Growth, structural, thermal and mechanical behavior of lithium para nitrophenolate (LPNP) single crystal for nonlinear optical applications

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Using slow evaporation solution growth technique, single crystal of Lithium para nitro phenolate (LPNP) has been grown from the equimolar mixture of para-nitro phenol and lithium hydroxide mono hydrate. Structural analyses were carried out by powder x-ray diffratcion method, FTIR and NMR methods to confirm the grown crystals. Thermal stability of the grown crystal is studied by Thermogravimetric (TG) and Differential Thermal analyses (DTA). The mechanical behavior of the grown crystal has been studied by Vicker's micro hardness method. UV-Vis spectral analysis has been carried out to find the transparency of the grown crystal. Nonlinear optical property has been confirmed by Kurtz powder technique. The observed properties have confirmed that the grown crystal is suitable for nonlinear optical applications.

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1. Introduction

Crystal growth is one of the thrust areas of research for the past few decades because of various industrial applications of single crystals. Depending upon the raw materials used for the growth of single crystals, the crystals are classified in to three categories which are organic, inorganic and semiorganic single crystal. Since the semiorganic single crystals prosses the good properties of both organic and inorganic crystal, Scientists and Researchers are focused their interest in growing as many semiorganic single crystals [1-3]. Para nitro phenol has been identified as potential organic material which gives variety of derivatives some hydroxides. Sodium para nitrophenolate (NPNa) has different hydrated form when it is grown from water solvent. The dihydrate form of NPNa has NLO activity; but, tetrahydrate does not [4]. Single crystal of Pottasium para nitrophenolate dihydrate has been grown and some new bonding properties have been reported by Boaz et al [5]. Lithium para nitrophenolate trihydrate crystal has been reported by same authors and studied the properties to some extent [6]. The title crystal has also been grown by recently developed SR method and some properties have been reported [7]. But still there are some characterizations like powder x-ray diffraction study left unstudied.

In the present study, bulk crystal larger in size than previously reported crystals of Lithium para nitrophenolate tryhydrate (LPNP) has been grown and Powder x-ray diffraction study, linear and nonlinear optical properties studies and thermal analysis were conducted and detailed report has been presented in this paper.

2. Experiment

2.1. Crystal growth

Para nitro phenol and Lithium hydroxide monohydrate were taken in 1: 1 molar ratio in excess of double distilled milli pore water as the starting material. The calculated amount of para nitro phenol dissolved in excess of double distilled milli pore water and the measured amount of lithium hydroxide monohydrate was added slowly with stirring to the mixture of water. After that the solution became homogeneous (ie., after continuous stirring for at least two hour), the solution was filtered to avoid the inclusion of impurities during the stirring and maintained at room temperature by using a constant temperature bath controlled to an accuracy of ± 0.01°C. The excess solvent was allowed to evaporate slowly so as to reach the saturation level of the solution. After the solution has attained the saturated level, well controlled evaporation was maintained to avoid the spurious nucleation. A Single crystal with dimension 20 × 20 × 5 mm^3 has been grown at room temperature (30°C) in the solution and it has been carefully harvested from the solution and the as grown crystal is larger than any other crystal that has been grown already as shown in the Fig. 1.

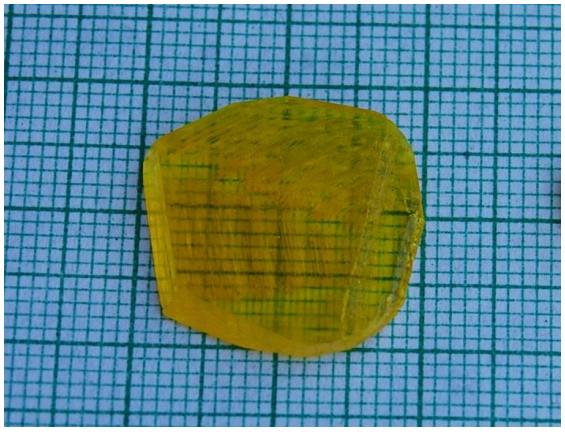

Fig. 1. Photograph of as grown crystal of LPNP.

