An Overview of Sophisticated Crystal Growth

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ABSTRACT

The arrangement of the atoms, ions, or molecules in a single crystal may lead to the formation of polycrystals or an amorphous material; these are all examples of solid state materials. In a perfect crystal, the atomic lattice repeats with a certain frequency and size in each of the three dimensions. True crystals have size constraints and flaws. A wide range of scientific disciplines are involved in crystal development, including chemistry, crystallography, mineralogy, metallurgy, chemical engineering, materials science, and physics. Fourier transform infrared analysis verified the existence of crystal vibration modes and functional groups. The crystal has a lower UV cutoff wavelength, as seen by the absorption spectra. The ZTS crystal was found to be of high quality and optically clear during UV-visible examination. The results of the microhardness test place the crystal in the category of rather soft materials. Thermal stability up to 236.92˚C, 238.77˚C, and 242.52˚C were verified by the thermo gravimetric analysis of the grown pure, 1 mole %, and 2 mole % KI doped ZTS crystals, respectively. Doping a ZTS crystal with KI increases its SHG efficiency. The crystals' elemental compositions were determined by using Energy Dispersive X-ray analysis.

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

Introduction

The arrangement of the atoms, ions, or molecules in a single crystal may lead to the formation of polycrystals or an amorphous material; these are all examples of solid state materials. In a perfect crystal, the atomic lattice repeats with a certain frequency and size in each of the three dimensions. True crystals have size constraints and flaws. Atoms arranged in three-dimensional periodic arrays with uniformly spaced repeats in a single direction constitute a single crystal (Dry burgh 1986). Communication, optical imaging, electronics, and laser technology are just a few of the many businesses that rely on crystals.

A wide range of scientific disciplines are involved in crystal development, including chemistry, crystallography, mineralogy, metallurgy, chemical engineering, materials science, and physics. The increasing need for materials for technological applications has led to a dramatic increase in the interest in crystal formation technologies during the last several decades (Brice 1986, Nalwa and Miyata 1997). Modern innovations in semiconductors, polarizers, transducers, infrared detectors, ultrasonic amplifiers, solid state lasers, nonlinear optics, acousto optics, microelectronics, optoelectronics, computers, and other fields attest to the pervasive impact of single crystals on science and technology.

Therefore, it is therefore essential for future research and technology to generate high-quality single crystals. More and more people are interested in learning about crystal formation processes recently, and that's probably due to the rising need for materials with technological uses (Laudise 1970, Brice 1986, Nawla and Miyata 1996). There is a vast variety of techniques for producing crystals, with the primary determinants being the size and properties of the material (Buckley 1951 and Mullin 1976). The time it takes for crystals to form may vary from minutes to hours to days to months, and the methods used to create them can be as basic or as complicated as the budget allows.

Non Linear Optical material (NLO)

Applications including telecommunications, optical data storage, and optical information processing rely heavily on non-linear optical material (NLO) (Meera et al. 2004). Mechanical strength, thermal stability, and transmittance are all high in inorganic NLO materials. However, their optical nonlinearity is low because they do not contain extensive π electron dislocation. As previously stated in many studies (e.g., Shaokang Gao et al., 2006; Ginson et al., 2006; Sun et al., 2005; Ramajothi et al., 2004; Ariponnammal et al., 2005; Min-hua Jiang et al., 1999), ZTS is a semiorganic nonlinear optical material.

