



GROWTH AND CHARACTERIZATION OF UNDOPED AND ZINC CHLORIDE DOPED L - ASPARAGINE CRYSTALS

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Abstract:

Single crystals of undoped and zinc chloride doped L-asparagine hydrate were grown by solution method. Solubility of the grown crystals was measured by gravimetric method. X-ray diffraction (XRD) studies reveal that the grown single crystals crystallize in orthorhombic structure. The UV-Vis-NIR spectral studies were carried out to find the absorbance of the samples. The Vickers microhardness test was carried out to test the mechanical stability. The second Harmonic generation (SHG) efficiency of the crystals was found by Kurtz and Perry technique. Dielectric constant and loss factor of the samples were determined at various temperatures and frequencies.

Key Words: Amino Acid, Doping, Single Crystal, Solution Method, Characterization, Solubility, XRD, Microhardness, SHG & Band Gap

1. Introduction:

There are many methods available to grow large crystals in laboratories and research institutions and the grown crystals are used in many scientific and technological fields. In recent years the need of nonlinear optical (NLO) single crystals are very much useful in the fields of second harmonic generation, fiber optic communication, optical computing, electro-optic modulation etc. It is confirmed that amino acids and their complexes have a lot of applications in the areas of nonlinear optics and laser spectroscopy [1-3]. Asparagine is one of the amino acids and it was first isolated in 1806, under a crystalline form, by French Chemists Louis Nicolas Vauquelin and Pierre Jean Robinquet from asparagus juice in which it is abundant. Hence the name they chose for that new matter becoming the first amino acid to be isolated. A few years later, in 1809, Pierre Jean Robinquet again identified a substance with properties that of asparagine and again Plisson in 1828 identified as asparagine itself. It is a non-essential amino acid which means that it can be synthesized from central metabolite pathway intermediates in humans and is not required in the diet. The precursor to asparagine is oxaloacetate and it is converted to aspartate using a transaminase enzyme. The enzyme transfers the amino group from glutamate to oxaloacetate producing alpha-ketoglutarate and aspartate. Some important properties of L-asparagine are molecular weight: 150.13 g/mol, melting point: 233-235 °C, boiling point : 438 °C at 760 mm Hg, Solubility : 30 g/L (20 °C) in water and appearance : white crystalline powder [4-6].

Similar to many other amino acids, L-asparagine hydrate (LAH) occurs in the dipolar form. L-asparagine hydrate crystallizes in an orthorhombic system belonging to space group $P2_12_12_1$. The structure is stabilized by a complex network of seven intermolecular hydrogen bonds involving all the hydrogen atoms bound to oxygen and nitrogen ones. Electron paramagnetic resonance and optical absorption studies of VO^{2+} ions in LAH have been conducted at room temperature [7-10]. L-asparagine has a tendency to form many stable organic and semiorganic compounds and their crystal structures have been solved [11-15]. A new compound of L-asparagine with L-tartaric acid was synthesized and its crystal structure, crystal growth, spectral, structural, thermal and SHG efficiency was reported [16]. The growth and characterization of the single crystals of the NLO material, viz., L-asparaginium picrate were reported by Srinivasan *et al.* [17]. Chemical analysis, FTIR and microhardness study to find out nonlinear optical property of L-asparagine lithium chloride crystals were reported in the literature [18]. Studies on growth and electrical properties of NLO crystals of L-asparaginium nitrate were carried out by Tamilselvan *et al.* [19]. A report on synthesis and various properties of L-asparagine sodium nitrate has been given by Venda *et al.* [20]. Impurity profiling of L-asparagine hydrate by ion pair chromatography was reported in the literature recently [21]. Yogam *et al.* have grown L-asparagine monohydrate crystals by solution method and various properties of the grown crystals have been reported [22]. L-asparagine hydrate crystals have been grown by SR method and LDT, SHG and other properties of the sample have been studied [23]. In this work, undoped and zinc chloride doped L-asparagine hydrate crystals have been grown by solution method at room temperature. Various studies such as structural, mechanical, spectral, electrical and SHG studies were carried out to analyze the properties of the grown crystals.

