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Thermal and optical properties of ZTS single crystals in the presence of 1,10-phenanthroline (Phen)

Crystalline perfection studies

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Abstract The influence of heteroaromatic N-base (1,10-phenanthroline) (Phen), a new additive as complexing agent on tris(thiourea)zinc(II)sulphate (ZTS) crystals from aqueous solutions at 30 °C is investigated. Crystals were grown using low concentration of the dopant (0.005 M L^{-1}) in the aqueous growth medium and the growth promoting effect (GPE) is much greater because of an increase in the metastable zone width. High dopant concentration decreases GPE. The crystalline perfection of the grown crystals is quite good both in doped and undoped crystals as evaluated by high-resolution X-ray diffractometry (HRXRD). The diffraction curve of a typical Phen doped as-grown ZTS crystal was observed to contain a single peak indicating that the crystal does not contain any epitaxial layer on the surface or internal structural grain boundaries. Not much variation is observed in FT-IR and XRD of pure and doped ZTS. Phen depresses the NLO efficiency of ZTS. It could be ascribed due to the disturbance of charge transfer in the presence of the dopant. The grown crystals were also characterized by UV–Vis, SEM and TG–DTA techniques.

Keywords Characterization · XRD · 1,10-Phenanthroline · Crystalline perfection · Nonlinear optical properties · Thermal analysis

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Introduction

Tris(thiourea)zinc(II)sulphate (ZTS) is a good engineering material for device application and laser fusion experiments. It is a novel organometallic crystal with potential application in electro-optic modulation. It belongs to the orthorhombic system with the space group $P_{ca}2_1$ and point group mm2. Although the crystal growth, kinetics and characterization of ZTS have been extensively investigated [1–6], a systematic investigation of the effect of a new organic dopant, Phen on ZTS crystal growth medium has not been reported.

It was observed that organic compounds like ethylenediamminetetraacetic acid (EDTA), urea and thiourea lead to an increase in the growth rate and improvement in quality of different crystals [7]. Likewise, catalytic effect on growth rates is also noticed with inorganic additives like KCl and NH_4Cl [8]. The growth promoting effect (GPE) is due to the complexation of trace metal ion impurities in solution. The resulting complex is not entering into the crystal. Since the complexing agent prevents the entry of impurities into the crystal by complex formation, the growth of the crystal is rapid. Also in the presence of these additives, secondary nucleation is effectively controlled.

In general, for crystallization to occur, the homogenous phase must be metastable, i.e. supersaturated. An impurity leads to an increase in the metastable zone width of the solution when the complex absorption on the growing surface is not very stable [7]. EDTA, a surfactant is a good additive and the main reason for the rapid growth process in the presence of EDTA is its ability to complex with impurities, particularly the trace metal ions in solution. We have reported [1] that EDTA enhances the second harmonic generation (SHG) efficiency of ZTS remarkably. It will be interesting to carry out the crystal growth and characterization studies in the presence of some other well-known complexing agent to substantiate the above said facts. X-ray, thermal, spectral, microhardness and microscopic studies are very useful techniques for materials characterization. Therefore, it is not surprising that many authors have used these techniques for various materials investigation [9–39]. In this study, we have made a detailed investigation on the influence of complexing agent, a new additive, Phen on ZTS crystals using various spectral, thermal, microhardness, SHG efficiency and microscopic analyses.

