Optik 127 (2016) 4928–4931

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Studies of L-malic acid doped ZTS crystals grown by solution method

B. Sivasankari[a,*], P. Selvarajan[b]

[a] Department of Physics, Kalasalingam Institute of Technology, Krishnankoil 626190, India
[b] Department of Physics, Aditanar College of Arts and Science, Tiruchendur 628216, India

ARTICLE INFO

Article history:
Received 11 December 2015
Accepted 18 January 2016

Keywords:
SHG
Supersaturation
LDT
NLO

ABSTRACT

Single crystals of L-malic acid doped ZTS were grown by slow evaporation technique. Structural studies were performed to find the *hkl* values and unit cell parameters. The grown crystals were characterized by UV – visible – NIR studies, SHG studies, LDT studies, Z-scan measurements and microhardness studies.

1. Introduction

The semi-organic crystals [1–5] are used as the new frequency generators due to the large nonlinearity, high resistance to laser induced damage [6], low angular sensitivity and good mechanical hardness [7–9]. Among the semi-organic nonlinear optical materials, metal complexes of thiourea are applicable for high power frequency conversion [10]. Growth of bulk single crystals of these materials has been a subject of perennial concern for enabling them to be useful for device applications. Some examples of semi-organic NLO materials are zinctris(thiourea) sulphate (ZTS) [11–25], bis(thiourea) cadmium chloride (BTCC), zincthiourea chloride (ZTC) and copper thiourea chloride (CTC). This article deals with the effect of L-malic acid doping on the morphology and properties of the ZTS crystals.

2. Synthesis, solubility and crystal growth

L-malic acid doped ZTS samples were synthesized by dissolving thiourea (Merck, 99%), zinc sulphate (Merck, 98%) and L-malic acid (Merck, 98%) in de-ionized water at room temperature. When L-malic acid (LMA) was added as a dopant in ZTS samples, the solubility was observed to be decreasing with the doping concentration of L-malic acid. Using the synthesized salts of L-malic acid doped ZTS and the solubility data, the saturated solutions were prepared and the solutions were stirred well using a hot plate magnetic stirrer for 2 h, and the solutions of doped ZTS samples were kept in different beakers. After 2 h of continuous stirring, the solutions were filtered into the growth vessels. The growth vessels with filtered solutions were porously sealed and placed in a dust free atmosphere at room temperature for slow evaporation. Optically transparent crystals were harvested in 25 days. The crystals were in general non-hygroscopic and colourless. The LMA doped crystals of ZTS are shown in Fig. 1(a–c). From the images, it was observed that prominent morphological changes occurred in the doped crystals.

3. Structural studies

In order to identify the grown crystals and to observe the changes in the lattice parameters, X-ray diffraction analysis was carried out for L-malic acid doped ZTS crystals. Powder X-ray diffraction data for L-malic acid doped ZTS were obtained from a microprocessor controlled X-ray diffractometer (XPERT PRO powder X-ray diffractometer) using nickel filtered Cu K_{α} radiation of wavelength 1.54060 Å. In the powder XRD patterns, it was observed that there was a change in intensity of diffraction peaks due to doping of ZTS crystals with L-malic acid. The powder XRD pattern is shown in Fig. 2. By employing an ENRAF-NONIUS CAD-4 single crystal X-ray diffractometer, the structure of crystals have been found out. Single crystal XRD results show that the doped crystals crystallize in orthorhombic system. The lattice parameter values of L-malic acid doped ZTS are presented in Table 1, which shows a slight variation in the cell volume for doped ZTS.

* Corresponding author. Tel.: +91 9789788914.
E-mail address: sivasathyan198@gmail.com (B. Sivasankari).

http://dx.doi.org/10.1016/j.ijleo.2016.01.148
0030-4026/

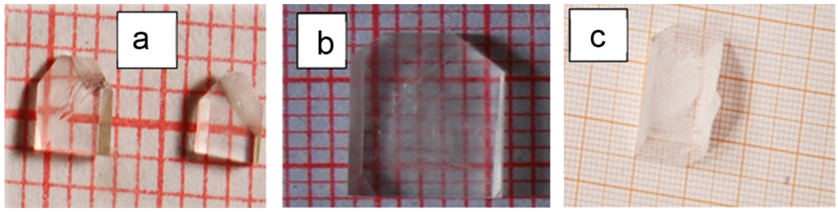

Fig. 1. (a–c): Grown crystals of 1, 2 and 3 mole% of L-malic acid added ZTS.