2. Growth of Crystals by Solution Method:

Undoped and zinc chloride doped L-asparagine hydrate (LAH) crystals have been grown by solution method with slow evaporation technique. GR grade L-asparagine and zinc chloride was purchased commercially. The solvent used here was double distilled water. 20 g of L-asparagine was taken in a borosil

beaker and water was used to prepare the saturated solution and it was stirred well for about 3 hours. Then the solution was filtered twice using Whatmann filter papers and it was kept in growth vessel covered with a porous paper. Colorless and transparent crystals were harvested after a period of 30 days. 1 mol % of zinc chloride was added to the solution of L-asparagine for the synthesis of the doped L-asparagine salt. Using the synthesized salt of zinc chloride doped L-asparagine and water, saturated solution was prepared and it was filtered. Then the solution was taken in a growth vessel and it was allowed in an undisturbed place for slow evaporation. After a period of about 35 days, the zinc chloride doped L-asparagine crystals were harvested. The grown crystals of undoped and zinc chloride doped L-asparagine crystals are shown in the figure 1.



Figure 1: Grown crystals of undoped and zinc chloride doped LAH crystals

3. Studies, Results and Discussion:

3.1 Solubility Study: Solubility study was carried out by gravimetric method and here the solubility of the sample in water at different temperatures was measured. Initially the temperature of solvent was maintained at 30°C and the solute was added step by step to the solvent in an airtight container kept on a hot plate magnetic stirrer and stirring was continued till a small precipitate was formed. Then, 25 ml of the solution was pipetted out and taken in a petri dish and it was warmed up at 40°C till the solvent was evaporated out. The deposited sample on the petri dish was measured and hence the solubility was determined at 30 °C. The same procedure was followed to find the solubility of undoped and zinc chloride doped L-asparagine hydrate samples at other temperatures. Variation of solubility with temperature for samples is presented in the Fig.2. It is observed from the results that the solubility increases with temperature for the both samples and it is found to be more for zinc chloride doped L-asparagine sample compared to the undoped sample. The increase in the values of solubility is due to the changes in the thermo dynamical parameters in the solution of zinc chloride added L-asparagine crystal.

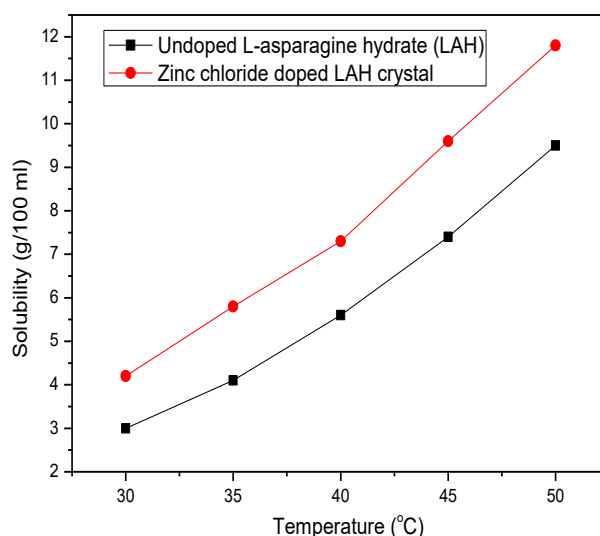


Figure 2: Solubility curves of undoped and zinc chloride doped LAH crystals

3.2 Single Crystal X-Ray Diffraction Studies: Undoped and zinc chloride doped LAH crystals were analyzed by single crystal XRD method and it is observed that the grown crystals crystallize in orthorhombic structure. The unit cell parameters of undoped and zinc chloride doped LAH crystals were shown in table 1. The diffraction data shows a very good match with data reported in the literature [22] and slight changes of lattice

parameters have been noticed for the zinc chloride doped sample compared to undoped LAH crystal. The changes in the lattice parameters are due to incorporation of zinc chloride in the lattice of L-asparagine hydrate crystal.

