F-T Raman, Microhardness and Photoconductivity study of Zinc Sulphate doped L-Threonine dihydrogen phosphate Single Crystal

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Abstract : Single crystals of Zinc sulphate doped L-Threonine dihydrogen phosphate (LTDP) have been successfully grown by slow evaporation method. FT-Raman spectra of doped crystal were recorded and interpreted. Photoconductivity of grown crystal was established by photoconductivity meter. Vickers hardness test was also carried out to elucidate the mechanical behaviour of the grown crystals. **Keywords:** Slow evaporation method, Photoconductivity, Microhardness and FT-Raman Study.

1. Introduction

Non-linear optical materials have wide applications in various fields like optical data storage, photorefractive phenomenon, frequency multipliers, fibreoptics, optical switches, etc. Nonlinear optics has been a rapidly growing field in recent decades. It is based on the study of effects and phenomenon related to the interaction of intense coherent light radiation with matter. For the last several years, scientists are working on nonlinear optical (NLO) materials which combine the high optical nonlinearity and chemical flexibility of organics with the high mechanical strength of inorganics [1-3]. Hence, new nonlinear optical material are needed for photonic applications and other device fabrications in optoelectronics.

Amino acid compound L-Threonine dihydrogen phosphate (LTDP) has been reported as a promising NLO material with SHG efficiency higher than that of KDP, and can be used for the fabrication of optoelectronic devices [4]. In the present study, the title compound L-Threonine dihydrogen phosphate (LTDP) doped with zinc sulphate was successfully grown by slow evaporation technique. Characterization studies such as Photoconductivity, Microhardness and F-T Raman analyses have been carried out for the grown crystal.

2. Growth of LTDP doped zinc sulphate crystal

Single crystals of LTDP doped zinc sulphate were grown from the aqueous solution of L-Threonine and orthophosphoric acid with 1: 2 molar ratio mixed with 2 mol % zinc sulphate. The aqueous solution was

stirred continuously using a magnetic stirrer. The prepared solution was filtered and kept undisturbed at room temp. The solution gradually achieved supersaturation due to slow evaporation. After a period of 32 days, transparent crystals with dimensions $17 \times 2 \times 2 \text{ mm}^3$ were harvested. Figure 1 shows the photograph of as - grown zinc sulphate doped LTDP crystal.

Figure 1: Photograph of the as- grown zinc sulphate doped LTDP crystal

3. Photo conductivity

Photoconductivity measurements were made using Keithly 485 picoammeter. The applied electric field was changed from 2 V / cm to 14 V / cm without exposing the sample to any radiation and the corresponding dark current was recorded. The sample was then illuminated with a halogen lamp of 100W power and the resulting photocurrent was measured by varying the applied field in the same range as used in the case of measurement of dark current. Figure 2 shows the plots of dark current (I_d) and photo current (I_p) against the applied field. It is seen from the plots that both I_d and I_p of the sample Increase linearly with the applied field. It is observed from the plot that the dark current is always higher than photocurrent.

The phenomenon of negative photoconductivity is explained by stockman model [5]. The negative photo conductivity in a solid is due to the decrease in the number of charge carriers (or) their life time, in the presence of radiation [6]. For negative photo conductor, forbidden gap holds two energy levels of which one is placed between the Fermi level and conduction band and the other is located close to the valence band. The second state has higher capture cross-section for electrons and holes. As it captures electron from the conduction band, the number of charge carriers in the conduction band gets reduced and the current decreases in the presence of radiation. Even though the material shows negative photoconductivity in the visible region, the material is capable of inducing electric polarization when the incident radiation is more intense for NLO activity.

Figure 2: Photoconductivity of Zinc sulphate doped LTDP Crystals

4. FT-IR Raman study

Raman spectra of Zinc sulphate doped LTDP crystal recorded at room temperature using a Nicolet 5700 spectrometer with NXP FT- Raman module was used (number of scans ; 256, laser power at sample: 0.44w, resolution: 4 cm^{-1} spectral range : 4000- 150 cm^{-1}). The wave number ranges from 0 to 3500 cm^{-1} and assignment for the modes is made on the basis of Raman vibrations in some similar complex molecules [7,8] . The peak at 2047 cm^{-1} shows N=C= S stretching vibrations. The peaks at 1346 cm^{-1} confirm the presence of sulphate. The peak due to 1318, 1479 cm^{-1} are due to Nitro groups. The peaks due to 1183,1247, 1109,931 cm^{-1} confirm the presence of phosphate in the crystal. The peak at 1040 cm^{-1} corresponds to amine group C-N stretching vibration. The bending vibrations of CH stretch are found corresponding to the peaks at 907,871,665,622 cm^{-1} . The peaks due to 701,739,769,804 , cm^{-1} reveal the presence of alkene group.

5.Vickersmicrohardness test

The fastest and simplest method to evaluate the mechanical properties of the crystal is the hardness measurement. Zinc sulphate doped LTDP crystals which are transparent and free from cracks, were selected for microhardness measurements. Micro hardness studies were carried out for the Zinc sulphate doped LTDP using LeitzWetzler Vickers microhardness tester by varying the applied load from 25g to 100g. The indentation time was kept at 5s for all the loads. Fig.3 shows the variation of Vickers hardness number with applied load P for (010) plane of the Zinc sulphate doped LTDP crystal. It is observed that the hardness number increases with the increases of load. The value of work hardening coefficient (n) of the Zinc sulphate doped LTDP crystals was determined as 2.2 from the slope (Fig.4) of the plot of $\log P$ vs $\log d$. According to Onitsch, if n is less than 3, the hardness number will increase with increase in load [9]. The hardness number is found to be increasing with the doping concentration of zinc sulphate in the lattice of LTDP doped with Zincsulphate confirming the prediction of onitch.

Figure 3: Plot of hardness number vs load P

Figure 4: Plot of $\ln P$ vs $\ln d$

6. Results and Discussion

Single crystals of zinc sulphate doped LTDP were grown by slow evaporation technique. Photoconductivity investigations reveal the Negative Photoconductivity nature of the title material. Vibrational spectra of zinc sulphate doped LTDP are registered and interpreted. Mechanical behaviour has been studied by Vickers micro hardness test. Spectral analysis measurement studies reveal that zinc sulphate doped LTDP is a better candidate for Non- linear optical applications compared to other members of the amino acid family.

Acknowledgements

The author wishes to thank SAIF IIT Madras, Loyola College, StJoseph'sCollege Autonomous Tiruchirappalli and NCNSNT (University of madras) for their kind support and help to complete this work.

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