Journal of Alloys and Compounds 523 (2012) 25–29

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Crystal growth, structural, spectral and mechanical studies of pure and KI doped ZTS single crystals

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ARTICLE INFO

Article history:
Received 6 May 2011
Received in revised form 11 January 2012
Accepted 22 January 2012
Available online 9 February 2012

Keywords:
Crystal growth
Slow evaporation technique
NLO
XRD
FT-IR
Micro hardness

ABSTRACT

Pure and KI doped single crystals of ZTS were grown by slow evaporation technique. The grown crystals were subjected to X-ray diffraction, UV–visible spectrum, FTIR analysis, micro hardness studies, TGA/DSC and SHG. X-ray diffraction analysis revealed that the structure of grown crystal belongs to orthorhombic system. The mechanical property of the grown crystals has been analyzed by Vickers microhardness method. Optical transparency of the grown crystals was studied by UV–visible spectroscopic method. The functional groups and modes of vibrational frequencies have been identified by using FTIR spectral data. The thermal stability of the grown crystal was investigated using thermo gravimetric analysis and differential scanning calorimetry (TGA/DSC) studies. Second harmonic generation was confirmed by using Nd: YAG laser. The analysis results confirmed that these crystals have better nonlinearity and good mechanical strength than KDP.

1. Introduction

Nonlinear optical material (NLO) plays a major role in applications such as telecommunications, optical data storage and optical information processing [1,2]. Inorganic NLO materials have large mechanical strength, thermal stability and good transmittance, but modest optical nonlinearity due to the lack of extended π-electron dislocation [3]. ZTS belongs to the family of semiorganic nonlinear optical material and it can be grown from aqueous solutions at room temperature [4–9]. Organic NLO material has poor mechanical strength, thermal strength and low laser damage threshold, but high nonlinearity compared to inorganic material [10]. Current research on crystal growth is focused on semiorganic NLO crystals for producing better nonlinear properties and having good properties crystal by combining the advantages of inorganic and organic materials. The semi-organic NLO materials have been attracting much attention due to high non-linearity, good mechanical strength, thermal strength and transmittance [10]. Many optically active organic amino acids are mixed with the inorganic salts in order to enhance their physical and chemical properties [11]. We know that utility of NLO crystal depends not only on the linear and nonlinear optical properties, but also on its quality and its ability to withstand thermal stress of high power laser. ZTS has high laser damage threshold, low angular sensitivity and wide range of transparency [11]. The molecular formula of the ZTS crystal is $Zn[CS(NH_2)_2]_3{\cdot}SO_4$ and the structure belong to orthorhombic system. ZTS is nearly 1.2 times more nonlinear than KDP [12]. ZTS exhibits a low angular sensitivity and hence, it is useful for type II second harmonic generation. ZTS crystal is a better alternative for KDP crystal in frequency doubling and laser fusion experiments because of high damage threshold and wide transparency [13]. Zinc tris-thiourea sulphate is a semiorganic nonlinear optical material which has better nonlinearity, excellent transmittance and good mechanical strength compared to many NLO materials [14]. In this present work, pure and KI doped ZTS were grown. The grown crystals were characterized by various studies, such as XRD, Fourier transform infrared (FT-IR) studies, UV transmittance studies, micro hardness studies, thermo gravimetric analysis and differential scanning calorimetry (TGA/DSC) studies, SHG studies and their results are reported in this article.

