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Effect of rare earth elements Neodymium, Cerium, Lanthanum and Soft transition element Niobium on L-Prolinium Picrate Single Crystal

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Abstract: L-Prolinium picrate, Rare earth elements, Neodymium, Cerium, Lanthanum doped L-Prolinium picrate and soft transition element Niobium doped L-Prolinium picrate were synthesized and grown as single crystals by slow evaporation method. The cell dimensions were obtained by single-crystal X-ray diffraction study. Optical properties, such as UV–visible–NIR absorption and second harmonic generation conversion efficiency were investigated to explore the optical characteristics of the grown crystals. Microhardness, Thermal and dielectric studies of the compound were also carried out.
Keywords: Growth from solution, Nonlinear optical crystal, X-ray diffraction, Semi organic compound, Micro hardness.

1. Introduction

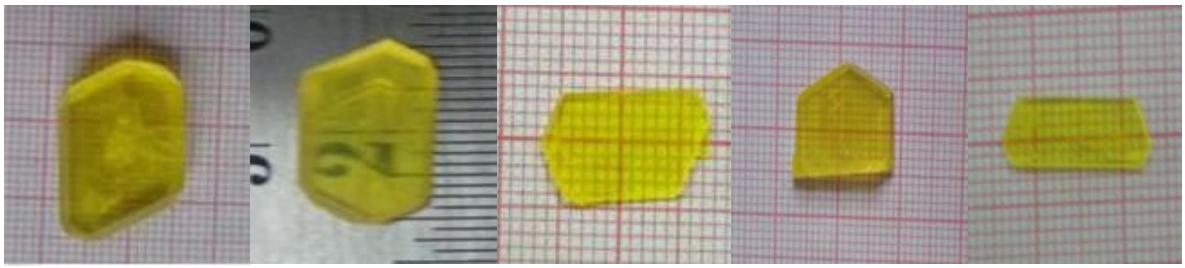
Recently, materials possessing non linear optical properties, especially those exhibiting second harmonic generation (SHG) have received considerable attention due to their wide range of technical applications. A novel class of SHG active compounds based on hydrogen bonded salts of inorganic oxyacids and polarizable organic cations seems to be very promising[1] because of the higher SHG efficiency and better physicochemical properties compared to the traditional classes (inorganic or organic salts) of SHG active materials. In the recent years, complexes of amino acids with inorganic acids and salts are promising materials for optical SHG, as they tend to combine the advantages of organic amino acid with that of inorganic acid[2-4]. A series of these compounds, such as L-argenine phosphate, L-argenine hydrobromide, L-argenine hydrochloride, L-hystidine dinitrate, L- hystidine tetrafluoroborate, L-threonine acetate, L-alanine maleate, L-Proline tartrate, L-Proline Picrate, L-cystine hydrochloride have been reported[5-11]. In this paper, we are presenting a report on synthesis and growth of L-Prolinium Picrate, rare earth elements, Neodymium, Cerium, Lanthanum doped L-Prolinium Picrate, soft transition element Niobium doped L-Prolinium Picrate and the grown crystals were subjected to various characterization studies.

Experimental

2.1. Crystal Growth

Commercially available AR grade L-Proline (Loba chemie) and Picric acid were mixed in equimolar ratio and dissolved in the mixed solvent of double distilled water and acetone in 1:1 ratio to synthesize L-Prolinium Picrate (LPP) source material. The synthesized salt was purified by repeated recrystallisation process and used for growing pure LPP. Rare earth elements Neodymium, Cerium, Lanthanum doped LPP crystals and soft transition element Niobium doped LPP crystal, were grown from mixed solvents of water and acetone in

the ratio of 1:1 using the well known solvent evaporation technique with 2 mol %, 5 mol % and 10 mol % of Niobium Penta oxide, Cerium Nitrate, Lanthanum Nitrate and Neodymium Nitrate added to the Pure LPP saturated solutions. Optical quality crystals were collected in a period of 30 to 45 days. From the physical observations of the grown crystals the 10 mol % Neodymium doped LPP (Nd10 : LPP), 5 mol % Cerium doped LPP (Ce5 : LPP), 5 mol % Lanthanum doped LPP (La5 : LPP) and 10 mol % Niobium doped LPP (Nb10 : LPP) crystals have good transparency and morphology and are shown in figure 1.



