GROWTH AND PHYSIO-CHEMICAL PROPERTIES OF PURE AND L-ALANINE ADMIXED TTZP SINGLE CRYSTALS

P. Sivakala[a], N. Joseph John[b*] and S.Perumal[c]

[a]Department of Physics, Udaya School of Engineering, Vellamodi – 629 204, India
[b]Department of Physics, Sethupathy Government Arts College, Ramanathapuram, India
[c]Physics Research Centre, S.T.Hindu College, Nagercoil-629004, India

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Abstract - *Single crystals of pure and L-alanine mixed Zinc Tris Thiourea Phosphate (LATTZP) were grown successfully by slow evaporation method at ambient temperature. Structural characterization of the grown crystals has been carried out by powder and single crystal X-ray diffraction methods. LATTZP crystallize in orthorhombic structure with $P2_12_12_1$. The existence of second harmonic generation signals in the crystal has been confirmed by performing the Kurtz powder test. The UV visible spectrum show that the grown crystals has wide optical transparency in the entire visible region. Vickers hardness value of the crystal is found to be increase with increase in load. The dielectric constant, dielectric loss and AC conductivity of the compound were calculated at different temperatures and frequencies, to analyze the electrical properties and the results were discussed.*

Key words : Solubility, crystal growth, XRD, hardness, SHG, dielectric constant, dielectric loss, AC conductivity.

I. INTRODUCTION

Nonlinear Optical (NLO) crystals have great technological significance in the fields of opto electronics, digital signal processing, instrumentation and optical communication . In the recent years semi-organic NLO crystals are attracting a great deal of attention due to their high NLO efficiency, low damage threshold and high mechanical strength as compared to their organic NLO counterparts. In semi-organic materials the organic ligand is attached to the inorganic host by an ionic bond. Therefore semi-organic crystals have higher chemical stability and mechanical strength. The thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment and ability to form extensive network of hydrogen bonds [1] .Among semi-organic NLO materials, the metal complexes of thiourea have a low UV cut-off wavelength. This feature of Thiourea finds significant application in the fields of high frequency conversion and second harmonic generation. Thiourea being a naturally centro-symmetric molecule doesn't exhibit NLO properties, however when it forms complexes with metal ions, it exhibit NLO characteristics [2].

Several interesting results have already been reported on several properties of impurity added thiourea complexes[3-7]. Bis thiourea cadmium chloride (BTCC) and L-Alanine doped BTCC, were grown by slow evaporation technique at room temperature [3]. It is reported L-alanine addition increases SHG efficiency of BTCC. Transparent and colourless crystal of Zinc (tris) thiourea chloride were grown using the slow solvent evaporation technique Revathi et al. Their studies confirm that the ZTTC crystal belongs to orthorhombic system[4] . Pure and Zn^{2+} doped bis(thiourea)cadmium acetate (BTCA), a nonlinear optical single crystal, was reported by Selva Kumar et al [5]. Metalcomplex of thiourea such as zinc tris(thiourea) sulphate(ZTS) have been grown by the slow cooling technique by Swetra Moitra and Tanusree Kas[6]. The grown crystals show good optical transmission in the entire visible region. Thos Jacob Pralash et al have grown Tetrakis thiourea potassium iodide (TTPI the slow evaporation technique and found its simple harmonic efficiency [7]. The SHG efficiency of TTPI was found to be higher than that of KDP. It is a potential material for frequency conversion. In the present study, we have grown pure Zinc tris thiourea phosphate (TTZP) crystals by slow evaporation technique and investigated the effect of L-alanine, the simple amino acid as an impurity on the optical, structural, mechanical and electrical properties of it. The results obtained are reported here in.

II. MATERIALS AND METHODS

2.1 Synthesis of pure TTZP and LATTZP

Commercially available Analar Reagent (AR) grade Thiourea, Zinc Chloride, Sodim Phosphate purchased from Merck India and double distilled water were used for synthesis of TTZP. Saturated solution of thiourea was made by dissolving 4.0g of AR grade thiourea in 25ml of double distilled water. To the saturated solution of thiourea was slowly added to the mixture of 9.2g $ZnCl_2$ and 5.0 g of Sodium phosphate in 40ml of hot distilled water at 45°C.This mixture was stirred well to get a clear solution and kept in glass vessels covered with perforated filter paper for crystallization [8-13]. After 3 days tiny crystals of TTZP were obtained.L-alanine mixed TTZP crystals (LATTZP) were grown by taking L-alanine and TTZP in 3 different molar ratios viz.,0.3:0.7, 0.5:0.5 and 0.7:0.3.

