INFLUENCE OF ORGANIC SOLVENT ON TRISTHIOUREA-ZINC(II)SULPHATE CRYSTALS

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It was observed that the addition of a very small quantity ($5\cdot10^{-3}$ M L^{-1}) of an organic solvent, benzene (C_6H_6) in the aqueous growth medium (pH ~5.9) of tristhioureazinc(II)sulphate (ZTS) markedly influences the SHG efficiency. The measurements using Nd:YAG laser source reveal that second harmonic generation (SHG) conversion efficiency which is one of the most important nonlinear optical (NLO) properties is enhanced by benzene dopant by a factor of nearly 1.5 times. The crystalline perfection of the grown crystals was evaluated by high-resolution X-ray diffractometry (HRXRD). The full width at half maximum (FWHM) of the diffraction curve (which gives an estimate for the degree of crystalline perfection) for undoped and benzene doped specimen crystals are 26 and 15 arc sec, respectively.

The reduction in FWHM due to the benzene solvent indicates the significant improvement in crystalline perfection. This very much suggests that the dissolution of trace impurities in the presence of benzene prevents the entry of impurities into the crystal lattice and at the same time enhances the growth promoting effect (GPE). Not much variation is observed in XRD, FTIR and TG-DTA of ZTS in the presence and absence of benzene in the aqueous growth medium.

Keywords: *characterization, growth from solutions, high resolution X-ray diffraction, nonlinear optical properties, zinc compounds*

Introduction

Tristhioureazinc(II)sulphate (ZTS) is a good engineering material for second harmonic generation (SHG) device application and laser fusion experiments. It is a novel metal organic crystal with potential application in electro-optic modulation. It belongs to the orthorhombic system with the space group $P_{ca}2_1$ (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 organic solvent in the growth medium of ZTS single crystals has not been reported.

It was observed that organic compounds like ethylenediaminetetraacetic acid (EDTA), urea and thiourea lead to an increase in the growth rate and improvement in quality of different crystals [1, 7]. Likewise, catalytic effect on growth rates is also noticed with inorganic additives like KCl and NH_4Cl [8]. The growth promoting effect is due to the complexation of trace metal ion impurities in solution. The process of complexation prevents the entry of impurities into the crystal and leads to increase the growth rate and enhances the crystalline perfection. Secondary nucleation is also effectively controlled in the presence of these additives. It is interesting to observe similar results in the presence of an organic solvent. It appears that the solvent because of dissolution of the trace organic impurities in the growth medium prevents their entry into the crystal lattice and thereby enhancing the crystalline perfection.

The solvent influences the crystallization process [9]. The solvent composition can markedly influence the growth rate through its influence on the crystal interface structure [10]. Further, the influence of solvent is ascribed to its influence on solution properties, the structure of solid liquid interface of the solubility [11]. Solvent also plays an important role on crystal morphology [12–14]. Growth promotion by H_2O in organic solvent has been observed [15] in the selective isolation of a target polymorph. Many authors have investigated organic-inorganic materials and also characterized them using various techniques such as thermal analysis, SEM, TEM, XRD and FTIR spectroscopy [16–48]. In the present investigation, effect of a small quantity of an organic solvent, benzene on the crystal structure, crystalline

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perfection, optical properties, SHG conversion efficiency has been studied by thermal analysis, powder XRD, SEM, HRXRD, FTIR and SHG measurements.

Experimental

Synthesis

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

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

The product was purified by repeated crystallization. Mainly, the crystal growth was carried out in the presence of a very small quantity of organic solvent under slightly acidic conditions. Under high acidity, the rate of crystal growth decreases considerably. High concentration of the organic solvent inhibits the growth process as reported in the case of dopants [49]. At high concentration of the dopants, the adsorption film formed by the complexation with impurities blocks the growth surface and inhibits the growth process [50]. Bulk crystals have been grown using the optimized growth parameters. Photograph of the as grown crystal in the presence and absence of benzene in the growth medium is shown in Fig. 1.

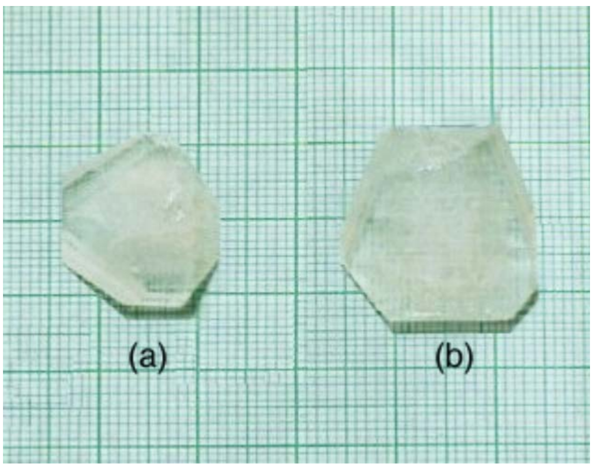

Fig. 1 ZTS in the a – absence and b – presence of benzene

Measurements

The powder X-ray diffractometry (XRD) analysis was performed with a graphite monochromated CuK_α radiation.