2. Experimental details

Single crystals of pure and KI doped ZTS were grown by low temperature solution growth method, especially slow evaporation technique at room temperature (30 °C) according to reaction (1) [14]. The analar grade of zinc sulphate ($ZnSO_4{\cdot}7H_2O$) and thiourea ($CS[(NH_2)_2]$) were taken in the molar ratio of 1:3 and were dissolved in deionised (DI) water. After an hour, the saturated homogeneous solution was prepared by using magnetic stirrer. The saturated solution was filtered in order to increase the purity of the solution. This saturated homogeneous solution was kept in

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doi:10.1016/j.jallcom.2012.01.123

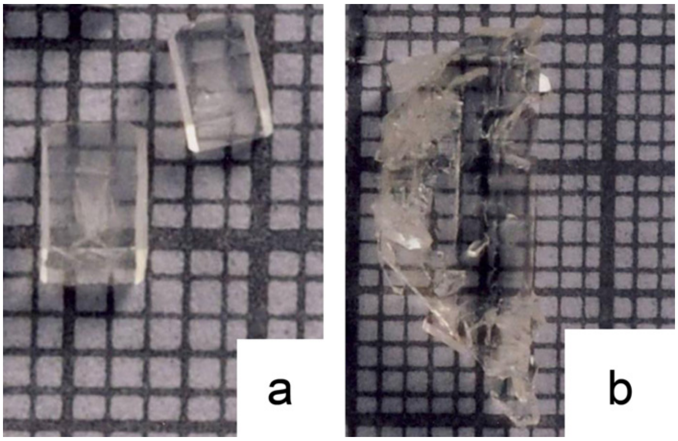

Fig. 1. As grown crystals of ZTS: (a) pure, and (b) KI doped ZTS.

a glass vessel covered with perforated filter paper for slow evaporation. Transparent colourless ZTS crystals were harvested in 15 days.

$$ZnSO_4{\cdot}7H_2O + 3CS[(NH_2)_2] \rightarrow Zn[CS(NH_2)_2]_3{\cdot}SO_4 \quad (1)$$

KI doped ZTS crystals were also grown by adding a 5 mol% of potassium iodide in ZTS solution according to the above reaction. Good quality, transparent single crystals were harvested in 20 days. Grown crystals were subjected to various characterization viz., powder X-ray diffraction, FTIR, UV–visible spectra, micro hardness analysis, TGA/DSC studies and SHG studies. The as-grown pure and KI doped ZTS single crystals are shown in Fig. 1(a) and (b) respectively.

3. Results and discussion

3.1. X-ray diffraction studies

Powder X-ray diffraction analysis of as-grown pure and KI doped ZTS crystals were carried using Rigaku diffractometer with Cu Kα radiation of wavelength 1.5418 Å. There are a number of good intensity peaks which were observed in the X-ray diffraction pattern, which are shown in Fig. 2(a) and (b). The well-defined peaks at specific 2θ values show high crystallinity of the grown crystals. All the peaks were indexed by XRD analysis software. The lattice parameters of grown crystals were calculated and tabulated in Table 1. The observed lattice parameter values are found to be in good agreement with the previously reported values [15,16]. The crystals belong to orthorhombic system with space group *Pca*21 [17]. The XRD analysis confirmed that the KI doping does not alter the basic structural properties of the crystal.

3.2. Fourier transform infrared spectral analysis

The FTIR spectroscopy was used to analyze qualitatively the presence of functional groups in grown crystals. The FTIR spectrum of grown pure and KI doped ZTS crystal was recorded using PerkinElmer spectrum FTIR spectrometer by KBr pellet technique in the range of 400–4000 cm^{-1}, which are shown in Figs. 3 and 4. The FTIR spectrum shows a broad envelope lying between 2750 and 3000 cm^{-1} arising out of the symmetric and asymmetric modes of the NH_2 group zinc coordinated thiourea. The presence of sulphate ions is evident by its peak around 717 cm^{-1}. The absorption band observed at 1602 cm^{-1} corresponds to the N—C—N stretching

Table 1
Lattice parameters of pure ZTS and KI doped ZTS crystals.