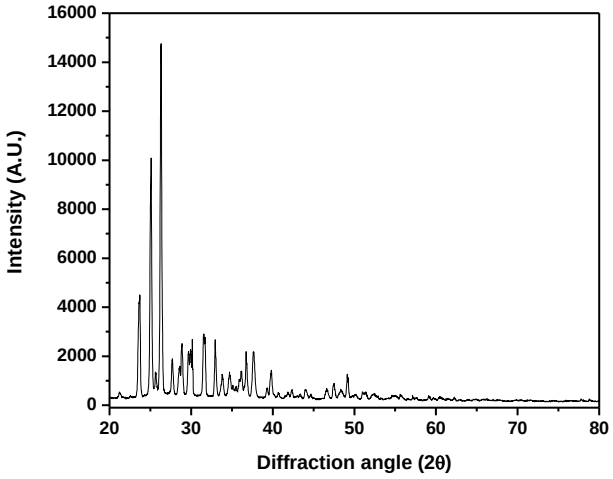

Fig. 2. Powder X-ray diffraction pattern of LPNP crystalline powder.

2.2 Characterization techniques

The grown seed crystals were powdered and used to study the properties using various techniques. Powder x-ray diffraction analyses were made on the fine crystalline powder sample to confirm the crystalline nature of the grown crystal using an X'PERT PRO diffractometer system. The powder sample was mixed with KBr 1:20 weight ratio and made as a pellet to study the Fourier transform infrared spectral analysis of the grown crystal by using Perkin Elmer Spectrometer and Proton NMR spectrum was recorded by Perkin Elmer, AMX 400 MHz. Linear optical properties of the crystals were studied by UV-Vis Spectrophotometer and nonlinear optical properties were tested by Kurtz Perry powder technique [8]. Thermo-gravimetry (TG), and Differential Thermal Analysis (DTA) for the crystal samples were carried out in nitrogen atmosphere by a Perkin Elmer Thermal Analyzer to study the thermal properties of the as-grown crystal. The Vicker's Microhardness method has been used to find study the mechanical behavior of the grown crystal.

3. Results and discussion

3.1. Powder x-ray diffraction analyses

The grown crystals were made as fine powder and subjected to powder x-ray diffraction analyses. The data have been collected at 298 K between 10° and 80° of diffraction angles with the source wave length of 1.5460 A°. The step size of 2θ and the scan step time were fixed as 0.017° and 10.3254 seconds respectively. The powder x-ray diffraction (PXRD) pattern of LPNP is shown in Fig. 2. The diffraction pattern contains various reflections corresponding to various crystallographic planes. The sharp peeks of the pattern have been observed due to the good quality of crystalline nature. The interplanar distance corresponding to the reflections at different 2θ values along with the intensity and relative intensity of the peeks have been tabulated in Table 1.

Table 1. Powder diffraction data of Lithium paranitro phenolate.

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
23.5031	2479.86	0.1020	3.78213	16.97
23.5944	3983.24	0.0669	3.77082	27.25
23.7332	4116.00	0.1004	3.74908	28.16
24.9832	7252.00	0.1020	3.56131	49.61
25.1046	10032.00	0.1171	3.54729	68.63
26.3143	14617.00	0.2175	3.38691	100.00
27.7269	1658.69	0.1338	3.21748	11.35
28.7996	2071.98	0.0816	3.09747	14.18
28.8837	2363.73	0.0612	3.08864	16.17
28.9697	1741.60	0.0408	3.08732	11.91
29.6148	1764.94	0.1632	3.01404	12.07
29.9192	2121.66	0.1020	2.98406	14.52
30.1437	2530.95	0.0612	2.96235	17.32
31.4970	2585.91	0.1428	2.83809	17.69
31.7185	2427.00	0.1020	2.81876	16.60
32.9424	2505.06	0.0816	2.71678	17.14
36.7264	1950.10	0.0612	2.44509	13.34
36.8358	1525.42	0.0612	2.43808	10.44
37.5558	1693.60	0.1632	2.39297	11.59
37.6910	2004.18	0.0816	2.39063	13.71