Pure LPP **Nd10 : LPP** **Ce5 : LPP** **La5 : LPP** **Nb10 : LPP**

Figure 1. As grown pure LPP and doped LPP crystals

2.2. Characterization

The grown single crystals of pure LPP, Nd10 : LPP, Ce5 : LPP, La5 : LPP and Nb10 : LPP were subjected to X-ray diffraction study using a Bruker AXS Kappa APEX II single crystal CCD diffractometer equipped with graphite monochromated MoKα (λ = 0.7107 Å). Energy dispersive and X-ray study (EDAX) was carried out using EDAX - AMETEK tester for the grown samples to analyze the percentage of dopants in the crystal. HIOKI 3532 – 50 LCR HITESTER was used for the dielectric study. The samples of size approximately 4 x 4 x 3 mm^3 were prepared from all the crystals 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 – 95 ºC. The thermo gravimetric and differential thermal analyses (TG – DTA) response curves were drawn for pure and doped LPP sample in the temperature range from 20 to 800 °C using the instrument NETZSCH STA 409C at the heating rate of 10 K/min. in nitrogen atmosphere. The optical transmission spectra were recorded using Shimadzu model - 1601 in the wavelength range of 300 – 900 nm. The study of NLO conversion efficiency was carried out by the powder technique of Kurtz and Perry. The crystals were 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.

3. Results and discussion

3.1. Single Crystal X-Ray Diffraction

Unit cell parameters of the grown LPP, Nd10 : LPP, Ce5 : LPP, La5 : LPP and Nb10 : LPP single crystals are listed in Table1. The observed values of LPP agree well with the reported values[10, 11]. It was observed that volume of the Nd10 : LPP, Ce5 : LPP and Nb10 : LPP crystals are reduced since the rare earth metal ions Nd, Ce and Nb occupies the void spaces of pure LPP crystalline matrix and there will be a local compressive strain in the lattice. LPP and doped LPP belongs to monoclinic system, space group $P2_1$ which is recognized as noncentrosymmetric, thus satisfying one the basic and essential material requirements for the SHG activity of the crystal.

Table 1. Comparison of Single Crystal X-ray data of pure LPP and doped LPP crystals

Parameters	Pure LPP	Nd doped LPP	Ce doped LPP	La doped LPP	Nb doped LPP
a (Å)	10.902	10.831	10.882	10.972	10.875
b (Å)	5.352	5.342	5.321	5.583	5.338
c (Å)	12.472	12.454	12.417	12.379	12.444
V ($Å^3$)	686	682	681	692.32	682.32
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
β(°)	109.11	108.76	109.37	109.14	109.17
Space group	$P2_1$	$P2_1$	$P2_1$	$P2_1$	$P2_1$

3.2. EDAX Analysis

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

Table 2. EDAX analysis of doped LPP crystals

Elements	10 mol % Nd doped LPP		5 mol % Ce doped LPP		5 mol % La doped LPP		10 mol % Nb doped LPP	
	Wt.%	**At.%**	**Wt.%**	**At.%**	**Wt.%**	**At.%**	**Wt.%**	**At.%**
C	32.08	37.9	33.18	38.6	37.25	38.1	38.81	46.01
N	23.16	23.47	20.13	20.27	18.72	18.57	17.22	17.51
O	43.39	38.50	40.15	37.26	41.25	37.83	40.38	35.93
Elements	Nd : 1.73	Nd : 0.17	Ce : 2.58	Ce : 0.24	La : 3.59	La : 0.52	Nb : 3.59	Nb : 0.55

3.3. Dielectric Studies

The variation of dielectric constant and dielectric loss as a function of frequency were determined for pure and doped crystals and are shown in the figures 2(a) and 2(b). 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. This may be attributed to space charge polarization due to charged lattice defects. The trend of the dielectric constants of LPP and doped 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 SHG coefficient[12].