2.2 Growth of pure and L-alanine mixed TTZP single crystals

Single crystals of pure and L-alanine mixed TTZP was grown by preparing super saturation solution of corresponding salts using solubility data. The temperature dependent solubility of pure and L-alanine admixed TTZP crystals is shown in Fig.1. It is observed that the solubility of L-alanine mixed TTZP crystals increases with increase of temperature from 25 °C to 50 °C as well as the concentration of L-alanine from 0.3 mole to 0.7 mole.

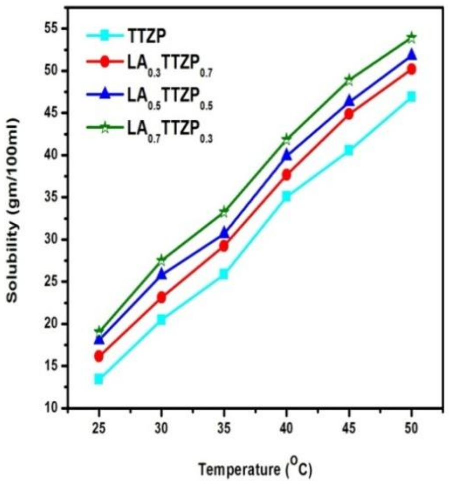

Fig 1 : Solubility curve of pure and L-alanine admixed TTZP crystals

According to the solubility data, the supersaturated solution of TTZP was prepared. L-alanine Zinc tris thiourea phosphate (LATTZP) with different concentration were grown. The semiransparent, good quality crystals were collected after 20 – 25 days. The obtained LATTZP crystals with different concentration of LA are shown in Fig 2.

Fig 2 : Photograph of grown crystal (from left to right) TTZP; $LA_{0.3}TTZP_{0.7}$; $LA_{0.5}TTZP_{0.5}$; and $LA_{0.7}TTZP_{0.3}$ single crystals

III. RESULTS AND DISCUSSIONS

3.1 Single crystal XRD

The single crystal XRD data were collected using an automatic X-ray diffractometer (MESSRS ENRAF NONIUS, The Netherlands) with MoK_{α} (λ = 0.717 Å). The obtained Single crystal XRD data were given in Table 1. It is observed that LATTZP crystals with different concentrations have Orthorhombic structure with a space group $P2_12_12_1$ and cell volume increases with increasing concentration of L-alanine. Such significant change in the unit cell parameters and increase in unit cell volume confirms the presence of L-Alanine in TTZP crystal lattice.

Table 1: Single Crystal XRD data of pure and L-alanine mixed TTZP single crystals

	TTZP	$LA_{0.3}TTZP_{0.7}$	$LA_{0.5}TTZP_{0.5}$	$LA_{0.7}TTZP_{0.3}$
System	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
a Å	8.52	8.75	8.96	9.06
b Å	11.23	11.54	12.12	12.39
c Å	15.41	15.75	15.86	15.98
V $Å^3$	1474.2	1590.35	1722.31	1793.81

3.2. UV-Vis spectral Analysis

The optical spectral analysis is an important study for any NLO material as it can be put into use only if it possesses the required cut off wavelength as well as a high optical transmittance. Efficient nonlinear crystals have lower cut off wavelength between 200 and 400nm [14].

The UV-Vis –NIR Transmittance spectra of pure and L-alanine admixed TTZP crystals are shown in Fig 3. It is observed from the Fig that the samples have absorption edge at 210,205,200 and 198nm respectively for pure TTZP, $LA0_{.3}TTZP0_{.7}$; $LA0_{.5}TTZP0_{.5}$; and $LA0_{.7}TTZP0_{.3}$ single crystals It is also observed that mixing of L-alanine increased the transmittance in the UV range. A wide transparent window is present between 210 nm and 1100 nm suggesting its use in optoelectronics devices.