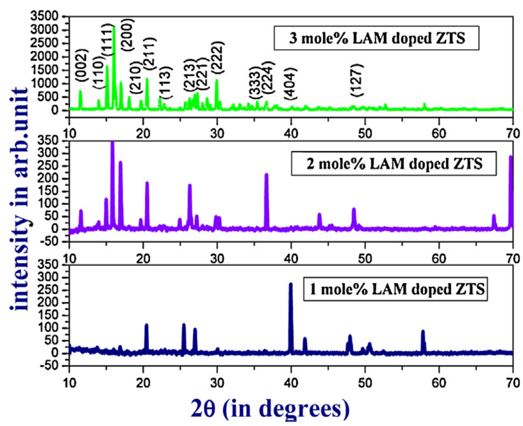

Fig. 2. Powder X-ray diffraction pattern of L-malic acid doped ZTS.

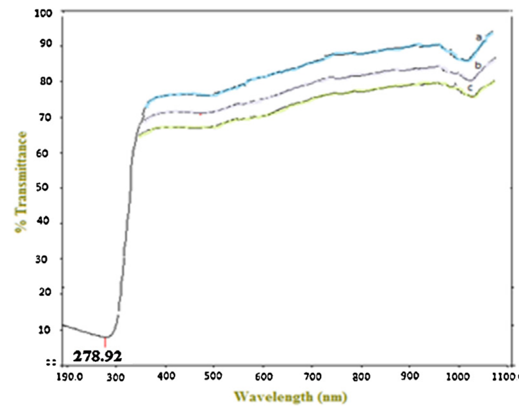

Fig. 3. UV – vis – NIR transmission spectra of (a) 1mole%, (b) 2 mole% and (c) 3 mole% of L-malic acid doped ZTS crystals.

4. Linear and nonlinear optical studies

4.1. UV – visible – NIR spectral studies

The UV – vis – NIR transmittance spectra of L-malic acid doped ZTS crystals (Fig. 3) were recorded at room temperature by using a SHIMADZU UV-240 IPC spectrophotometer within the range of 190 – 1100 nm. The spectra were taken across 1.5 mm thick well-polished doped crystals. The relative study of the optical transmission of L-malic acid doped ZTS crystals shows a low cut-off wavelength around 280 nm and the spectra show a wide transparency range from 330 to 1000 nm. The plots show the transmission percentage has decreased with the percentage of doping. The optical absorption coefficient (α) was calculated from the transmittance values using the relation

$$\alpha = \frac{2.303 \log \left(\frac{1}{T}\right)}{t}$$

The Tauc's plots are shown in the Fig. 4. The optical band gap (E_g) was evaluated by the extrapolation of the linear part to $h\nu$-axis. The obtained band gap values are 4.45 eV (from the Fig. 4) and it is found to be same for all the samples. As a consequence of wide band gap, the grown crystals have large transmittance in the visible region and hence these crystals are useful for opto-electronic applications.

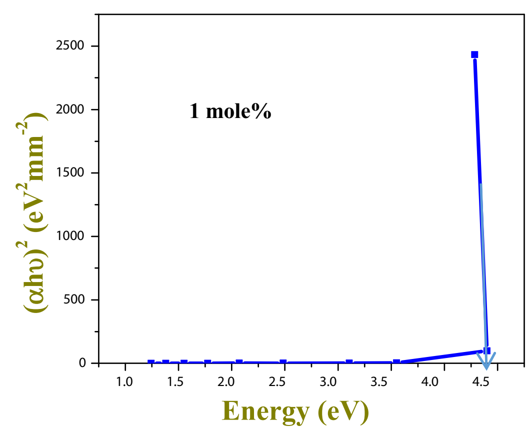

Fig. 4. $(\alpha h\nu)^2$ versus $(h\nu)$ for L-malic acid doped ZTS crystal samples.

4.2. Second harmonic generation efficiency

The second harmonic generation efficiency of L-malic acid doped samples of ZTS was determined by powder technique of Kurtz and Perry [26]. The relative conversion efficiency was calculated from the output power with reference to KDP sample. When a laser input of 0.68 J was passed through L-malic acid doped ZTS crystal samples, it was found that the output power was 11 mJ, 12.5 mJ and 13.6 mJ and the relative SHG efficiencies were 1.25, 1.42 and 1.55 times that of KDP. It was reported that the SHG efficiency for pure ZTS crystal is 1.2 times of KDP [27] and hence the SHG efficiency is increased when L-malic acid is added as dopant into the lattice of ZTS crystals.

Table 1
Unit cell parameters of pure and LMA doped ZTS crystals.

	a (Å)	b (Å)	c (Å)		V (Å^3)
Pure ZTS [16]	11.178	7.765	15.594	α = 90.00(0)°; β = 90.00(0)°; γ = 90.00(0)°	1353.64
ZTS doped with 1 mole% of L-malic acid	11.148 (1)	7.720 (2)	15.421 (1)		1327.248 (1)
ZTS doped with 2 mole% L-malic acid	11.139 (1)	7.739 (3)	15.439 (3)		1331.102 (2)
ZTS doped with 3 mole% L-malic acid	11.154 (2)	7.835 (4)	15.258 (1)		1333.669 (1)