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Synthesis, Growth and Characterisation of Nonlinear Optical La-doped L-Prolinium Picrate Single Crystals

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Abstract : A nonlinear optical material L-Prolinium Picrate and Lanthanum doped L-Prolinium Picrate were synthesized and grown as single crystals by slow evaporation method. The grown crystals were subjected to structural, elemental, thermal, optical, mechanical and dielectric studies. The structural analysis reveals that pure LPP and La doped L-Prolinium Picrate belongs to the monoclinic crystallographic system with space group P_{21}. Optical transparency of the grown crystals was investigated by UV-vis-NIR spectrum. The thermal analyses reveal that La doped L-Prolinium Picrate is thermally stable up to 188°C. The dielectric constant and dielectric loss of the crystals were studied as a function of frequency. The nonlinear optical property of the doped crystal was confirmed by the Kurtz-powder second harmonic generation test and the result is compared with pure L-Prolinium Picrate. Mechanical strength of the crystals was also carried out by Vicker's micro hardness test.
Keywords : Growth from solution, Nonlinear optical crystal, X-ray diffraction, Semi organic compound, Micro hardness.

Introduction

Nonlinear optical (NLO) materials play a major role in nonlinear optics and in particular they have a great impact on information technology and industrial applications. In the last decade, however, this effort has also brought its fruits in applied aspects of nonlinear optics. This can be essentially traced to the improvement of the performances of the NLO materials. The understanding of the nonlinear polarization mechanisms and their relation to the structural characteristics of the materials has been considerably improved. The new development of techniques for the fabrication and growth of artificial materials has dramatically contributed to this evolution. The aim is to develop materials presenting large nonlinearities and satisfying at the same time all the technological requirements for applications, such as wide transparency range, fast response and high damage threshold. But in addition to the processability, adaptability and interfacing with other materials improvements in nonlinear effects in devices led the way to the study of new NLO materials. Nonlinear optical crystals, due to their nonlinear properties, have been found to have enormous applications in frequency conversion, image processing, data storage and fiber optical communication etc.

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Rare earth ions introduced as dopant during the crystal growth have important consequences on the growth kinetics, morphology and quality of crystals, improving in many cases their physical properties for specific applications. Efforts have been made to improve the NLO properties of the L-Prolinium Picrate (LPP) crystal by doping with various rare earth elements. The growth, optical absorption and mechanical studies on pure LPP were studied and reported [1,2], The availability of the rare earth elements is of great interest to scientists doing basic research. In the present investigation, attempts were made to study the role of Lanthanum as dopant on growth and physical properties of pure LPP.

1. Experimental

1.1 Crystal Growth

Commercially available L-Proline and Picric acid were mixed in stoichiometric ratio and dissolved in the mixed solvent of double distilled water and acetone in 1:1 ratio to synthesize LPP source material. The synthesized salt was purified by repeated recrystallisation process and used for growing pure LPP. Lanthanum doped LPP crystal was grown from mixed solvent of water and acetone in the ratio of 1:1 using the well known solvent evaporation technique with 5 mol % and 10 mol % of Lanthanum Nitrate added to the LPP saturated solutions.

Optical quality crystals were collected in a period of 35 days from the supersaturated solution and are shown in figure 1. From the physical observation of the grown crystals the 5 mol % Lanthanum doped LPP (La5 : LPP) crystals have good transparency and morphology.

