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Crystalline perfection and optical studies of L-Histidinium dihydrogen phosphate orthophosphoric acid (LHDP) single crystals

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ABSTRACT

Single crystals of L-Histidinium dihydrogenphosphate orthophosphoric acid (LHDP) were grown by slow evaporation solution growth technique. The grown crystals were confirmed by single crystal X-ray diffraction techniques. The HRXRD rocking curve measurements revealed the crystalline perfection of grown crystal and the absence of structural grain boundaries. The lower optical cut-off wavelength for this crystal was observed at 240 nm. The third order nonlinear refractive index (n_2), nonlinear absorption coefficient (β) and susceptibility ($\chi^{(3)}$) were calculated by Z-scan studies using Nd: YAG laser as a source. The single shot laser damage threshold of grown crystal was measured to be 6.286 GW/cm^2 using Nd: YAG laser.

1. Introduction

Nonlinear optical (NLO) materials are playing a key role in optical fields such as laser frequency conversion and optical parametric oscillators [1]. Organic NLO crystals had more attention because of the low cost and flexibility of molecular design, which we need for applications with using suitable donor and acceptor. Organic crystals are having some special properties of large optical nonlinearity and low cut-off wavelengths in UV region, therefore the organic NLO crystals are required for use in optical devices [2]. L-Histidine ($C_6H_9N_3O_2$) is one of the basic amino acids and attracting researchers in the field of nonlinear optics, as it acts as a proton donor, proton acceptor and nucleophilic reagent. It has a five membered imidazole ring attached to alanine [3]. Generally organic materials contain donor and acceptor groups positioned at either end of a suitable conjugation path. Extension of benzene derivatives has permitted an increase in the number of π electrons as well as their delocalization length, so as to lead to remarkable enhancement in hyperpolarizability [4]. The large π delocalization length has been recognized as a factor leading to large third order nonlinearity [5].

In the present investigation, we discuss about the optical properties and crystalline perfection of L-histidinium orthophosphate (LHDP) has been reported.

2. Experimental

The analytical grade of L-histidine and ortho phosphoric acid were taken in 1:2 amount of material was dissolved in deionized water with the resistivity of 18.2 MΩ cm at room temperature. The reaction scheme, morphology, solubility of grown crystals had been reported already [6]. Photograph of as grown LHDP crystal is shown in Fig. 1.

2.1. Single crystal X-ray diffraction

The grown LHDP single crystals have been subjected to various characterization studies. The Bruker kappa APEXII single crystal X-ray diffractometer, using Mo Kα (λ = 0.71073 Å) was used to estimate the cell parameters of LHDP crystal. From the single crystal X ray diffraction data, it is observed that the crystal belongs to monoclinic system with space group P21 and lattice parameter values as a = 8.8051 (07) Å, b = 8.722(8) Å, c = 9.36(2) Å and $\alpha = \beta = 90°$ β = 111.33(2)°. The unit cell parameters and space group are in good agreement with the reported values [7].

2.2. HRXRD studies

A PANalytical X'Pert PRO MRD high-resolution XRD system, with CuKα1 radiation, was employed to assess the crystalline perfection of grown crystal. The rocking curves of the crystals for

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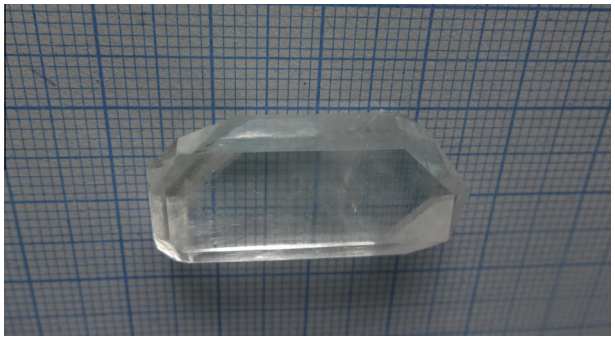

Fig. 1. Photograph of as grown LHDP crystal.

the diffraction planes were recorded in symmetrical Bragg geometry using the natural facets by performing the ω scan [8] with double-axis geometry. The monochromated X-ray beam incident on the specimen was obtained using a high-resolution four-bounce Ge (2 2 0) monochromator. The diffracted beam from the specimen was detected using a scintillation detector without using any analyzer at the receiving stage (i.e. before the detector) to get all the possible information like the individual peaks from structural grain boundaries, scattered intensity from the dislocations and other defects from the specimen crystal.

