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Synthesis And Characterization Of Non-Linear Optical Crystal: L-Valinium Picrate

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Abstract: Nonlinear optical single crystals of L-Valinium picrate were conveniently grown by slow evaporation method. The good quality single crystal has been harvested in a period of 25 days. The crystal structure and space group were confirmed by single crystal X-ray diffraction analysis. The optical transmission studies has been carried out and found that the tendency of transmission observed from the specimen with respect to wavelength of light is practically more suitable for opto-electronic applications. FTIR confirms the presence of all functional groups in the grown crystal. Thermal stability and decomposition process were studied by means of thermogravimetric analysis and differential thermal analysis. The Vicker's microhardness values were measured for the grown crystal. The relative second harmonic generation efficiency of L-Valinium picrate crystal has been tested by Kurtz-Perry powder technique.
Keywords: Single crystal, NLO, FTIR analysis, Thermal analysis, Microhardness test, Second harmonic generation.

1. Introduction

Organic crystals have been extensively analysed due to their nonlinear optical (NLO) coefficient existing much larger than those of inorganic. Combination of amino acids with organic salts is predicting materials for optical second harmonic generation. New nonlinear optical frequency conversion materials can have a significant impact on laser technology, optical communication and optical data storage technology [1]. The explore for new frequency conversion materials over the past decade has focused primarily on organic compounds [2,3] and many organic NLO materials with high nonlinear susceptibilities have been found. In the issuing advanced technologies, many efforts have been chosen to get the new higher order nonlinear optical materials for various optoelectronic applications. This technology is continuing to grow and refinement in the development of the lasers and higher nonlinear optical materials have resulted in a form of commercially available nonlinear optical devices [4]. Among nonlinear optical (NLO) materials, organic materials have greater attention due to their large optical susceptibilities, inherent ultrafast response times and high damage resistance when compared to other materials [5]. Organic molecules with long conjugated systems usually exhibit large molecular hyperpolarizability (β) and macroscopic susceptibilities $\chi^{(2)}$ values which are the basis of a strong second harmonic generation response [6]. In the present investigation, the growth aspects of the L-Valinium picrate (LVP) single crystals have been carried out by slow evaporation technique. The grown crystal is subjected to different characterization such as single crystal X-ray analysis, FTIR analysis, optical analysis, thermal study, microhardness and SHG studies. The results of these studies have been discussed.

2. Crystal Growth

Single crystals of L-Valinium picrate were grown, from aqueous solution by slow evaporation technique. The solution was prepared by dissolving equimolar amounts of picric acid and L-Valine in deionized water and stirred well to yield a homogenous mixture of solution. A saturated solution was prepared and the solution was filtered. The filtered solution was taken in a beaker which was hermetically sealed to avoid the evaporation of the solvent. Single crystals of L-Valinium picrate were grown within a period of 25 days by slow evaporation technique. Photograph of as grown L-Valinium picrate single crystal as shown in Fig.1.

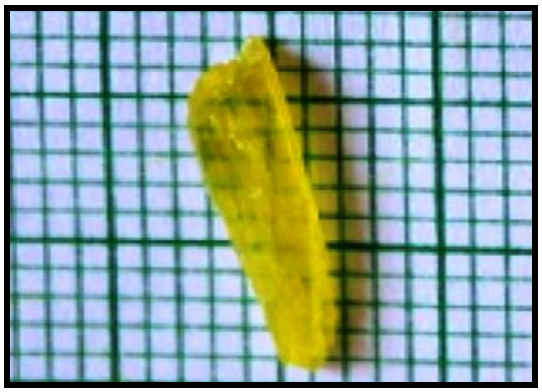

Fig. 1 As grown LVP crystal

3. Single Crystal X-Ray Diffraction Studies

The grown crystals of L-Valinium picrate were subjected to single crystal X-ray diffraction studies using ENRAF NONIUS CAD4-F diffractometer. The X-ray diffraction studies confirm that the grown crystals of L-Valinium picrate belongs to monoclinic crystal system with space group $P2_1$. The cell parameter values are a = 9.96 Å; b = 6.23 Å; c = 12.64 Å, β = 110.40°. The structure of the grown crystal has been confirmed by single-crystal XRD which is very good agreement with Anitha et al [7].