Table 1: XRD data of undoped and zinc chloride doped LAH crystals $\alpha = \beta = \gamma = 90^\circ$, $Z = 4$

Sample	Lattice parameters (Å)			Unit cell volume (Å ³)
	A	b	C	
Undoped LAH crystal	5.589 (4)	9.867(3)	11.890(2)	655.68 (3)
Zinc chloride doped LAH crystal	5.591(3)	9.858(4)	11.903(5)	656.04(2)

3.3 SHG Studies: Second harmonic generation (SHG) is one of the second order NLO phenomena and it was created from a non-centrosymmetric crystal. The method used to measure the SHG efficiency is the Kurtz and Perry method [24]. The grown crystal was ground into a homogenous powder and densely packed between two transparent glass slides. A Q-switched Nd:YAG laser beam of wavelength 1064 nm with an input power of 0.68 J/pulse, pulse width of 6 ns and repetition rate of 10 Hz was directed on the sample. The SHG output of wavelength 532 nm (green light) from the sample was detected by the photomultiplier tube (PMT). The powdered material of potassium dihydrogen phosphate (KDP) was used in the same experiment as a reference material. The values of SHG efficiency of LAH sample and zinc chloride doped LAH sample were found to be 0.83 and 1.13 times that of KDP. The powder SHG test confirms the second order NLO property of the grown crystals. It is noticed that SHG of the doped crystal is higher than that of LAH crystal. Thus, the zinc chloride doped LAH crystal is found to be the better candidate for NLO application. A small distortion of the crystal structure due to incorporation of dopant may have a great influence on the nonlinear optical properties like second harmonic generation.

3.4 Vickers Microhardness Testing: There are many hardness testing methods and Vickers hardness testing method is one of best methods to understand the mechanical properties of materials such as fracture behavior, yield strength, brittleness index and temperature of cracking. Transparent crystals free from cracks were selected for microhardness measurement. Before indentations, the crystals were carefully lapped and washed to avoid surface effects. Microhardness analysis was carried out using Vickers microhardness tester fitted with a diamond indenter. The well polished crystal was placed on the platform of the Vickers microhardness tester and the loads of different magnitude were applied over a fixed interval of time. The microhardness number was calculated using the relation $H_v = 1.8544 P/d^2$ kg/mm², where P is the applied load in kg and d is the diagonal length of the indentation impression in millimeter. The variation of hardness number (H_v) with the applied load (P) for samples are shown in figure 3. The hardness increases gradually with the increase of load.

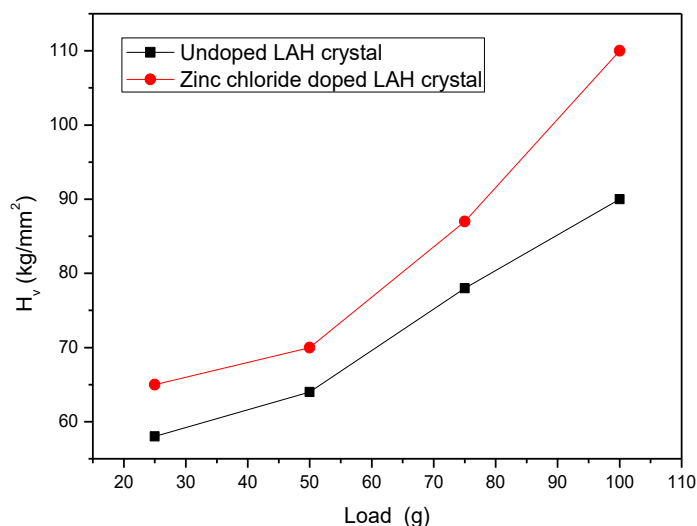


Figure 3: Plots of hardness number versus the applied load for undoped and zinc chloride doped L-asparagine (LAH) crystals

