Journal of Crystal Growth 311 (2008) 141–146

Contents lists available at ScienceDirect

Journal of Crystal Growth

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

Growth and studies of pure and potassium iodide-doped zinc tris-thiourea sulphate (ZTS) single crystals

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ARTICLE INFO

Article history:
Received 5 June 2008
Received in revised form
11 October 2008
Accepted 13 October 2008
Communicated by M. Roth
Available online 5 November 2008

PACS:
81.10.Dn
61.50.Nw
81.70.Pg
81.40.Tv

Keywords:
A1. Characterization
A1. Doping
A2. Growth from solutions
B2. Nonlinear optical materials

ABSTRACT

Single crystals of pure and potassium iodide (KI)-doped Zinc Tris-thiourea Sulphate (ZTS) were grown from aqueous solutions by slow evaporation technique. The grown crystals have been subjected to single crystal X-ray diffraction to determine the unit cell dimensions. The grown crystals were also characterized by recording the powder X-ray diffraction patterns and by identifying the diffracting planes. The Fourier Transform Infrared (FT-IR) spectra have been recorded in the range 400–4500 cm^{-1}. Second harmonic generation (SHG) for the materials of this work was confirmed using Nd:YAG laser. The UV–visible spectra show that the grown crystals have wide optical transparency in the entire visible region. The Thermogravimetric/Differential Thermal Analyses (TG/DTA) thermograms reveal that the materials have good thermal stability. Atomic absorption study reveals the presence of potassium in the doped f crystals. The electrical measurements were made in the temperature range 40–130 °C along *c*-direction of the grown crystals. The dielectric studies show that there may be a ferroelectric transition at 50 °C for both pure and KI-doped ZTS crystals. DC conductivity for both the samples is found to be increasing with increase in temperature. Activation energy values were also determined for both AC and DC conduction processes in the samples.

1. Introduction

Zinc Tris-thiourea Sulphate (ZTS), $Zn[CS(NH_2)_2]_3SO_4$, is a metal-organic crystal with potential application in Second Harmonic Generation (SHG) and in electro-optic modulation. Its SHG efficiency is 1.2 times as that of KDP crystals [1]. Salient features of ZTS include a comparable nonlinear optical (NLO) coefficient (d_{31}=0.13 pm V^{-1}, d_{32}=0.35 pm V^{-1} and d_{33}=0.23 pm V^{-1}) with that of KDP (d_{14}=0.39 pm V^{-1}). A wide acceptance angle, good transparency down to 290 nm and a single shot laser damage threshold of 3 GW cm^{-2} at 1064 nm, makes it a good candidate for NLO applications [2,3]. This crystal crystallizes in the non-controsymmetric orthorhombic space group $Pca2_1$ (point group mm2) with lattice parameters a=11.261 Å, b=7.773 Å and c=15.491 Å [4]. The morphology of ZTS crystals grown from aqueous solution is composed of (1 0 0), (0 1 0), (0 0 1) and (0 1 2) prominent faces [5]. The elastic property of ZTS was studied by ultrasonic wave interferometric technique [6]. Effect of organic dopants on ZTS crystals has been reported by Subbiah Meenakshisundaram et al. [7]. Theoretical estimation of the electro-optic coefficients of ZTS has been carried out and reported by Sastry [8]. Heat capacity, thermal expansion coefficients and thermal conductivity of ZTS crystals have been reported by Kerkoc et al. [9]. Further, various studies of ZTS crystals have been reported in a number of publications [10–15]. It has been reported that doping NLO crystals with organic and inorganic additives can alter various physical and chemical properties and doped-NLO crystals may find wide applications in optoelectronic devices compared to pure NLO crystals [16,17]. In this work, we have made an attempt to investigate AC and DC electrical properties of pure and KI-doped ZTS at different temperatures ranging from 40 to 130 °C. The results of the growth, X-ray Diffraction (XRD) studies, Fourier Transform Infrared (FT-IR) studies, atomic absorption study, SHG, UV–visible transmittance studies, Thermogravimetric/Differential Thermal Analysis (TG/DTA) studies, density, melting point, DC conductivity, AC conductivity, dielectric constant and activation energy of the grown crystals are reported in this paper.

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doi:10.1016/j.jcrysgro.2008.10.089

2. Experimental procedure

ZTS salt was synthesized according to the reaction

$$3CS(NH_2)_2 + ZnSO_4 \rightarrow Zn[CS(NH_2)_2]_3SO_4$$

ZTS salt was synthesized from stoichiometric amount of Analar Grade (AR) thiourea and zinc sulphate heptahydrate taken in the molar ratio 3:1. Aqueous solutions were prepared separately with the calculated amounts of $ZnSO_4$ and thiourea. Both these solutions were then mixed together (mother solution) using a magnetic stirrer for about 2 h and the mixture was heated at 50 °C till a white crystalline salt of ZTS was obtained. Temperature was maintained at 50 °C to avoid decomposition of the salt. The yield was found to be homogeneous. The synthesized salt of ZTS was purified further by re-crystallization. To obtain potassium iodide (KI)-doped ZTS salt, 1 mol% of KI was added to the mother solution and the same procedure was followed as given above.

Single crystals of ZTS and KI-doped ZTS were grown from saturated solutions of synthesized salts by the solution growth employing slow evaporation technique at room temperature (31 °C). Details of the growth procedure were published elsewhere [18,19]. Pure ZTS crystals of size of about $7 \times 7.5 \times 5\,mm^3$ were harvested in 15–20 days and KI-doped ZTS crystals of size $10 \times 7.2 \times 12.7\,mm^3$ were harvested in 30–35 days. Both pure and doped ZTS crystals were observed to be transparent and colourless.