4. Optical Transmission Spectrum Analysis

The optical transmission range and the transparency cut-off wavelength are essential since single crystals are used in opto-electronic applications. Finely powdered sample was dissolved in water and transmission spectrum was recorded using Varian Cary 500 Spectrophotometer where the transparency of the sample is high in the region 300-1100 nm. The absence of absorption in this region is suitable for second harmonic generation of Nd:YAG laser radiation. The maximum absorbance is found to be 470 nm. The recorded spectrum is shown in Fig 2. The crystal has good optical transmission in the visible region. The transparency in the visible region for this crystal suggests its suitability for second harmonic generation.

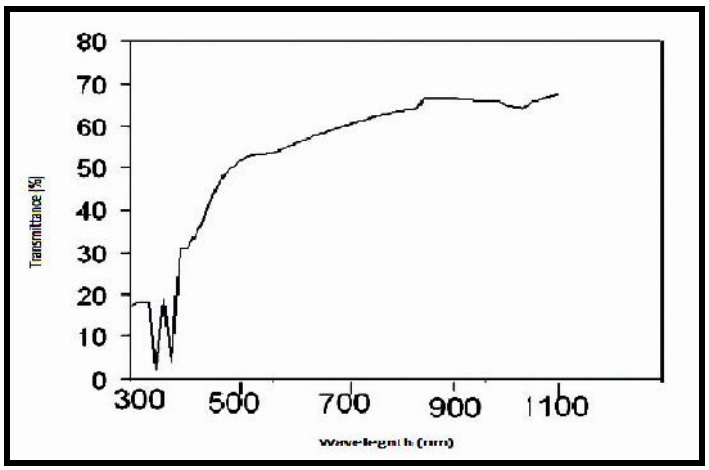

Fig. 2. Transmittance spectrum of LVP

5. FTIR Analysis

The presence of various functional groups of the grown crystal was confirmed by FTIR. The powder form of L-Valinium picrate was mixed with KBr to form pellets for obtaining optical transmission spectrum. The various functional groups present in L-Valinium picrate were identified and confirmed by recording the Fourier Transform Infra Red spectrum in the range 4000-400cm-^{1} using BRUKKER IFS 66V spectrometer. The FTIR spectrum of L-Valinium picrate is shown in Fig 3. A strong peak at 3087 cm^{-1} corresponds to the stretching bond of the NH^{3+} ion of the amino acid. It was due to superimposed O-H and NH^{3+} stretching bonds. The strong peak at 1714 cm^{-1} due to presence of COOH and COO^{-} groups of the compound and it confirms the reaction of picric acid with L-Valine. The asymmetric mode of NH^{3+} group vibration appears at 1626 cm^{-1}. The strong peaks at 1338 cm^{-1} was due to CH_3 rocking vibrations. A strong band arising from C-COO^{-} stretching was found at 1272 cm^{-1}. The absorption peak appears at 911 cm^{-1} was due to presence of CH_2 group. The bending vibration of NO_2 was found at 782 cm^{-1}. The ionization of the carboxyl group was confirmed from the absorption bands observed at 540 cm^{-1}. The functional groups predicted agree very well with work of Kirubavathi et al [8]. The link between the molecules in each layer is through hydrogen bonds. The two layers are also interlinked by hydrogen bonds. Hydrogen bonds provide an imbalance charges. This imbalance of charges makes the material non-centrosymmetric which is an important requirement for the material to generate Second Harmonic Generation (SHG).