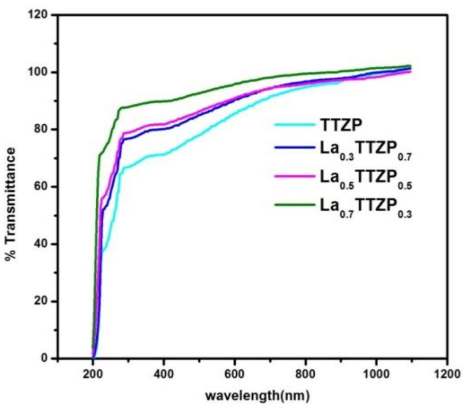

Fig 3: UV-Vis. transmittance spectrum of pure and L-alanine admixed TTZP single crystals

Plot of optical bandgap determination from UV-Vis.-NIR absorption data of pure and L-alanine admixed TTZP single crystals were shown in Fig 4 . The bandgap energy of TTZP; $LA_{0.3}TTZP_{0.7}$; $LA_{0.5}TTZP_{0.5}$; and $LA_{0.7}TTZP_{0.3}$ single crystals are 5.77 ev, 5.9 ev,6.02ev and 6.26 eV respectively. This indicates that the grown LAP crystals considered in the present study are higher band gap energy materials. The obtained bandgap values for all the admixed samples increases systematically with L-alanine concentration . The wide band gap usually happens due to the large transmittance in the visible region [15].

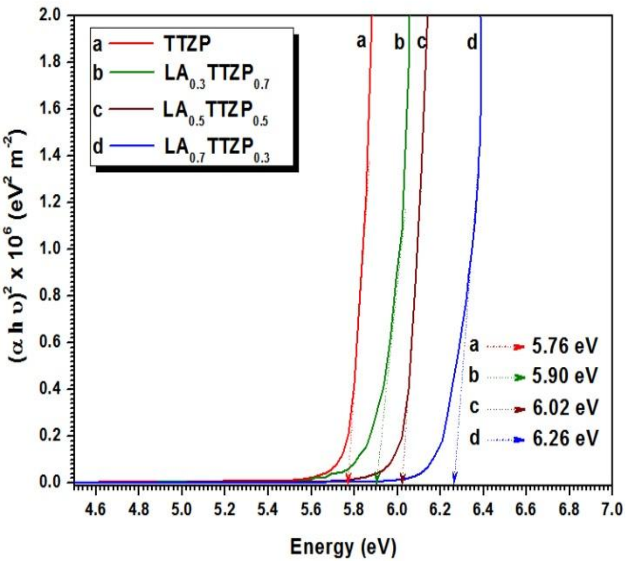

Fig 4: Plot for optical bandgap energy of pure and L-alanine admixed TTZP single crystals

3.3 NLO studies

Second harmonic generation measurements were done on the pure and L-alanine admixed TTZP using Kurtz and Perry technique [16]. Using Nd:YAG Q-switched laser source, the crystal was illuminated by laser beam with a wavelength of 1064 nm. The SHG signal generated in the crystalline sample was collected and displayed as green light radiation (λ=532 nm) on a cathode ray oscilloscope. A SHG signal of 7.5,9.8,16.2,19.5 mJ was obtained for pure TTZP, $LA_{0.3}TTZP_{0.7}$, $LA_{0.5}TTZP_{0.5}$ and $LA_{0.7}TTZP_{0.3}$ crystals respectively when compared to 8.8 mJ of that of standard KDP crystal for the same input energy of 2.9 mJ/pulse. The SHG efficiency of the grown crystals were compared to that of KDP crystal and the results are tabulated in Table 2. From the observed results, L-alanine mixed TTZP crystals are greater SHG efficiency than pure TTZP as well as KDP crystals.The NLO efficiency of $LA_{0.3}TTZP_{0.7}$, $LA_{0.5}TTZP_{0.5}$ and $LA_{0.7}TTZP_{0.3}$ crystals are found to be1.31,2.16 and 2.6 times respectively than that of pure TTZP crystals.