The grown crystals were subjected to single crystal XRD studies using an ENRAF NONIUS CAD4 diffractometer with MoK_α radiation (λ=0.71073 Å) to determine the unit cell dimensions. The powder XRD patterns were obtained using a powder X-ray diffractometer (Model: Ritz-170 with Nickel filtered CuK_α radiations (1.54056 Å), 35 KV, 10 mA). It is to be mentioned here that powder XRD studies were performed on the grown crystals to check the correctness of the values of unit cell parameters obtained by single crystal XRD studies and to find diffracting planes of the crystals.

The FT-IR spectra of the samples were recorded using JASCO FT-IR 460 spectrometer by the KBr pellet technique in the range 400–4500 cm^{-1}. Atomic absorption study of KI-doped ZTS crystals was carried out using an atomic absorption spectrometer (Model: AA 6300).

The SHG test for the grown pure and KI-doped ZTS was performed by the powder technique of Kurtz and Perry [20] using a pulsed Nd:YAG laser. The grown crystals were ground to powder of grain size 1500–1800 μm and the SHG was confirmed by the emission of green radiation (532 nm) which was detected by a photomultiplier tube.

For single crystals to be used in optical applications, the optical transmittance range and the transparency cutoff are important. A Varian Cary 5E UV–Visible–NIR spectrophotometer was used for spectral transmission studies. A crystal thickness of about 2 mm was used for transmission studies.

TGA and DTA were carried out using Seiko thermal analyzer. The analyses were carried out simultaneously in air at a heating rate of 20 °C min^{-1} for a temperature range 30–600 °C.

The floatation method was employed for the precise determination of density and this method is sensitive to point defects and insensitive to dislocations of crystals [21]. Bromoform (density: 2.89 g cm^{-3}) and carbon tetrachloride (density: 1.59 g cm^{-3}) were used for this experiment. After mixing bromoform and carbon tetrachloride in a specific gravity bottle, a small piece of crystal was immersed in the mixture of the liquids. When the sample was attained in a state of mechanical equilibrium, the density of the crystal would be equal to the density of mixture of liquids. The density was calculated using the relation $\rho=(w_3-w_1)/(w_2-w_1)$, where w_1 is the weight of empty specific gravity bottle, w_2 the weight of the specific gravity bottle with full of water and w_3 the weight of the specific gravity bottle with full of bromoform and carbon tetrachloride mixture. The melting point of the grown crystals was measured using a melting point apparatus (Model: Tempo 120).

The electrical measurements were carried out for pure and KI-doped ZTS crystals at various temperatures ranging from 40 to 130 °C along the *c*-direction. Crystals with high transparency and large defect-free size were selected and used for the electrical measurements. The extended portions of the crystals were removed completely.

DC electrical conductivity measurements were carried out using the conventional 2-probe technique [parallel plate capacitor method] at different temperatures ranging from 40 to 130 °C in a way similar to that followed by Perumal and Mahadevan [22]. The resistance of crystals was measured using a million megohm meter. The observations were made while cooling the samples. The samples were cut in to rectangular shape to the desired thickness of 2–3 mm and polished. For good conduction, opposite faces of the sample crystals were coated with good quality graphite. The samples were annealed in the holder assembly at ~130 °C before making observations. The dimensions of the crystals were measured using a traveling microscope (L.C.=0.001 cm). The DC conductivity (σ_{dc}) of the crystal was calculated using the relation $\sigma_{dc}=d/RA$, where R is the measured resistance, d the thickness of the sample, and A the area of cross section of the crystal.

The capacitance and dielectric loss factor ($\tan\delta$) measurements were carried out using an LCR meter (Agilent 4284A) with a constant frequency of 1 KHz at different temperatures ranging from 40 to 130 °C in a way similar to that followed by Neelakanta pillai and Mahadevan [23]. The observations were made while cooling the sample. The samples were prepared and annealed in a way similar to that followed for the resistance measurements. Air capacitance was also measured. The dielectric constant of the crystal was calculated using the relation (as the crystal area was smaller than the plate area of the cell)

$$\varepsilon_r = \left\{\frac{C_{crys} - C_{air}(1 - A_{crys}/A_{air})}{C_{air}}\right\}\frac{(A_{air})}{(A_{crys})}$$

where C_{crys} is the capacitance with crystal (including air), C_{air} is the capacitance of air, A_{crys} is the area of the crystal touching the electrode and A_{air} is the area of the electrode.

The AC conductivity (σ_{ac}) was calculated using the relation

$$\sigma_{ac} = \varepsilon_o \varepsilon_r \omega \tan\delta$$

where ε_o is the permittivity of free space ($8.85 \times 10^{-12}\,C^2\,N^{-1}\,m^{-2}$) and ω is the angular frequency ($\omega=2\pi f$, f=1 KHz in the present study), ε_r is the dielectric constant and $\tan\delta$ is the dielectric loss of the sample.

The activation energy values were calculated using the relation

$$\sigma_{ac} = \sigma \exp(-E_{ac}/KT)$$

$$\sigma_{dc} = \sigma \exp(-E_{dc}/KT)$$

where K is the Boltzmann's constant, T is the absolute temperature, σ is a constant depending on the material and E_{ac} and E_{dc} are the activation energies for AC and DC conduction processes, respectively.

3. Results and discussion

The photograph of the grown pure and KI-doped ZTS crystals is displayed in Fig. 1. The external appearance or morphology of the