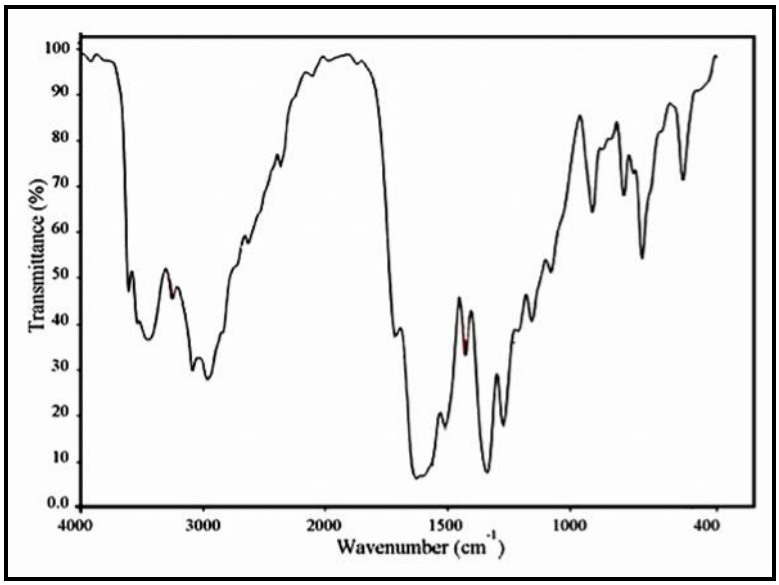

Fig.3 FTIR Spectrum of LVP

6. Thermal Analysis

The thermal stability of L-Valinium picrate has been studied by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) using NETZSCH STA 409C instrument under nitrogen atmosphere with a heating rate of 20 ºC/min. From the TGA curve the percentage of weight loss with temperature can be determined. The origin of the temperature difference in the sample lies in the energy difference between the products and reactants or between the two phases of the substance. This energy difference is manifested as enthalpic changes-either exothermic or endothermic. The thermal effects are observed as peaks whose sequence, sign, magnitude and shape reflect the physical or chemical changes taking place. The DTA method is applicable to all the studies listed for TGA and also to phase transitions including polymerization, phase equilibria and chemical reactions. From the curves (Fig. 4) it is inferred that the melting of the material takes place in the vicinity of 268°C. The DTA response curve also shows a sharp endothermic peak at 268°C, which indicates decomposition temperature. Thus from the thermal analysis, it is seen that LVP crystal decomposes without melting and is stable up to 268°C temperature. This was also confirmed by the Monarch melting point apparatus. Hence it can be utilized for device applications till 268 °C. Further, it indicates no phase transition before melting. There is a gradual and significant weight-loss as the temperature is increased above the melting point.

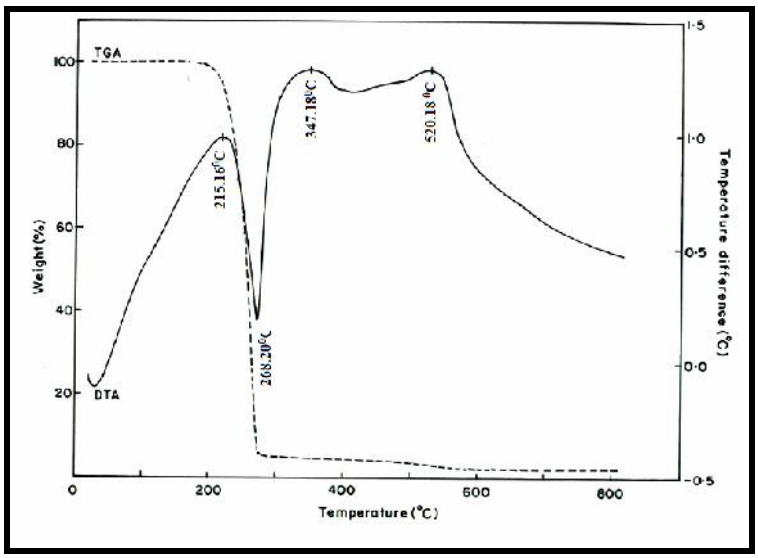

Fig.4 TG/DTA of LVP

7. Microhardness Studies

To find surface hardness of the as grown LVP crystal, microhardness was measured using Shimadzu HMV – 2000 Microhardness tester. The applied load was varied from 10 to 60 g for a constant indentation period of 10 s. The Vicker's hardness number H_v is calculated using the relation,

