present in synthesized material. The FTIR spectral analysis of pure and 1 mol % of KCl doped ZTS crystals were carried out by Perkin Elmer FTIR spectrometer by KBr pellet technique in the range 400 - 4000 cm^{-1} is shown in figure 5.

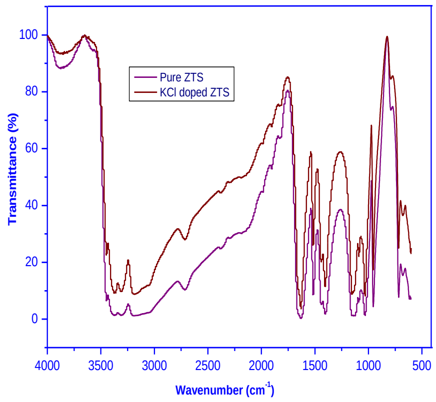

Figure 5. FTIR spectra of pure and KCl doped ZTS

In the ZTS complex, there are two possibilities by which the coordination with the metal can occur. It may be either through nitrogen or Sulphur. From the spectra of thiourea and zinc sulphate it follows that the coordination of thiourea with zinc occurs through sulfur in ZTS [15]. The spectra of pure and 1 mol % of KCl doped ZTS shown that the broad envelope lying in between 2750 and 3500 cm^{-1} arising out of symmetric and asymmetric modes of the NH_2 group of zinc coordinated thiourea. The absorption band at around 1631 cm^{-1} in the spectra of pure and KCl doped ZTS corresponds to the NH_2 bending vibration [15]. The presence of sulphate ion in the coordination sphere of ZTS is evident from its peak at 717 cm^{-1}. The N-H absorption band at higher frequency region does not shift to lower frequency on the formation of metal thiourea complex. The absorption peaks are observed at around 1516 cm^{-1} and 955 cm^{-1} corresponds to N-C-N stretching vibration. The absorption band at 1403 cm^{-1} assigned to the C=S asymmetric vibration [16]. The FTIR spectrum of 1 mol % of KCl doped ZTS crystal shown that there is broadening or narrowing of some absorption peaks are observed and this may be due to the incorporation of K^+ ions in the lattice of ZTS [17-18].

UV visible studies

The UV visible studies of grown crystals were carried out using Lambda 35 model UV visible spectrophotometer in the range of 190-1100 nm. The recorded absorption spectrum is shown in figure 6.

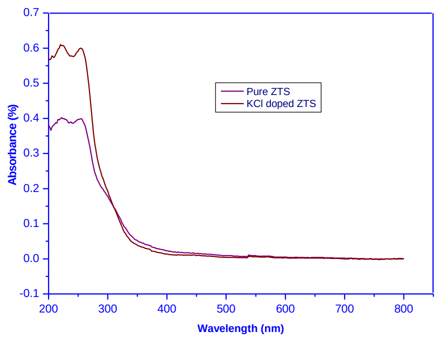

Figure 6. Absorption spectra of pure and KCl doped ZTS

The absorption spectra revealed that the grown pure and KCl doped ZTS crystals have lower cut off wavelengths. The energy band gap was calculated using the relation $E_g = hc/\lambda$, where h is the Planck's constant, c is the velocity of light and λ is the wavelength. The obtained forbidden energy band gap values of pure and 1 mol % of KCl doped ZTS crystals are 3.46 eV and 3.54 eV. These results are confirmed that both pure and doped materials belong to the category of typical insulating materials. The increase in energy band gap may be attained due to the incorporation of KCl in ZTS crystals [19].

SHG measurement

The second harmonic generation (SHG) test for the grown pure and KCl doped ZTS was performed by the Kurtz powder technique [20] using Q-switched Nd: YAG laser (λ= 1064 nm) as a source. The photo multiplier tube was used as detector and 90° geometry was employed. The generated second harmonic signal was confirmed by the emission of green radiation of wavelength 532 nm from the sample. The estimated relative second harmonic efficiencies of pure and 1 mol % of KCl doped ZTS crystals are 1.29 and 1.31 times higher than that of KDP crystals. The doped ZTS crystal slightly increases the non-centro symmetry due to incorporation of K^+ ion in ZTS [21].

Table 1. Lattice parameters of pure and 1 mol % KCl doped ZTS single crystals.

Grown crystal	a (Å)	b (Å)	c (Å)	V ($Å^3$)
Pure ZTS	11.121	7.773	15.499	1339.7883
KCl doped ZTS	11.311	8.014	15.283	1385.3482

Dielectric studies

The variation of dielectric constant as a function of frequency of pure and 1 mol % of KCl doped ZTS crystals are shown in figures 7, 8.