Other mechanical properties such as yield strength (σ_y) and stiffness constant (C_{11}) were calculated at different loads. The relations for determining yield strength ($\sigma_y = (H_v/3)$ N/m²) and the stiffness constant ($C_{11} = (H_v)^{7/4}$ N/m²) where H_v is the Vickers microhardness number of the material. The variations of yield strength and stiffness constant for undoped and zinc chloride doped LAH crystals with the applied loads are shown in the figures 4 and 5. It is observed from the results that the mechanical properties like hardness, yield strength and stiffness constant increase with increase in the applied load. As the values of hardness, yield strength and

stiffness constants are found to be more for the zinc chloride doped LAH crystal than that of undoped sample and hence it is concluded that the zinc chloride doped LAH crystal is more suitable for device fabrication [25, 26].

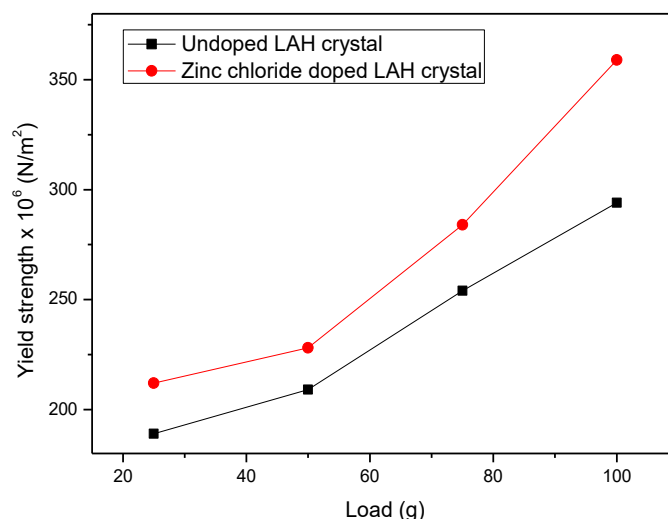


Figure 4: Plots of yield strength versus the applied load for undoped and zinc chloride doped L-asparagine (LAH) crystals

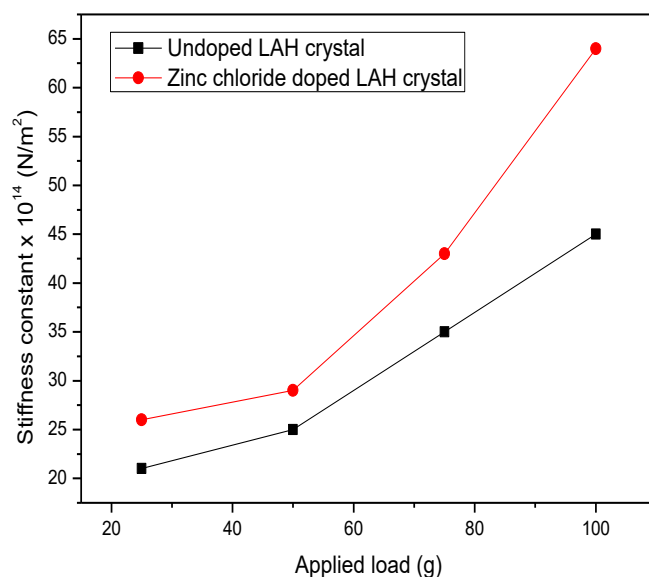


Figure 5: Plots of stiffness constant versus the applied load for undoped and zinc chloride doped L-asparagine (LAH) crystals