3.2. FTIR and Proton NMR spectral analysis

For the purpose of analyzing the presence of various functional groups in the grown LPNP the Fourier transform infrared spectrum has been recorded in the frequency range between 400 and 4000 cm^{-1}. The recorded FTIR spectrum is shown in Fig. 3. Because of the presence of various modes of vibrations, the spectrum is found to be complex [9]. The symmetric and asymmetric stretching vibrations due to -OH of lattice water have been observed in the high frequency region near 3400 cm^{-1} as abroad

envelop. Generally these modes of vibration have not been resolved clearly which confirm the presence of hydrogen bonded lattice water in the material. The bending vibration of H-OH of water molecule has been observed at 1687 cm^{-1}. The peak at 1112 cm^{-1} is due to C-O vibration of stretching mode. The para substitution usually gives its vibration around 856 cm^{-1} is observed in the spectrum at cm^{-1}. The para substitution NO_2 gives its symmetric stretching vibration at 1310 cm^{-1} and the asymmetric stretching vibration is observed at 1590 cm^{-1}. The presence of lithium hydrates is confirmed by the strong absorption peak at 500 cm^{-1}. Bending vibration of the ring C-H is observed at 1490 cm^{-1}. The important vibrations observed in the present study agree with the existing literature [5]. Proton NMR spectral analysis has also been carried out in order to confirm the structure of the synthesized material. The recorded proton NMR spectrum is shown in Fig. 4. In addition to the solvent peek at 4.67 ppm two signals have been observed. The ortho hydrogen in the aromatic structure can be seen each other as aligned (parallel) or opposed (antiparallel) and usually come to resonance twice. But, in this study the signals with multiple splitting at 6.4 is due to the ortho hydrogen of benzene ring and the signal at 6.9 is due to the meta hydrogen of benzene ring [10].

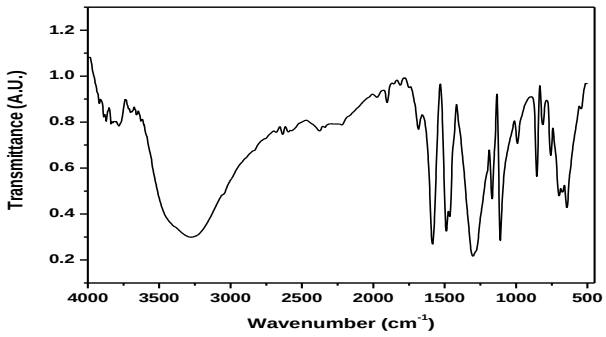

Fig. 3. FTIR Spectrum of LPNP.

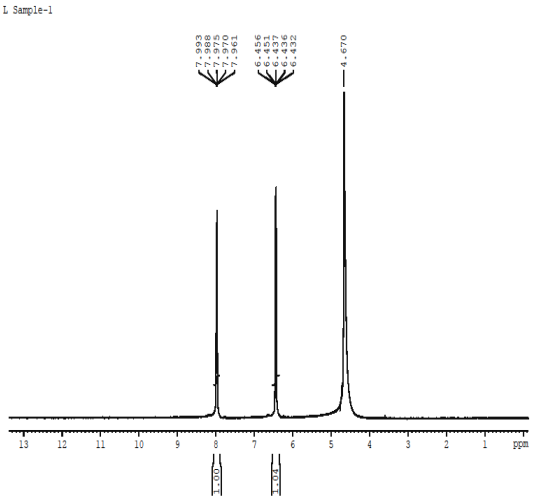

Fig. 4. Proton NMR Spectrum of LPNP.

