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Growth and Characterization of New Semi-Organic L-Asparagine Potassium Di-Hydrogen Phosphate Crystals

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The studies on the growth and characterization of a new semi-organic non-linear optical crystal, L-asparagine potassium dihydrogen phosphate have been successfully carried out by slow evaporation technique using deionized water as a solvent. The grown crystal is characterized by powder X-ray diffraction analysis and FT-IR analysis. The results of X-ray diffraction analysis showed that it possess orthogonal structure having lattice parameters a = 5.582 Å, b = 9.812 Å and c = 11.796 Å, $\alpha = \beta = \gamma = 90°$ and V = 514 Å^3. The fourier transform infrared spectroscopy of L-asparagine potassium dihydrogen phosphate crystal were recorded between wave-number 4000 to 400 cm^{-1} showed very weak bands appearing around 1232 and 1147 cm^{-1} are due to P–O–H stretching and bending. The observed broad intense band in 3385-3119 cm^{-1} region is assigned to NH stretch of NH_2 vibration of L-asparagine potassium dihydrogen phosphate molecule. The CH_2 vibration of the amino acid shows its peak at 2945 cm^{-1}. The combination band observed at 2149 cm^{-1} is due to asymmetric NH_3^+ vibration at 1643 cm^{-1} and NH_2^+ tensional oscillation at 512 cm^{-1} and optical transmission spectral analysis. The lower cut off wavelength of L-asparagine potassium dihydrogen phosphate crystal occurs at 198 nm and it reveals that the material has good optical transparency in the entire visible region. The results of hardness test showed that the presence of dopant has enhanced the mechanical strength of the L-asparagine potassium dihydrogen phosphate crystals and the second harmonic generation of L-asparagine potassium dihydrogen phosphate crystals was tested using Kurtz and Perry method also showed good results.

Keywords: Characterization, Slow evaporation technique, Non-linear optical material, Second harmonic generation.

INTRODUCTION

In recent years there is a growing interest in the non-linear optical (NLO) materials in view of their applications in opto-electronics and photonic devices[1]. Optical crystals with a high degree of perfection find wide spread applications in critical technology areas such as high power lasers, higher harmonic generation and also in the field of nuclear fusion[2]. Inorganic non-linear optical materials have large mechanical strength, thermal stability and good transmittance but modest optical non-linearity due to the lack of extended π electron dislocation[3,4]. Purely organic non-linear optical material have large non-linearity compared to inorganic material but low optical transparency, poor mechanical and thermal strength and low laser damage threshold. In spite of the importance the present research is focused on semi-organic non-linear optical material crystal in order to obtain superior non-linear optical crystal by combining the advantages of organic and inorganic materials. The semi-organic non-linear optical materials have been attracting much attention due to high non-linearity, chemical flexibility, high mechanical and thermal stability and good transmittance[5]. The search of new non-linear optical materials has been of great interest in the recent years because of their significant impact on laser technology, optical communication and optical data storage technology[6,7]. Over the past two decades, amino acid family crystals are gaining importance because of their higher second order non-linear optical efficiency. Considerable efforts have been made to combine amino acids with interesting organic and inorganic materials to produce outstanding materials like niobates and borates. Such types of materials have already been reported by many researchers[8-10]. In this view, a new semi-organic L-asparagine potassium dihydrogen phosphate crystals (LAKDP) material has been synthesized and bulk single crystals have been grown by slow evaporation solution growth technique. The grown single crystal has been subjected to different characterization analyses in order to know its suitability for device fabrication and the results are reported.

EXPERIMENTAL

Crystal growth: The title compound was synthesized by taking equimolar ratio of high pure L-asparagine potassium dihydrogen phosphate salt (E-Merck) and dissolved in deionized water. The concentrated solution was taken in a beaker and covered by a perforated cover for controlled evaporation. The good quality L-asparagine potassium dihydrogen phosphate crystal has been harvested after 25 days (Fig. 1).

