Synthesis, Growth and Characterisation of Nonlinear Optical Nb-doped L-Valinium Picrate Single Crystals

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Abstract: ***A nonlinear optical material Niobium doped L-Valinium Picrate was synthesized and grown as single crystals by slow evaporation method. The grown crystals were subjected to structural, elemental, thermal, optical and dielectric studies. The structural analysis reveals that Nb : LVP 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 Nb doped L-Valinium Picrate is thermally stable up to 185 °C. The dielectric constant and dielectric loss of the crystal were studied as a function of frequency. The nonlinear optical property of the grown crystal was confirmed by the Kurtz-powder second harmonic generation test and the results are compared with pure LVP. Mechanical strength of the crystal was also carried out by Vicker's micro hardness test.***

Keywords: Growth from solution, X-ray diffraction, Semi organic compound, Nonlinear optical crystal, Micro hardness

1. Introduction

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. 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. The growth, optical absorption and mechanical studies on pure LVP 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 Niobium as dopant on growth, physical, mechanical and optical properties, thermal, dielectric and hardness of pure LVP.

Crystal Growth

Commercially available L-Valine 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 L-Valine Picrate (LVP) source material. The synthesized salt was purified by repeated recrystallisation process. Niobium doped LVP crystals were grown from mixed solvents of water and acetone in the ratio of 1:1using the well known solvent evaporation technique with 5 mol % and 10 mol % of Niobium Penta oxide added to the LVP saturated solutions.

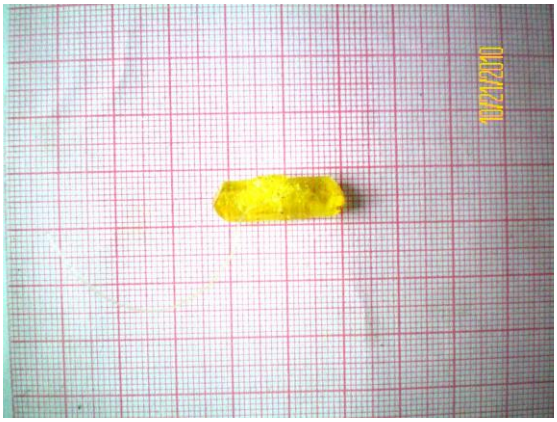

Figure 1: As grown crystals of 10 mol % Nb doped LVP (Nb10 : LVP)

Optical quality crystals were collected in a period of 35 days from the supersaturated solution and are shown in figure 1. From the physical observations of the grown crystals the 10 mol % Niobium doped LVP (Nb10 : LVP) crystals have good transparency and morphology.

Single Crystal X-Ray Diffraction

Lattice parameter values of pure LVP (LVP) and Nb10: LVP single crystals are listed in Table1. The observed values for LVP are in good agreement with the reported values [1, 2].

Table 1: Comparison of single crystal X-ray data of LVP and Nb10: LVP crystals

Parameters	LVP	Nb10 : LVP
a (Å)	10.902	10.875
b (Å)	5.352	5.338
c (Å)	12.472	12.444
V (Å^3)	687.60	682.32
System	Monoclinic	Monoclinic
β(°)	109.11	109.17
Space group	P_{21}	P_{21}

EDAX Studies

In order to analyze quantitatively the presence of Niobium in the crystal, EDAX study was carried out using EDAX - AMETEK tester for the grown sample and the percentage of dopant present in the LVP was confirmed and tabulated. From EDAX analysis, it is observed that the amount of Niobium atoms present inside the LVP lattice is very less.

Table 2: EDAX analysis of Nb10: LVP crystals

Elements	Wt.%	At.%
Nb	3.59	00.55

Dielectric Studies

The dielectric constant and dielectric loss were calculated for pure and doped crystals. The figures 2(a) and 3(b) show the variation of dielectric constant and dielectric loss as a function of frequency. It is found that the dielectric constants of LVP and doped LVP crystals are high at lower frequencies and they decrease with increase in frequency. The trend of the dielectric constants of LVP, 5 mol % Nb doped LVP (Nb5 : LVP) and 10 mol % Nb doped LVP (Nb10 : LVP) crystals are almost the same. But at fixed frequency, the dielectric constants of doped LVP 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].