When contrasted with inorganic NLO materials, organic NLOs exhibit strong nonlinearity but low thermal strength, mechanical strength, and laser damage threshold (Sweta Moitra et al., 2007). To improve nonlinear and good-property crystal production, researchers are concentrating on semiorganic NLO crystals, which combine the best features of inorganic and organic materials. High nonlinearity, excellent mechanical strength, thermal strength, and transmittance are some of the reasons why semiorganic NLO materials have been garnering a lot of interest recently (Sweta Moitra et al 2007). In order to improve the chemical and physical characteristics of the inorganic salts, they are combined with several organic amino acids that are optically active. The linear and nonlinear optical characteristics, as well as the quality and resiliency to high power laser thermal stress, determine the practicality of NLO crystals. According to Kurtz et al. (1968), ZTS has a high laser damage threshold, low angular sensitivity, and a broad range of transparency. The ZTS crystal has an orthorhombic structure and a chemical formula of Zn [CS (NH2)2]3. SO4. According to Arunmozhi et al. (2004), ZTS has roughly 1.2 times greater nonlinearity than KDP. Because of its low angular sensitivity, ZTS is well-suited for second harmonic generation of type II. Due to its high damage threshold and broad transparency, ZTS crystal is preferable to KDP crystal in frequency doubling and laser fusion investigations (Sangwal et al 2004). Semiorganic nonlinear optical materials, such as zinc tris thiourea sulphate, outperform many NLO materials in terms of nonlinearity, transmittance, and mechanical strength (Sangwal et al., 2004). Here, ZTS was produced at room temperature both pure and doped with KI. The grown crystals were examined using a range of techniques, including XRD, FTIR, UV transmittance, microhardness, TGA/DSC, SHG, and EDX, and the outcomes of these investigations are detailed in this publication.

Experimental Details

The low temperature solution growth approach, particularly the slow evaporation technique at room temperature (30˚), was used to form single crystals of both pure and KI doped ZTS in accordance with the reaction in equation (1) (Ramasamy et al 1999). Thiourea (CS [(NH2)2)) and analar grade zinc sulphate (ZnSO4.7 H2O) were dissolved in deionized (DI) water in a molar ratio of 1:3. We used a magnetic stirrer to get a saturated homogenous solution after an hour. To make the saturated solution even more pure, it was filtered. For gradual evaporation, this uniform saturated solution was placed in a glass container covered with perforated filter paper. In only fifteen days, transparent, colorless ZTS crystals may be collected.

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

Fig-1 (a) As grown crystal of Pure ZTS

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

The grown crystals were characterized in a number of ways, including powder X-ray diffraction, Fourier transform infrared spectroscopy, microhardness testing, thermogravimetric analysis, electrochemical dissolution spectroscopy, and scanning hybrid microscopy. The pure ZTS single crystals as generated and the ones doped with KI are shown in Figure 2.1 (a), (b), and (c), correspondingly.

RESULTS AND DISCUSSION

X-ray diffraction studies

Pure, 1 mole %, and 2 mole % potassium iodide (KI) doped ZTS crystals were analyzed by powder X-ray diffraction using a Rigaku diffractometer equipped with CuKα radiation at a wavelength of 1.5418Å.Figure 2.2 (a), (b) and (c) show a number of excellent intensity peaks that were seen in the x-ray diffraction pattern. The produced crystals' high crystallinity is shown by the clearly defined peaks at various 2θ values. Utilizing XRD analysis software, all peaks were indexed. The generated crystals' lattice properties are listed in Table-2.1. We find that the observed values of the lattice parameters coincide well with the values published before (Alex et al., 2001; Goma et al., 2006). The orthorhombic system with space group Pca21 is represented by the crystals (Charles Kittle 2007). The XRD results show that the crystal's fundamental structural characteristics are unaffected by the KI doping.

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	11.24	7.766	15.488	90˚	90˚	90˚
1 mole % KI doped ZTS	11.24	7.790	15.487	90˚	90˚	90˚
2 mole % KI doped ZTS	11.33	7.786	15.454	90˚	90˚	90˚

