PUBELESE PUBLISHER

JOAASR Journal of Advanced Applied Scientific Research

Synthesis, Growth and characterization of pure L-Asparagine and its based crystal: L-Asparagine admixtured with cadmium chloride using different solutions

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Abstract:

Pure L-Asparagine and L-Asparagine admixtured with cadmium chloride using de-ionised water as solvent of size of 19mm x 14mm x6mm and 6mm x 4mmx2mm were grown by slow evaporation technique. Structural confirmations of grown crystals were done by powder x-ray diffraction. The various absorption peaks were obtained from FTIR study. The grown crystals were optically transparent and cut off wavelengths were 220nm and 203 nm and corresponding energy gap values were 5.46 eV and 6.11eV respectively. From the mechanical results, it is noticed that the hardness number increases with the applied load and the value of hardening coefficients of the grown crystals were greater than 1.6. So the grown crystals belonged to the soft material category.

Key words: slow evaporation, PXRD, FTIR, UV-VIS, Micro hardness.

1. Introduction:

In the past few decades, there has been a growing interest in crystal growth process, particularly, in view of the increasing demand for materials for technological application [1-3].In recent years, there is a growing need for nonlinear optical (NLO)materials in view of their applications in opto-electronics and photonicdevices [4].In terms of nonlinear optical properties, organic compound posses more advantage as compared to their inorganic counter parts [5,6].The naturally occurring α-amino acids are ideal precursors for the synthesis of new materials for NLO applications in view of their chiral nature (expecting glycine)and ready availability. Although the simplest α-amino acid glycine is achiral, it is known to form several solids which crystallize in non-centrosymmetric space group. crystalline salts of amino acids have recently attracted considerable interest among researchers. Amino acids are interesting materials for NLO applications. The importance of amino acids in NLO applications is due to the fact that all the amino acids have chiral symmetry and crystallize in non centro –symmetric space group [7]. The presence of zwitter ions influence the physical and chemical properties of amino acids. The proten donor carboxyl acid (-coo) group donates its proton to acceptor amino ($-NH_2$) group. The neutral asparagines molecule exists as zwitterions, where the carboxyl group is dissociated and amino group is protonated. Thus L-Arginine, L-Histidine, L-Alanine and L-Asparagine have been exploited for the formation of salts with different organic/inorganic acids. The compounds of L-Asparagine have been much less explored. Several new complexes of amino acid L-Asparagine have been recently crystallized and their structural,optical and thermal properties have been investigated[8-12].The crystal structure of L-Asparagine mixed with nitric acid ratio 1:1 has already been reported[13].

2. Synthesis and Growth:

Analytical reagent (AR) grade samples L-Asparagine , cadmium chloride and distilled water were used for the preparation of L-Asparagine admixtured with cadmium choloride(LACC).LACC was synthesised by dissolving 2:1 ratio of L-Asparagine and cadmium chloride in double distilled water at 30^0C.small (seed)crystals were grown from saturated aqueous solution by the free slow evaporation technique at room temperature. Good quality crystals were selected for the growth of large single crystals. The pure L-asparagine and LACC crystal grown in the present study are found to be stable, colourless and transparent, Photograph of a grown crystals are shown in figs 1 and 2.

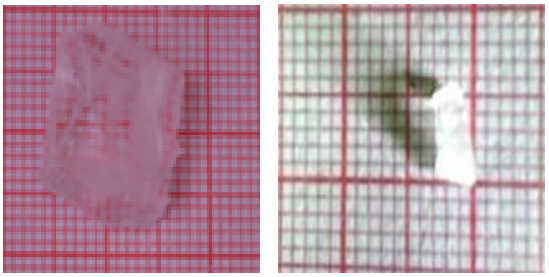


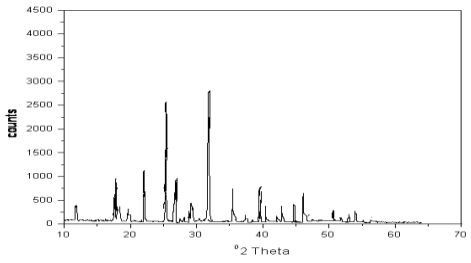
Fig. 1. Photograph of a) pure L-asparagine b)LACC crystal

3.Characterization:

The powder x-ray diffraction data recorded for as grown pure L-Asparagine based crystals were finely powdered and subjected to powder XRD anaiysis using X'PERT-PRO diffractometer system.The samples were examined with Cuk$_\alpha$ radiation (λ=1.54056A) in a 2Θ range of 10^0-80^0 at a scan rate of 2^0/min and in step size [2Θ].From the X-ray diffraction spectra, the 2Θ values were read directly and relative intensities of the diffraction peaks were estimated. In order to qualitatively analyse the presence of functional group in the grown crystals, the FTIR spectrum were recorded in the range 400-4000cm^{-1} using KBr pellet on SHIMADZU-FTIR-8400S spectrometer. The UV-Vis transmission of grown crystals were recorded between 190nm and 1200nm using perkin Elmer Lambda 35 UV-Vis spectrometer. The microhardness studies of pure L-Asparagine and based crystals were carried out by using a Leitz microhardness tester fitted with a dimond pyramidal indentor. The crystals were mounted properly on the base of the microscope and the selected faces were indented gently by loads varying from 25-100g for a period of 10s using Vickers diamond indenter attached to an optical microscope.

3.1 Powder XRD:

The powder XRD patterns of L-Asparagine and LACC samples are compared in Fig 2and 3.From the figures 2 and 3 the presence of sharp peaks confirms the good crystalline [14]nature of the grown crystals. However a slight variation in intensity is observed as a result of dopping .The most prominent peaks with maximum intensity of the XRD patterns of pure and doped specimens are quite different.



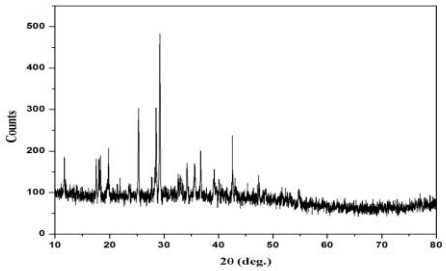


Fig. 2.PXRD pattern of pure L-asparagine Fig. 3. PXRD pattern of LACC

3.2 FTIR:

The recorded FTIR of L-Asparagine and based single crystals are shown in fig 4and5 the various observed peaks are assigned [15-18]. In the spectrum,O-H,NH_2 asymmetric and NH_3^+ symmetric stretching vibration modes are observed as a weak intensity broad absorption peaks are expected in 4000-3000cm^{-1}region**.** In 3000-1500cm^{-1}region,and they are assigned as CH_2 stretching at 2294 and 2298cm^{-1},NHstretching at 2001-2006cm^{-1},symmetric bending and deformation of NH_3^+ are obtained at 1640,1642,1527,and 1528cm^{-1} as medium and weak intensity bands respectively. While in 1500-1000cm^{-1} region, absorption peaks are observed and they are assigned as COO^-symmetric stretching at 1146,1147,1148,1429 and 1430cm^{-1},C-O stretching at 1232,1233,and 1402cm^{-1},CH_3 rocking at1072 and 1073 cm^{-1},CH bonding at 1357 and 1358cm^{-1},Wagging mode of (CH_2)at 1307 and 1308cm^{-1},COO^-bending at 1427cm^{-1},rocking mode of (NH^+_3) at 1103 and 1145cm^{-1},(8)NH_2rocking at1232cm^{-1} and (9)C-N stretching at 1074 cm^{-1}.In 1000-400cm^{-1} region ,C-C-N deformation vibration was observed at 562 and 559 cm^{-1},CH_2,H_2O,NO_2 and COO^-rocking modes are observed at 892,675,674,672,596,598,561 and 511cm^{-1}.Hence the presence of various functional groups were confirmed from the above band assignment.

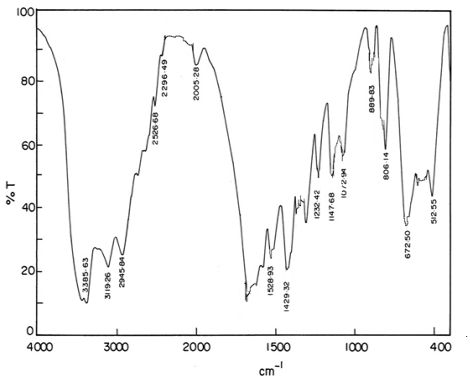


Fig. 4.FTIR spectrum of pure L-asparagine

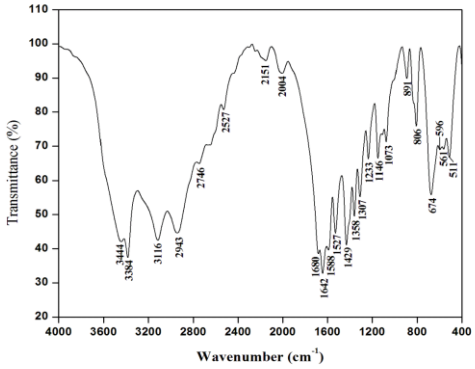
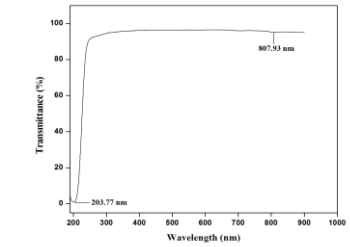