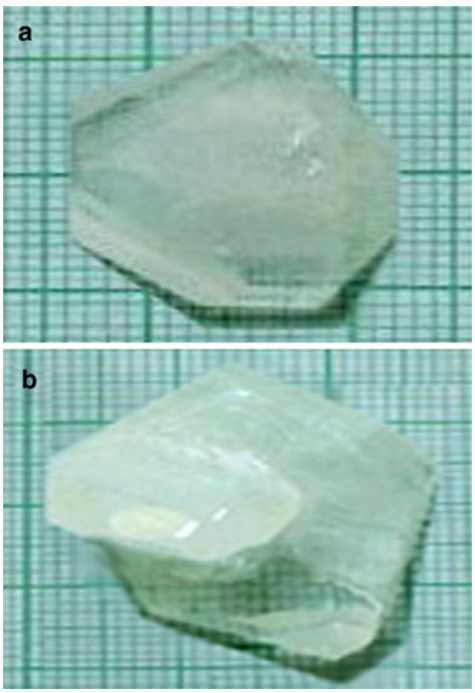

Fig. 1 Photograph of (**a**) pure ZTS and (**b**) Phen-doped ZTS

Experimental

Synthesis and crystal growth

The starting material was synthesized in the stoichiometric ratio of 1:3 for Zinc Sulphate Heptahydrate (EM) and thiourea (SQ). To avoid decomposition, low temperature (<70 °C) was maintained during the preparation of the solution in deionized water.

$$ZnSO_4 \cdot 7H_2O + 3\left(CS(NH_2)_2\right) \rightarrow Zn\left(CS(NH_2)_2\right)_3SO_4$$

The product was purified by repeated recrystallization. The crystal growth was carried out in the presence of a small quantity (5×10^{-3} M L^{-1}) of organic dopant in the growth medium. At low concentrations of Phen, the GPE is much greater than that observed in the absence of dopant.

The crystal growth was tried under different acidic conditions at pH values in the range of 3.0–6.0. The pH variations were carried out using dilute sulphuric acid. The crystal growth rate and the quality of the crystals are much better when the solution is slightly acidic and the studies were mainly carried out at pH ~5.9. Under high acidity, the rate of crystal growth decreases considerably.

Studies follow the general trend that the growth rate of the crystals in the presence of impurities always decreases with an increase in the impurity concentration. At high concentration of the dopants, the adsorption film blocks the growth surface and inhibits the growth process [40]. Bulk crystals have been grown using the optimized growth parameters. Photographs of the crystals grown from (a) pure ZTS and (b) Phen-doped ZTS solutions are shown in Fig. 1.

Measurements

Powder X-ray diffractometry (XRD) analysis was performed with a graphite monochromated Cu Kα radiation.

The FT-IR was recorded for pure ZTS and Phen-doped ZTS using AVATAR 330 FT-IR by KBr pellet technique in the range 500–4000 cm^{-1}.

UV–Visible absorption spectra were recorded using a Hitachi UV–VIS spectrophotometer in the spectral range 250–800 nm.

Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out using a NETZSCH STA 409C thermal analyzer in nitrogen atmosphere. The sample was heated between 30 and 800 °C at a heating rate of 20 °C/min.

Vickers microhardness was evaluated for the well polished grown crystal and dominant (001) plane using Reichert 4000E Ultramicrohardness Tester.

The SEM images were taken at magnification values from 50× to 5,000× with maximum value of EHT 15.00 kV using a JEOL JSM 5610 LV instrument.

Solubility was analyzed gravimetrically. Metastable zone width was measured by conventional polythermal method [41, 42].

Results and discussion

Solubility and metastable zone width

Metastable zone width is an essential parameter for the growth of large size crystals from solution since it is a direct measure of the stability of the solution in its supersaturated region [43]. Metastable zone width is determined for ZTS/Phen system. Comparison shows that it is wider than in the case of pure ZTS (Table 1). In the present investigations, it is very interesting to note that the metastable zone width increases with increase in temperature for ZTS/Phen system. Also in the presence of Phen, secondary nucleation is controlled to a considerable extent. It effectively depresses the shearing action of the solution tearing off the small particles from crystal surface and thus preventing the secondary nuclei formation.

X-ray diffraction study

XRD pattern of ZTS crystals grown rapidly in 5×10^{-3} M L^{-1} Phen added solution is compared with that of pure ZTS crystal. X-ray diffraction patterns of the product are consistent with that of the pure ZTS crystal. No change in basic structure is observed except for the slight reduction in intensity with organic dopant (Fig. 2). The XRD data is analyzed with Rietveld method with RIETAN-2000.