Table 2: SHG efficiency of pure and L-alanine mixed TTZP single crystals

Samples	Input	Output	SHG efficiency (compared with KDP)
	J	mJ	
TTZP	0.68	7.5	0.85 times
$LA_{0.3}TTZP_{0.7}$	0.68	9.8	1.11 times
$LA_{0.5}TTZP_{0.5}$	0.68	16.2	1.84 times
$LA_{0.7}TTZP_{0.3}$	0.68	19.5	2.21 times

3.4. Microhardness Analysis

Hardness testing provides useful information concerning the mechanical behaviour of solids. The Mechanical property of the grown crystals has been studied using a microhardness tester fitted with a Vickers diamond pyramidal indenter. A well polished LATTZP crystal was placed on the platform of Vickers microhardness tester and the loads of different magnitudes were applied over a fixed interval of time. The indentation time was kept (8 s) for all the loads. The hardness number was calculated using the relation

$$Hv = \frac{1.8544*P}{d^2} \text{Kg/m}^3$$

where *k* is the material constant and '*n*' is the Meyer's index. A graph is plotted between log P *vs* log d is shown in Fig 6. The slope of the straight line gives the work hardening coefficient (n). The work hardening coefficients are found to be 3.53,3.63,2.92 and 3.79 . The Meyer's relation indicates that H_v should increase with P, if n > 2 and decrease with P when n < 2.This is well satisfied shown in Fig 6.

According to Hanneman [18] work hardening coefficient (n) should be between 1 and 1.6 for hard materials and above 1.6 for soft ones.Thus the grown crystals are soft crystals.

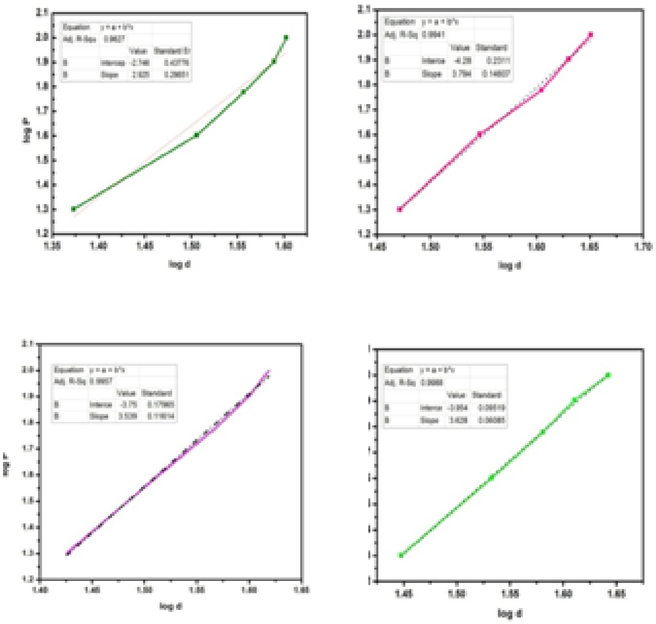

Fig 6: Plot of log p vs. log d for pure TTZP, $_{0.3}$TTZP$_{0.7}$, La$_{0.5}$TTZP$_{0.5}$, La$_{0.7}$TTZP$_{0.3}$ single crytsals

3.5 Electrical Analysis

Studies on the temperature and frequency dependences of dielectric parameters, viz. dielectric constant, dielectric loss factor and AC electrical conductivity unveil useful information about structural nges, defect behaviour, and transport phenomenon. Figs 7-8 shows the temperature and frequency dependences of dielectric constants observed for the L-alanine admixed TTZP crystals.

These plots exemplify the fact that the dielectric constant is inversely proportional to the frequency and directly proportional to the temperature.

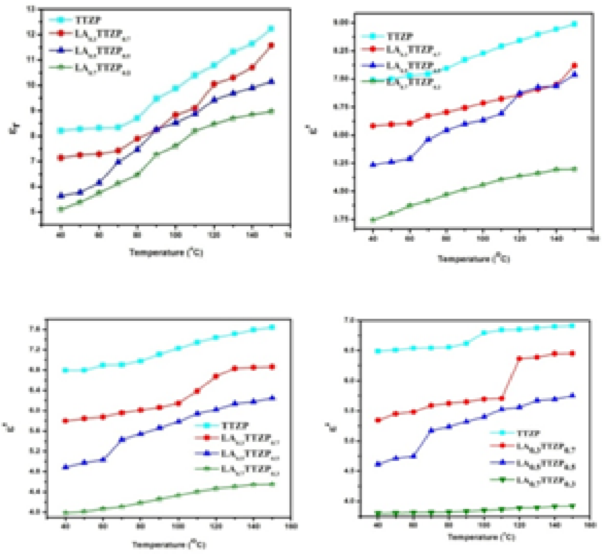

Fig 7: Variation of ε' with temperature for pure and L-alanine admixed TTZPsingle crystals at (a) 1kHz, (b) 10kHz, (c) 100kHz and (d) 1MHz