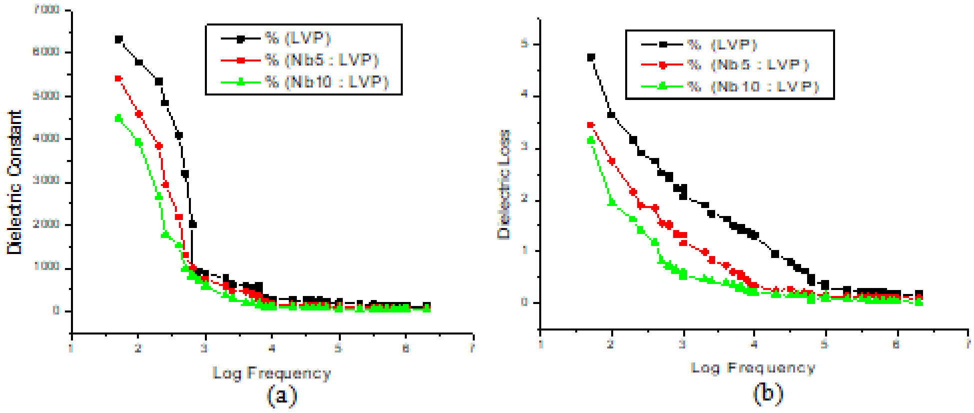

Figure 2: (a) Dielectric Constant vs. Log frequency for pure and doped LVP crystals **(b)** Dielectric loss vs. Log frequency for pure and doped LVP crystal

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 LVP is slightly lesser than that of pure, which indicates that the dopant further enhances the optical quality of LVP and reduces the defects.

Thermal Analysis

The TG - DTA curves of LVP and Nb10 : LVP samples appear 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 LVP, 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 LVP is found at 160 ºC and for Nb10 : LVP it is found at 185 ºC. This shows that the doped crystal possess better thermal stability compared to pure crystal.

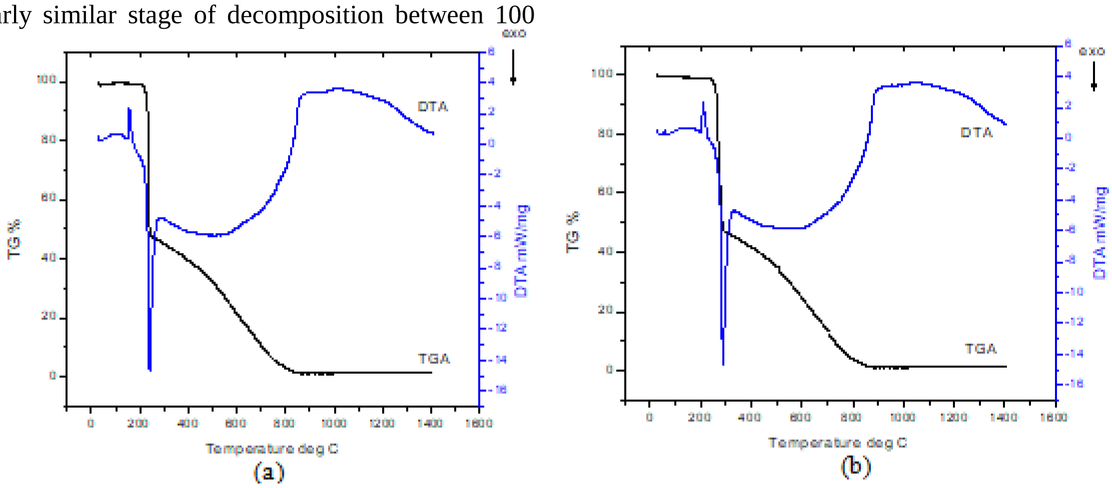

Figure 3: (a) TG-DTA graph for LVP sample **(b)** TG-DTA graph for Nb10: LVP sample

Optical Transmission Study

The figure 4 show the optical transmission spectra of LVP and Nb10: LVP crystals. The thickness of the sample used for this study was 1.5 mm for LVP and Nb10 : LVP. It is found that LVP crystal has transmittance of 66 % and Nb10 : LVP crystal has the transmittance of 70 %. The lower cut off for LVP and Nb10: LVP crystals are 470 nm. This shows that doping the crystal with Niobium did not shift the lower cut-off value, but, the percentage of transmission is increased due to Niobium addition.

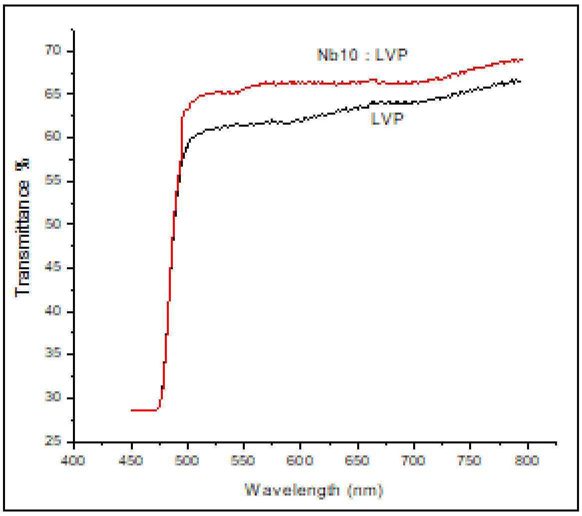

Figure 4: Optical transmission for LVP and Nb10: LVP crystals

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 441 mV was obtained for an input energy of 3.2 mJ/pulse for Nb10: LVP. 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 Nb10: LVP is nearly 29 times higher than that of KDP. 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.

