Effect of 100keV N^+ ion irradiation on semi-organic single crystal of L-Arginine phosphate monohydrate single crystal for nonlinear optical applications

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The potential Semi-organic nonlinear optical material of L-Arginine phosphate monohydrate (LAP) single crystal has been grown by slow evaporation solution growth technique using water as the solvent. The well prepared single crystals of pure LAP were irradiated at room temperature with 100 keV Nitrogen (N^+) ions at fluences $1x10^{16}$, $5x10^{16}$ and $1x10^{17}$ ions/cm^2. The pure and irradiated LAP single crystals were characterized by different characterization technique. The structural changes were analyzed by means of powder X-ray diffraction analysis. The functional groups of the pure and irradiated compound have been identified by FTIR. The photoluminescence and UV-Vis. absorption were done at room temperature and found that there is insignificant absorption in entire visible region. Vicker's microhardness technique was used to study effect on mechanical strength of crystal at different ion fluences. The surface studies of the grown and irradiated single crystal were done by using the optical microscope and found that roughness of surface increases with increasing ion fluences.

Keywords: Single crystal**,** solution growth, non-linear optical material, irradiation

1. Introduction

Non-linear optical (NLO) single crystals has emerged as one of the most attractive fields of research in view of its potential applications in the area of optical switching, optical computing, optical data storage, optical bi-stability etc [1-4]. LAP is one of the promising non linear optical (NLO) material having chemical formula $(H_2N)_2^+CNH(CH_2)_3CH(NH_3)^+COO^-H_2PO_4{\cdot}H_2O$. It crystallizes in monoclinic system with space group $P2_1$. Organic NLO materials are attracting much attention due to their high conversion efficiency for second harmonic generation, good transparency in the visible region and high resistance to optical damage and so on. However uses of organic materials are impended due their poor mechanical and thermal properties [5]. On the other hand, Inorganic NLO materials have good chemical stability, excellent mechanical strength, high optical quality and thermal properties. But Inorganic materials have low nonlinear properties relative to organic materials due to lack of □ electron delocalization. In semi organic NLO materials, high optical nonlinearity of organic material is combined with the favourable mechanical and thermal properties of inorganic materials [6]. The single crystals of LAP have been grown by slow evaporation solution growth technique at room temperature. The good quality single crystals have been grown with the time span of 10 days. The grown single crystals of LAP were subjected to N^+ ions beam with different ions fluences. Interactions of energetic ions with crystalline materials induce the physical & chemical changes in crystal. When energetic N^+ ions impinge on the crystal, it causes displacement of lattice ions via collisions and cascade of displacements depending on ions, energy and properties of the medium [7]. These lattice displacements induce modifications in property of crystal including mechanical, optical absorption, luminescence and crystalline perfection [8,9]. In the present experimental study, the grown crystals were irradiated by 100 keV N^+ ions at fluence of $1x10^{16}$ ions/cm^2, 5×10^{16} and 1×10^{17} ions/cm^2 from the Low Energy Ion Beam Facility (LEIBF) at IUAC, New Delhi. The pure single crystals of LAP are shown in Fig.1. The title compound (LAP) belongs to semiorganic NLO material, and crystallizes in monoclinic system with unit cell parameters a=10.85 Å, b=7.91 Å, c =7.32 Å and space group $P2_1$ [10]. After the irradiation, its lattice dimensions, other optical, mechanical, dielectric and structural properties have been

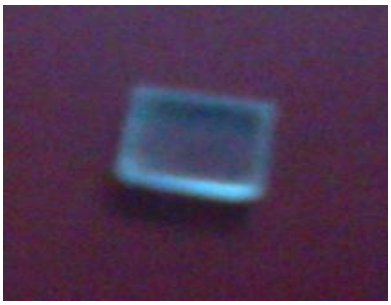

Fig.1: Photograph of LAP single crystal

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evaluated by different instrumentation technique. Many studies on L-Arginine phosphate monohydrate are already reported [11]. However this is the first report which carries information regarding the effect of ion irradiation on LAP single crystal. The observed results pure and irradiated LAP crystal will be presented in detail.

