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Bulk crystals of L-Histidinium dihydrogen phosphate orthophosphoric acid grown by Sankaranarayanan–Ramasamy method

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ABSTRACT

L-Histidinium dihydrogen phosphate orthophosphoric acid (LHDP) crystal of length 80 mm long and 20 mm diameter has been grown from aqueous solution along *c*-axis using Sankaranarayanan–Ramasamy method. The unit cell parameters were confirmed by single crystal X-ray diffraction analysis and it belongs to orthorhombic system. The UV–vis–NIR spectrum showed that the grown crystal is transparent in the entire visible region. The lower optical cut-off wavelength for this crystal was observed at 240 nm. Fluorescence studies were carried out in range of 200–700 nm. SHG efficiency was analyzed using Kurtz–Perry powder technique.

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1. Introduction

The rapid growing advancement of optical fiber communication systems has enthused the explore for highly nonlinear materials proficient of high-speed and competent processing of optical signals [1,2]. 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 The growth of optically good quality, large size SHG crystals with orientation control is required for SHG and Photonic applications [3–5]. The Sankaranarayanan–Ramasamy (SR) method is suitable to control the orientation during bulk crystal growth from solution. The crystals grown by unidirectional solution growth (SR) method boast low dielectric loss, enhanced mechanical stability and optical transparency and good crystalline perfection [6–8] compared to conservative solution grown crystals. Hence, we spotlight the foremost instant on the growth of bulk size single crystals of the title compound by SR method in the present swat.

2. Experimental

The analytical grade of L-histidine and orthophosphoric acid were taken in 1:2 amount of material was dissolved in deionized water with the resistivity of 18.2 M Ω cm at room temperature. The reaction scheme, morphology, solubility of grown crystals had been reported already [9]. The grown LHDP crystals were harvested when they attained an optimal size and shape. The grown crystals are optically transparent, non-hygroscopic and are shown in Fig. 1(a).

The SR method was employed using controllable ring heater, transparent glass tubes made by borosilicate and seed mounting pad. Two ring heaters are positioned in the top and bottom of the ampoule. Saturated solution of LHDP was taken for the SR method. The seed crystals collected from the conventional slow solvent evaporation technique were used for the unidirectional growth [9]. A suitable seed crystal cut along *c* axis with size of $5 \times 5 \times 3$ mm^3 was selected for single crystal growth. The ampoule was carefully designed to avoid growth of other faces. The seed crystal was mounted in the 18 mm diameter and 300 mm length ampoule. The ampoule was filled with saturated solution of LHDP The temperature of the top and bottom portion was set at 38 °C and 33 °C respectively. The temperature gradient creates a concentration gradient along the growth ampoule, having a maximum super saturation at the bottom of the ampoule and a minimum at the top of the ampoule. The growth rate of 2 mm per day was found in optimized condition. The grown crystal is shown in the Fig. 1(b).

3. Single crystal x-ray diffraction

The Bruker kappa APEXII single crystal X-ray diffractometer, using MoKα (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 $P2_1$ and lattice parameter values as a=8.8051 (07) Å, b=8.722(8) Å, c=9.36(2) Å and α=β=90 β=111.33 2 . The

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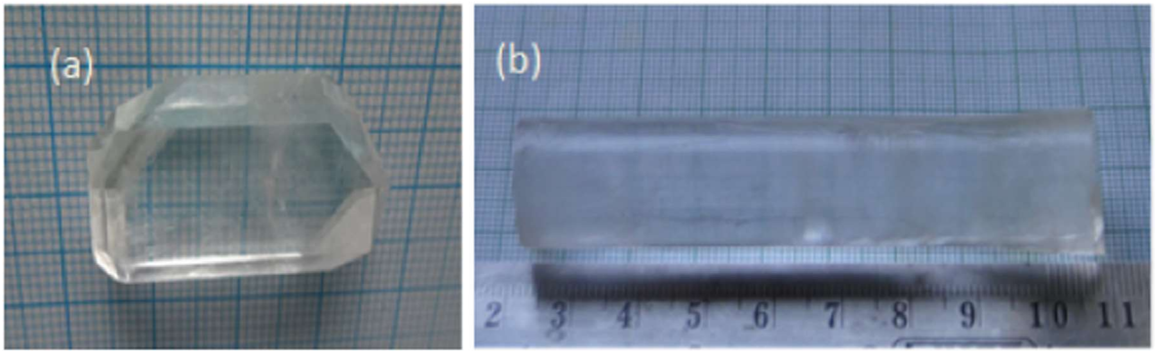

