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Crystal Growth: An Introductory Survey in Advanced Crystal Growth

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Abstract:

Single crystals are a type of solid state material that can be classed, depending on the arrangement of the component atoms, ions, or molecules, polycrystals and amorphous materials are formed. An ideal crystal is an infinite lattice of atoms arranged in patterns that repeat with repeat distances in all three dimensions. Real crystals are limited in size and contain defects. Crystal growth is a multidisciplinary field that encompasses physics, chemistry, materials science, chemical engineering, metallurgy, crystallography, and mineralogy. 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 possess lower UV cut off wavelength. UV- visible analysis revealed that the ZTS crystal is good in quality and optically transparent. Microhardness study indicates that the crystal belongs to the class of soft materials. The Thermo gravimetric analysis confirmed that the grown pure, 1 mole % and 2 mole % of KI doped ZTS crystals are thermally stable up to 236.92˚C, 238.77˚C and 242.52˚C respectively. The SHG efficiency of KI doped ZTS crystal is enhanced by KI dopant. Elemental compositions of grown crystals were obtained by using Energy Dispersive X-ray analysis.

Key words: Crystals, component atoms, ions, molecules, polycrystals, amorphous materials

Introduction:

Single crystals are a type of solid state material that can be classed, depending on the arrangement of the component atoms, ions, or molecules, polycrystals and amorphous materials are formed. An ideal crystal is an infinite lattice of atoms arranged in patterns that repeat with repeat distances in all three dimensions. Real crystals are limited in size and contain defects. A single crystal is made up of periodic atomic arrays in three dimensions with equal repeated distances in one direction (Dry burgh 1986). Crystals are used in a variety of industries, including communication, laser technology, optical imaging, and electronics.

Crystal growth is a multidisciplinary field that encompasses physics, chemistry, materials science, chemical engineering, metallurgy, crystallography, and mineralogy. There has been a surge in interest in crystal formation technologies in recent decades, owing to the growing demand for materials for technological applications (Brice 1986, Nalwa and Miyata 1997). The strong influence of single crystals in the present day technology is evident from the recent advancements in the field of semiconductors, polarizers, transducers, infrared detectors, ultrasonic amplifiers, solid state lasers, nonlinear optics, acousto optics, microelectronics, optoelectronics and computer industries.

Hence, growth of good quality single crystals has become inevitable for further research and technology. Presently, there has been growing interest in crystal growth process, particularly in view of the increasing demand for materials for technological applications (Laudise 1970, Brice 1986, Nawla and Miyata 1996). The methods of growing crystals are very wide and mainly dictated by the characteristic of the material and its size (Buckley 1951 and Mullin 1976). Methods of crystal growth ranges from a simple inexpensive technique to a complex sophisticated expensive process and crystallization time range may be in minutes, hours, days and months.

Non Linear Optical material (NLO)

Non Linear Optical material (NLO) plays a major role in applications such as telecommunications, optical data storage and optical information processing (Meera et al 2004). 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. ZTS belongs to the family of semiorganic nonlinear optical material and it can be grown from aqueous solutions at room temperature (Shaokang Gao et al 2006, Ginson et al 2006, Sun et al 2005, Ramajothi et al 2004, Ariponnammal et al 2005 and Min-hua Jiang et al 1999). Organic NLO material has poor mechanical strength, thermal strength and low laser damage threshold, but high nonlinearity compared to inorganic material (Sweta Moitra et al 2007). Thus the research is focused on semiorganic NLO crystals for producing better nonlinear and having good properties crystal by combining the advantages of inorganic and organic materials. The semiorganic NLO materials have been gaining much attention due to high nonlinearity, good mechanical strength, thermal strength and transmittance (Sweta Moitra et al 2007). Many optically active organic amino acids are mixed with the inorganic salts in order to enhance their physical and chemical properties. The 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 (Kurtz et al 1968). The molecular formula of the ZTS crystal is $Zn\ [CS\ (NH_2)_2]_3.\ SO_4$ and the structures belong to orthorhombic system. ZTS is nearly 1.2 times more nonlinearity than KDP (Arunmozhi et al 2004). 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 (Sangwal et al 2004). 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 (Sangwal et al 2004). In this present work, Pure and KI doped ZTS were grown at room temperature. The grown crystals were characterized by various studies, such as XRD, Fourier transform infrared (FTIR) studies, UV transmittance studies, microhardness studies, Thermo gravimetric analysis and Differential scanning calorimetry (TGA/DSC) studies, SHG studies, EDX analysis and their results have been reported in this paper.