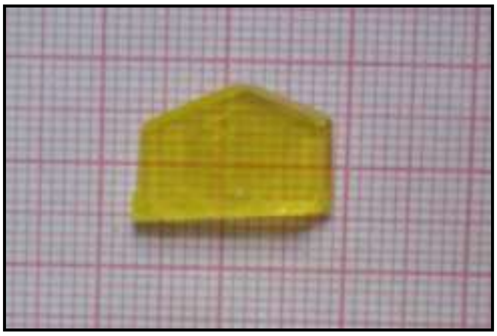


Figure 1. As grown crystal of La5 : LPP

1.2 Characterization

The Grown single crystals of pure and La5 : LPP were subjected to X-ray diffraction studies using a Bruker AXS Kappa APEX II single crystal CCD diffractometer equipped with graphite monochromated Mo(Kα) (λ = 0.7107 Å). EDAX study was carried out using EDAX - AMETEK tester for the grown sample to analyze the percentage of dopants in the crystal. HIOKI 3532 – 50 LCR HITESTER was used for the dielectric study. The sample of size 4 x 3 x 3 mm^3 was prepared and mounted between copper electrodes. In order to ensure good electrical contact between the crystal and the electrodes, the crystal faces were coated with silver paint. The dielectric measurements were carried out in a frequency range 100 Hz – 5 MHz and temperature range 35 – 95ºC. The thermo gravimetric and differential thermal analyses (TG – DTA) response curves were drawn for pure and La5 : LPP powder sample in the temperature range from 20 to 1200 °C using the instrument NETZSCH STA 409C at the heating rate of 10 K/min. in nitrogen atmosphere. The optical transmission spectra was recorded using Shimadzu model - 1601 in the wavelength range of 300 – 1200 nm. The study of NLO conversion efficiency was carried out by the powder technique of Kurtz and Perry. The sample was ground into fine powder and tightly packed in a micro capillary tube. It was mounted in the path of the laser beam. A Q-switched flash lamp pumped Nd:YAG laser of power 3.2 mJ with a wavelength of 1064 nm, pulse duration of 8 ns, a repetition rate of 10 Hz and a spot size of 1 mm diameter was used for SHG test. Vickers hardness study was made on the as grown crystal using Leica- Reichert Polyvar2 model hardness tester fitted with a diamond indenter.

2. Results and discussion

2.1 Single Crystal X-Ray Diffraction

Lattice parameter values of pure LPP and La5 : LPP single crystals are listed in Table1. The observed values for LPP are in good agreement with the reported values [1,2].

Table 1. Comparison of single crystal X-ray data of LPP and La5 : LPP crystals

Parameters	LPP	La5 : LPP
a (Å)	10.902	10.972
b (Å)	5.352	5.583
c (Å)	12.472	12.379
V (Å^3)	687.60	692.32
System	Monoclinic	Monoclinic
β(°)	109.11	109.14
Space group	P_{21}	P_{21}

2.2 EDAX Analysis

In order to analyze quantitatively the presence of Lanthanum in the crystal, EDAX study was carried out for the grown sample and the percentage of dopant present in the LPP was confirmed and tabulated in Table 2. From EDAX analysis, it is observed that the amount of Lanthanum atoms present inside the LPP lattice is very less.

Table 2. EDAX analysis of La5 : LPP crystal

Element	Wt.%	At.%
La	3.59	0.52

2.3 Dielectric Studies

The dielectric constant and dielectric loss were calculated for pure and doped crystals. The figures 2(a) and 2(b) show the variation of dielectric constant and dielectric loss as a function of frequency. It is found that the dielectric constants of LPP and doped LPP crystals are high at lower frequencies and they decrease with increase in frequency. The trend of the dielectric constants of LPP and La5 : LPP crystals are almost the same. But at fixed frequency, the dielectric constants of doped LPP crystals are less than that of pure one. In accordance with Miller rule, the lower value of dielectric constant is a suitable parameter for the enhancement of Second Harmonic Generation (SHG) coefficient [3]. Since the dielectric constant of doped crystals is lower than that of the pure crystals they are less polarized in comparison with pure crystal. The lower polarization may be due to ineffective transportation of polarization from one molecule to its neighbor in the presence of dopants [4].