Fig.5. FTIR spectrum of LACC crystal

3.3.UV-Visible spectroscopy:

The recorded spectrum is shown in Figs 6 and 7. The transparent wave band of grown crystal lies in the range of 200-900 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 transparency was checked by carrying out UV-Visible studies for both pure and L-Asparagine based crystals. The cut-off wavelength values for pure and L-Asparagine based samples were found to be 220 and 203 nm corresponding energy gap values are 5.46 and 6.11 eV respectively.



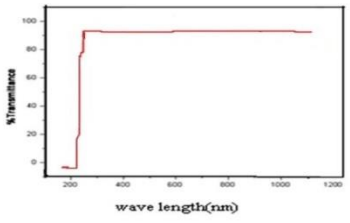


Fig. 6.UV-Vis spectrum of pure L-asparagine Fig. 7. UV-Vis spectrum of LACC crystal

3.4 . Microhardness:

The length of the two diagonals of diamond indenter was measured by a calibrated micrometer attached to the eyepiece of the microscope after unloading and the average was found out. For a particular load, at least three well defined indentations were considered and the average value (d) was measured. The Vickers hardness (H_v) numbers at different loads were calculated using the relation,

$$H_v=1.8544P/d^2 Kg\text{-}mm^{-2}$$

Where p is the applied load in kilogram and d is the average diagonal length of the indentation marks in millimetre and 1.8544 isa constant of a geometrical factor for the diamond pyramid.The Vickers microhardness number as a function of the applied test load shown in figure 8.

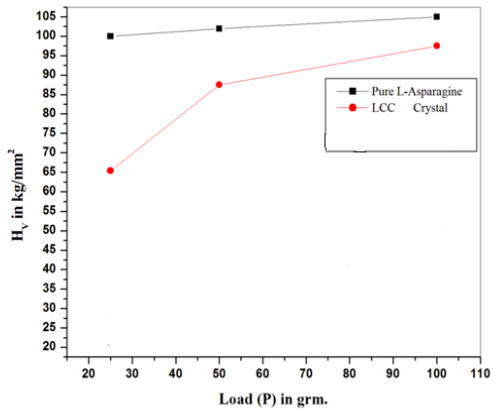
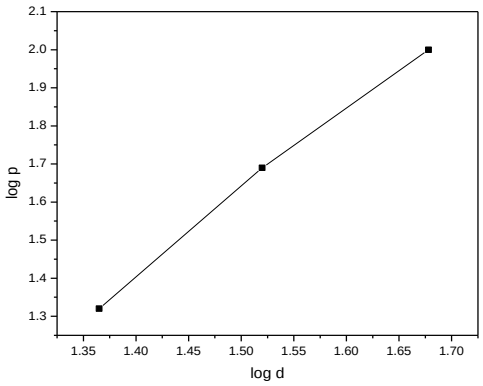


Fig. 8. Plots between hardness number (H_v) and applied load for pure L-Asparagine and its based crystals.

From the results, it is noticed that the hardness number increases with applied load and this is due to reverse indentation size effect[19].This increase in the hardness value of admixture sample can be attributed to the incorporation of an impurity in the lattice of the L-Asparagine crystal [20].

3.4.1. Estimation of Work hardening coefficient (n):

The load variation can be interpreted using Meyer's law ,$p=ad^n$, Where P is load applied, d is the diagonal length of impression, A is a constant and n is the Meyer's index or work hardening co-efficient. The work hardening coefficient can be estimated from the slope of log P versus log d plot shown in figures 9 and 10 using square fit method and the obtained values are reported in table 1.