3.3. Linear and nonlinear optical properties studies

It is necessary to have good optical transparency in an NLO crystal in the green visible region. Optical absorption spectrum has been recorded in the range between 180 to 800 nm and is shown in Fig. 5. The grown crystal has UV cutoff below 500 nm and above which the grown crystal is transparent in the entire visible range of the spectrum which has good agreement with the literature. So, the grown crystal is useful for optoelectronic applications and the second harmonic generation (frequency conversion) from the Nd: YAG Laser.

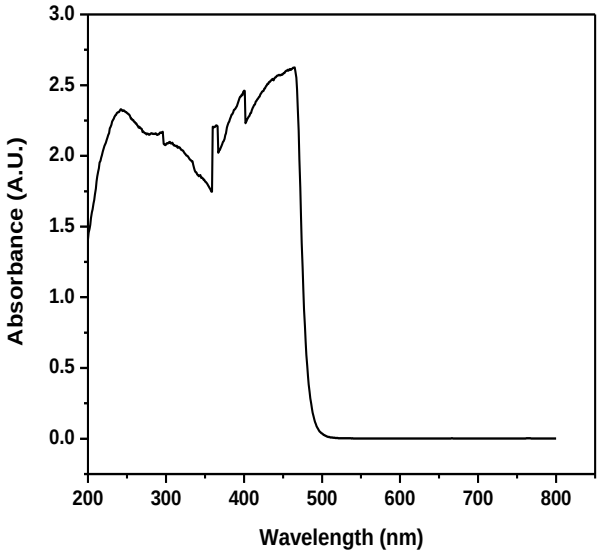

Fig. 5. UV-Visible absorption spectrum of LPNP crystal sample.

The SHG efficiency of LPNP crystalline sample has been found by Kurtz and Perry powder technique [8]. The powder samples prepared from the grown crystals have been subjected to this test. The second harmonic output has been generated by irradiating the powder samples by a pulsed laser beam of Nd: YAG laser with a pulse width of 8 ns. The capability of the energy (frequency) conversion is confirmed by the emission of green light from the powder sample of the grown crystal. KDP sample has been used as the reference material and output power intensity of the LPNP sample has been found to be six times as that of output power intensity of KDP.

3.4 Hardness study

Hardness of a crystal plays a key role in the device fabrication. It is a measure of a material's resistance to localized plastic deformation. The Vickers's hardness number of the grown crystal has been calculated using the relationship $H_v = 1.8544\ P/\ d^2$ where, H_v is the Vicker's micro hardness number, P is the applied load in kg and d is

the average diagonal length of the impression in mm. Fig. 6 shows the variation of hardness number with load. Before indentations, these crystals have been lapped carefully and washed to avoid surface defects, which may influence the hardness values. The indentations were made on the prominent plane of the grown crystal for the loads varying from 10 to 50g with a dwell time of 10s. The distance between two indentation points was maintained to be more than three times the diagonal length, in order to avoid any mutual interference of indentations. It is observed that the hardness value is apparently higher at lower loads for the prominent plane of the crystal because these loads are insufficient to soften the bonding in the molecules. Cracks were formed above 50g load due to release of internal stress generated locally by indentation and hence the hardness value decreased further. The mayer's index has been calculated from the Mayer's law, which is the relation between the applied load and indentation diagonal length.

$$P = kd^n$$

$$\log P = \log k + n \log d.$$

In the above equations, k is the material constant and n is the Mayer's index and it is also called as work hardening coefficient. The value of 'n' has been found by plotting a graph between log d and log P. The slope of the graph gives the value of n and it is found to be 1.73. Since this value is greater than 1.6 the grown crystal is a soft material [11].