Grown crystal	*a* (Å)	*b* (Å)	c (Å)
Pure ZTS	11.12	7.773	15.499
KI doped ZTS	11.22	7.863	15.489

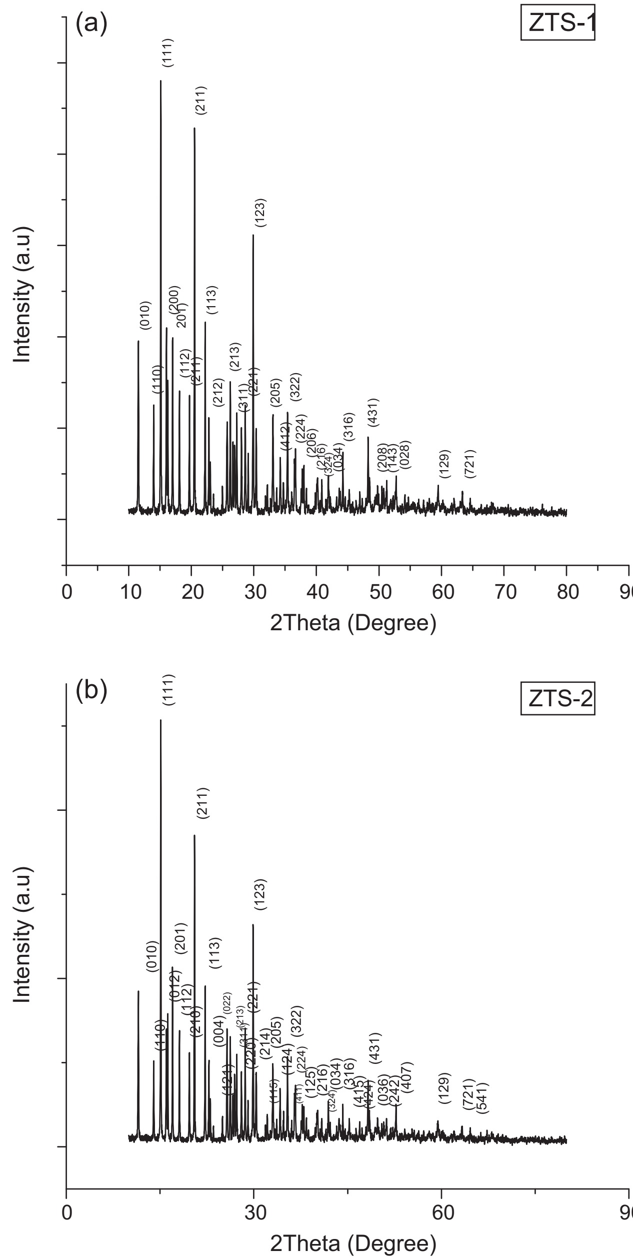

Fig. 2. XRD pattern of ZTS (a) pure (ZTS-1) and (b) KI doped (ZTS-2).

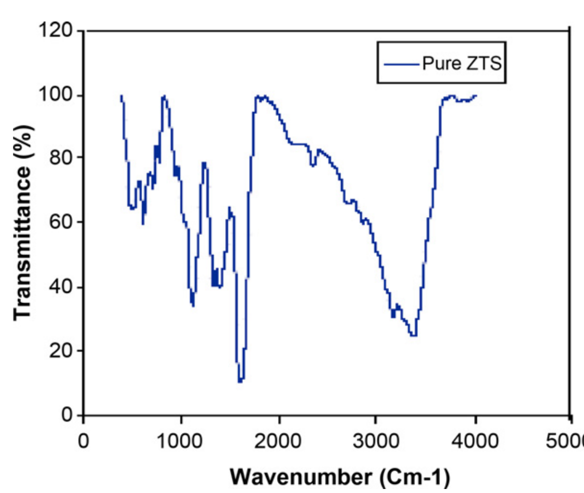

Fig. 3. FTIR spectrum of ZTS crystal.