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˚) according to reaction in equation (1) (Ramasamy et al 1999). The analar grade of zinc sulphate ($ZnSO_4\ .7\ H_2O$) and thiourea ($CS\ [(NH_2)_2)$ were taken in the molar ratio of 1:3 are 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 a glass vessel covered with perforated filter paper for slow evaporation. Transparent colourless ZTS crystals were harvested in 15 days.

$ZnSO_4 .7 H_2O + 3 CS [(NH_2)_2] \rightarrow Zn [CS (NH_2)_2]_3. SO_4 \rightarrow (1)$

KI doped ZTS crystals were also grown by adding a 1 mole % and 2 mole % of potassium iodide in ZTS solution according to the above reaction. Good quality transparent single crystals were harvested in 20 days.

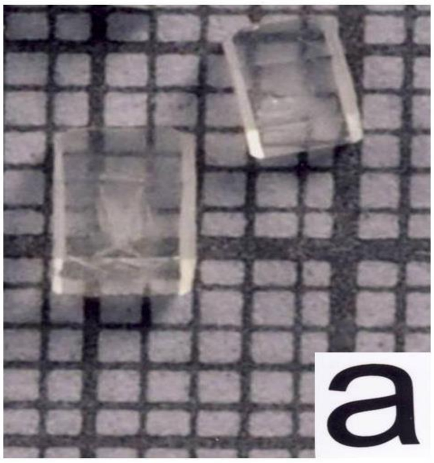

Fig. (a) As grown crystal of Pure ZTS

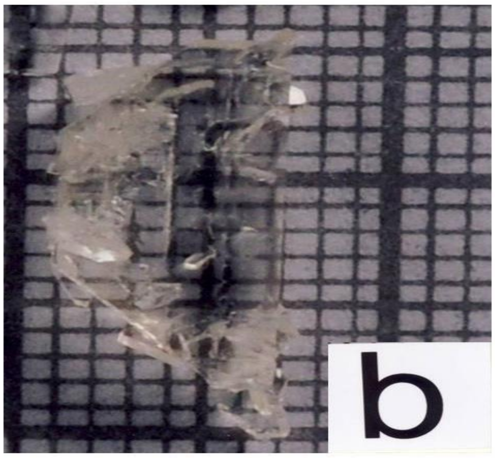

Fig. (b) As grown crystal of 1 mole % KI doped ZTS

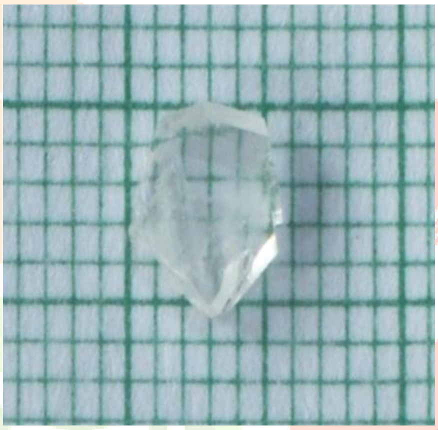

Fig. (c) As grown crystal of 2 mole % KI doped ZTS

Grown crystals was subjected to various characterizations viz., powder X- ray diffraction, FTIR, UV-visible spectra, microhardness analysis, TGA/DSC studies, EDX analysis and SHG studies. The as grown pure and KI doped ZTS single crystals are shown in the Fig. 2.1 (a), (b) and (c) respectively.

RESULTS AND DISCUSSION

X-ray diffraction studies

Powder X-ray diffraction analysis of as grown pure, 1 mole % and 2 mole % of potassium iodide (KI) doped ZTS crystals were carried using Rigaku diffractometer with CuKα radiation of wavelength 1.5418Å.There are a number of good intensity peaks which were observed in the x-ray diffraction pattern, which are shown in Fig. 2.2 (a), (b) and (c). 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-2.1. The observed lattice parameter values are found to be in good agreement with the previously reported values (Alex et al 2001 and Goma et al 2006). The crystals belong to orthorhombic system with space group $Pca2_1$ (Charles Kittle 2007). The XRD analysis confirmed that the KI doping does not alter the basic structural properties of the crystal.