3.5 Dielectric Constant and Dielectric Loss Factor: Dielectrics are insulating materials with no free charges. But in the presence of an electric field, the material gets polarized. The dielectric constant and dielectric loss are the basic electrical properties of solids. The dielectric constant is a physical measure of the electric polarizability of a material. Polarization is due to atomic mechanisms like electronic, ionic, orientational and space charge polarizations. The amount of power loss in a dielectric material when subjected to an electric field is known as dielectric loss. A low value of dielectric loss is desired for a dielectric material for device applications. Determination of dielectric constant as a function of frequency and temperature, provides insight into the polarization mechanisms within the dielectric under the influence of an electric field. The values of dielectric constant and loss factor were measured for the samples at various frequencies and temperatures using an LCR meter and the obtained values are presented in the figures 6-9. The high values of observed at low frequencies in pure and zinc chloride doped LAH crystals may be due to the dominant presence of various polarizations arising as a consequence of the charge transfer complex in the samples and also the large value of at low frequency and

at low temperature is due to the presence of space charge polarization which depends on the purity and perfection of the sample. Low values of dielectric constant at high frequency are due to the decay of the dominant polarization. The grown crystals exist as a charge transfer complex which contribution mostly for polarization in the direction of the applied field. As frequency increases, a situation will be reached where space charges cannot sustain and comply with the external field. It is noticed that the dielectric constant and dielectric loss factor increase when the temperature of the samples increases. The addition of dopant (zinc chloride) in L-asparagine crystal also increases the values of the dielectric parameters and this is due to increase in space charge polarization [27, 28].

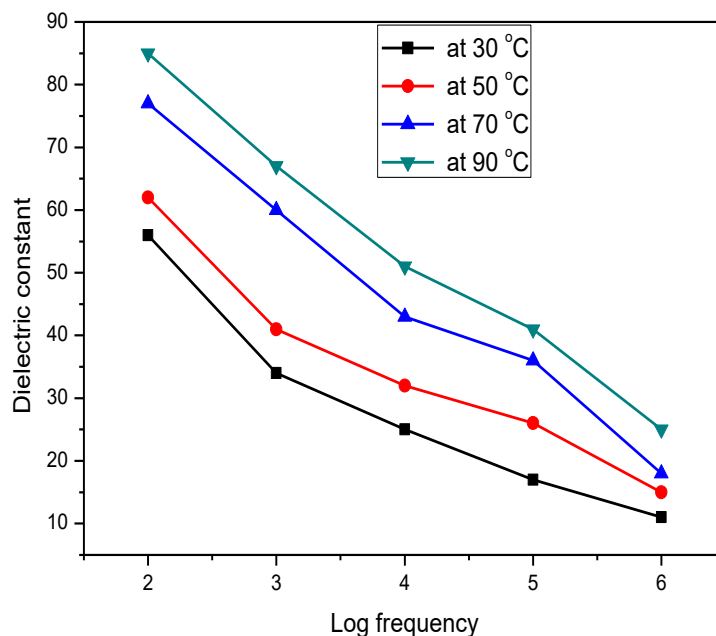


Figure 6: Plots of dielectric constant versus frequency for undoped LAH crystals at different temperatures

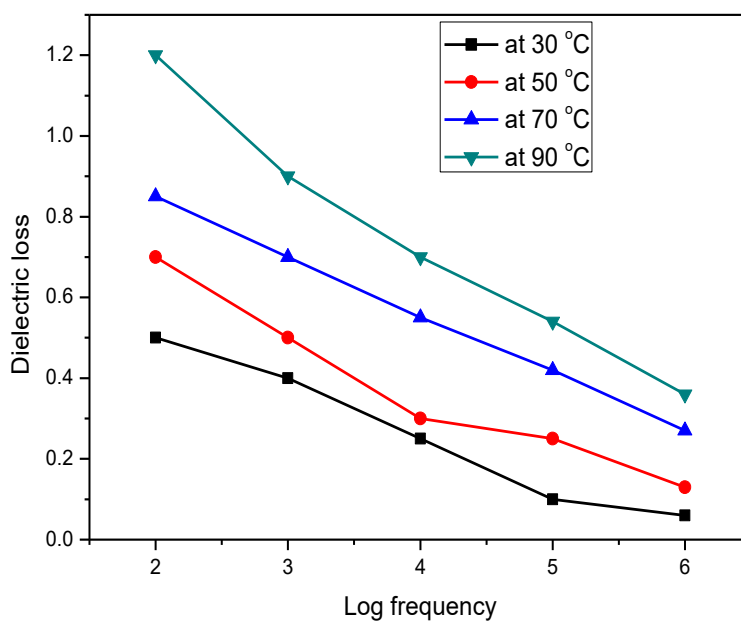


Figure 7: Plots of dielectric loss factor versus frequency for undoped LAH crystals at different temperatures