Fig. 1. (a). Conventional grown LHDP crystal (b) Photograph of SR grown AAP single crystal along *c*-axis.

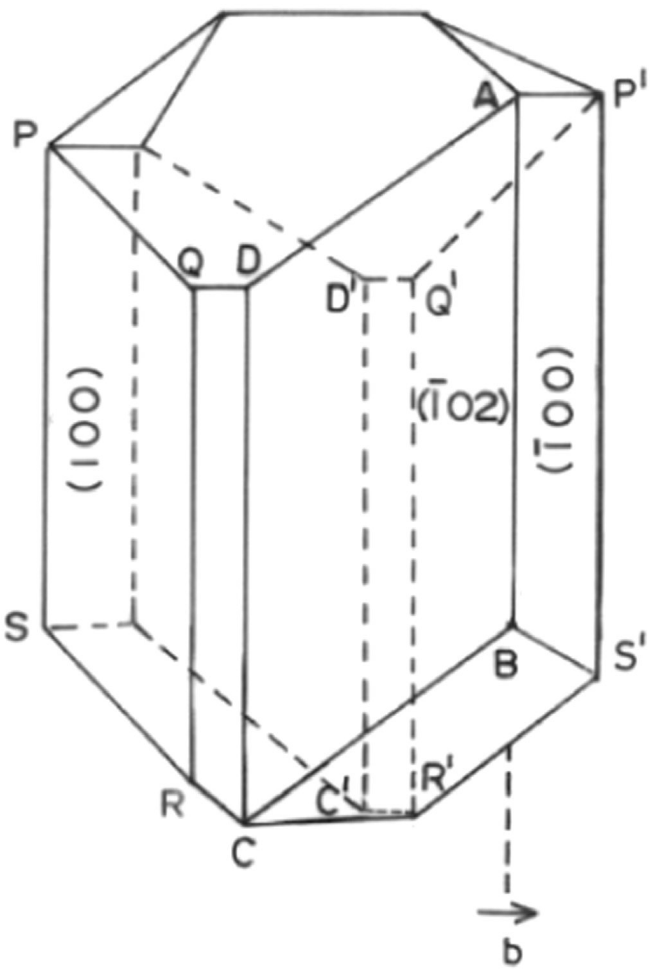

Fig. 2. Morphology of conventional grown LHDP crystal.

unit cell parameters and space group are in good agreement with the reported values [10]. Morphology of the conventional method (Fig. 2) grown crystal illustrates that the crystal is polyhedron with 12 well developed faces. Faces ABCD and A′B′C′D′ are (102) and (102) planes, which form the most prominent faces for the crystal Faces PQRS and P′Q′R′S′ are 001 planes.

4. 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. 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 anti-reflection coatings. The lower cut off wavelength of LHDP is around 240 nm and it have sufficient transmittance in the entire visible and NIR regions. The recorded transmission spectra of conventional and SR method grown LHDP single crystals are shown in the Fig. 3. The LHDP crystal grown by the Sankaranarayanan–Ramasamy method has 8% higher transparency. This is because the unidirectional grown crystals may have lesser defects compared to conventional solution grown crystals, which in turn decreases the scattering centers in the crystals and increases the output intensity [11].