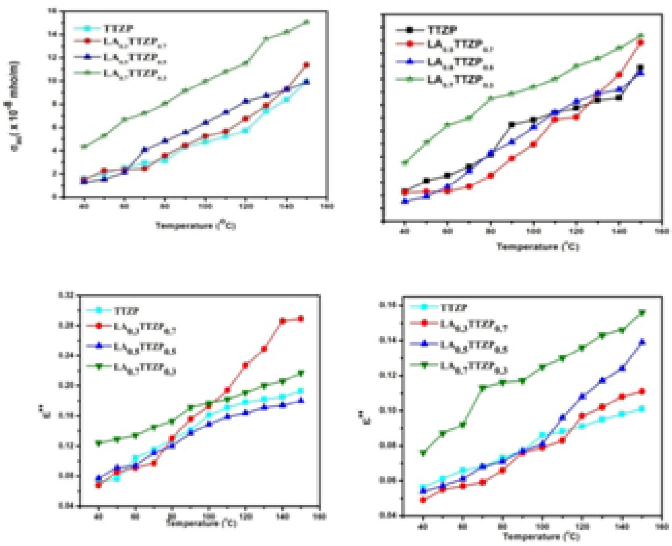

Fig 8: Variation of ε'' with temperature for pure and L-alanine admixed TTZP single crystals at (a) 1kHz, (b) 10kHz, (c) 100kHz and (d) 1MHz

The dielectric loss factor obtained for the pure and L-alanine admixed TTZP crystals. Variation of dielctric loss with temperarture and frequency are shown in Fig 9.The amount of power loss in a dielectric under the action of the voltage applied to it is commonly known as dielectric losses. When considering dielectric losses, we usually mean the losses precisely under an alternating voltage. When a dielectric is subjected to an alternating field E, there will be a phase lag between the

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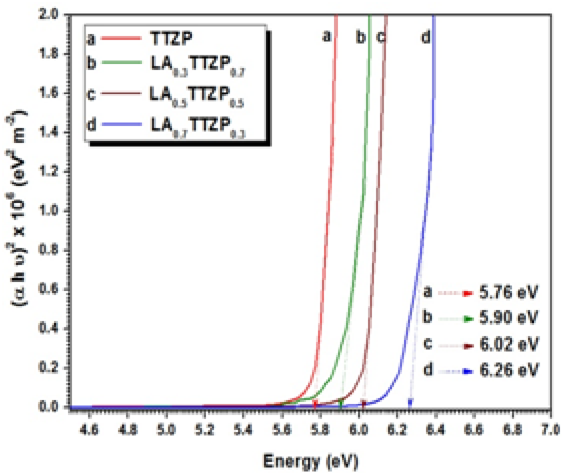

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$$Hv = \frac{1.8544 * P}{d^2} \mathrm{Kg/m^2}$$

Where H_v is the Vickers microhardness number, P is the applied load in kg and d is the diagonal length of the indentation impression in the hardness number (Hv) and applied load (P) as shown in Fig 5.From the graph, the hardness of the grown crystals was increased with increasing loads can be observed. On further increasing the load beyond 100 g cracks were developed on the surface of the crystals. This is due to release of internal stress locally initiated by indentation

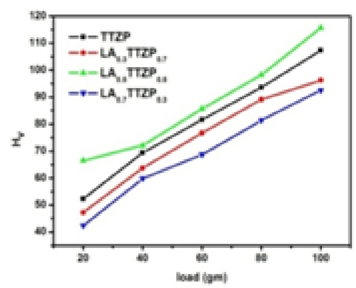

Fig 5: **Variation of H_v with load for pure and L-alanine admixed TTZP single crystals**

Meyer's index number(n) was calculated from Meyer's law [17] which relates the load and indentation diagonal length as

$$P = kd^n,$$
$$\log P = \log k + n \log d,$$

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