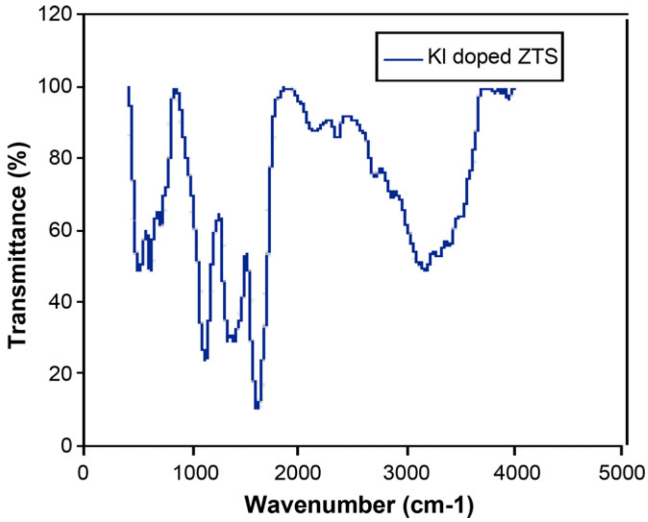

Fig. 4. FTIR spectrum of KI doped ZTS crystal.

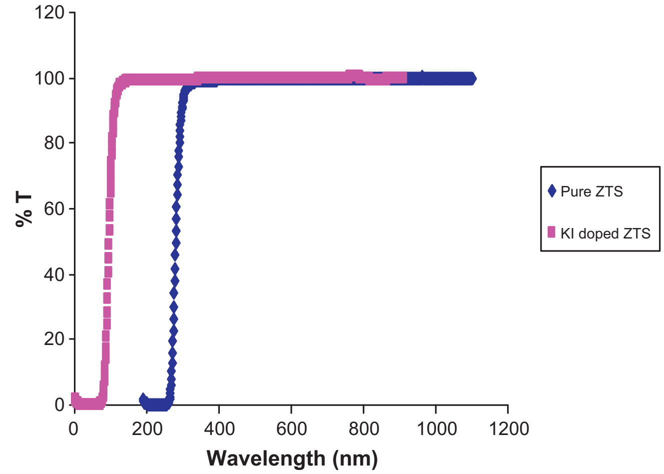

Fig. 6. Transmittance spectra of ZTS and KI doped.

vibration. The presence of band at 393 cm^{-1} and 948 cm^{-1} corresponds to the asymmetric stretching vibration. The peak observed at 3170 cm^{-1} corresponds to NH_2 symmetric stretching vibration. The absorption band observed at about 3376 cm^{-1} corresponds to the NH_2 asymmetric stretching vibration [18–20]. Comparison of IR spectra of ZTS and 5 mol% of KI doped ZTS showed a slight shift in the absorption bands. This shift in absorption bands is attributed to the incorporation of KI in ZTS.

3.3. UV–visible spectral studies

The single crystals are mainly used for optical applications. The optical transmittance range and transparency cut off are important for any crystal. The UV–visible study of pure and KI doped crystals were carried out by Lambda 35 model UV–visible spectrometer in the spectral range 190–1100 nm. The absorption and transmission spectra of crystals are shown in Figs. 5 and 6. The absorption spectra showed that the grown crystals have lower cut off wavelength less than 240 nm. These values are found to be in good agreement with the literature values. The forbidden band gaps for the grown crystals were calculated using the relation $E = hc/\lambda$, where 'c' is the velocity of light and 'λ' is the wavelength. The obtained value for the forbidden band gap for pure and KI doped ZTS crystals are 5.308 eV and 5.480 eV. The percentage of transmittance of grown crystals is very high.

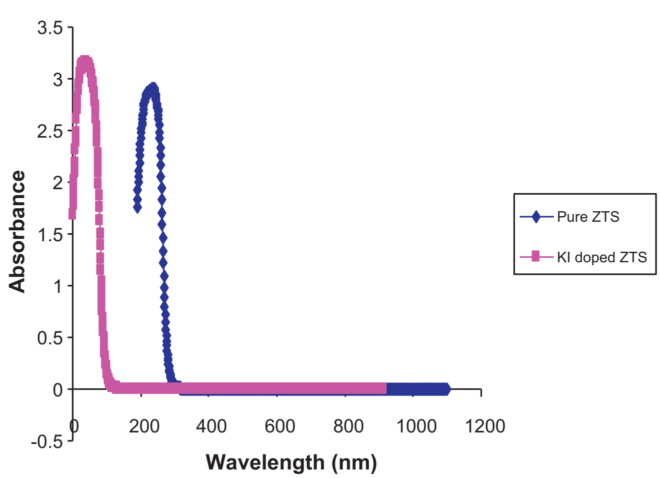

Fig. 5. Absorption spectra of ZTS and KI doped.