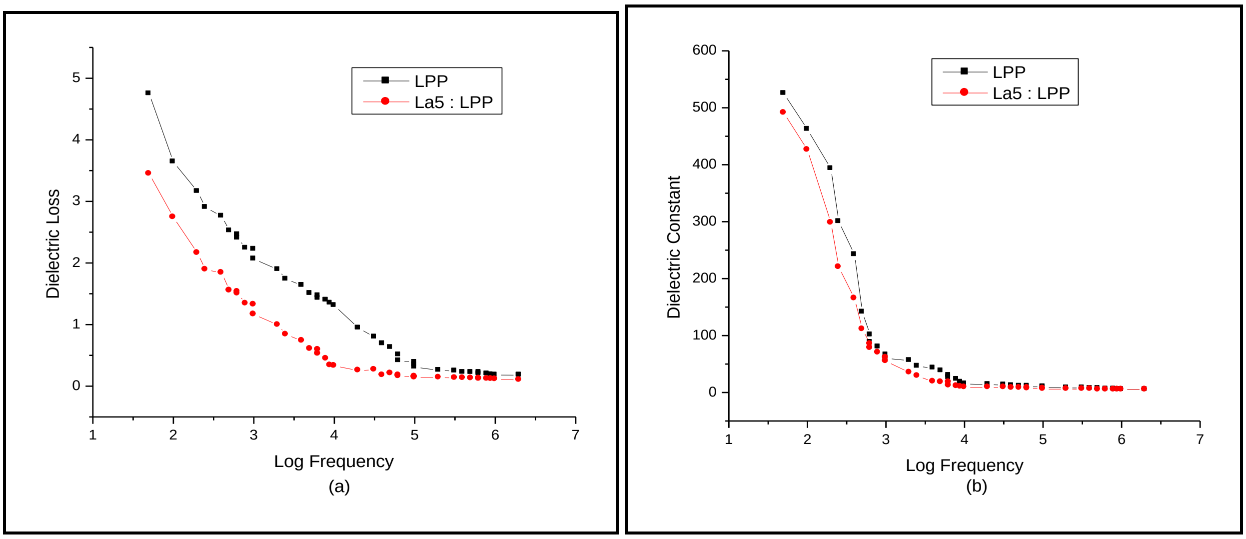


Figure 2 (a). Dielectric Loss vs. Log frequency for pure and doped LPP crystals (b). Dielectric Constant vs. Log frequency for pure and doped LPP crystals.

The characteristic of low dielectric loss at high frequencies for these samples suggest that the pure and doped crystals possess enhanced quality with lesser defects [5]. For a particular frequency, the dielectric loss of doped LPP is slightly lesser than that of pure, which indicates that the dopant enhances the optical quality of LPP and reduces the defects.

2.4 Thermal Analyses

The TG - DTA curves of LPP and La5 : LPP samples exhibits nearly similar stage of decomposition between 100 and 1200 ºC as shown in figures 3(a) and 3(b). In order to study the influence of the dopant on the thermal stability of LPP, the temperature corresponding to a peak maximum of first stage of phase transition in DTA trace is taken into account for comparison. The temperature on the first state of transition for the LPP is found at 158 ºC and for La5 : LPP it is found at 188 ºC. This shows that the doped crystal possess better thermal stability compared to pure crystal.

