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Effect of pH, thermal, electrical and thermomechanical properties of nonlinear optical L-threonine single crystals

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Abstract

Nonlinear optical L-threonine single crystals have been grown at various pH values. The crystals were subjected to dielectric and thermomechanical measurements at various temperatures. The thermal strength of the grown crystal was also determined by differential scanning calorimetry (DSC) analysis. The results have been discussed in detail.

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1. Introduction

In our earlier works [1,2], we have reported the structural, linear and nonlinear optical properties of L-threonine amino acid single crystals. The present investigation deals with pH influence, thermal, thermomechanical (TMA) and dielectric properties of L-threonine single crystals at various temperatures. L-Threonine ($C_4H_9O_3N$) is a small chiral naturally occurring amino acid. The system crystallizes in the noncentrosymmetric $P2_12_12_1$ space group with four zwitterionic molecules in the unit cell, linked by a three dimensional network of four hydrogen bonds of unequal strength [3–5]. The unit cell parameters are $a = 13.611$ Å, $b = 7.738$ Å and $c = 5.144$ Å. In general, amino acid single crystals have special features like wide transparency in UV as well as in the visible range, higher acentricity, good thermal and mechanical strength which are usually considered as the essential criterion for second harmonic nonlinear optical (NLO) application based devices.

2. Experimental procedure

2.1. Crystal growth

High purity L-threonine (99.9%) was used for the crystal growth experiments. Seed crystals of L-threonine were taken from slow evaporation technique from the saturated solution of various pH viz. 4.4, 5.87 and 6.70. For the bulk growth of L-threonine crystals at various pH values, slow cooling technique was adopted and crystals were harvested after a typical growth period of 30 days. The pH values of the growth solutions were adjusted using dilute acetic acid. The crystals grown at pH 5.87 called isoelectric pH (PI) possess good transparency over other crystals of pH 4.4 and 6.70.

2.2. Characterization studies

The grown crystals of L-threonine at different pH were subjected to different studies like Kurtz–Perry powder SHG measurement, differential scanning calorimetry (DSC-NETZSCH), dielectric and thermomechanical measurements at various temperatures using a solartron impedence analyzer and Mettler TA 3000 TMA analyzer.

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3. Results and discussion

3.1. Effect of pH on powder SHG efficiency

Transmission range of L-threonine single crystal was reported as too wide (250–1500 nm) [6]. This property can be a good sign for a second order NLO material for photonic applications using various laser sources. Hence powder SHG efficiencies were measured using a Nd:YAG laser (1064 nm, 10 ns; 10 Hz repetition rate) for the polycrystalline samples of various pH values. The average grain size of all samples were found to be same. The powder SHG efficiency of L-threonine sample at isoelectric pH was found to be higher than the other two polycrystalline samples. The determination of powder SHG efficiency measurement [18] was carried out with the calibrated polycrystalline powder under test and the second one with a reference powder sample potassium dihydrogen phosphate (KDP) of same calibration. The second harmonic powers generated by the sample under study and the reference are proportional to the square of the effective coefficients d_{eff} and d_{reff} and to the square of the incident beam power of the fundamental wave. The relation can be written as:

$$P_{2\omega} = K(d_{\mathrm{eff}})^2 P_{\omega}^2, \qquad P_{\mathrm{r}2\omega} = K(d_{\mathrm{reff}})^2 P_{\omega}^2$$

where the factor K depends on the refractive indices of the sample. But it may be considered approximately as a constant in this evaluation test [19]. Based on the above relations the relative powder SHG efficiency of L-threonine polycrystalline sample at the isoelectric pH was found to be 1.2 times that of KDP. The powder efficiencies of the samples grown at other pH 4.40 and 6.70 were 0.70 and 0.5 times relative to KDP. This has been shown in Fig. 1.