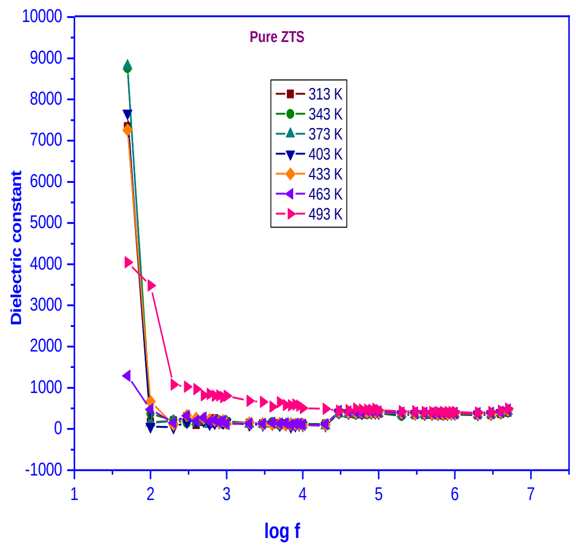

Figure 7. Variation of dielectric constant with frequency of electric field of pure ZTS single crystal

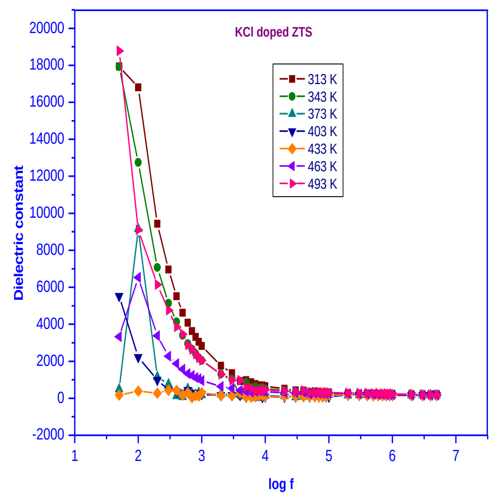

Figure 8. Variation of dielectric constant with frequency of electric field of KCl doped ZTS single crystal

Dielectric constant and dielectric loss of grown crystals has been calculated using the relation $\varepsilon_r = C_p\, t/ \varepsilon_o A$, where C_p is the capacitance of the material, t is the thickness of the specimen, ε_o is the permittivity of free space ($8.85 \times 10^{-12}\ C^{-1}N^{-1}m^{-2}$) and A is the area of the sample. The observations are made in the frequency range 50 Hz – 5 MHz at different temperatures. The dielectric constants of both pure and KCl doped ZTS crystals are high at low frequencies and decreases with increase in frequencies was observed in figures 7, 8. Beyond 1 KHz the dielectric constant of the material remains constant. The high dielectric constant value of the crystals at low frequency is attributed to space charge polarization. At low frequency the dielectric constant of KCl doped ZTS is greater than the pure ZTS, which may be due to the lower polarizabilities of KCl in ZTS. The decrease in dielectric constant of pure and KCl doped ZTS crystals at higher frequencies may be attributed to the contribution of electronic, ionic and orientational polarization. The variation of dielectric loss with frequency is also shown in figures 9, 10.

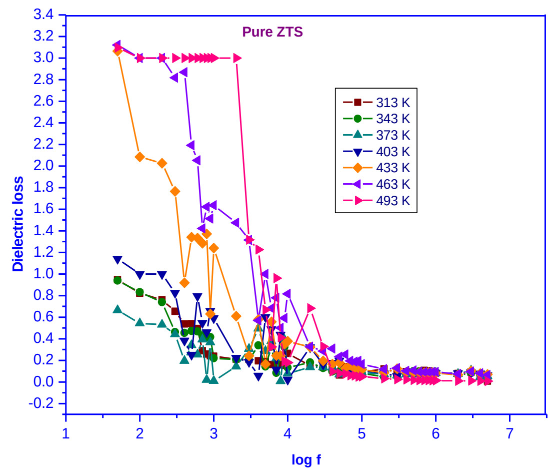

Figure 9. Variation of dielectric loss with frequency of electric field of pure ZTS single crystal

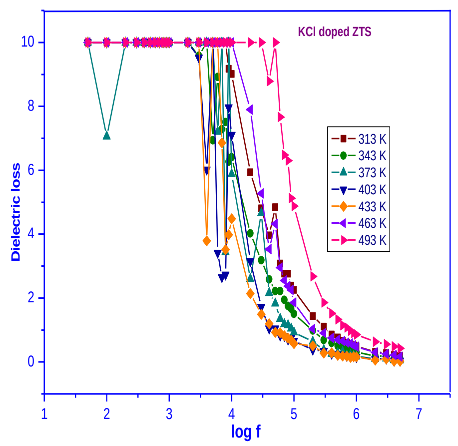

Figure 10. Variation of dielectric loss with frequency of electric field of KCl doped ZTS single crystal

The characteristic of low dielectric loss at high frequencies for grown sample suggests that the sample posses an enhanced optical quality with lesser defects [22]. The observations of results confirmed that the grown crystals is well suitable candidate for construction of photonic and optoelectronic devices [23].