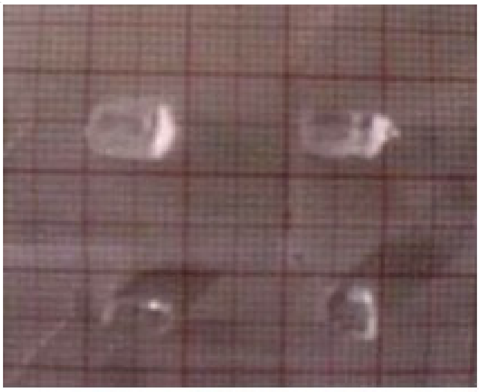

Fig. 1. Photograph of LAKDP crystal

RESULTS AND DISCUSSION

X-Ray diffraction analysis: The powder X-ray diffraction analysis has been carried out to confirm the crystallinity and to calculate the lattice parameters of the specimen. Finely crushed specimen of L-asparagine potassium dihydrogen phosphate was subjected to powder X-ray diffraction analysis. The sample was scanned over the range 10-80° with a scan rate of 2 °/min. The recorded X-ray pattern of LAKDP is shown in Fig. 2. The observed results indicates that LAKDP belongs to orthorhombic system belonging to space group P212121 with lattice parameters a = 5.582 Å, b = 9.812 Å and c = 11.796 Å, $\alpha = \beta = \gamma = 90°$ and V = 514 $Å^3$ and four molecules per unit cell which occupy general sites of C1 symmetry. This is compared with L-asparagine monohydrate[11-14].

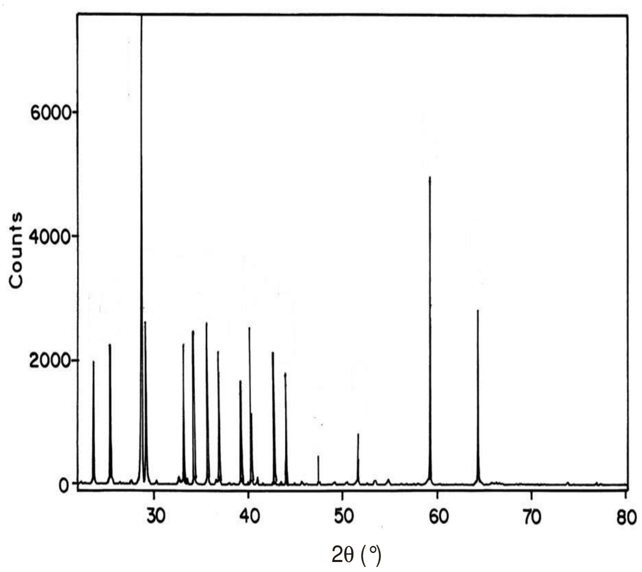

Fig. 2. Powder X-ray diffraction spectra of LAKDP crystal

Fourier transforms infrared analysis: The fourier transform infrared analysis is a technique in which almost all the functional groups in a molecule absorb characteristic frequencies. The FT-IR spectrum of LAKDP crystal has been recorded in the KBr phase in the frequency region of 4000-400 cm^{-1} using Perkin-Elmer 783 spectrometer. The recorded spectrum has been compared with the available review literature values[15,16]. The broad intense band in the higher energy region around 3385-3119 cm^{-1} is assigned to NH stretch of NH_2 vibration of LAKDP molecule[17]. The CH_2 vibration of the amino acid shows its peak at 2945 cm^{-1}. The combination band observed at 2149 cm^{-1} is due to combination of asymmetric NH_3^+ vibration at 1643 cm^{-1} and NH_2^+ tensional oscillation at 512 cm^{-1}. The C=O vibration of COO group occurs at 1679 cm^{-1} and the peaks at 1528 cm^{-1} and 1429 cm^{-1} are due to asymmetric and symmetric vibrations of COO^-. The peaks observed at 1643 and 1528 cm^{-1} due to NH_3^+ asymmetric, symmetric bends respectively. The CH_2 bends of amino acid are seen[18] at 1357 and 1429 cm^{-1}. The spectrum shows strong absorptions bands at 1232.42 and 1102.59 cm^{-1} which could be assigned to P=O stretching and P-O stretching mode of vibration. The O-H stretching modes have intense broad absorption band between 3500 and 2400 cm^{-1}. The absorption bands at 2526 and 2945 cm^{-1}, is assigned to O-H stretching vibrations. The PO_4^{3-} symmetric bending is at 541.73 cm^{-1} and P-O and $(PO_4)_3$ plane bending at 836.80 cm^{-1} and 672.50 cm^{-1}. The broad absorption bands appearing at 1232.42 cm^{-1}, 1147.68 cm^{-1} are assigned to P-O-H stretching vibrations.