From the dielectric study, it is observed that the pure LPP crystal has high dielectric constant compared to that of the doped crystal. It shows that the pure LPP has higher polarization than that of the doped LPP crystals. This may be attributed that the polarization in one molecule is not well transported to neighboring molecules in the presence of dopants[13].

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[14]. 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.

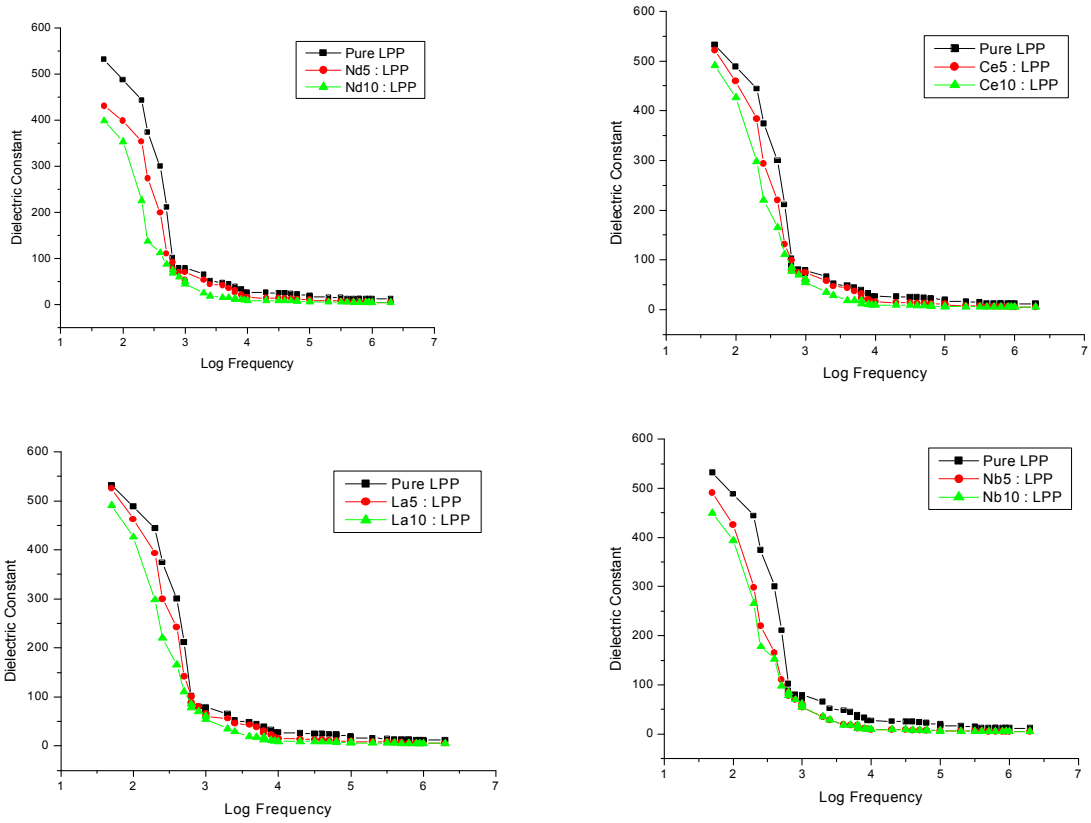


Figure 2 (a). Dielectric Constant vs. Log frequency for pure and doped LPP crystals