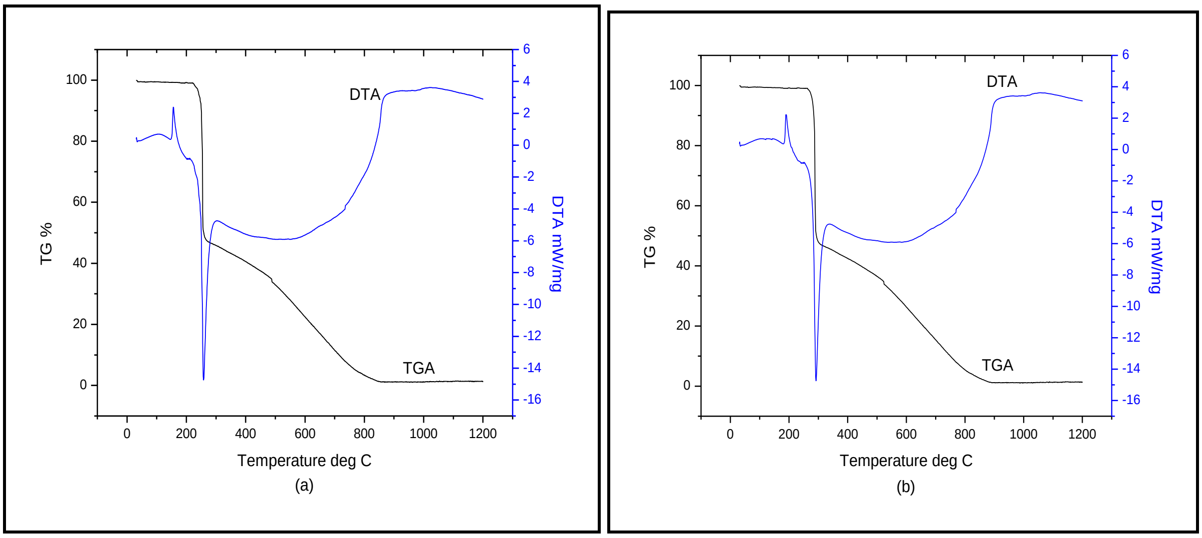


Figure 3 (a). TG-DTA graph for LPP sample (b). TG-DTA graph for La5 : LPP sample

2.5 Optical Transmission Study

The figure 4 shows the optical transmission spectra of LPP and La5 : LPP crystals. The thickness of the sample used for this study was 1.5 mm. It is found that LPP crystal has transmittance of 66 % and La5 : LPP crystal has the transmittance of 63 %. The lower cut off for LPP is 467 and for La5 : LPP it is found at 470 nm. This shows that doping the crystal with Lanthanum did not make much difference in the lower cut-off value, but, the percentage of transmission is decreased due to Lanthanum addition.

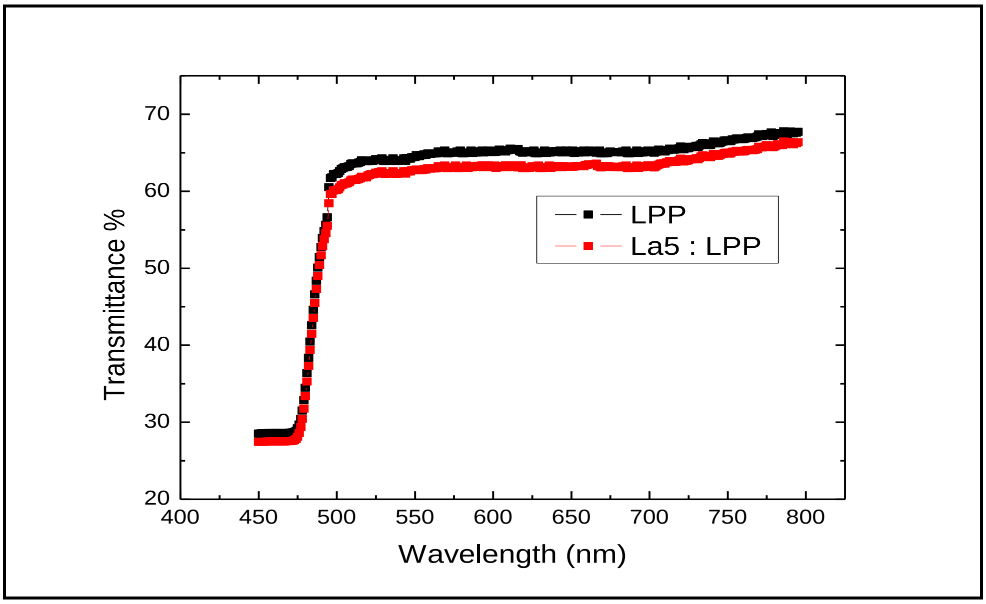


Figure 4. Optical transmission for LPP and La5 : LPP crystals *Powder SHG Measurement*

The study of NLO conversion efficiency was carried out by the powder technique of Kurtz and Perry [6]. Second harmonic signal of 512 mV was obtained for an input energy of 3.2 mJ/pulse for La5 : LPP. But the standard KDP sample gave a SHG signal of 15 mV/pulse for the same input energy. The results obtained by this method shows that SHG efficiency of La5 : LPP is nearly 34.1 times higher than that of KDP but pure LPP shows the SHG efficiency of 48 times higher than that of KDP. The reduction in SHG efficiency for La5 : LPP compared to pure LPP is attributed to ineffective transportation of polarization from one molecule to its neighbor in the presence of dopants. Since the second order non linear efficiency will vary with the particle size of powder sample [7], the care has been taken to maintain uniform particle size of source and the reference material.