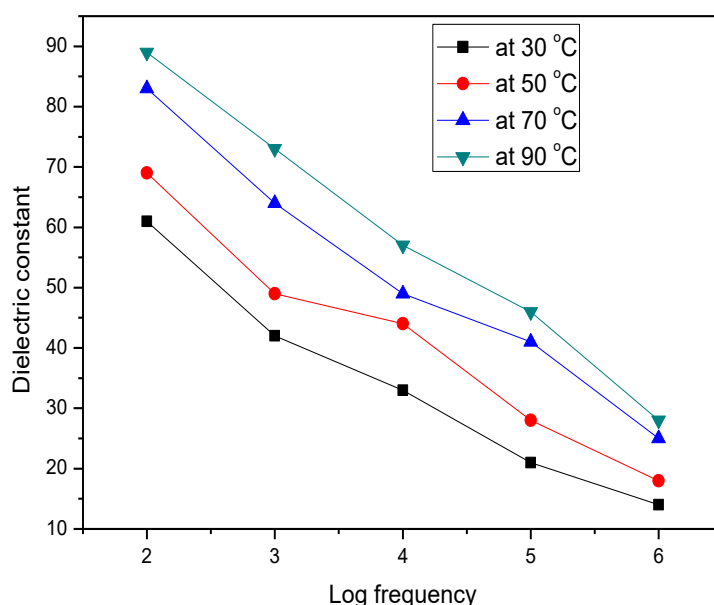


Figure 8: Plots of dielectric constant versus frequency for zinc chloride doped LAH crystals at different temperatures

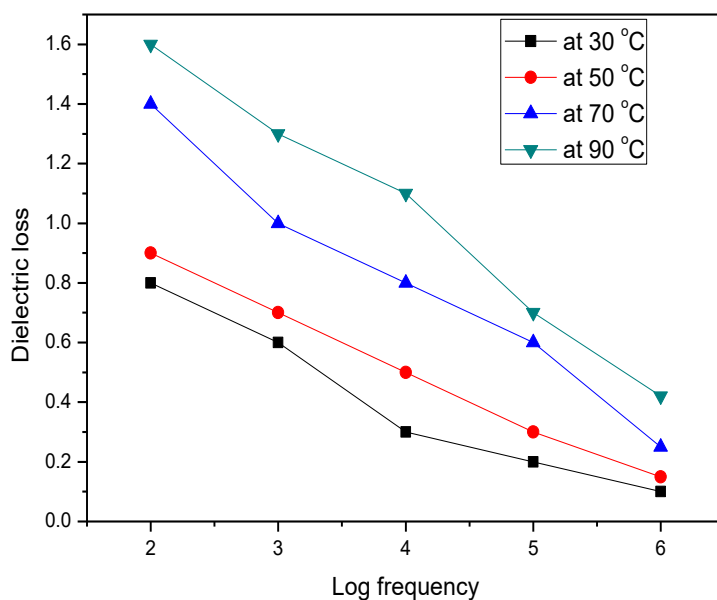


Figure 9: Plots of dielectric loss factor versus frequency for zinc chloride doped LAH crystals at different temperatures