3.2. Differential scanning calorimetry (DSC)

The thermal strength of the crystal has been investigated through differential scanning calorimetry measurements in the

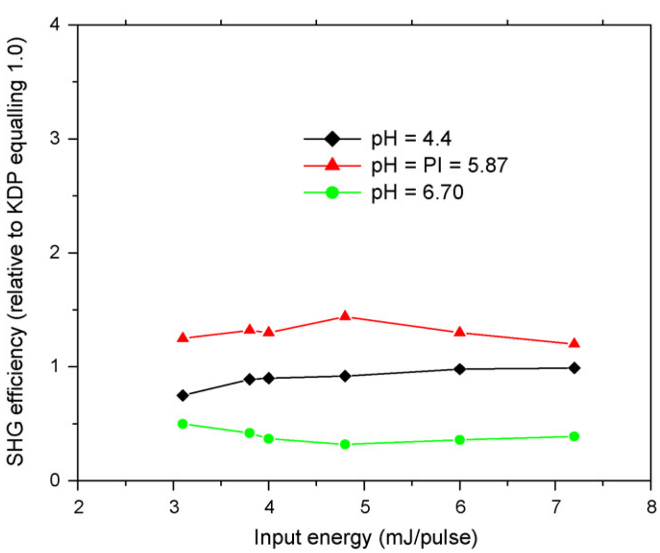

Fig. 1. Powder SHG efficiencies of L-threonine at different pH values.

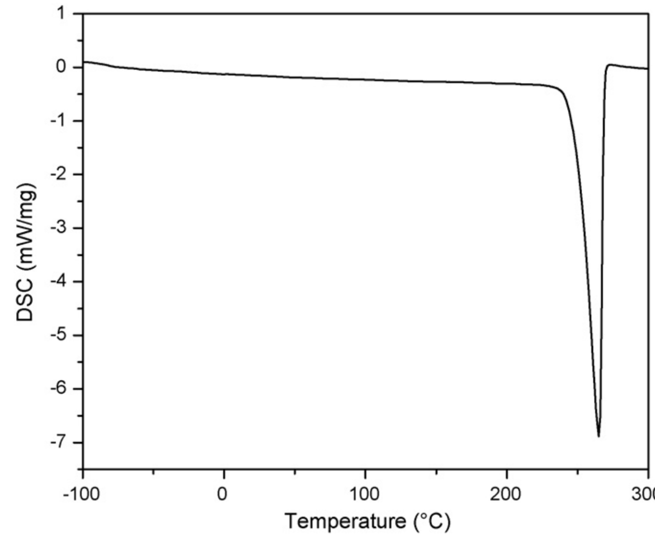

Fig. 2. DSC curve of L-threonine crystal.

temperature −100 to 300 °C at a heating rate of 5 °C/min using a NETZSCH Geratebau Gmbh thermal analyzer in nitrogen atmosphere. From Fig. 2, it is clear that no anomalous behaviour (phase transition) was observed in both lower and higher temperature region. It is worthwhile to note that some kind of structural instability has been found out around −30 to −33 °C ($\Delta C_{\mathrm{p}} \simeq 0.01$ W/g) in similar neutral amino acid, L-alanine single crystal [7]. But, such a possibility of second order structural phase transition is ruled out to our case as the presented compound shows a single endothermic peak at 265.2 °C which corresponds to decomposition temperature of L-threonine molecules.

3.3. Dielectric measurements

Dielectric studies was performed from 50 to 150 °C. Rectangular shaped crystal of dimension (l = 3.35 mm, b = 4.45 mm and t = 1.25 mm) has been pasted with conductive silver paint for metallic contacts. Dielectric constant and dielectric loss (tan δ) values have been found using a Solartron impedence analyzer in the frequency range 1 kHz to 1 MHz. It was found that at all temperatures, there were sudden shoot ups in the dielectric constant (ε_{r}) at low frequencies. This can be attributed to space-charge polarization mechanism of molecular dipoles. After that the dielectric permittivity of the compound remains almost constant in the range 175–180 in the entire temperature range studied. The dielectric constant was found to be 175 at 1 MHz at 100 °C. It is important to note that temperature has not influenced much on the dielectric behaviour of the crystals. Similarly the dielectric loss value increases at lower frequencies and this may be due to the fact that the natural frequency of the molecular dipoles matches with frequency of the applied a.c. field and thus causes the dissipation of energy in the form of heat. As expected the dielectric loss decreases at higher frequencies and it was found to have negligible values at all temperatures. The results have been presented in Figs. 3 and 4.