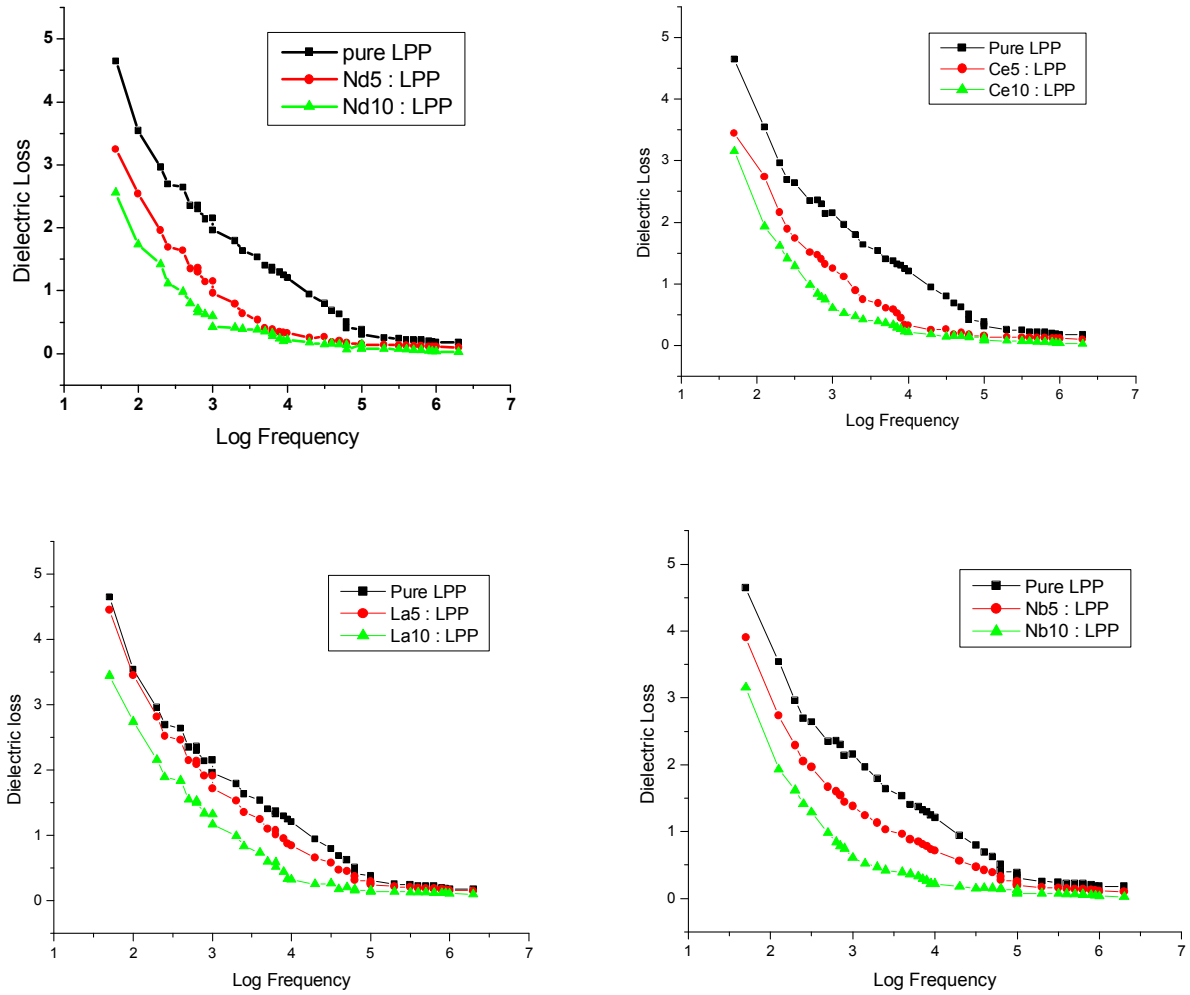


Figure 2 (b). Dielectric Loss vs. Log frequency for pure and doped LPP crystals

3.4. Thermal Analyses

The TG - DTA curves of LPP and doped LPP samples exhibit nearly similar stage of decomposition between 100 and 900 ºC as shown in figure 3. In order to study the influence of the dopant on 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.