2.6 Vicker's Microhardness Study

The good quality crystals are needed not only with good optical performance but also with good mechanical behavior [8] for applications. In order to study the mechanical behavior of the grown LPP crystal, Indentations were made on the cleaved (100) plane of pure LPP and La5 : LPP crystals with the applied load ranging from 5 to 100 g. The time of indentation was kept constant as 5 s for all indentations. The Vicker's hardness number was calculated using the relation [9].

$$H_V = \frac{1.854P}{d^2} kg/mm^2$$

where P is the applied load and d is the diagonal length. The Vicker's hardness for LPP and La5 : LPP crystals as a function of load are shown in figure 5.

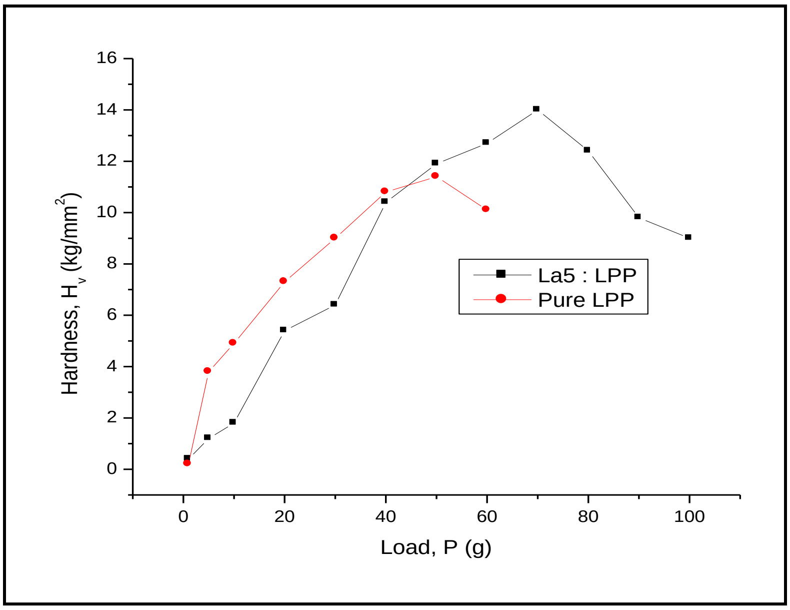


Figure 5. Micro hardness value of LPP and La5 : LPP crystals

The hardness values of LPP have been found to be lower than that of La5 : LPP crystal. Vicker's hardness increases with increase of load till 70 g for La5 : LPP crystal but upto 50 g for LPP crystal. The Loads above 70 g for La5 : LPP and 50 g for LPP developed multiple cracks around the indentation mark and hardness decreases with the further increase of load. By plotting log P versus log d, the value of the work hardening coefficient (n) was found to be 3.71 for LPP and 3.01 for La5 : LPP. According to Onitsch, $1.0 \leq n \leq 1.6$ for hard materials and $n > 1.6$ for soft materials [10]. Hence it is concluded that LPP and La5 : LPP are soft materials. In order to find the increase in strength that accompanies plastic deformation of the grown crystal, yield strength (σ_y) of the crystals was also calculated using the relation [11]

$$\sigma_y = (\frac{H_V}{3})0.1^{n-2} MPa.$$

where 'H_v' is the maximum hardness and 'n' is the work hardening coefficient. Yield strength for LPP and La5 : LPP crystals are found to be 0.07 MPa and 0.08 MPa respectively.