$$H_V = 1.8544P / d^2 kg / mm^2 \qquad (1)$$

where P is the indentor load in kg and d is the diagonal length of the impression in mm. The variation of H_v with applied load is shown in Fig.5. It is evident from the plot that the microhardness of the crystal increases with increasing load. The increase in the microhardness values of LVP with increasing load is in agreement with the reverse indentation size effect (ISE) [9].

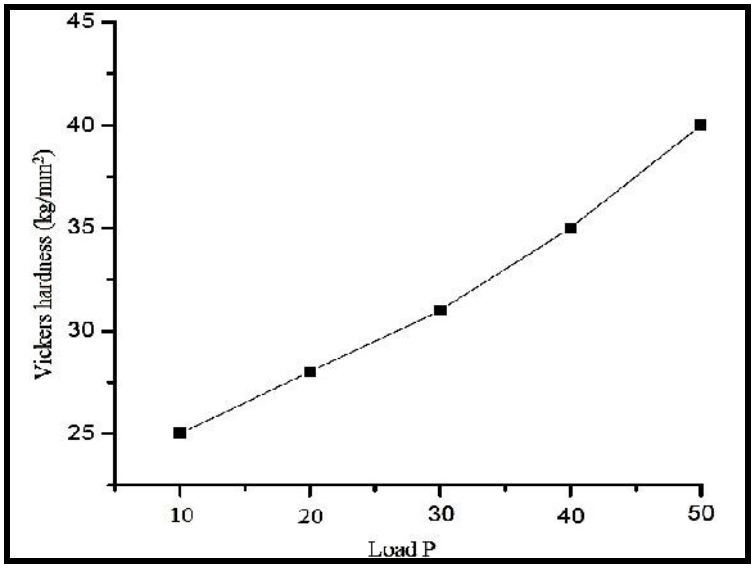

Fig.5. Vickers hardness profile of LVP as a function of applied load

8. Kurtz Powder Technique

Nonlinear optical property of the sample was tested by Kurtz and Perry technique and the efficiency of the sample was compared with microcrystalline powder of KDP and urea as the reference material. A Q-switched mode locked Nd:YAG laser operates at the fundamental wavelength of 1.64 nm, generating 6mJ/pulse. In the present investigation the laser pulse of 8ns with spot radius of 1mm was used. The input laser beam was passed through the Infrared reflector and then directed on the microcrystalline powdered sample packed in a capillary tube of 0.154 mm. When a laser beam of 2.7 mJ/pulse was passed through the sample, second harmonic signal of 532 nm were generated and the output voltage of 1.33V was obtained. The experimental data shows that the second harmonic efficiency of the sample was nearly 57 times than that of KDP crystal [10].

9. Conclusion

Single crystals of L-Valinium picrate were grown by slow evaporation technique. Single crystal X-ray diffraction analysis shows the crystal belongs to monoclinic system. Functional groups were analyzed by using FTIR analysis, which have revealed the characteristic vibration modes of L-Valinium picrate crystal. The optical property of the grown crystal was studied by optical transmission spectrum and UV cut off wavelength of the grown crystal was found to be 470 nm. From the thermal analysis it is concluded that the grown crystal decomposes without melting at about 268°C and is stable till that temperature. Vickers microhardness of studies was carried out. The second harmonic generation efficiency by Kurtz-Perry powder technique reveals that the crystal was 57 times that of KDP.

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