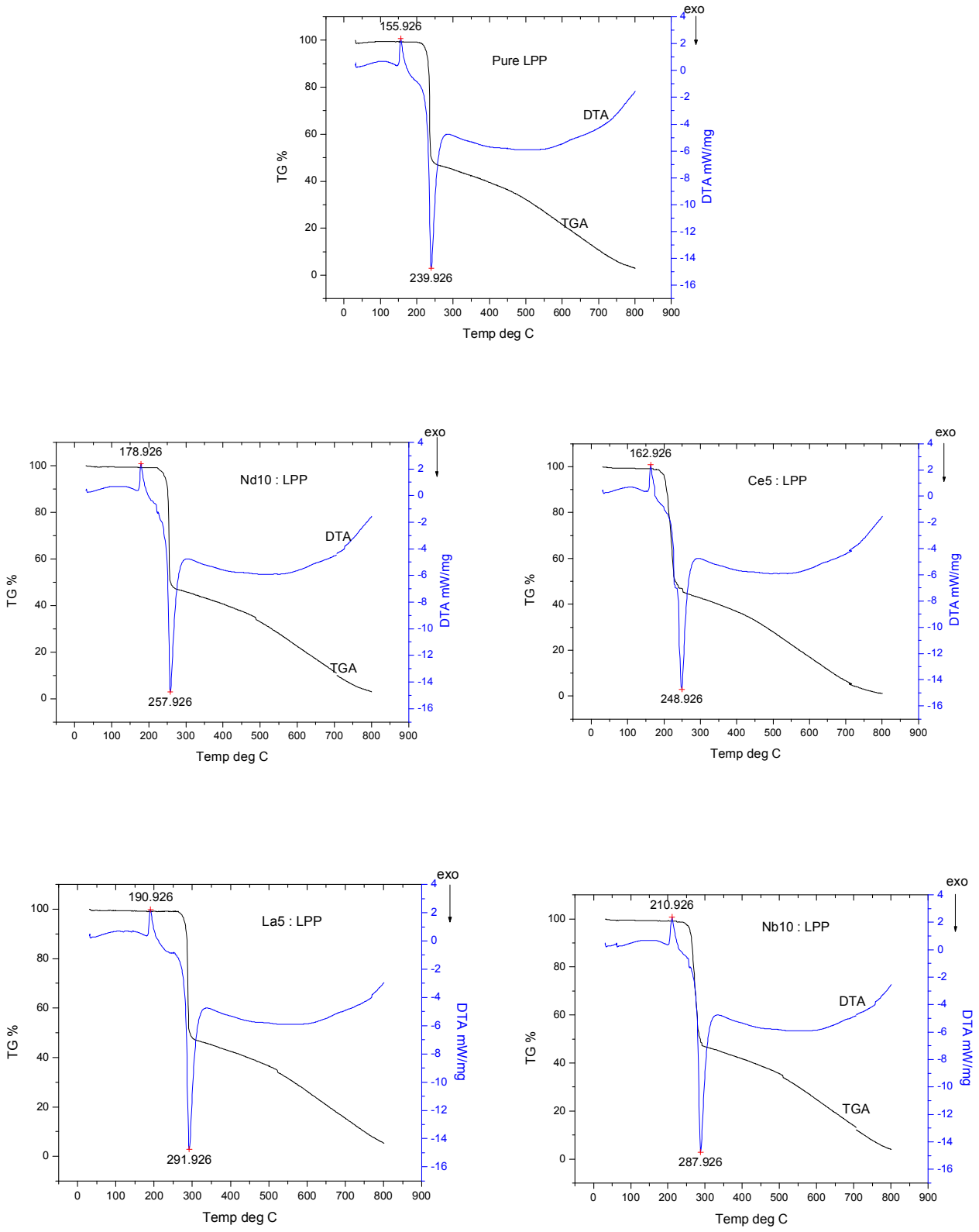


Figure 3. TG-DTA graph for pure and doped LPP samples

The temperature on the first stage of transition for the pure LPP and doped LPP crystals are mentioned in the figure 3. This shows that the doped crystal possess good thermal stability compared to pure crystal.