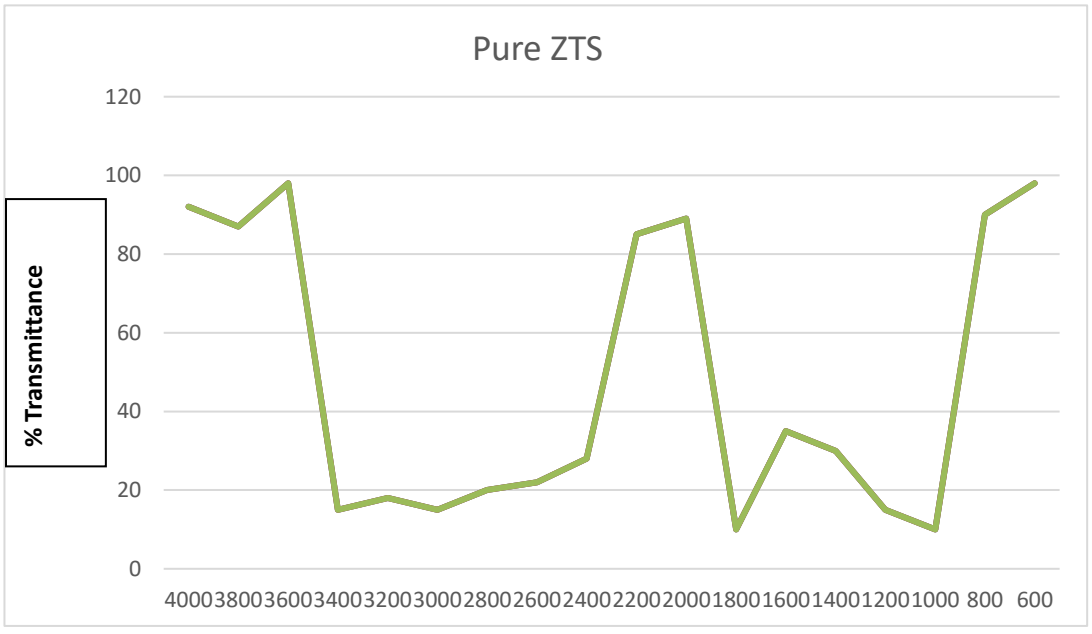


Fig-2 (a) FTIR spectrum of Pure ZTS crystal

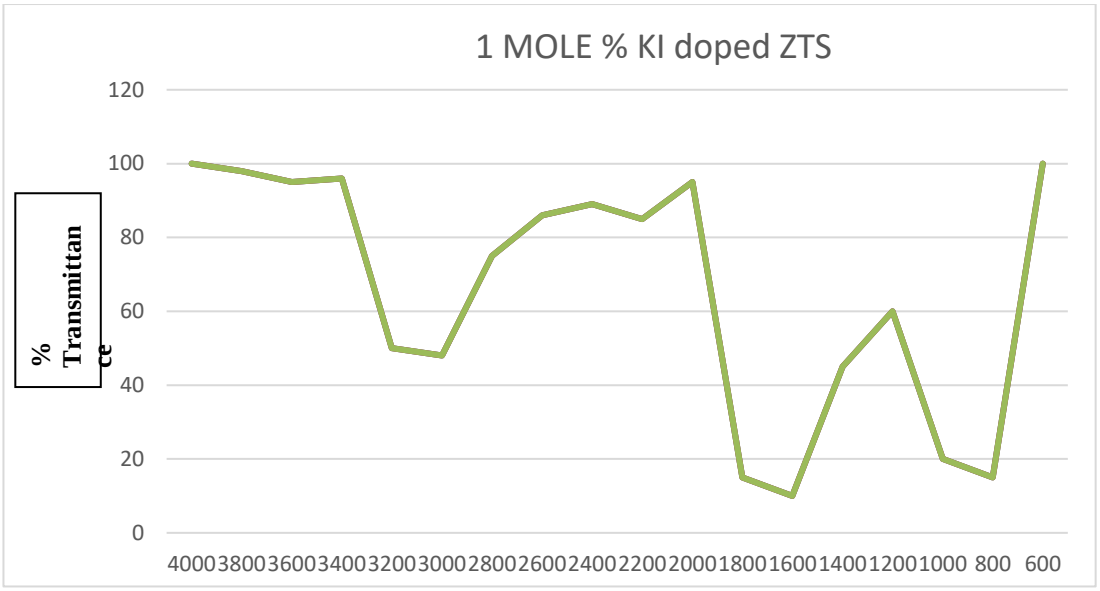
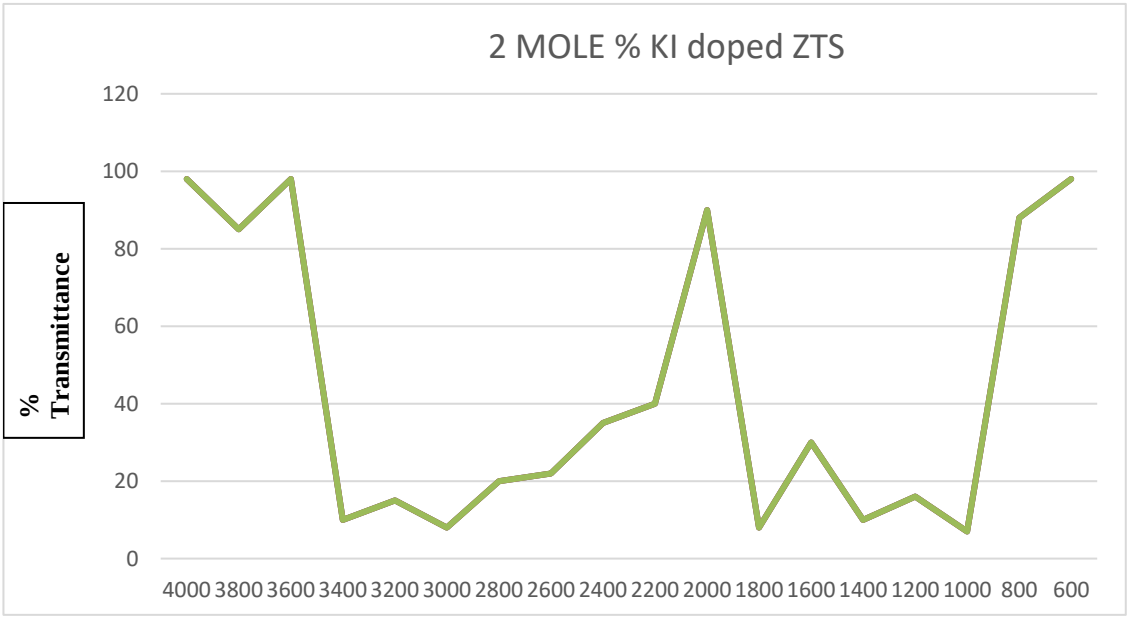