Vicker's Microhardness Studies

The good quality crystals are needed not only with good optical performance but also with good mechanical behavior [8] for applications. Indentations were made on the (100) planes of pure and Nb10 : LVP crystals with the applied load ranging from 5 to 100 g. The time of indentation was kept constant for 5s. The Vicker's hardness was calculated using the relation.

$$H_V = \frac{1.8544P}{d^2} kg/mm^2 .$$

where P is the applied load and d is the diagonal length. The cleaved surface was polished and then subjected to micro hardness studies. The Vicker's hardness for LVP and Nb10 : LVP crystals as a function of load are shown in figures 5(a) and 5(b) respectively. The hardness values of LVP have been found to be lower than that of Nb10 : LVP crystal. Vicker's hardness increases with increase of load till 70 g for Nb10 : LVP crystal and upto 50 g for LVP crystal. Test loads above 70 g for Nb10 : LVP and 50 g for LVP developed multiple cracks around the indentation mark and hardness decreases with the increase of load. By plotting log P versus log d, the value of the work hardening coefficient (n) was found to be 3.73 for LVP and 3.01 for Nb10 : LVP. According to Onitsch, $1.0 \leq n \leq 1.6$ for hard materials and $n > 1.6$ for soft materials [9]. Hence it is concluded that LVP and Nb10 : LVP 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 [10]

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

where 'H_v' is the maximum hardness and 'n' is the work hardening coefficient. Yield strength for LVP and Nb10 : LVP crystals are found to be 0.07 MPa and 0.08 MPa respectively.

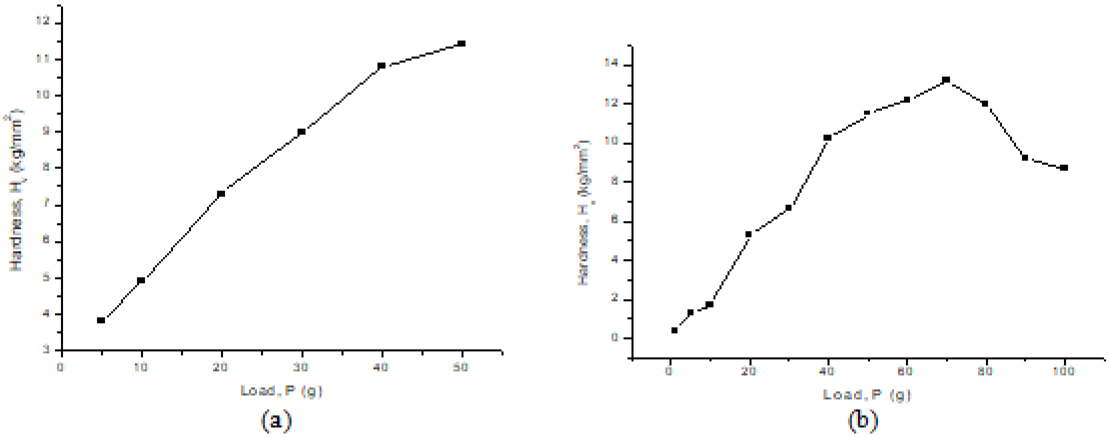

Figure 5 (a): Micro hardness for LVP crystal **(b)** Micro hardness for Nb10: LVP crystal

2. Conclusion

LVP and Niobium doped LVP crystals were grown from mixed solvent of water and acetone in the ratio of 1:1 by the solvent evaporation method. From the XRD studies, it is observed that the LVP and Nb doped LVP crystals retain the monoclinic structure and the calculated lattice parameter values are comparable with the reported values of LVP. The presence of Niobium in LVP crystal was confirmed by EDAX analysis. Optical transmission studies show that the grown Niobium doped LVP crystal has high transparency in the wavelength ranges from 470 nm to 800 nm. The dielectric constant and dielectric loss of Nb doped LVP is found to be lesser than that of LVP. This shows that the doped crystal possess better optical quality with lesser defects compared to pure crystals. The thermal studies of the samples suggest that the thermal stability is better for doped crystals. Hardness studies reveal that the LVP and Nb10: LVP crystals are soft materials. Higher hardness is obtained for Nb10: LVP than that of the LVP crystals. Yield strength of the crystals was also calculated. The NLO efficiency for Nb10: LVP crystals is 29 times higher than that of KDP crystals.

3. Acknowledgements

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