The FTIR spectra were recorded for both samples using an AVATAR 330 FTIR by KBr pellet technique in the range 500–4000 cm^{-1}.

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

The thermogravimetric and differential thermal analyses 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^{-1}.

Results and discussion

Metastable zone width

Omar and Ulrich [9] and Matynia and Wierzbowska [51, 52] have investigated the effect of addition of alcoholic miscible co-solvents on the crystallization process. The solvents increase the thermodynamic driving force and width of the metastable zone. In the present investigations, addition of small quantities of nonaqueous solvent benzene ($5{\cdot}10^{-3}$ M L^{-1}) results in the GPE because of increase in metastable zone width. Morphology of ZTS crystal grown under the experimental conditions is shown in Fig. 2.

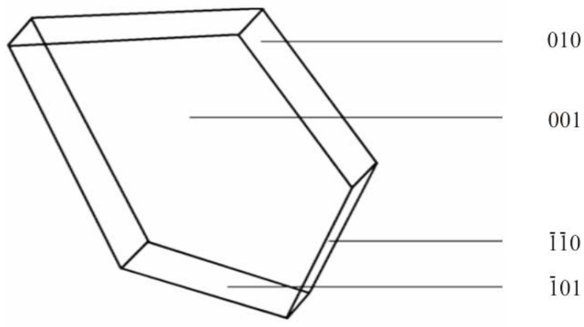

Fig. 2 Morphology of benzene doped ZTS crystal

X-ray diffraction study

XRD pattern of ZTS crystal grown rapidly in ($5{\cdot}10^{-3}$ M L^{-1}) benzene 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 solvent (Fig. 3). The XRD data is analyzed with Rietveld method with RIETAN-2000.

FTIR and optical transmission spectra

The characteristic vibration frequencies of pure ZTS and organic solvent 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 FTIR spectra [53].

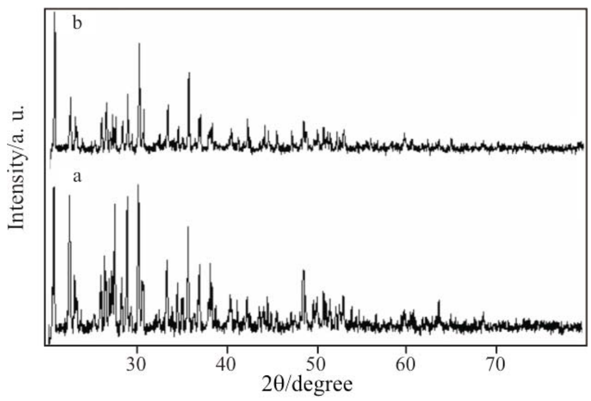

Fig. 3 XRD patterns of a – pure ZTS and b – benzene doped ZTS

The band ~1500 cm^{-1} is assigned to N–C–N stretching vibration. It appears that the growth promoting effect of organic solvent 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 [54]. The rapid growth process is caused by the dissolution of the trace impurities. The optical transmissions are not altered much for benzene addition.

Thermal studies

The simultaneous TG-DTA curves in nitrogen for ZTS and ZTS/benzene systems at a heating rate of 20°C min^{-1} are given in the Figs 4a and b. The presence of crystallization water in the molecular structure is indicated by the absence of mass loss around 100°C. Melting point of the sample is slightly lower in the case of benzene added ZTS (Fig. 4b). A very good thermal stability of the material is observed up to ~225°C and the thermal behavior is not very much altered in the presence of the dopant, benzene. 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.

High-resolution X-ray diffractometry (HRXRD)

Figures 5a and b show the high-resolution diffraction curves recorded with the multicrystal X-ray diffractometer [55] in symmetrical Bragg geometry for (001) diffracting planes. A well collimated and monochromated MoKα_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. For pure ZTS the DC curve contains a single peak with FWHM of 26 arc sec which shows that the crystal does not contain any epitaxial layer (Fig. 5a). The curve, belongs to benzene