Fig-2 (b) FTIR spectrum of 1 mole % KI doped ZTS crystal



Fi-2 (c) FTIR spectrum of 2 mole % KI doped ZTS crystal

The symmetric and asymmetric modes of the NH2 group zinc coordinated thiourea give rise to a wide envelope in the FTIR spectrum, which lies between 2750 and 3000 cm11. Peaking at around 717 cm-1, it clearly indicates the presence of sulfate ions. It is the N-C-N stretching vibration that causes the absorption band at 1602 cm-1 to be detected. The asymmetric stretching vibration is shown by the existence of bands at 393 cm-1 and 948 cm-1. The stretching vibration of NH2 is correlated with the peak at 3170 cm-1.

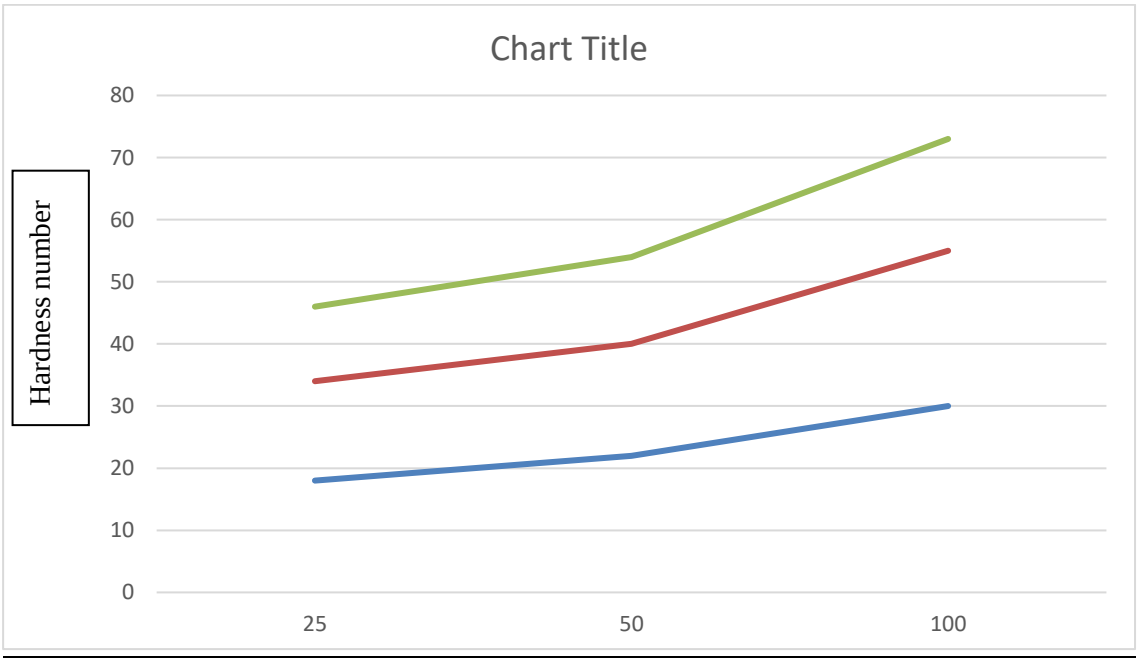
According to Silverstein et al. (1998), Nakamoto (1978), and Kalsi (2009), the NH2 symmetric stretching vibration is corresponding to the absorption band at about 3376 cm-1. A little change in the absorption bands was seen when comparing the infrared spectra of ZTS, 1 mole % KI doped ZTS, and 2 mole % KI doped ZTS. The addition of KI to ZTS is responsible for the change in absorption bands.