3.4. Microhardness analysis

The grown crystals were also subjected to Vickers microhardness testing (model no. HMV-2) with a diamond indenter. The well-polished crystals were mounted on the platform of the micro hardness tester and a load of different magnitudes (25–100 g) was applied over a fixed interval of time about 10 s. Graphs plotted between load and hardness numbers are shown in Figs. 7 and 8. From these graphs, the hardness of the grown crystals were increased with increasing loads can be observed. On further increasing the load beyond 100 g, cracks were developed on the surface of the crystals. For lower load, hardness value is relatively low and found to be higher for higher load. A graph is also plotted between log p vs log d, which gives a straight line. From these graphs, the value of n was obtained. This result confirmed that the grown crystals belong to the class of soft material.

3.5. Kurtz powder SHG test

Second harmonic generation (SHG) for the powder pure and KI doped ZTS has been carried out by Kurtz powder technique. Powder samples illuminated by using Q-switched Nd:YAG laser

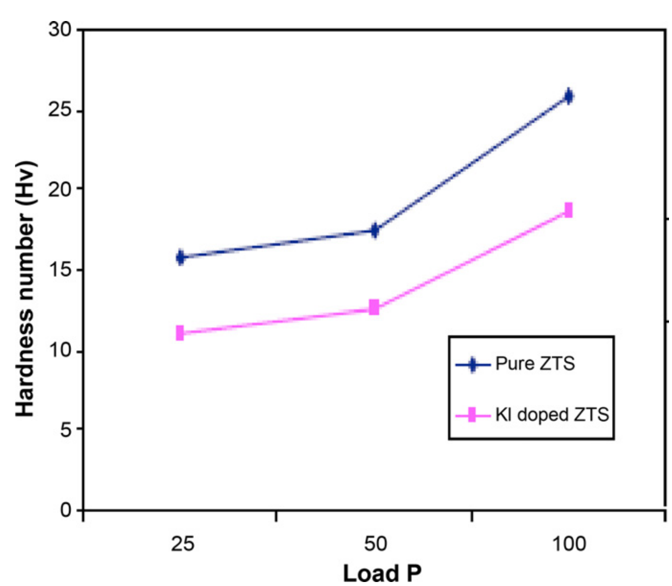

Fig. 7. Load (p) vs hardness number for both pure and doped ZTS Crystals.

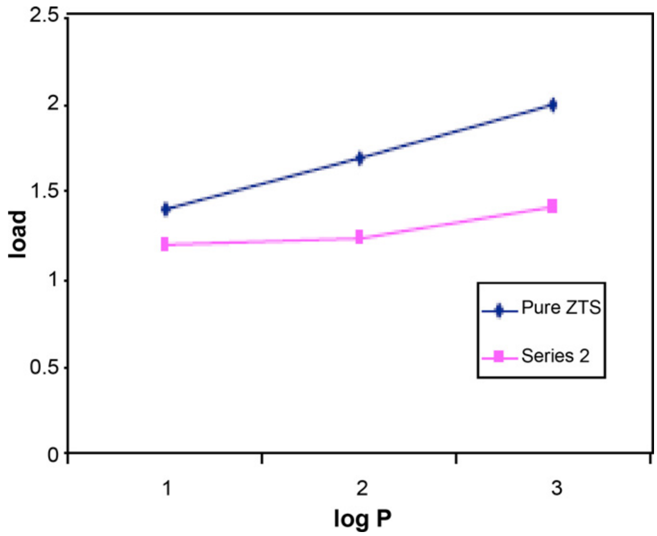

Fig. 8. log *p* vs log *d* for both pure and doped ZTS Crystals.