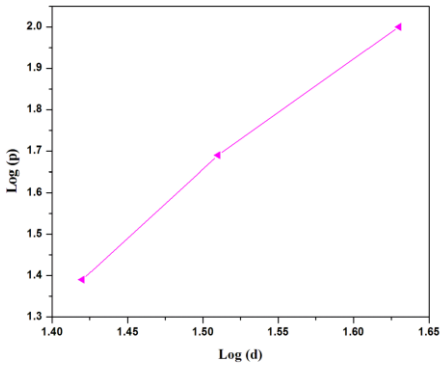


Fig.9 and 10.Plot of log P versus log d for pure L-asparagine

Samples	Work hardening coefficient(n)
Pure L-Asparagine	2.1749
LACC crystal	2.8873

Table1: Work hardening coefficient (n) of pure L-Asparagine and it is based crystals

From the table 2, the work hardening coefficients (n)values for all the grown crystals are greater than 1.6.Accordingto Onitsch[21]and Hanneman [22], if n is greater than 1.6, the material belongs to the category of soft materials [23].In the present study,the work hardening coefficients of all the grown crystals are greater than 1.6.Thus the present crystal under study belongs to soft material category.Because of the high mechanical strength ,both crystals can be very well used for device fabrication.

References:

[1]R.A.Laudise,R.Ueda.J.B.Millin(Eds),Crystal Growth and characterization, North-Holland puplishing co.,(1975).

[2]J.C.Brice,Crystal Growth processes, Halsted press, John Wiley and sons, Newyork,(1986).

[3]H.S.Nalwa,S.Miyata,Nonlinear potics of organic molecules and polymers,CRC press Inc.,Newyork,1996.

[4]D.S.Chemla, J.Zyss (Eds), Nonlinear optical properties of organic molecules and crystals,vols.1 and 2,Acedemic press, Newyork (1987).

[5]R.Hierle, J.Badamn, J.cryst.Growth 69 (1984) 545-554.

[6]C.A.Discoll, H.J.Hoffmann, R.E.Stone, P.E.Perkins, J.opt.Soc.Am.B 31 (1986) 683-686.

[7]M.N. Bhat, S.M. Dharmaprakash, J.Cryst.Growth 236 (2002) 376.

[8]C. Razzetti, M. Ardoido, L.Zanotti, M.Zha,C.Parorici,Cryst.Res.Technol.,37(2002)121.

[9] S. Dhanuskodi, K. Vasantha, Cryst.Res.Technol.,39 (2004) 259.

[10] K. Vasantha, S. Dhanuskodi, J.Cryst.Growth,263 (2004) 466.

[11] D.R.Babu, D.Jeyaraman, R.M,Kumar, R.Jayavel, J.Cryst.Growth,245(2002)121.

[12]P.Srinivasan, T.Kanagasekaran, R.Gopalakrishnan, G.Bhagavannarayana, and P.Ramasamy, Crystal Growth and Design, 6 (2006) 1663.

[13]A.Aarthy, K.Anitha, S.Athimoolam, S.Asath Bahadur and R.K.Rajaram. Acta Cryst.,E61(2005) 2042.

[14] S. Masilamani, P. Ilayabarathi, P. Maadeswaren, J. Chandrasekaran, K. Tamilarasan, "Synthesis, Growth and characterization of a novel semi organic Nonlinear optical single crystal",Optik123(2012) 1304.

[15]T.vela. "Growth Of L-Asparagine sodium choloride Acetate (LASCA) crystal and its studies such as structural, optical, mechanical, thermal and dielectric properties", Archives of physics Research,2014,5(3):49-58.

[16]K.seyed suresh babu, M.Anbuchezhiyan, M.Gulam Mohamed, P.A.Abdullah Mahaboob and R.Mohan, "Growth,optical,dielectric,thermal and mechanical properties of pure and sr(11)-doped L-Asparagine monohydrate single crystals",Archives of physics Research (2013) 4(2) 31.

[17]A.S.I. Joy Sinthiya and P. Selvarajan, "Growth,XRD,Spectroscopic,Hardness and SHG studies of L-Asparagine monohydrate single crystals :,International Journal of advanced scientific and technical research, (2013) 3.

[18]S.Masilamani, A.Mohamed Musthafa ,P.krishnamurthi, "Synthesis,growth and Characterisation of a semiorganic nonlinear optical material:L-threonine cadmium chloride single crystals :,Arabin Journal of chemistry (2014).

[19]S.Karan, S.P.S.Gupta, Mater. Sci. Eng., A 398 (2005)198.

[20]Mott,B.W.,"In:Microindentation Hardness Testing",vol.206.Butter worths, London (1956).

[21] E.M.Onitsch,Mikroskopie 2 (1942)131.

[22] Hanneman, Metallyrgia Manchu 23(1941)135.

[23]P.Selvarajan, J.Glorium Arulraj, S.Perumal, Physica B 405 (2010) 738-743.