5. Fluorescence studies

Fluorescence analysis provides relatively direct information about the physical properties of materials at the molecular level [12]. The fluorescence measurements were carried out on a Jobin Yvon-Spex Spectrofluorometer Fluor log 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 emission peak is observed at 375 nm for both the conventional and SR method grown crystals. But intensity of the peak depends upon the crystallinity. Hence from the PL spectrum changes it is clear that the SR grown crystal possesses high crystallinity compared to conventional solution grown LHDP crystal.

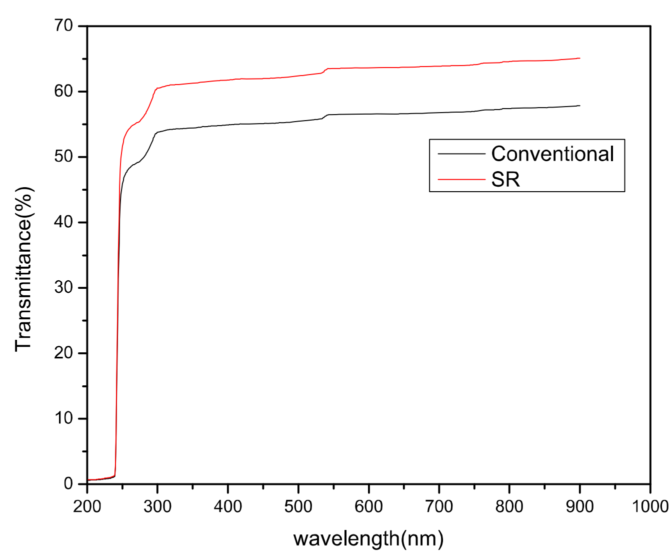

Fig. 3. Transmittance spectrum of conventional and SR grown LHDP single crystal.

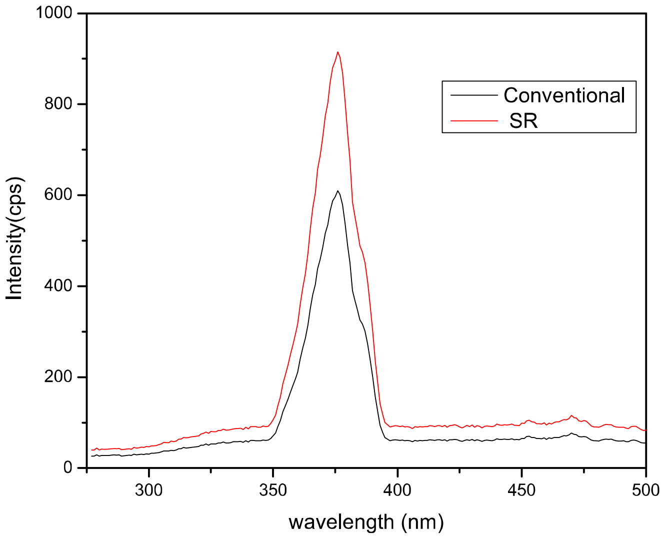

Fig. 4. Emission spectrum of LHDP.

6. Laser damage threshold

A nonlinear optical crystal's ability to withstand very high power densities of laser energy is an important factor in various applications particularly that involves Q-switched lasers. Hence, the determination of the laser damage threshold for crystal is essential as this would decide the upper limit of the laser power density to which a crystal could be exposed. A linearly polarized second harmonic output 532 nm of a Q switch Nd: YAG laser was used for the laser damage threshold measurement. The laser was operated at a repetition rate of 10 Hz, pulse duration 7 ns and beam diameter 8 mm in TEM00 Gaussian mode. The laser pulses were focused onto LHDP sample by a 90 mm focal length lens, a 1 mm thick LHDP sample was mounted on a computer-controlled motorized X–Y translation stage. The occurrence of laser damage was characterized by audible cracking and damage was confirmed at test site by microscope. The measurement was made in different sites on the crystal surface for single shot irrespective of whether damage had occurred on the surface or not [13,14] The surface damage threshold of the crystal was calculated using the expression, $Pd=E/\tau\ \pi r\ 2$ where E is the input energy mJ, τ is the pulse width ns and r is the radius of the spot mm. Laser damage threshold ~6.286 GW/cm^2 (conventional) and 7.034 GW/cm^2 (SR). SR grew LHDP to possess higher laser stability than conventional grown LHDP.