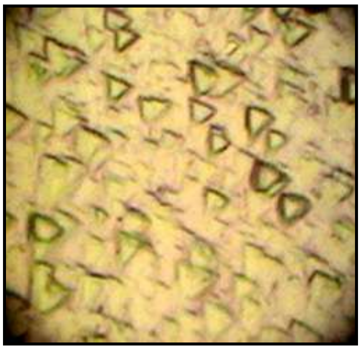
(a) Indentation image for 12 g

(b) Indentation image for 50 g

Figure 6. Indentation image observed in La5 : LPP

Moreover while analyzing the optical image of the indentation in the crystal for LPP and La5 : LPP, it is observed that mild crack started at 10 g load for both LPP and La5 : LPP and multicracks developed at 70 g load for La5 : LPP and 50 g load for LPP. Crack length was measured for various loads applied on the crystal. It was about 35 µm length from the indentation center for the load between 10 g and 50 g which can be seen in the optical image shown in the Figure 6. There were no remarkable changes found in the indentation length and crack length in this range of load. But when the applied load reached 80 g for LPP and 82 g for La5 : LPP, the crystals were found to be deformed more. Elastic stiffness constant was calculated from the microhardness by Wooster's empirical relation $C_{11} = (Hv)^{7/4}$ [12]. The maximum stiffness constants for the LPP and La5 : LPP crystals are 71.8 x 10^{12} pascals and 101.32 x 10^{12} pascals respectively.

Fracture toughness, Kc, is the resistance of a material to failure from fracture starting from a pre existing crack. It was calculated using the formula $Kc = P/\beta C^{3/2}$, where C is the crack length from the center of the indentation, P is the applied load and β (= 7) is the geometrical constant for Vicker's indenter [13]. The crack length developed with maximum hardness at 70 g applied load for La5 : LPP crystal was 41 µm and the crack length developed with maximum hardness at 50 g applied load for LPP was 44 µm. Hence the fracture toughness was calculated as 24,390 kg $m^{-3/2}$ for La5 : LPP and 16,233 kg $m^{-3/}$2 for LPP. Brittleness is an important property of the crystal which determines its fracture without any appreciable deformation. It is expressed in terms of brittleness index [14]. Brittleness index was calculated using the formula, Bi = Hv/Kc as 6.77 x 10^{-3} $m^{-1/2}$ for LPP and 5.74 x 10^{-3} $m^{-1/2}$ [15]. Figures 7(a) and 7(b) show the etch patterns produced for 2 s and 5 s for La5 : LPP. Etching produces triangular shaped etch pits. It is observed that etch pit is symmetrical in nature. The possible reason for the formations of these etch pits is due to the impurity in the crystal during growth, which introduces strain in the crystal lattice and serves as sites of dislocation [16].



(a) Etch Pits for 2 s Average Width 2.85 µm

(b) Etch Pits for 5 s Average Width 5.75 µm

Figure 7. Triangular Etch Pits observed in La5 : LPP Crystals

3. Conclusion

LPP and Lanthanum doped LPP crystals were grown from mixed solvent of water and acetone in the ratio of 1:1 by the solvent evaporation method. From the XRD analysis, it is observed that the LPP and La doped LPP crystals retain the monoclinic structure and the calculated lattice parameter values are comparable with the reported values of LPP. The presence of Lanthanum in LPP crystal was confirmed by EDAX analysis. Optical transmission study shows that the grown Lanthanum doped LPP crystal has high transparency in the wavelength range from 470 nm to 800 nm. The dielectric constant and dielectric loss of La doped LPP is found to be lesser than that of LPP. This shows that the doped crystal possess better optical quality with lesser defects compared to pure crystal. The thermal studies of the samples suggest that the thermal stability is better for doped crystal. Hardness study reveals that the LPP and La5 : LPP crystals are soft materials. Higher hardness is obtained for La5 : LPP than that of the LPP crystals. Elastic stiffness of the La5 : LPP crystals was also reported. The NLO efficiency for La5 : LPP crystal is 34.1 times higher than that of KDP crystals.

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