2. Experimental Details

2.1 Sample preparation

The single crystals of promising NLO material-LAP have been grown from the solution by slow evaporation technique using water as a solvent. The concentrated solution of LAP was prepared by dissolving the crystallized material with continuous stirring of the solution. Then the saturated solution was filtered by using Whatmann filter paper for further purification of the solution. The filtered solution was tightly packed and housed in a constant temperature bath (CTB) with a setting temperature of 30^0C. Good quality single crystals have been harvested from the mother solution, within 10 days.

2.2 Ion Irradiation Details

The as grown LAP crystals were well polished and then subjected to irradiation at different ion fluences. The projected ranges N^+ ions in the LAP crystals were calculated by SRIM-2006 which ascertains the penetration of ions into the crystal lattice. The nuclear energy loss (S_N) and the electronic energy loss (S_E) values in the LAP crystals are given in Table.1 for N^+ respectively, as obtained from the SRIM-2006 calculations. Since the S_E value is larger than the S_N value, the incident N^+ ions lose energy predominantly via inelastic collisions with the target electrons.

Table.1: Energy loss, projected range and energy straggling for 100keV N^+ ions

Ion energy	dE/dx(elec.) eV/ Å	dE/dx (nuc.) eV/ Å	Projected Range	Longitudinal straggling	Lateral straggling
100.0 0keV	1.448E+01	3.537E+00	5346 Å	1192 Å	1092 Å

3. Results & Discussions

3.1 Powder X-ray Diffraction

The pure and irradiated single crystal of semi-organic LAP were analyzed by adopting Bruker D-8 Advance X-ray powder diffractometer using CuKα radiation of wavelength 1.54 Å at a scan speed of 1^0 /sec. The recorded patterns are shown in Fig.2. The observed peaks were analyzed with POWDERX software and the observed lattice dimensions of pure and irradiated LAP acid are shown in Table.2, which is in good agreement with the reported single crystal XRD data. From the XRD pattern, we found that relative intensity of peak is decreasing and width of the peaks increases on irradiation which indicate that crystallinity of the irradiated samples is decreasing with irradiation, which may be due to production of point/clusters defects along the ion trajectory [12]. It is clear that the lattice strain in crystal increases due irradiation. Hence, it can be concluded that the strain developed due to the created defects is responsible for the modification of different properties of LAP crystals. From the analysis, we observed that there is no change in the phase structure of the irradiated samples, but there are changes in the lattice parameters (Table.2).

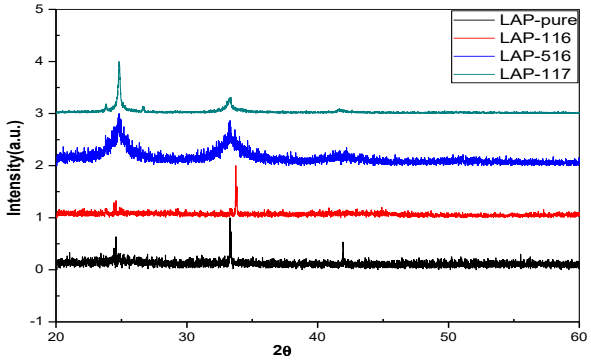

Fig.2: Powder X-ray diffraction pattern of pure and irradiated single crystal

Table.2: The lattice parameters of pure and irradiated single crystal of LAP

Sample Name	a	b	c
LAP-pure	10.8698	7.8451	7.2983
LAP -1x10^{16}	10.8713	7.9211	7.3018
LAP -5x10^{16}	10.8409	7.9461	7.3286
LAP -1x10^{17}	10.8506	7.9201	7.3059