Fig. 2 shows the high-resolution X-ray diffraction curve (DC) recorded for a typical AK1 specimen crystal in symmetrical Bragg geometry by employing the MRD X-ray diffractometer described above with Cu $K\alpha_1$ radiation. As seen in the figure, the curve is not having a single diffraction peak. The solid line, which follows well with the experimental points (filled circles), is the convoluted curve of two peaks using the Lorentzian fit. The additional peak with very low peak intensity depicts the structural grain boundary. According to our earlier convention [9], depending upon the tilt angle i.e. the misorientation angle (α) of the boundary with respect to the two adjacent crystalline regions on both sides of the boundary, the observed structural boundary may be named as low angle grain boundary ($\alpha > 1$ arc min but less than a deg). The tilt angle of the observed structural grain boundary is 440 arc s (equivalent to 7.33 arc min) from the main crystalline block. The FWHM (full width at half maximum) of the main crystal block is 52 arc sec which shows that crystalline perfection is reasonably good [10]. The low angle boundary with very low peak intensity reveals that the entrapped impurities or solvent molecules during the growth process are responsible for the formation of such grain boundaries due to segregation of point defects through the self-generated strains [11]. It may be mentioned here that such a low angle boundary could be detected with well-resolved peak in the diffraction curve only because of the high-resolution of the diffractometer with four bounce monochromator. The influence of such defects may not influence much on the NLO properties. However, a quantitative analysis of such unavoidable defects is of great importance, particularly in case of phase matching applications [12].

2.2.1. Uv–Vis–NIR studies

UV–Vis–NIR transmittance spectrum of LHDP was recorded using 'Perkin Elmer UV' spectrophotometer in the wavelength range from 200 to 1100 nm and shown in Fig. 3. For optical applications, the material considered must be transparent in the wavelength region of interest. A sample of thickness 1.5 mm is used for the measurements. These measurements were carried out without any antireflection coatings. The lower cut off wavelength of LHDP is around 240 nm and it has sufficient transmittance in the entire visible and NIR regions. The absence of absorption in the region

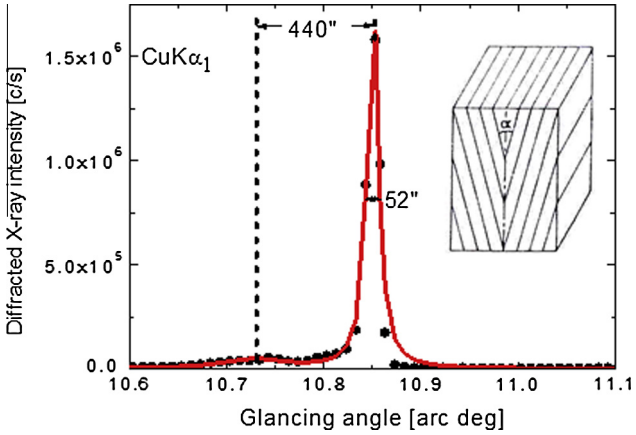

Fig. 2. Diffraction curve recorded for a typical LHDP single crystal.

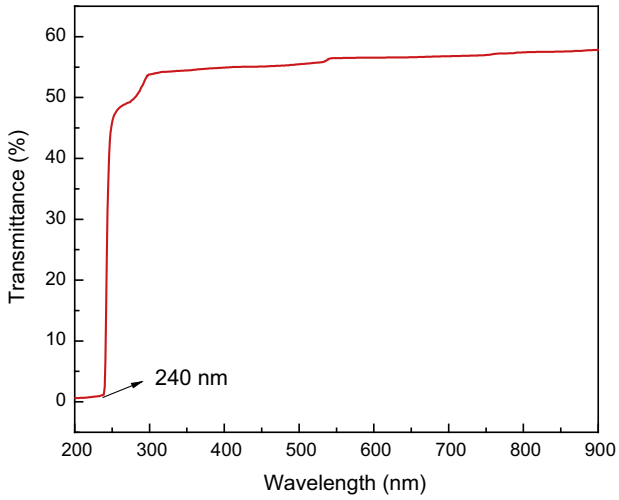

Fig. 3. Transmittance spectrum of LHDP single crystal.

between 240 and 900 nm shows that the crystal can be used for optical window applications.

2.3. Fluorescence studies

Fluorescence analysis provides relatively direct information about the physical properties of materials at the molecular level [13]. The fluorescence measurements were carried out on a Jobin Yvon–Spex Spectrofluorometer (Fluorolog version – 3; Model FL3-11. The slit width was 2 nm. The fluorescence emission was recorded by exciting the crystal with a wavelength 250 nm and the resultant emission spectrum is shown in Fig. 4.

The Z-scan method is a standard technique for the accurate measurement of intensity dependent nonlinear susceptibilities, nonlinear refractive index (NLR) n_2 and the nonlinear absorption coefficient (NLA) β. Generally typical Z-scan data with fully open aperture is insensitive to nonlinear refraction. Therefore, the data are expected to be symmetric with respect to focus. The maximum transmittance at the focus ($Z = 0$) reveals the saturation of absorption at high intensity. For materials with multi-photon absorption, there is a minimum transmittance in focus (valley) and for saturable absorber samples there is maximum transmittance in the focus (peak). Saturation of absorption enhances the peak and suppresses the valley, while saturation produces the opposite effect [13,14]. The peak followed by a valley transmittance which is the