Optical transmission spectral analysis: For studying optical transparency of the grown LAKDP crystals in the UV-visible-near infrared, an optical absorption spectrum was recorded in the wavelength range 200-1100 nm using Perkin-Elmer Lambda UV-visible-near infrared spectrometer. The obtained transmission spectrum is shown in Fig. 3. The transparent wave band of LAKDP crystal lies in the range of 300-900 nm. This is the advantage of using amino acids, where the absence of strongly conjugated bonds leads to higher optical transparency in the visible and UV spectral regions. The lower cutoff wavelength was observed at 200 nm, it enhances the usefulness of LAKDP in optoelectronic applications and it is

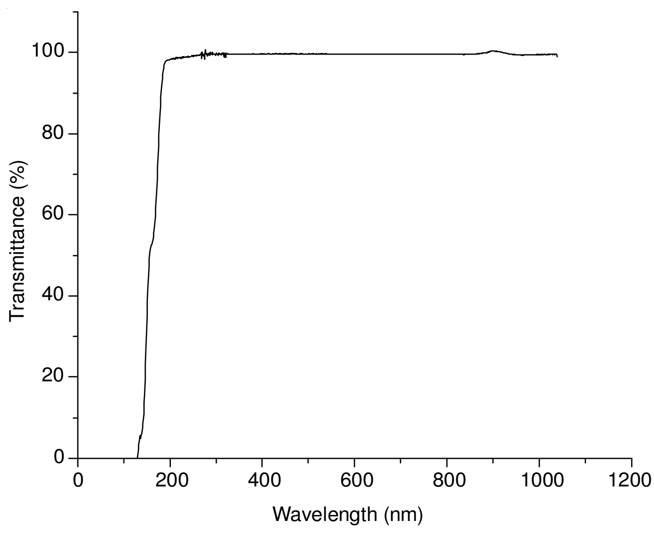

Fig. 3. UV-visible transmission spectra of LAKDP crystals

an essential parameter for non-linear optical applications[19]. The UV spectra reveals that the material has good optical transparency in the entire visible region. Therefore, the title compound can be used as a good non-linear optical material.

Vickers micro hardness study: Micro hardness is an important for good quality crystals along with good optical performance[20]. It can be used as a suitable measure for the plastic properties and strength of a material. A well polished L-asparagine potassium dihydrogen phosphate crystal was placed on the platform of vickers micro hardness tester and the loads of different magnitudes were applied over a fixed interval of time. The indentation time was kept (8 s) for all the loads. The hardness number was calculated using the relation Hv = (1.8544 × P) / (d2) kg/mm^2, where P is the applied load in kg and d is the diagonal length of the indentation impression in the micrometer. The vickers hardness number for the grown crystal is 75 kg/mm^2. Beyond the load of 50 g multiple cracking were developed in the crystal surface due to the release of internal stress generated locally by indentation (Fig. 4).

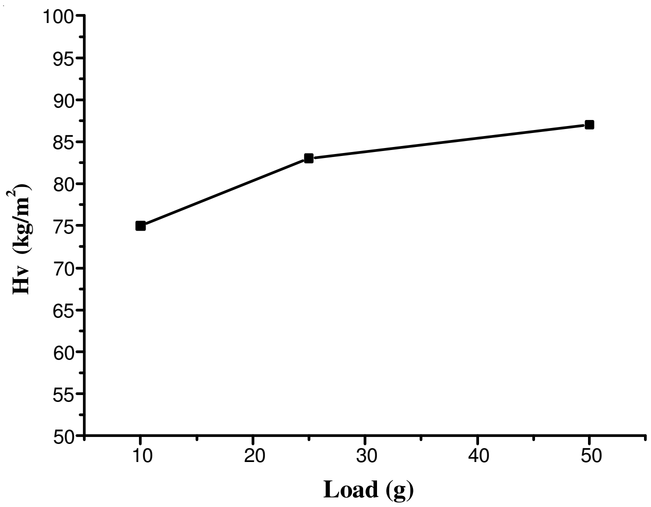

Fig. 4. Variation of micro hardness of LAKDP crystals with load

Powder second harmonic generation measurement: The second harmonic generation conversion efficiency of L-asparagine potassium dihydrogen phosphate was measured by Kurtz and Perry powder technique[21,22]. The crystal was grounded into a homogenous powder of particles and densely packed between two transparent glass slides. A Q-switched Nd:YAG laser emitting a fundamental wavelength of 1064 nm was allowed to strike on the sample cell normally. The grown crystals were crushed into a fine powder and then packed in a micro capillary of uniform bore and exposed to laser radiation. The 532 nm radiation was finally collected by the monochromater after separating the 1064 nm pump beam with an infrared blocking filter. Second harmonic radiation generated by the randomly oriented micro crystals was focused by the photomultiplier tube. The emission of green light property confirms the second harmonic generation property of the crystal.

