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# Growth, Thermal and Mechanical Studies on a Semi organic NLO Crystal : L-Lysine 4-nitrophenolate monohydrate (LLPNP)

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**Abstract:** Semi organic nonlinear optical (NLO) crystal L-Lysine 4-nitrophenolate (LLPNP) monohydrate was grown by slow evaporation technique. The grown LLPNP crystal was subjected to single crystal X-ray diffraction. Solubility of the LLPNP was carried out for different temperature. Thermal stability of the grown material was carried out by TG/DTA analysis. The hardness of the material was found by Vickers micro hardness technique. Laser damage threshold value was determined by Nd: YAG laser. SHG efficiency was determined by Kurtz Perry Powder SHG technique.
**Keywords**: Solubility, Single crystal, Thermal analysis, Nonlinear optical material.

## Introduction

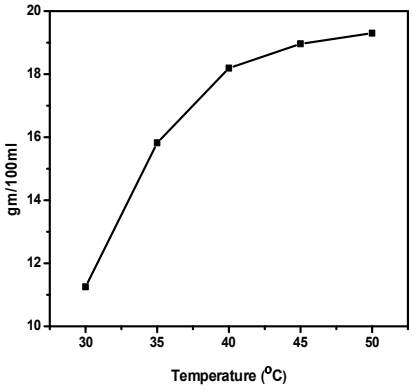
Semi organic nonlinear optical materials (NLO) play a major role in nonlinear optics for the fast processing of information and for data storage applications [1]. Of these organic materials, NLO crystals composed of L-Lysine are deeply investigated because of its chirality, which induces an asymmetric molecular structure [2–4]. We have developed several NLO crystal materials that possess excellent properties, such as L-arginine phosphate mono hydrate crystal (LAP) and L-arginine bis (trifluoroacetate) crystal [5–7]. These materials generally have a high second harmonic generation (SHG) efficiency [8]. 4-nitrophenol totally matches this criterion with its electron donor substituent ''–OH'' and electron acceptor substituents ''–$NO_2$'' – OH,–$NO_2$ and phenyl group form a conjugated molecular configuration. In the present investigation we report for the first time, the synthesis, growth, crystal structure and TG/DTA, hardness, Laser damage value and SHG efficiency of the L-Lysine 4-nitrophenolate monohydrate single crystal.

## 1. Experimental

LLPNP material were synthesised by L-Lysine monohydrate and 4-nitrophenol in equimolar ratio in water used as solvent. The mechanism of formation of LLPNP is given by the following chemical reaction,

$$C_6H_{14}N_2O_2 \bullet H_2O + C_6H_5NO_3 \rightarrow C_{12}H_{21}N_3O_6$$

The solubility test of LLPNP in water was performed in the temperature range between 30° and 50 °C. The solubility was measured by adding excess amount of LLPNP in water at constant temperature and it was continuously stirred using magnetic stirrer to achieve homogeneous concentration over the entire volume of the solution. On reaching saturation the content of the solution was analyzed gravimetrically and this was repeated for all the temperature. The solubility curve is shown in Fig.1. At room temperature prepared solution was allowed to slow evaporation. After 30 days, dimension of 18mm X 6mm X 8mm yellow colour, transparent LLPNP single crystals were obtained as shown in Fig.2.



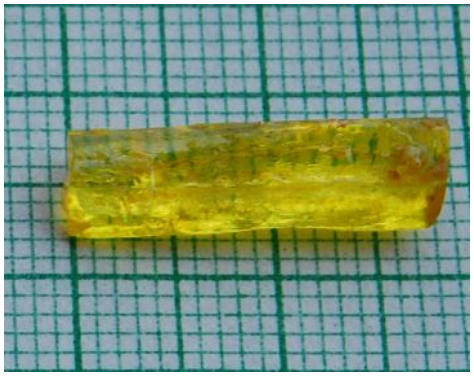



**Fig.1. Solubility diagram of LLPNP crystal.** **Fig.2. As-grown LLPNP single crystal**

## 2. Results and Discussion

### 2.1 Single crystal X-ray diffraction

The LLPNP crystal was subjected to single crystal X-ray diffraction ENRAF (bruker) NONIUS CAD4 MV3. The cell parameters are obtained a = 5.4382(2) Å, b = 8.5023(4) Å, c = 30.9204(15) Å and V=1429.67(11) $A^3$ and LLPNP crystal belongs to Orthorhombic system'$P2_12_12_1$'.

### 2.2. Thermal studies

Thermal behaviour of LLPNP has been identified from the TG/DTA. The TG/DTA of LLPNP crystal has been carried out between room temperature (28°C) and 800° C at a heating rate of 10° C per min. TG/DTA curve is shown in Fig.3. From the TG curve it is observed that 12 % of weight has been lost below 200° C due to loss of water molecule in the crystal structure. A careful observation in the DTA curve infers that this region has three endothermic transitions at 93.5, 137.2 and 175.1° C. The first one is due to the removal of water physically absorbed by the material which has only very meagre amount of weight loss in TG curve. The second one is due to the removal of water molecule at 137° C associated with corresponding weight loss in TG curve and the material melts at 175° C which is not associated with weight loss at TG. After the material melts completely, it started to decompose which is confirmed by the steep weight loss in the TG curve. The 88.8% weight loss has been observed between 200° C and 800° C due to the decomposition of the compound in association with the exothermic peak around 261° C in DTA curve. From this study it is observed that the grown crystal is stable up to 175° C. Hence, the LLPNP material has reasonably good thermal stability which satisfies the requirement for the device fabrication.