3.2 FTIR Analysis

The different functional groups of pure and irradiated LAP were identified by FTIR studies in the range 4000-400 cm^{-1}. The band vibrations of PO_4 is tentatively assigned at

wave number 526 cm^{-1} in the IR spectrum and OH out of plane deformation is observed at 611.4cm^{-1}. The N-H wagging (out of plane bending) of the compound are identified at peaks with wavenumber of 690.6 cm^{-1}. The rocking vibration of NH_2 is observed at 775.4 cm^{-1}. The P-OH stretching is observed at 873.75 and 948.9 cm^{-1} in the IR spectrum. A band at 1149.6 cm^{-1}, 1195.9 cm^{-1}, may be due to C-N stretching. The C-H bending vibrations are identified at 1417 cm^{-1}. The band at 1660.7 and 1670.4 cm^{-1} are observed due to stretching vibrations of COO^-. The band at 2343.5 cm^{-1} and 1924.9 cm^{-1} due to hydrogen bonding interaction in compound. The band at 2943.7 cm^{-1} is due to asymmetric stretching vibrations of δ (CH_2). The band at 3161.3 cm^{-1} is observed at NH_3^+ asymmetric stretching. The sharp and intense band is observed at 3325.8 cm^{-1} may be due to N-H stretching vibration and the band at 3425.6 cm^{-1} are the evident of ν(OH)H_2O vibrations. NH_2 stretching vibration is observed at 3732 and 3714 cm^{-1}. The FTIR spectrum of irradiated LAP shown in Fig.3 is closely similar to that of pure compound. Hence, we can say that there is no change in the chemical nature of L-Arginine Phosphate monohydrate due to irradiation and irradiation on the sample might give energy to dislocate molecules in the lattice which may in turn weakens the intermolecular bonding. Hence it can be concluded that there is no change in functional group for grown as well as irradiated crystals.

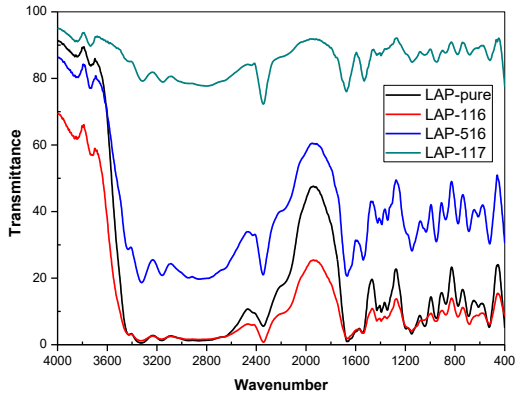

Fig.3: FTIR spectrum of pure and irradiated single crystal

3.3 UV-Vis-NIR analysis:

The UV-Vis-NIR analysis was carried out between 200 to 1100 nm using SHIMADZU (model-1601) UV-Visible-NIR spectrophotometer. The recorded UV-absorption spectrum is shown in Fig.4. From these measurements, we found that the cut-off wavelength are 321nm, 264nm, 250 and 247nm for pure and irradiated L-Arginine Phosphate single crystal at fluence $1x10^{16}$, $5x10^{16}$, $1x10^{17}$ respectively. It is noted that there is no significant absorption in the entire visible region, which enables it to be a potential candidate for optoelectronic applications. The cut off wavelength was found to decrease with increase in fluence of ions which indicate that band gap of crystal is increasing with increasing dose. The change in band gap may be due to structural changes which have been created by N^+ ions. The absorption is decreased with increase of ion fluences which may be due to formation of defect centre which forms scattering of light within the sample [13].

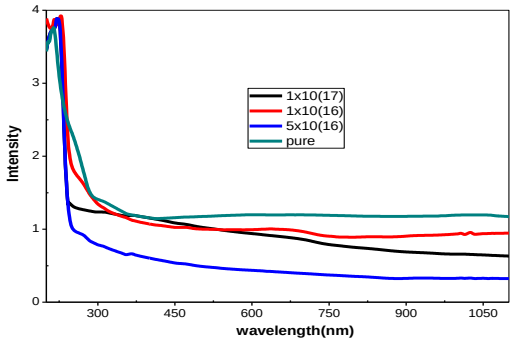

Fig.4: Plot of Absorbance vs. wavelength (nm) for pure and irradiated LAP single crystal