FT-IR spectra

The characteristic FT-IR vibrational frequencies of pure ZTS and dopant added ZTS are very similar. The symmetric and asymmetric C=S stretching vibrations at 740 and 1417 cm^{-1} of thiourea are shifted to lower frequencies in all the FT-IR spectra [44]. The band $\sim$1500 cm^{-1} is assigned to N–C–N stretching vibration. It appears that the GPE of organic dopants is not connected with the additive entering into the crystal. When the impurity distribution coefficient is very low, the impurities are practically not incorporated into the crystal [45]. The rapid growth process is caused by the adsorption of the impurity at the flat surface or at the step edge [46]. At low dopant concentrations, adsorption can take place at kink sites (Bliznakov mechanism) or at the surface terrace (Cabrera Vemilyea mechanism). Interestingly at high Phen concentrations, there are some variations in FT-IR spectra [47]. Explanations require a detailed study. The work is in progress.

Table 1 Nucleation temperature and metastable zone width of pure and Phen (5×10^{-3} mol/dm^3) added ZTS solution at different saturation temperatures

Saturation temperature/°C	Nucleation temperature/°C		Metastable zone width/°C	
	Pure	Phen added	Pure	Phen added
35	32.0	28.5	3.0	6.5
40	34.5	32.0	5.5	8.0
45	38.2	34.5	6.8	10.5
50	43.0	38.5	7.0	11.5

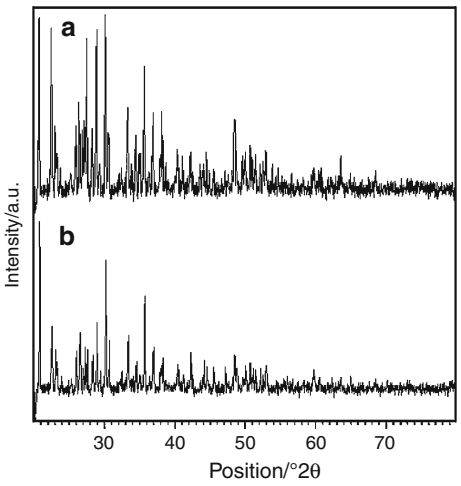

Fig. 2 XRD patterns of (**a**) pure ZTS and (**b**) Phen-doped ZTS

Optical transmission spectra

The UV–Vis absorption spectra were recorded using a Hitachi UV–Vis spectrophotometer in the spectral range 250–800 nm for pure and Phen-doped ZTS sample. The percentage transmission is much better in the case of Phen doping. The lower cut-off wavelength is <250 nm.

Microhardness measurements

Hardness is the resistance offered by a material to localized plastic deformation caused by scratching or by indentations.

Microhardness number, $H_V = 1.8544\ p/d^2$,

where p is the load in kg and d is the diagonal length of indentation (mm). There is not much of variation in H_V for a test load of 25 g (Table 2).

During indentations, radical cracks have been observed on the prism faces at higher loads (>30 g).

Thermal studies

The simultaneous TG–DTA curves in nitrogen for ZTS and ZTS/Phen systems at a heating rate of 20 °C/min are given

Table 2 H_V values

System	Plane	H_V/kg/mm^2
ZTS	100	120
ZTS/Phen	100	121

H_V value for ZTS taken from Ref. [49]

in the Fig. 3a, b. The absence of water of crystallization in the molecular structure is indicated by the absence of weight loss around 100 °C. Melting point of the sample is slightly lower in the case of Phen added ZTS (Fig. 3b). A very good thermal stability of the material is observed up to ~225 °C and the thermal behaviour is not very much altered in the presence of the dopant, Phen. No decomposition up to the melting point ensures the suitability of the material for application in lasers, where the crystals are required to withstand high temperatures.

Scanning electron microscopic studies

Scanning electron microscopic (SEM) study gives information about the surface nature and its suitability for device fabrication. Also it is used to check the presence of imperfections. It has been reported [48] that the effectiveness of different impurities in changing the surface morphology is different. At low concentrations of dopants the effects are reflected by changes in configuration of grown structures [49]. The SEM pictures of pure and Phen-doped ZTS are given in Fig. 4a, b. SEM photograph of ZTS (Fig. 4a) shows dendritic growth. Larger scatter centres are observed in Phen-doped ZTS (Fig. 4b). The scatter centre can be understood as a kind of liquid inclusion, mainly mother solution.