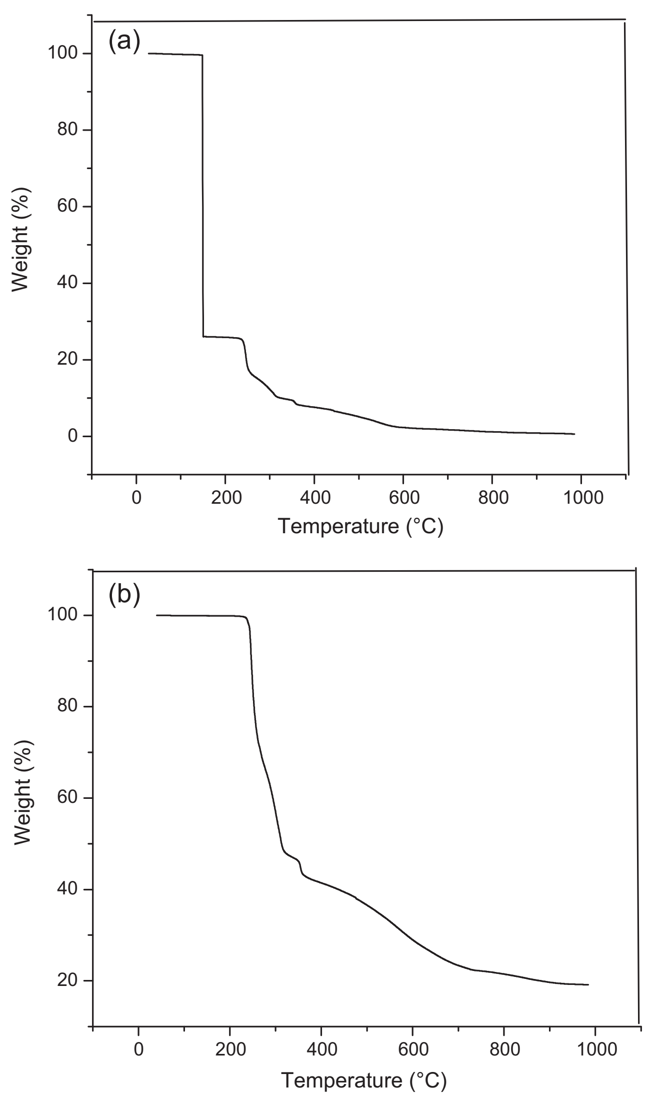

Fig. 9. The TGA curve of ZTS (a) pure ZTS and (b) KI doped ZTS.