Conclusion

The compound L-asparagine potassium dihydrogen phosphate (LAKDP) has been synthesized and the crystals were grown successfully using slow evaporation method. The Lattice parameter was determined using powder XRD method. Functional groups were analyzed using FT-IR analysis, which shows the mode of vibration of L-asparagine potassium dihydrogen phosphate crystal. The optical property of the grown crystal was studied by UV-visible-near infrared spectrometer and the lower cut off wavelength of the crystal was observed at 200 nm. The L-asparagine doped potassium dihydrogen phosphate is found to suppress the inclusions and improve the quality of crystal with higher transparency in the entire visible region. The experiment for hardness confirmed that the presence of dopant has enhanced the mechanical strength of the LAKDP crystals. The Kurtz-Perry powder technique confirmed that the crystal has high second harmonic generation efficiency and laser damage energy density.

REFERENCES

1. S. Masilamani, P. Ilayabarathi, P. Maadeswaran, J. Chandrasekaran and K. Tamilarasan, *Optik*, **123**, 1304 (2012).
2. P. Kumaresan, S. Moorthy Babu and P.M. Anbarasan, *Optic. Mater.*, **30**, 1361 (2008).
3. M. Amalanathan, I.H. Joe and V.K. Rastogi, *J. Mol. Struct.*, **985**, 48 (2011).
4. S. Ariponnammal, S. Radhika, R.S. Vennila and N.V. Jeya, *Cryst. Res. Technol.*, **40**, 786 (2005).
5. M. Jiang and Q. Fang, *Adv. Mater.*, **11**, 1147 (1999).
6. D. Eimerl, S. Velsko, L. Davis, F. Wang, G. Loiacono and G. Kennedy, *IEEE J. Quantum Electron*, **25**, 179 (1989).
7. L.N. Rashkovich and B.Y. Shekunov, *J. Cryst. Growth.*, **112**, 183 (1991).
8. M.D. Aggarwal, J. Choi, W.S. Wang, K. Bhat, R.B. Lal, A.D. Shields, B.G. Penn and D.O. Frazier, *J. Cryst. Growth*, **204**, 179 (1999).
9. D. Rajan Babu, D. Jayaraman, R. Mohan Kumar and R. Jayavel, *J. Cryst. Growth*, **245**, 121 (2002).
10. R. Ittyachan and P. Sagayaraj, *J. Cryst. Growth*, **249**, 557 (2003).
11. G. Bhagavannarayana and S.K. Kushwaha, *J. Appl. Cryst.*, **43**, 154 (2010).
12. M. Senthil Pandian and P. Ramasamy, *J. Cryst. Growth*, **312**, 413 (2010).
13. T. Balakrishnan and K. Ramamurthi, *Spectrochim. Acta A*, **68**, 360 (2007).
14. J.J. Verbist, M.S. Lehmann, T.F. Koetzle and W.C. Hamilton, *Acta Crystallogr. B*, **28**, 3006 (1972).
15. H.Q. Sun, D.R. Yuan, X.Q. Wang, X.F. Cheng, C.R. Gong, M. Zhou, H.Y. Xu, X.C. Wei, C.N. Luan, D.Y. Pan, Z.F. Li and X.Z. Shi, *Cryst. Res. Technol.*, **40**, 882 (2005).
16. P. Maadeswaran, S. Thirumalairajan and J. Chandrasekaran, *Optik*, **121**, 773 (2010).
17. S. Selvasekarapandian, K. Vivekanandan, P. Kolandaivel and T.K. Gundurao, *Cryst. Res. Technol.*, **32**, 299 (1997).
18. S. Balamurugan and P. Ramasamy, *Spectrochim. Acta A*, **71**, 1979 (2009).
19. J.T.J. Prakash and S. Kumararaman, *Mater. Lett.*, **62**, 4003 (2008).
20. B. Vengatesan, N. Kanniah and P. Ramasamy, *Mater. Sci. Eng.*, **104**, 245 (1988).
21. A. Senthil, R. Ramesh Babu, N. Balamurugan and P. Ramasamy, *J. Cryst. Growth*, **311**, 544 (2009).
22. S.K. Kurtz and T.T. Perry, *J. Appl. Phys.*, **39**, 3798 (1968).