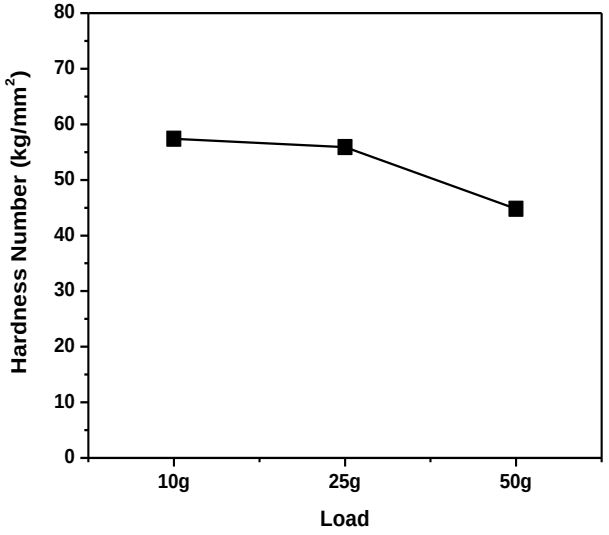

Fig. 6. A plot of Hardness Number versus applied load on the prominent plane.

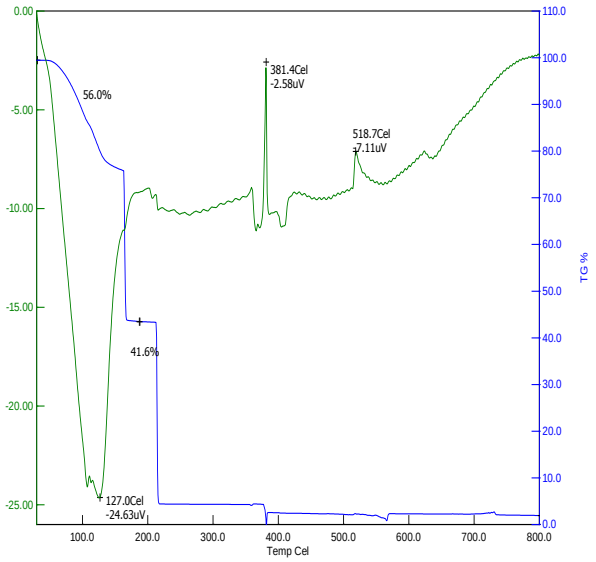

Fig. 7. TG/DTA Curve of LPNP.

3.5 Thermal analysis

As far as fabrication technology is concerned TG and DTA analyses are of immense importance, as they provide thermal stability of the material for fabrication where a considerable amount of heat is generated during the cutting process. Thermal analysis has been performed on the grown crystal powder to study the thermal stability and melting point. The thermo gravimetric analysis (TGA) of LPNP has been carried out between room temperature (28°C) and 800°C at a heating rate of 10°C per min. The experiment has been performed in nitrogen atmosphere and the TG & DTA plot as shown in the Fig. 7. There is a weight loss equal to 56% and it is assigned to loss of water in the TGA Curve. A careful examination of TG curve shows the weight loss in two stages, one by occurring below 120°C due to weakly entrapped lattice water and the other one occurring above it, due to the removal of strongly entrapped lattice water. This is followed by a major weight loss at 381°C due to decomposition of the substance [6]. The high temperature weight loss may be attributed to melting and volatilization of LiO_2. The DTA analysis of the substance is also carried out under the same condition of the above experiment. The onset of the first endothermic peak just above 180°C coincides with the initial weight loss in TGA. Although the overlapping of two weight losses in this endothermic peak is evident due to two different types of water losses, as said above, the shape of the endothermic curve clearly confirm the above view. This endothermic transition followed by a sharp exothermic at 127°C coincides with the major weight loss in the above TGA trace. The sharp peek at 381°C is due to melting of the material. Though the material melts at higher temperature, its application is restricted bellow 120°C.

4. Conclusions

Good quality single crystal of LPNP has been grown from the slow evaporation solution growth technique. The structural properties of the grown crystals have been characterized by Powder x-ray diffraction, FTIR and NMR methods. Thermal properties have been analyzed and thermal stability has been reported that the material can withstand till the material reaches 120°C. Hardness of the grown crystal has been studied by Vickers hardness test. The linear and nonlinear optical property studies confirm that the grown crystal is useful for nonlinear optical applications.

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