UV- Visible spectral studies

The primary use of the individual crystals is in optical applications. Any given crystal's optical transmittance range and transparency cutoff are crucial parameters. Using a Lambda 35 model UV Visible spectrometer, which operates in the 190–1100 nm spectral range, we examined both pure and KI doped crystals in the ultraviolet light spectrum. Figures 2.4 and 2.5 show the crystals' transmission and absorption spectra, respectively. A reduced cutoff wavelength of less than 297 nm was seen in the absorption spectra of the produced crystals. The values contained in literature are found to be in excellent harmony with these ideals. The formula E= hc/ λ, where c is the velocity of light and λ is the wave length, was used to determine the prohibited band gaps for the produced crystals. The calculated prohibited band gaps for ZTS crystals doped with 0, 1, and 2 moles of KI are 4.18 eV, 4.2 eV, and 4.24 eV, respectively. Transmittance percentages of produced crystals are quite high.

Microhardness analysis

Additionally, the produced crystals were tested for microhardness using a diamond indenter and Vicker's Microhardness Testing (Model No. HMV-2T). Mounted on the micro hardness tester's platform, the crystals were subjected to loads ranging from 25 to 100 grams for a set duration of around 10 seconds. Figure 2.6 shows a curve that is plotted against the load and hardness values. The hardness of the produced crystals was shown to increase with increasing stresses, as seen in these graphs. Surface fractures appeared on the crystals when the weight was increased above 100 gm. The hardness value is low at low load and increases with increasing load. Additionally, a straight line is produced when the graph of log P vs log d is displayed (Fig. 2.7). The n-values that were derived from this graph are 2.0, 1.85, and 1.78. This finding provided more evidence that the crystals formed are really from a pliable substance.



Load

Fig-3: load vs hardness number for pure, 1 mole% and 2 mole % KI doped ZTS

Kurtz powder SHG test

We used the Kurtz powder approach to generate second harmonics (SHG) for both powder-pure and KI-doped ZTS. The basic wavelength radiated by powder samples lit with a Q-switched Nd: YAG laser was 1064 nm. An emission of green light at 532 nm was used to validate the second harmonic generation.

The findings show that compared to pure ZTS crystal, KI-doped ZTS crystal has a higher SHG efficiency. One possible use for these materials is in frequency conversion.

Conclusion

The synthesis of pure and doped ZTS single crystals using low temperaturesolution growth and, more specifically, the slow evaporation methodology, resulted in a novel semi-organic nonlinear optical material (NLO). The crystal structure was determined to be an orthorhombic system with space group Pca21 by powder XRD analysis. Fourier transform infrared analysis verified the existence of crystal vibration modes and functional groups. The crystal has a lower UV cutoff wavelength, as seen by the absorption spectra. The ZTS crystal was found to be of high quality and optically clear during UV-visible examination. The results of the microhardness test place the crystal in the category of rather soft materials. Thermal stability up to 236.92˚C, 238.77˚C, and 242.52˚C were verified by the thermo gravimetric analysis of the grown pure, 1 mole %, and 2 mole % KI doped ZTS crystals, respectively. Doping a ZTS crystal with KI increases its SHG efficiency. The crystals' elemental compositions were determined by using Energy Dispersive X-ray analysis.

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