7. SHG studies

NLO efficiency of LHDP crystal sample was measured by Kurtz and Perry technique [15]. A Q-switched Nd: YAG laser was used as light source. A laser beam of fundamental wavelength 1064 nm with 8 ns pulse width, and 10 Hz pulse rate was made to fall normally on the sample cell. KDP crystal was powdered and used as reference material in the SHG measurement. The second harmonic signal of 192 mV was obtained for LHDP while KDP gave SHG signal of 45 mV for the same input beam energy. Thus the relative SHG efficiency of LHDP is found to be 4.26 times higher than that of KDP.

8. Conclusion

Optical quality single crystal of LHDP was grown using slow evaporation solution growth technique and along *c*-axis using Sankaranarayanan–Ramasamy method. The cell parameter of LHDP was determined by single crystal X-ray diffraction analysis. Optical transmission studies showed that LHDP was optically transparent in the entire visible region. The LHDP crystal grown by the Sankaranarayanan–Ramasamy method has 8% higher transparency. PL studies show emission at 375 nm for both conventional solution grown crystal and SR grown single crystal Single shot surface laser damage threshold is 7.034 GW/cm^2 for at 532 nm laser radiation. Investigations showed that the Sankaranarayanan–Ramasamy method grown LHDP crystal has better perfection than conventional method grown LHDP crystal. The SHG efficiency of LHDP is found to be 4.26 times that of KDP crystal.

References

[1] P.N. Prasad, D. Williams, Introduction to Nonlinear Optical Effects in Organic Molecules and Polymers, Wiley, New York, 1991.
[2] S. John, T. Quang, Phys. Rev. A 54 (1996) 4479–4488.
[3] D.S. Chemla, J. Jyss, Nonlinear Optical Properties of Organic Molecules and Crystals, Academic Press, NewYork, 1987.
[4] H.A. Petrosyan, H.A. Karapetyan, A.M. Petrosyan, J. Mol. Struct. 794 (2006) 160–167.
[5] P. Srinivasan, T. Kanagasekaran, G. Bhagavannarayana, R. Gopalakrishnan, P. Ramasamy, Cryst. Growth Des. 6 (7) (2006) 1663–1670.
[6] P.V. Dhanaraj, N.P. Rajesh, J. Kalyana Sundar, S. Natarajan, G. Vinitha, Mater. Chem. Phys. 129 (2011) 457–463.
[7] A. Arunkumar, P. Ramasamy, J. Cryst. Growth (2013).
[8] K. Sankaranarayanan, P. Ramasamy, J. Cryst. Growth 280 (2005) 467.
[9] R. Ittyachan, P. Sagayaraj, J. Cryst. Growth 249 (2003) 553–556.
[10] R.H. Blessing, Acta Cryst. B42 (1986) 613–621.
[11] V. Vasudevan, et al., Physica B 406 (2011) 936–994.
[12] Bernard Valeur, Molecular Fluorescence: Principles and Applications, Wiley-VCH Verlag GmbH, New York, 2001.
[13] N.L. Boling, G. Dub, Appl. Phys. Lett. 23 (1973) 658–660.
[14] G.C. Bhar, A.K. Chaudhury, P. Kumbhakar, Appl. Surf. Sci. 161 (2000) 155–162.
[15] S.K. Kurtz, T.T. Perry, J. Appl. Phys. 39 (1968) 3798–3813.

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