3.4 Photoluminescence Analysis

Photoluminescence (PL) spectroscopy is the standard technique for characterizing defects, vacancies and other imperfections existing in the single crystal. Emission spectrum of pure and irradiated LAP single crystals was recorded at the excitation wavelength of 261 nm using a Perkin-Elmer luminescence spectrometer (model: LS-55) at room temperature as shown in Fig.5. The pure and irradiated LAP single crystals exhibit a high intensity PL emission at 652 nm respectively. The absorption leads to a strong emission in the red region. From the graph, we observed that the PL intensity is affected by defects created by N^+ ions. Initially, a strong PL intensity indicates dominant radiative transitions. The observed PL spectra of pure and irradiated samples do not show any shift in the band position. This observation suggests the existence of states, which remain unaffected by irradiation. The peak intensity has decreased when compared to that of the pure sample. The PL intensity is sensitive to the damage created by low energy N^+ ions. With increase of fluences, the sample becomes rich with defects, which affect the radiative transitions. Thus, due to the excessive defects, the radiative transition rate decreases, resulting a decrease of the integrated PL intensity from the LAP sample with increase of fluence [14]. The decrease in PL intensity may be recognised to lattice deformation produced by displacement of cations in the irradiated region.

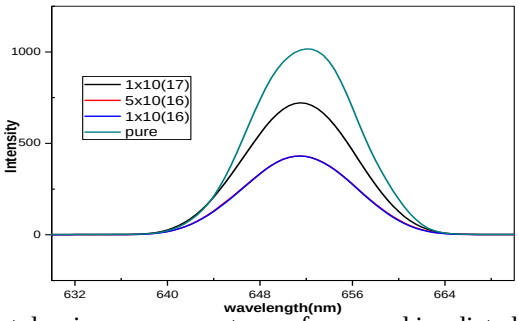

Fig.5: Photoluminescence spectrum of pure and irradiated single crystal of LAP.

3.5 Hardness Measurement

The Vickers micro hardness studies were carried out using a Vickers hardness (Make: Metatech, Pune) tester equipped with a diamond square indenter. The Vickers micro indentation hardness of pure and irradiated semi-organic LAP single crystals were investigated on crystallographic plane at indentation test loads ranging from 5 to 75 gram and time of indentation was kept 10 sec. The average value of the diagonal lengths of indentation mark was used to calculate the hardness of the sample. The hardness of the crystals is calculated using the relation [15]

$$H_v = \frac{1.854 * P}{d^2} (kg/mm^2)$$

where H_v is the Vickers hardness number, P is the indentation load in kg and d is the diagonal length of the indentation in mm. The calculated hardness values for LAP single crystals are plotted in Fig.6 and it is observed that initially the hardness value increases nonlinearly with load. The nonlinear variation may be due to imperfections like interstitials defects, impurities, vacancies, dislocations, low angle grain boundaries etc. It is also observed that hardness decreased with increase of N^+ ions fluence, which may be recognized due to high porosity. According to the Hays – Kendall approach, load dependent hardness is given by [16]

$$P = W + A.d^2$$

Where W is the minimum load to initiate plastic deformation and A is a load independent constant. The estimated values of W and A which were calculated from the plots drawn between P and d^2 (Fig.6a), where W is the intercept along the load axis and A is the slope. The corrected hardness H_0 for these crystals has been estimated using the relation, H_0 = 1854 A. The W and Ho values for pure, irradiated single crystals are given in Table.3 respectively. The relationship between load P and size of the indentation is given by Meyer's law [17] as, $P = kd^n$, Where P is the load applied, d is the diagonal length of impression, k is a constant of material and n is

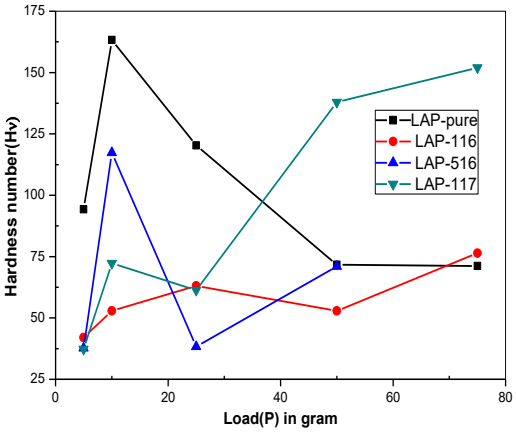

Fig.6: Variation in the Vickers hardness H_v with load P (grams).