Table-1 Lattice parameters of Pure, 1 mole % and 2 mole % KI doped ZTS

Grown crystal	a (Å)	b (Å)	c (Å)	α	β	γ
Pure ZTS	11.12	7.773	15.499	90˚	90˚	90˚
1 mole % KI doped ZTS	11.12	7.870	15.492	90˚	90˚	90˚
2 mole % KI doped ZTS	11.22	7.863	15.489	90˚	90˚	90˚

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, 1 mole % and 2 mole % of KI doped ZTS crystal was recorded using Perkins Elmer spectrum FTIR spectrometer by KBr pellet technique in the range of 400 to 4000 cm^{-1}, which are shown in Fig. 2.3 (a), (b) and (c).

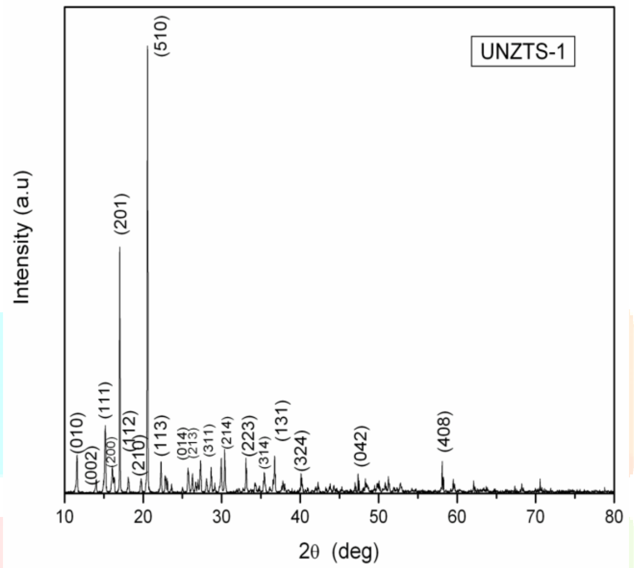

Fig. (a) XRD pattern of Pure ZTS (UNZTS-1)

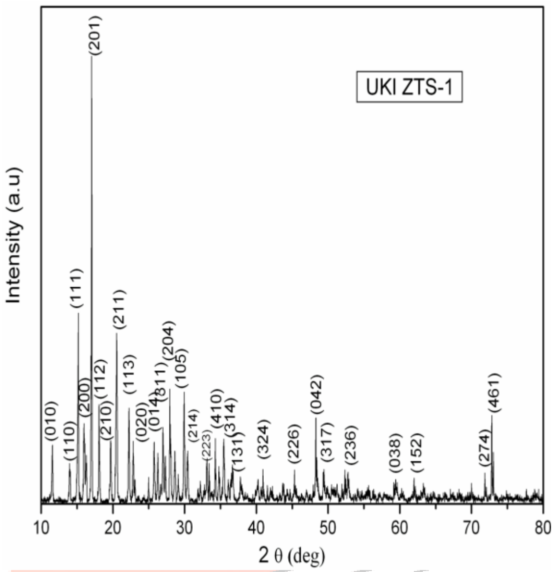

Fig.(b) XRD pattern of 1 mole % KI doped ZTS (UKIZTS-1)

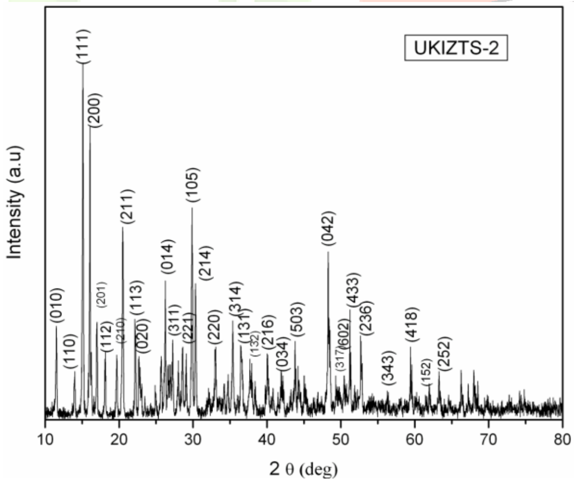

Fig. (c) XRD pattern of 2 mole % KI doped ZTS (UKIZTS-2)