Microhardness measurement

Microhardness testing is one of the earliest methods for understanding the mechanical properties of the materials. Hardness of a material is a measure of its resistance it offers to local deformation [24, 25]. The grown pure and KCl doped ZTS crystals were subjected to Vickers microhardness test using HMV-2T microhardness tester. The indentations were made on the surface of the grown crystals by varying the load from 25 gm, 50 gm and 100 gm at room temperature with constant indentation time of 5 second. Cracks were developed on the surface of the crystals beyond 100 gm of applied load. Figure 11 shows that the hardness number was found to increase with addition of KCl in ZTS crystal due to incorporation of metal K^+ ions.

The relation between load and size of indention is given by Mayer's law as $P= ad^n$, where P is the load in kg , d is the mean diagonal length and n is the work hardening coefficient. A graph was plotted between load P and hardness number (Hv) found to be a straight line (Figure 11). A graph was also plotted between log P and log d which gives a straight line (Figure 12).

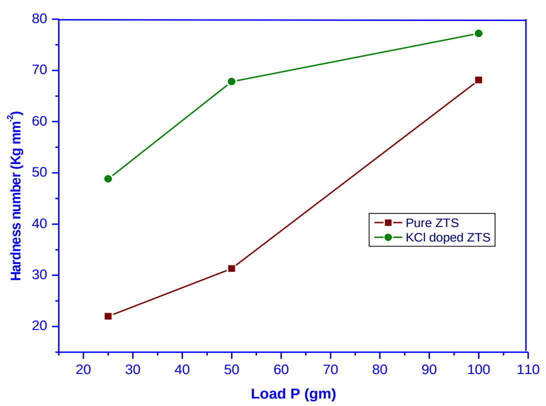

Figure 11. Load (P) Vs Hardness number for pure and KCl doped ZTS

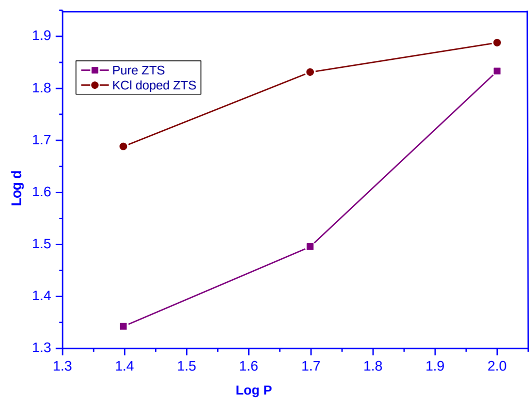

Figure 12. Log P Vs Log d for pure and KCl doped ZTS

The slope of the straight line gives the work hardening coefficient (n). The calculated work hardening coefficient of the pure and 1 mol % of KCl doped ZTS crystals are 1.9 and 2.1. According to Onitsch [26], the work hardening coefficient value (n) for soft materials would be more then 1.6 where as for hard materials the n value lies between 1 and 1.6. The obtained results of work hardening coefficient shown that the grown both pure and 1 mole % KCl doped materials belong to the category of soft in nature.

Conclusion

Good optical quality of pure and KCl doped zinc tris thiourea sulphate single crystals were grown at ambient temperature by slow evaporation solution growth method. The powder X ray diffraction pattern of grown materials confirmed that there is no change in basic structure of ZTS while KCl as dopant. The estimated lattice parameters confirmed that the grown crystals belong to the system of orthorhombic. The modes of vibration and presence of functional groups was identified by using FTIR spectrometer. By using UV-visible absorption studies the forbidden energy band gap of material was calculated and which has shown that the grown both pure and KCl doped material belong to the typical insulating materials. The relative second harmonic efficiencies of pure and KCl doped ZTS are 1.20 and 1.31 times higher than that of KDP. So it is a potential candidate for frequency conversion. Vicker's microhardness measurements revealed that the grown crystals in the category of soft in nature. The dielectric constant of both pure and doped ZTS crystals was increased at low frequencies and it's decreased at higher frequencies. The dielectric constant of doped ZTS is greater than the pure because of the addition of KCl in ZTS.

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