### 2.3. Microhardness studies

Micro hardness is a general microprobe technique for assessing the bond strength, apart from being a measure of bulk strength. The selected smooth surfaces of the crystal were subjected to indentation test. For each load, the micro hardness value was calculated using the equation [9] $Hv = 1.8544P/d^2$ kg $mm^{-2}$ .where, $H_v$ is the Vickers hardness number, P is the applied load (Kg), d is the average diagonal length of indentation mark (mm). Fig.4 shows that the Vickers hardness number linearly increases with increasing the applied load. Due to the application of mechanical stress by the indenter, dislocations are generated locally in the region of indentation. The increase in microhardness ($H_v$) with increasing load is in agreement with the reverse indentation size effect (RISE). The RISE can be caused by the relative predominance of nucleation and multiplication of dislocations.

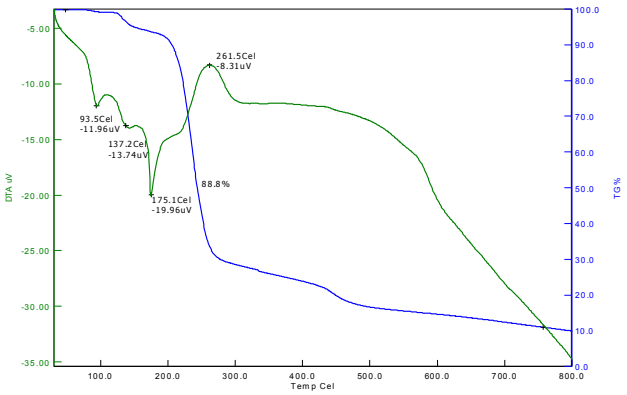



**Fig.3. TG/DTA curve of LLPNP**

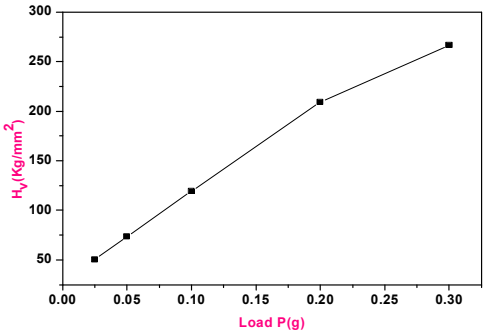



**Fig.4. Hardness number Vs load for LLPNP**

### 2.4. Laser damaged studies

NLO crystals are susceptible to optically induced catastrophic damage. Optical damage in non-metals (dielectrics) may severely affect the performance of high power laser systems as well as the efficiency of optical systems based on nonlinear process and has therefore been subjected to extensive research since three decades. Laser Damage threshold of LLPNP single crystal was assessed by Q-switched Nd: YAG laser with 6 ns pulse width, 10Hz repetition rate and source wavelength of 1064 nm. The laser damage threshold was calculated using the expression Power density ($P_d$) = E / $\tau \pi r^2$ where E is the energy (mJ), $\tau$ is the pulse width (ns) and r is the radius of the spot (mm) [10]. The calculated power density of the LLPNP single crystal is 38.36 GW/cm$^2$.

### 2.5. Nonlinear optical studies

Second harmonic generation (SHG) conversion efficiency measurement was carried out using Kurtz and Perry technique [11]. A Q-switched Nd: YAG laser beam of wavelength 1064 nm with input beam energy 2.1 mJ/pulse and pulse width 10 ns with a repetition rate of 10 Hz was used. The grown single crystal was powdered with a uniform particle size and tightly packed in a micro-capillary of uniform bore and exposed to the laser radiation. The bright green light emission (k = 532 nm) was observed which indicates the SHG behaviour of the title material. The relative SHG efficiency of the title crystal (114 mV) is 4.45 and 1.4 times that of KDP (25.6 mV) and urea (82 mV) respectively.

## Conclusion

L-Lysine 4-nitrophenolate monohydrate (LLPNP) was synthesized and grown by the slow evaporation solution growth technique at room temperature using water as solvent. The single crystal X-ray diffraction was confirmed the cell parameter and crystal system of orthorhombic $P2_12_12_1$. From TG/DTA measurement the LLPNP single is stable up to 175° C. The hardness of the crystal was assessed by the Vicker's hardness test. It shows the reverse indentation size effect. The laser damage threshold value of LLPNP crystal is 38.36 GW/cm$^2$. SHG efficiency LLPNP crystal is found to be 4.45 than KDP.

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