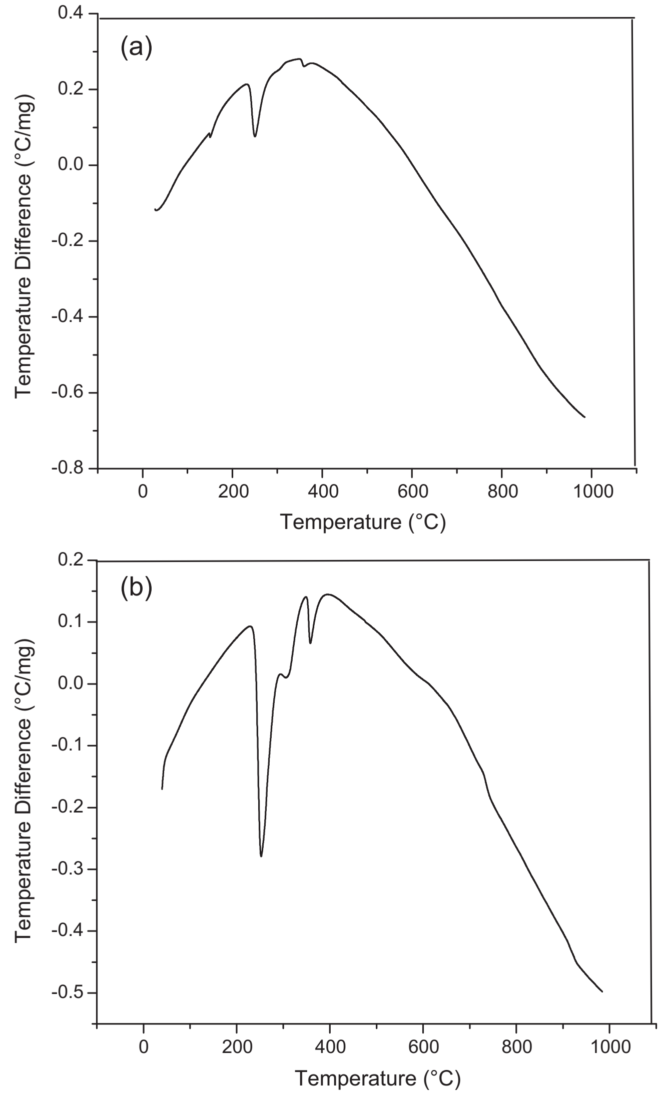

Fig. 10. The DSC curve of ZTS (a) pure ZTS and (b) KI doped ZTS.

emitting the fundamental wavelength of 1064 nm. The second harmonic generation was confirmed by the emission of green radiation (532 nm). From observed results, KI doped ZTS crystal have greater SHG efficiency than pure one. These are potential materials for frequency conversion.

3.6. Thermo gravimetric analysis (TGA) and differential scanning colorimetry (DSC) studies

The thermo gravimetric analysis (TGA) and differential scanning colorimetry (DSC) were carried out using SDT D 600 at heating rate 20 °C/min in nitrogen inert atmosphere to determine the thermal stability of the compound. The TGA curves of pure ZTS and KI doped ZTS show that materials have very good thermal stability up to 148.60 °C and 242.52 °C. The weight losses of pure and doped ZTS are about 73.79% and 33.70% in temperature range 148.60–150.26 °C and 242.52–253.80 °C may be due to liberation of volatile substances like sulfur oxide in the compound. Thermal stability of doped ZTS has more compared to undoped ZTS, which implies that KI doped ZTS can be used for NLO applications in a wide temperature range than undoped ZTS. Fig. 9(a) and (b) shows TGA curves for pure ZTS crystals.

The DSC spectrum of pure and KI doped ZTS shown in Fig. 10(a) and (b), shows a minor endothermic peak at 149.34 °C and a major peak at 249.76 °C. There is a sharp endothermic peak at 252.59 °C which represents the melting point of the doped ZTS crystal. The sharpness of these peaks show good degree of crystallinity of the sample. The TGA and DSC studies of pure and KI doped ZTS crystals are stable up to their melting point. From the studies of both thermograms it is clear that the melting points of grown crystals are nearly same.

4. Conclusion

Semi organic nonlinear optical material of pure and KI doped ZTS single crystals was grown by low temperature solution growth method and especially slow evaporation technique. Powder XRD confirmed that the structure of grown crystal belongs to orthorhombic system with space group *Pca*21. The presence of functional groups and modes of vibration of crystals were confirmed by Fourier transform infrared analysis. The absorption spectrum revealed that the crystal possesses lower UV cut off wavelength. UV–visible analysis revealed that the ZTS crystal is good in quality and optically transparent. Micro hardness study indicates that the crystal belongs to the class of soft materials. Both the thermo gravimetric analysis and differential scanning calorimetry exhibit that the crystals are thermally stable up to 149.34 °C and 252.59 °C temperature. The SHG efficiency of KI doped ZTS crystal is enhanced by KI dopant.

Acknowledgements

One of the authors (M.S.) would like to thank Dr. R. Vijayaraghavan, School of Advanced Sciences, VIT University, Vellore, India, for his kind help to carry out XRD. The author also thanks Dr. S Victor Williams, Department of Physics, St. Joseph College, Trichy, India for extending the characterization facilities of FTIR, UV and micro hardness analysis.

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