Meyer's index. The value of 'n'(shown in Table.3) is estimated from the slope of ln P vs. ln d plot which is shown in the Fig.6b. Onitsch and Hanneman [18] had shown that the value of n comes out to be 1–1.6 for hard materials and more than 1.6 for soft ones. From this analysis, we found that the present crystal belongs to the category of soft material.

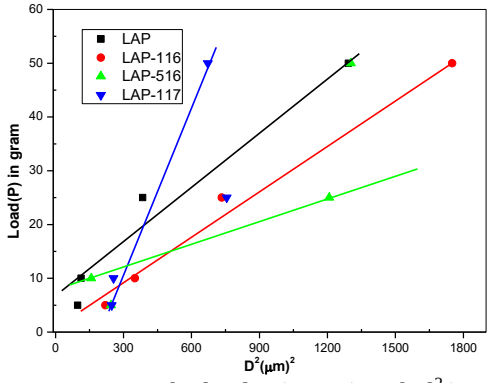

Fig.6a: Variation in the load P (grams) with d^2(mm^2).

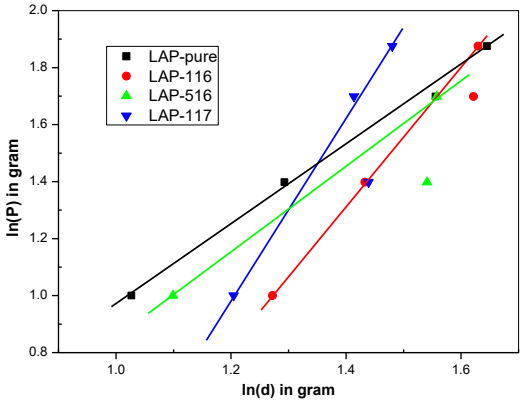

Fig.6b: Variation in the ln(P) with ln(d).

3.6 Surface Studies

The Micrograph patterns of the pure and irradiated LAP singles have been recorded with help of optical microscope in transmission mode. In this mode, Polarisor and analyser have crossed positions at 45^0 angle. The recorded patterns of the pure and irradiated single crystal are given in Fig.7. From the figure, we analysed that grown single crystal has uniform surface having pits. The surface of the irradiated samples is having non-uniform defects and the surface defects are increased with the increase of ions. As the ions fluence is increased, surface became more and more amorphous. Its crystalline nature is decreased with increased of the ions fluence.

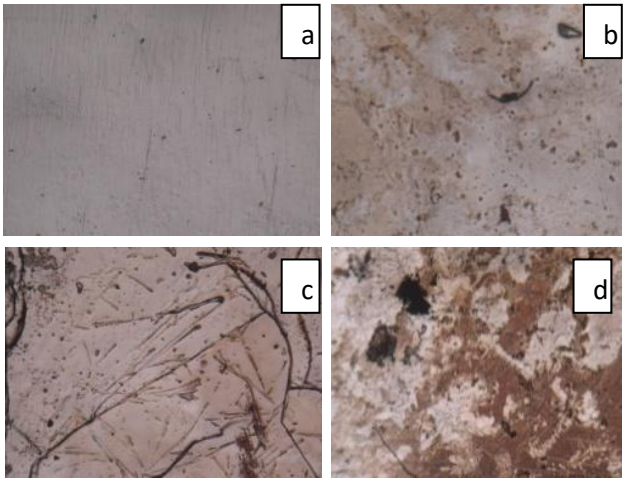

Fig.7: Micrograph of pure LAP and irradiated single crystals (a:pure,b:1x10(16)c: 5x10(16,d: 1x10(17).

4 Conclusion

The grown good quality single crystal of LAP was subjected to irradiation at different ions fluences. The lattice parameter values were determined from Powder X-ray diffraction and found that the compound crystallizes in monoclinic crystal system. The presence of various functional groups was identified from FTIR spectroscopic analyses. The UV-Vis and PL studies shows that there is no absorption in the entire visible region and band gap of material increase with increase of ion dose. From the Vickers hardness analysis we found that the meyer index (n) of the crystal is increasing with irradiation, sample is becoming more soft after irradiation. Micrograph studies of the pure and irradiated single crystal shows that roughness of the surface is increased with increased of the ion fluencies. Surface is becoming more and more amorphous with increase of the ion dose.

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