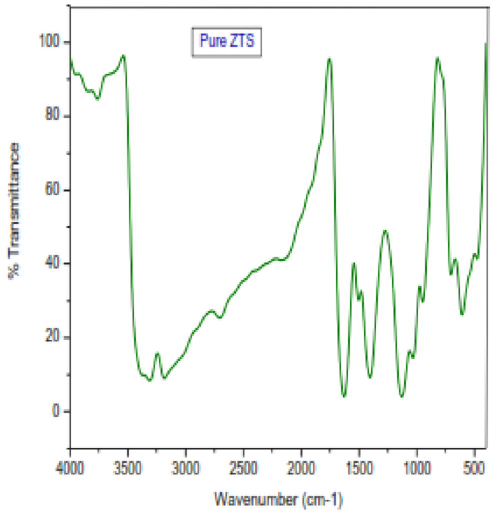

Fig. (a) FTIR spectrum of Pure ZTS crystal

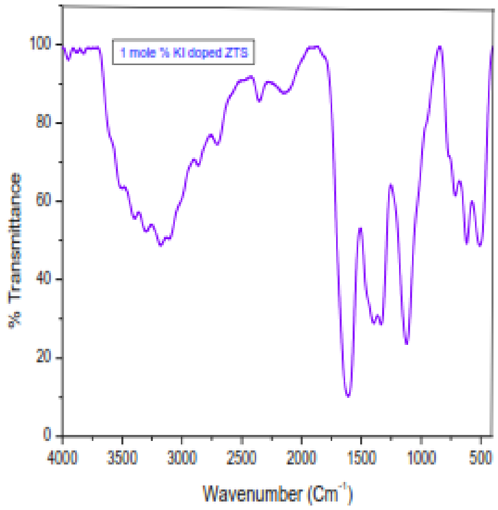

Fig. (b) FTIR spectrum of 1 mole % KI doped ZTS crystal

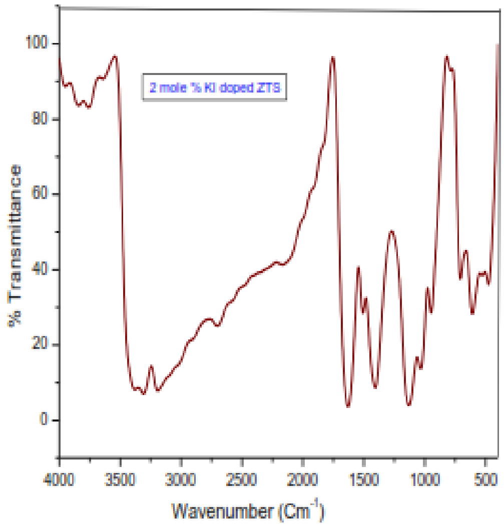

Fig. (c) FTIR spectrum of 2 mole % KI doped ZTS crystal

The FTIR spectrum shows a broad envelope lying between 2750 and 3000 cm1[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 1602cm^{-1} corresponds to the N-C-N stretching 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 symmetric stretching vibration (Silverstein et al 1998, Nakamoto 1978 and Kalsi 2009). Comparison of IR spectra of ZTS, 1 mole % and 2 mole % 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.

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 crystals. The UV Visible study of pure and KI doped crystals were carried out by Lambda 35 model UV Visible spectrometer in the spectral range of 190 – 1100 nm. The absorption and transmission spectra of crystals are shown in Fig. 2.4 and 2.5. The absorption spectra showed the grown crystals have lower cut off wavelength that is less than 297 nm. These values are found to be in good consonance with the literature values. The forbidden band gaps for the grown crystals were calculated using the relation E= hc/ λ, where c is the velocity of light and λ is the wave length. The obtained value for the forbidden band gap for pure, 1 mole % and 2 mole % of KI doped ZTS crystals are 4.18 eV, 4.2 eV and 4.24 eV. The percentage of transmittance of grown crystals is very high.

Microhardness analysis

The grown crystals were also subjected to Vicker's Microhardness Testing (Model No. HMV-2T) 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 gm) were applied over a fixed interval of time about 10 sec. A graph plotted between load and hardness numbers are shown in the Fig. 2.6. From these graph, the increase in the hardness of the grown crystals with increasing loads could be observed. On further increasing the load beyond 100 gm, 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 (Fig. 2.7), which gives a straight line. From this graph, the obtained n values are 1.78, 1.85 and 2.0. This result confirmed that the grown crystals belong to the soft material.