3.6 UV-Visible Absorption Analysis: As far as NLO crystals are concerned, the lower cut-off wavelength and band gap are important and these values could be obtained from absorption or transmittance spectra. The amount of absorption depends upon the wavelength of the radiation and the structure of the compound. The absorption of radiation is due to subtraction of energy from the beam of radiation when electrons in orbitals of lower energy get excited into orbitals of higher energy. UV-visible absorption spectra of samples were recorded in the wavelength range of 220-1100 nm and it is shown in the figure 10. From the spectra, it is observed that the samples have low absorbance in the visible region and the lower cut-off wavelength for the undoped L-asparagine crystal is 252 nm and that for zinc chloride doped L-asparagine is 258 nm. Hence, the values of

optical band gap for undoped L-asparagine and zinc chloride doped L-asparagine hydrate crystals are 4.931 eV and 4.813 eV respectively.

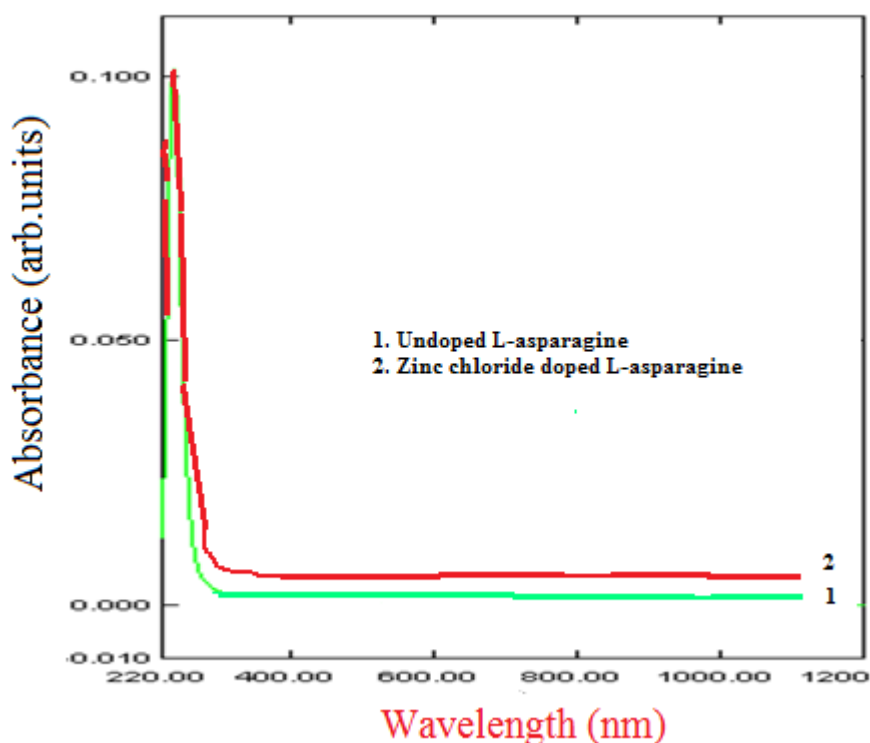


Figure 10: UV-visible absorption spectra for undoped and zinc chloride doped L-asparagine hydrate crystals

4. Conclusion:

Undoped and zinc chloride doped L-asparagine hydrate crystals were grown by slow evaporation method. Solubility was found to be more for zinc chloride doped LAH crystal than that of the undoped crystal. X-ray diffraction studies confirmed that the undoped and zinc chloride doped crystals crystallize in orthorhombic system. The UV-Vis-NIR spectral studies reveal that the absorbance is more for the zinc chloride doped sample compared to the undoped one. The Vickers microhardness study of the crystals was carried out and mechanical parameters such as hardness, yield strength and stiffness for the samples were determined. SHG studies reveal that the suitability of the grown crystals for NLO applications. The dielectric parameters like dielectric constant and dielectric loss of zinc chloride doped LAH sample are observed to be more than that of undoped LAH crystal.