3.5. Optical Transmission Study

The figure 4 shows the optical transmission spectra of LPP and doped LPP crystals. The thickness of the samples used for this study was 1.5 mm.

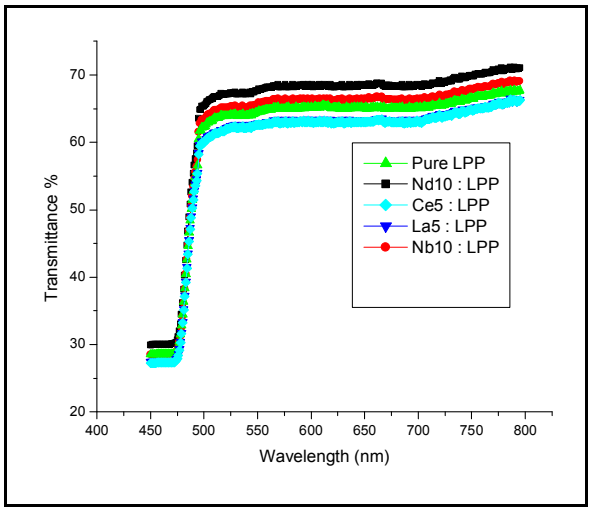


Figure 4. Optical transmission for pure and doped LPP crystals

The lower cut off for LPP and doped LPP crystals are around 470 nm. This shows that doping the crystal with Neodymium, Cerium, Lanthanum and Niobium do not influence the lower cut-off value, but, the percentage of transmission is varied. It is observed from the graph that 66 % for Pure LPP, 63 % for Ce5 : LPP and La5 : LPP, 70 % for Nb10 : LPP and 72 % for Nd10 : LPP.

3.6. Powder SHG Measurement

The study of NLO conversion efficiency was carried out by the powder technique of Kurtz and Perry[15]. It shows the second harmonic signal and SHG efficiency for pure and doped LPP crystals for an input energy of 3.2 mJ/pulse and is compared with standard KDP sample. The standard KDP sample gave a SHG signal of 15 mV/pulse for the same input energy. The result obtained by this method shows that SHG efficiency of doped LPP crystals are less than the pure LPP. SHG efficiency for pure LPP is 48 times that of KDP, 31 times that of KDP for Nd10 : LPP, 31.6 times that of KDP for Ce5 : LPP, 34.1 times that of KDP for La5 : LPP and 29 times that of KDP for Nb10 : LPP. This is due 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[16], the care has been taken to maintain uniform particle size of source and the reference material.

3.7. Vicker's Microhardness Study

The good quality crystals are needed not only with good optical performance but also with good mechanical stability[17] for applications. In order to study the mechanical behavior of the grown LPP crystal, indentations was made on the cleaved (100) plane of pure LPP and doped 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[18],