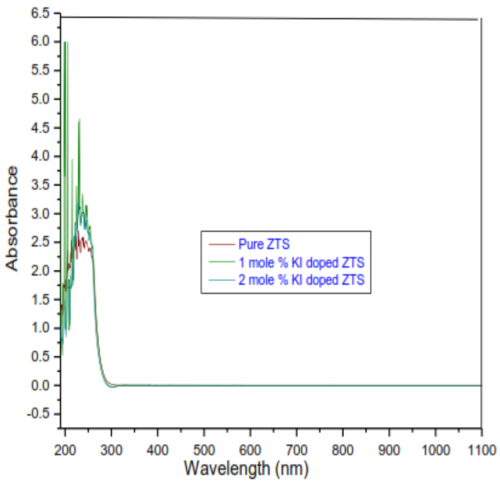

Fig. Absorption spectra of Pure ZTS, 1 mole % and 2 mole % KI doped ZTS crystal

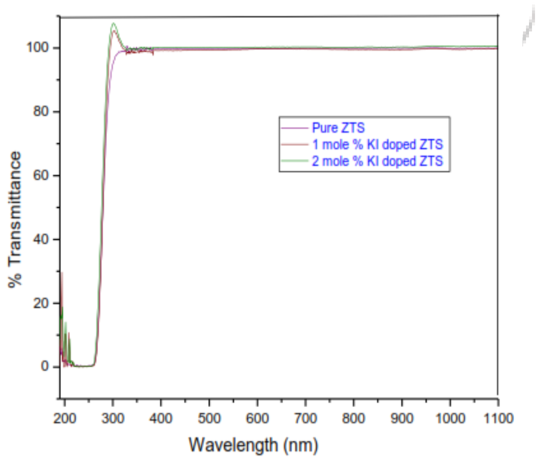

Fig. Transmittance spectra of Pure ZTS, 1 mole % and 2 mole % KI doped ZTS crystal

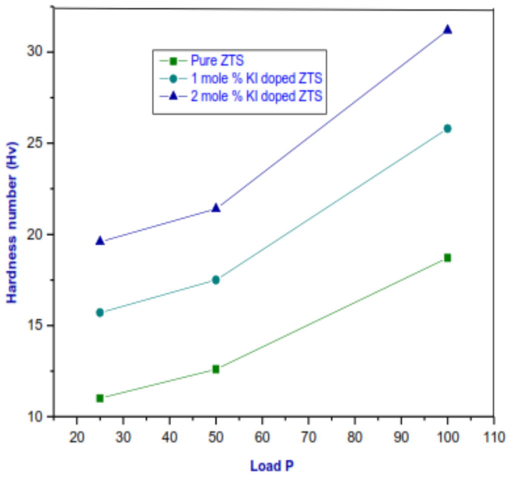

Fig. Load (P) vs Hardness number for Pure, 1 mole % and 2 mole % KI doped ZTS

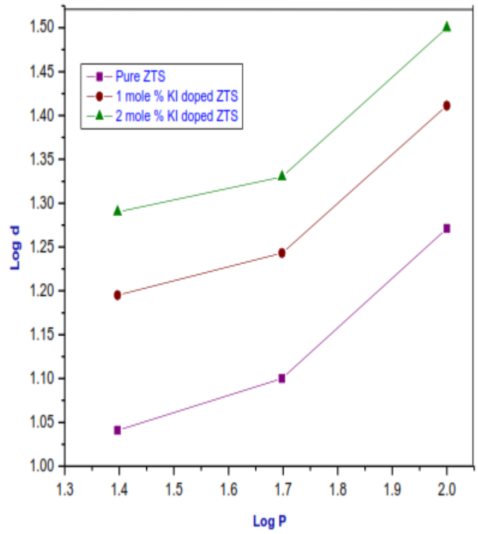

Fig. log P vs log d for Pure, 1 mole % and 2 mole % KI doped ZTS

Kurtz powder SHG test

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

Conclusion

A new semi organic nonlinear optical (NLO) material of Pure and KI doped ZTS single crystals were 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 Pca21. 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 possess lower UV cut off wavelength. UV- visible analysis revealed that the ZTS crystal is good in quality and optically transparent. Microhardness study indicates that the crystal belongs to the class of soft materials. The Thermo gravimetric analysis confirmed that the grown pure, 1 mole % and 2 mole % of KI doped ZTS crystals are thermally stable up to 236.92˚C, 238.77˚C and 242.52˚C respectively. The SHG efficiency of KI doped ZTS crystal is enhanced by KI dopant. Elemental compositions of grown crystals were obtained by using Energy Dispersive X-ray analysis.

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