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6. References:

1. L. Wood, F. J. Sharp, Nonlinear Optics & Electro-Optics hand book, McGraw Hill Ltd, New York (1994).
2. Robert A. Meyers, Encyclopedia of lasers and optical technology, Elsevier, London (1991).
3. V. V. Rampal, Photonics: Elements and devices, Wheeler Publishers, Allahabad (1992).
4. R.H.A. Plimmer & F.G. Hopkins, The chemical composition of the proteins.
5. Monographs on biochemistry. Part I. Analysis (2nd Ed.), London, Longmans, Green and Co. (2008).
6. J. J. Verbist, M.S. Lehman, T.F. Koetzla, W.C. Hamilton, Acta Cryst. Vol.B 28 (1972) 3006.
7. K. Syed Suresh Babu, M. Anbuezhayan, M. Gulam Mohamed, P. A. Abdullah Mahaboob and R. Mohan, Archives of Physics Research, 4 (2013) 31.
8. Grace Sahaya Sheba, P. Omegala Priyakumari, M. Gunasekaran International Journal of Chemical, Nuclear, Metallurgical and Materials Engineering 8 (2014) 99.
9. R. Kripal, Mishra, S. K. Gupta, M Arora, Spectrochim Acta A, 71(5) (2009) 1969.
10. Ram Kripal, Pragya Singh, Physica B, 387 (2007) 222.
11. K. Anitha, S. Athimoolam, R.K. Rajaram, Acta Crystallogr. E 61 (2005) 1463.

12. F. Guenifa, L. Bendjeddou, A. Cherouana, S. Dahaoui, C. Lecomte, Acta Crystallogr. E 65 (2009)2264.
13. A. Aarthy, K. Anitha, S. Athimoolam, S.A. Bahadur, R.K. Rajaram, Acta Crystallogr. E 61 (2005) 2042.
14. N. M. Slimane, A. Cherouana, L. Bendjeddou, S. Dahaoui, C. Lecomte, Acta Crystallogr. E 65 (2009)2180.
15. S. Natarajan, V. Hema, J.K. Sundar, J. Suresh, P.L.N. Lakshman, Acta Crystallogr. E 66 (2010) 2239.
16. K. Moovendaran, Bikshandarkoil R. Srinivasan, J. Kalyana Sundar, S.A. Martin Britto Dhas, S. Natarajan, Spectrochim. Acta B 92 (2012) 388.
17. P. Srinivasan, T. Kanagasekaran, R. Gopalakrishnan, G. Bhagavannarayana, P. Ramasamy, Crystal Growth Des. 6 (2006) 1663.
18. S. Masilamani, A. Mohamed Musthafa, Microchemical Journal 110 (2013) 749.
19. S. Tamilselvan, X. Helan Flora, A. Cyrac Peter, M. Gulam Mohamed, C.K. Mahadevan, M. Vimalanand J. Madhavan, Archives of Applied Science Research, 3 (1) (2011) 235.
20. S. Venda, S. Gunasekaran, S. Srinivasan, Optik, 127(2016) 848-851.
21. Klaus Schilling, Maria Cecilia Amstalden, Lorenz Meinel, Ulrike Holzgrabe, J. Pharm. Biomed. Analysis, 131 (2016)202-207.
22. F. Yogam, I. Vetha Potheher, R. Jeyasekaran, M. Vimalan, M. Antony Arickiaraj, P. Sagayaraj, J. Therm. Anal. Calorimetry 114(2013) 1153.
23. Mohd Shakir, B. Riscob, K. K. Maurya, V. Ganesh, M. A. Wahab, G. Bhagavannarayana, J. Crystal Growth, 312 (2010)3171.
24. S. K. Kurtz and T. T. Perry, J. Appl. Phys., 39 (1968) 3798-3813.
25. B. W. Mott, Microindentation hardness testing, Butterworths, London (1956).
26. K. Sangwal, A. Klos, Cryst. Res. Technol. 40 (2005) 429.
27. J. C. Anderson, Dielectrics, Chapman and Hall, London, (1963).
28. J. B. Birks, J. Hart, Progress in Dielectrics, Vol. I-V, Heywood, London, (1959)