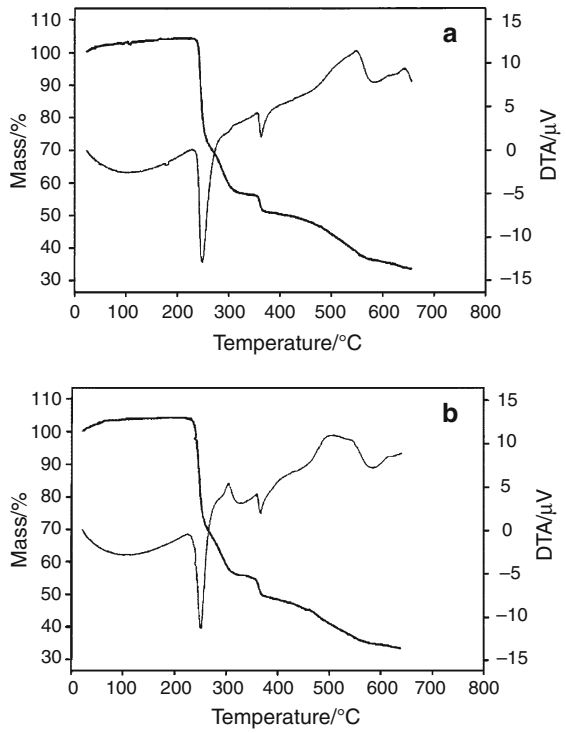

Fig. 3 TG–DTA curve of (**a**) pure ZTS and (**b**) Phen-doped ZTS

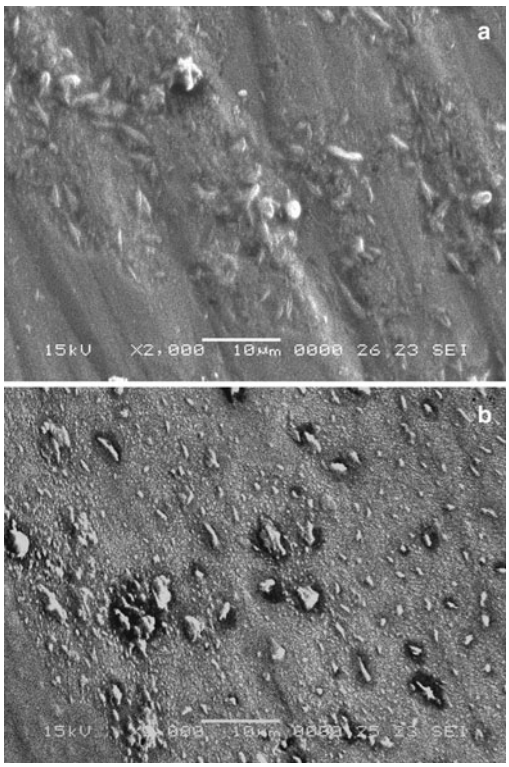

Fig. 4 SEM photograph of (**a**) pure ZTS and (**b**) Phen-doped ZTS

High-resolution X-ray diffractometry (HRXRD)

Figure 5a, b shows the high-resolution diffraction curves recorded with the multicrystal X-ray diffractometer [48] in symmetrical Bragg geometry for (001) diffracting planes. A well collimated and monochromated Mo $K\alpha_1$ beam obtained from a set of three plane (111) Si monochromator crystals set in dispersive (+, −, −) configuration has been used as the exploring X-ray beam. Due to this dispersive configuration of the monochromator crystals, the dispersion broadening in the diffraction curve of the specimen crystal is insignificant and the full width at half maximum (FWHM) of the diffraction curve of the specimen does not alter. The specimen crystal is aligned in the (+, −, −, +) configuration. The curves in Fig. 5a, b are having single sharp peaks with FWHM much less than a minute of arc showing good crystalline perfection. The single peak in the curves indicates that the crystal does not contain any epitaxial layer on the surface or internal structural grain boundaries. In general, one can come to a conclusion that the presence of organic dopant improves the crystalline