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

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

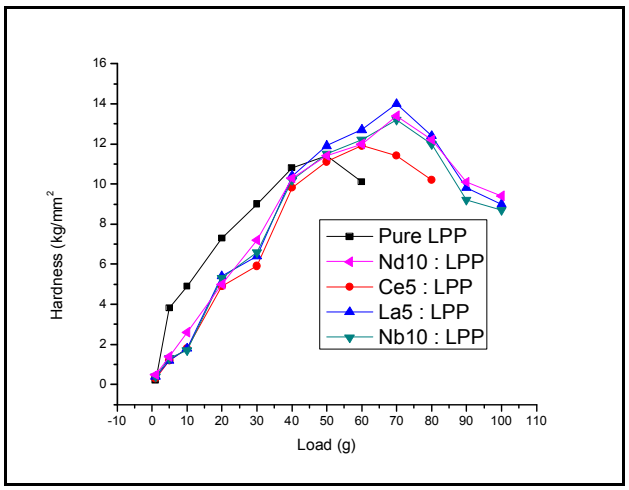


Figure 5. Microhardness measurement for pure and doped LPP crystals

The hardness values of LPP were found to be lower than that of the doped LPP crystals. Vicker's hardness increases with increase of load till 60 g for Ce5 : LPP, 70 g for Nd10 : LPP, La5 : LPP and Nb10 : LPP crystals but upto 50 g for pure LPP crystal. The Loads above 60 g for Ce5 : LPP, 70 g for Nd10 : LPP, La5 : LPP, Nb10 : LPP crystals and 50 g for pure LPP developed multiple cracks around the indentation mark and hardness decreases with the further increase of load. The value of H_v increases on doping because dopant ions enters into the lattice and hinder the formation of dislocation. By plotting log P versus log d, the value of the work hardening coefficient (n) was found out for pure and doped LPP crystals. Work hardening coefficient for pure LPP is 3.73, 3.08 for Nd10 : LPP and 3.01 for Ce5 : LPP, La5 : LPP and Nb10 : LPP. According to Onitsch, $1.0 \leq n \leq 1.6$ for hard materials and $n > 1.6$ for soft materials[19]. Hence it is concluded that LPP and doped LPP crystals 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[20]

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

where 'H_v' is the maximum hardness and 'n' is the work hardening coefficient. Yield strength for LPP is 0.07 MPa and for doped LPP crystals it is 0.08 MPa respectively.

Elastic stiffness constant was calculated from the microhardness by Wooster's empirical relation[21] $C_{11} = (H_v)^{7/4}$. Fracture toughness, K_c, is the resistance of a material to failure from fracture starting from a preexisting crack. It was calculated using the formula $K_c = P/\beta C^{3/2}$, 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[22]. Brittleness is an important property of the crystal which determines its fracture without any appreciable deformation. It is expressed in terms of brittleness index[23]. Brittleness index[24] was calculated using the formula $B_i = H_v/K_c$. Elastic stiffness constant, fracture toughness and brittleness index for pure LPP, Ce5 : LPP and La5 : LPP are tabulated in table 3.

Table 3. Elastic Stiffness, Fracture Toughness and Brittleness index for pure LPP, Ce5 : LPP and La5 : LPP crystals.

Crystals	Elastic Stiffness Constant (C_{11})	Fracture Toughness (K_c)	Brittleness index (B_i)
Pure LPP	71.8 x 10^{12} pascal	16,233 kg $m^{-3/2}$	6.77 x 10^{-3} $m^{-1/2}$
Ce5 : LPP	76.24 x 10^{12} pascal	30,398 kg $m^{-3/2}$	3.55 x 10^{-3} $m^{-1/2}$
La5 : LPP	101.3 x 10^{12} pascal	24,390 kg $m^{-3/2}$	5.74 x 10^{-3} $m^{-1/2}$

4. Conclusion

The experimental results of pure LPP, Niobium doped LPP, rare earth elements Neodymium, Cerium and Lanthanum doped LPP can be summarized as follows.

1. Pure LPP, Niobium doped LPP, Rare earth elements Neodymium, Cerium 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.
2. From the XRD analysis, it is observed that the pure LPP and doped LPP crystals retain the monoclinic structure and the calculated lattice parameter values are comparable with the reported values of LPP.
3. The presence of fewer amounts of Neodymium, Cerium, Lanthanum and Niobium as a dopant in LPP crystal was confirmed by EDAX analysis.
4. Optical transmission study shows that the grown Neodymium and Niobium doped LPP crystals have high transparency in the wavelength range from 470 nm to 800 nm.
5. The dielectric constant and dielectric loss of Niobium, Neodymium, Cerium and Lanthanum doped LPP crystals are found to be lesser than that of LPP. This shows that the doped crystals possess better optical quality with lesser defects compared to pure crystals.
6. The thermal studies of the samples suggest that the thermal stability is better for doped crystals.
7. Hardness study reveals that the LPP and doped LPP crystals are soft materials and higher hardness is obtained for doped LPP crystals than that of the LPP crystals.
8. Yield strength, elastic Stiffness, fracture toughness and brittleness index of the pure and doped LPP crystals were also reported.
9. The NLO efficiency for the doped LPP crystals is less than that of the pure LPP crystals.

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