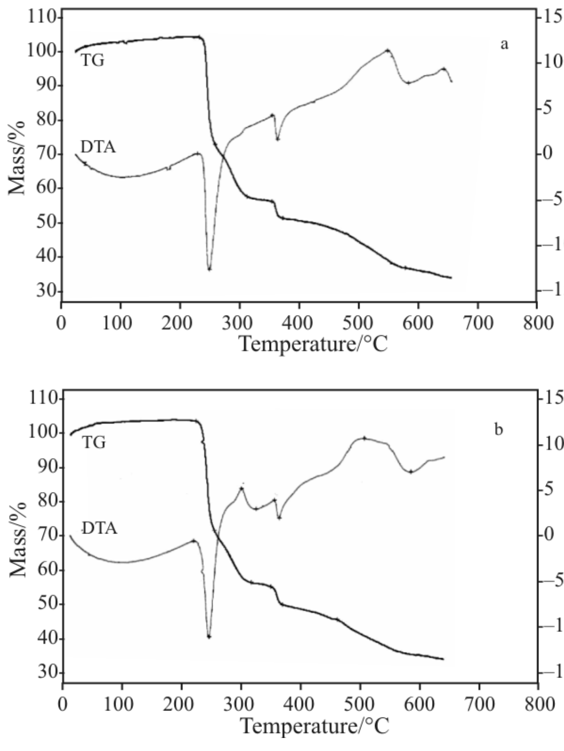

Fig. 4 TG-DTA curve of a – pure ZTS and b – benzene doped ZTS

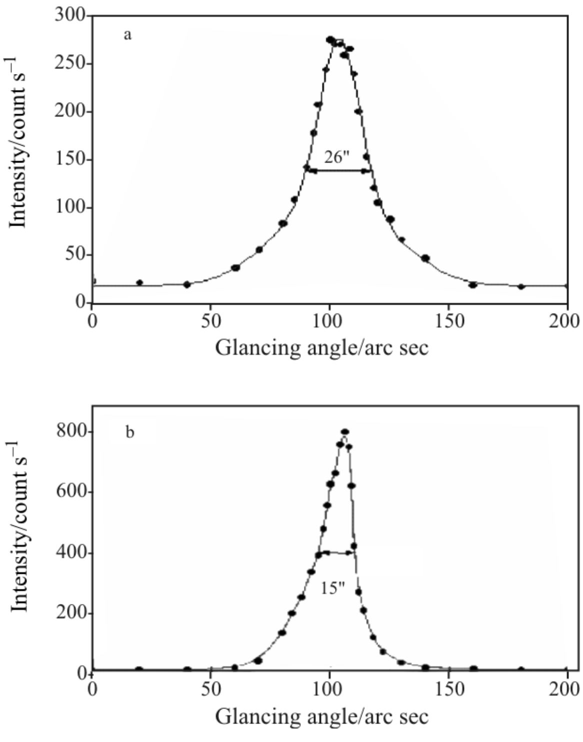

Fig. 5 HRXRD patterns of a – pure ZTS and b – benzene doped ZTS

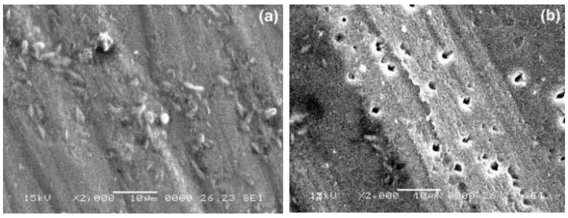

Fig. 6 SEM photographs of a – pure ZTS and b – benzene doped ZTS

doped ZTS also contains one peak with FWHM of 15 arc sec showing good crystalline perfection (Fig. 5b). The reduction in FWHM of DC for doped specimen from 15 arc sec from its initial value of 26 arc sec in its undoped condition shows that the presence of organic solvent improves the crystalline perfection to a considerable extent. High-resolution diffuse X-ray scattering (DXS) studies [56] are in progress to understand the residual point defects and their aggregates in these samples.

Scanning electron microscopic studies

SEM study (JEOL JSM 5610 LV) 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 [57] that the effectiveness of different impurities in changing the surface morphology is different. At low concentrations of dopant, the effects are reflected by changes in configuration of grown structures [57]. SEM image of ZTS (Fig. 6a) shows dendritic growth and ZTS/benzene system (Fig. 6b) shows bubble voids. It could be quite likely due to the evaporation of the solvent from the crystal surface.

SHG efficiency

Second harmonic generation test on the crystals was performed by Kurtz powder SHG method [58]. An Nd:YAG laser with a modulated radiation of 1064 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 non-linearities, the attainment of second-order effects requires favorable alignment of the molecule within the crystal structure [59]. To elaborate, the efficient SHG demands specific molecular alignment of the crystal to be achieved facilitating nonlinearity in the presence of solvent. 5 millipoise/pulse input radiation is used. Intensity of second harmonic generation gives an indication of NLO efficiency of the material. We have compared the SHG efficiency in the presence of organic dopant, benzene (Table 1). Solvent benzene enhances the NLO efficiency of the ZTS crystal nearly 1.5 times and this is in tune with the relatively high magnitude of crystalline perfection observed as indicated by narrow peak (15 arc sec) (Fig. 4b).

Table 1 SHG output showing the relative SHG efficiency of pure and doped ZTZ crystals

System	$I_{2\omega}$/mV
ZTS	48–49
ZTS/benzene	70–72

Conclusions

The incorporation of small quantities of organic solvent benzene well promotes the crystal growth process of ZTS in slightly acidic solutions (pH ~5.9). The studies reveal that the growth promoting effect is caused by dissolution of trace organic impurities by the added organic solvent in the aqueous growth medium. High concentrations of the added organic solvent inhibit the growth process. The optical transmissions are not altered much for benzene addition. The detailed HRXRD studies reveal that the crystalline quality is increased when the crystals are grown in the presence of benzene in the aqueous growth medium at small concentrations. Benzene prevents the entry of unwanted impurities into the crystal by dissolving the impurities in the solution and thereby improves the crystalline quality. SHG efficiency is enhanced by nearly 1.5 times due to benzene than that of undoped ZTS crystals which may be attributed to the better crystalline quality with less impurity. The current experiment proves that the addition of an organic solvent in small quantities to the aqueous growth medium is advantageous in the crystallization process of ZTS.

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