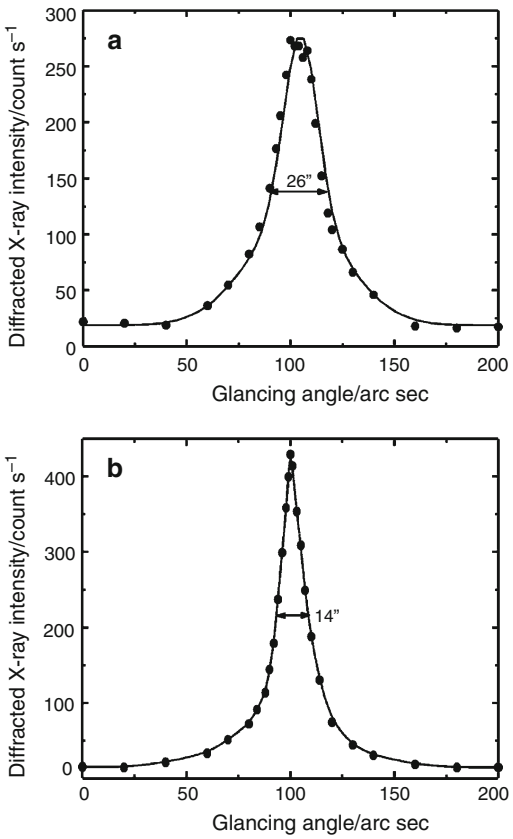

Fig. 5 HRXRD patterns of (**a**) pure ZTS and (**b**) Phen-doped ZTS

perfection to a considerable extent as indicated by low FWHM values. High-resolution diffuse X-ray scattering (DXS) studies [50] are in progress to understand the residual point defects and their aggregates in these samples.

SHG efficiency

SHG test on the crystals was performed by Kurtz powder SHG method [51]. The Nd:YAG laser with a modulated radiation of 1,064 nm was used as the optical source and directed on the powdered sample through a filter. The doubling of frequency was confirmed by the green radiation of 532 nm.

Although many materials have been identified that have higher molecular nonlinearities, the attainment of second-order effects requires favourable alignment of the molecule within the crystal structure [52]. To elaborate, the efficient SHG demands specific molecular alignment of the crystal to be achieved facilitating non-linearity in the presence of a dopant. It has been reported that the SHG can be greatly enhanced by altering the molecular alignment through inclusion complexation [53] (Table 3).

Input radiation used is 5 millipoise/pulse. Intensity of SHG gives an indication of NLO efficiency of the material. Depressed SHG output in the case of Phen dopant is quite

Table 3 SHG output

System	$I_{2\omega}$/mV
ZTS	48–49
ZTS/Phen	20–22

likely due to the disturbance of charge transfer. It appears that because of the orientational cancellation, the second order susceptibility for SHG vanishes. By changing the growth conditions and the method, Phen can be an effective dopant. Our belief is based on the fact that the presence of delocalized aromatic organic molecule can result in much higher second order NLO efficiencies.

Conclusions

The metastable zone width of ZTS solutions in their supersaturated region was found to be enhance by the incorporation of small quantities of 1,10-phenanthroline, a new additive. Phen well promotes the crystal growth process of ZTS in slightly acidic solutions (pH $\sim$5.9). XRD and FT-IR studies reveal that the GPE of organic dopant is not caused by adsorption of dopant on the flat surface or the step edge of the crystal. High concentrations of Phen inhibit the growth process. Optical transmission spectral studies reveal that the percentage of transmission is much better with Phen-doped ZTS. Not much variation in microhardness values is observed. HRXRD studies indicate single peak in the diffraction curves of ZTS and ZTS/Phen systems revealing the absence of any epitaxial surface layer or internal structural boundaries that lead to improved crystalline quality. Depressed SHG efficiency with Phen dopant is rationalized by envisaging an unfavourable molecular alignment affecting the nonlinearity.

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