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Growth, optical, dielectric, thermal and mechanical properties of pure and Sr(II)-doped L-asparagine monohydrate single crystals

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ABSTRACT

Single crystal organic nonlinear optical materials of pure and Sr(II)-doped L-asparagine monohydrate (LAM) were successfully grown by slow evaporation method at room temperature. The lattice parameter of the grown crystals was subjected to single crystal X-ray diffraction method. The UV-Vis-NIR spectrum of pure and doped LAM possess a wide optical transmission window of range 230 - 1100 nm. The grown compounds were also characterized by FTIR analysis. The presence of Sr(II) in the grown crystal was confirmed by Inductively-Coupled Plasma (ICP) elemental analysis. The dielectric behaviour of the grown crystals has been studied at room temperature in the frequency range 50 Hz - 5 MHz. Thermal stability of the crystal was also studied by TGA/DTA and DSC analyses. The mechanical strength of the grown crystal has been determined with the aid of Vickers hardness test. The nonlinear optical property of the crystal was tested by Nd:YAG laser source.

Keywords: Solution growth; Optical analysis; Dielectric studies; Thermal analysis; Microhardness analysis.

INTRODUCTION

The search and design of highly efficient nonlinear optical (NLO) crystals for visible and ultraviolet (UV) region are extremely important for laser processing. In view of this, it is desired to find new NLO crystals which have a shorter cut-off wavelength. High quality organic NLO crystals must possess sufficient large NLO coefficient, transparent in UV region and high laser damage threshold power easily grow with large dimensions [1, 2]. Amino acid families of crystals are under extensive investigations in recent times owing to their favourable nonlinear optical properties [3]. In general, most of the organic molecules designed for nonlinear optical applications are the derivatives of an aromatic system substituted with donor and acceptor substituent's [4, 5].

Asparagine is one of the twenty most common natural amino acids in living organism. It is a very important amino acid because it plays a role in the metabolic control of some cell functions in nerve and brain tissues and is also used by many plants as a nitrogen reserve source [6] besides this being part of different drug and food. L-asparagine monohydrate $C_4H_8O_3N_2.H_2O$ (LAM) single crystal have orthorhombic structure [7] and belong to space group $P2_12_12_1$ with four molecules per unit cell and lattice parameters: a = 5.593 Å, b = 9.827Å, c = 11.808 Å. The molecule is in the zwitterions form and is linked together by seven distinct hydrogen bonds forming a three dimensional network. It is an interesting material to investigate as it crystallizes in structures exhibiting a complex network of hydrogen bonds among asparagines and water molecules [8]. Based on this, asparagine compound materials such as L-asparagine-L-tartaric acid (LALT) [9], L-asparaginium picrate (LASP) [10], L-asparaginium nitrate (LAsN) [11] and L-asparagine cadmium chloride monohydrate [12] are proved to be good NLO application materials. Recently, investigation of Mn^{2+} doped L-asparagine monohydrate single crystal has been found to improve the crystallinity, optical transparency and mechanical strength that are useful for optoelectronic application

as reported by Mohd.Shakir *et al* [13]. In this perspective the present work involves growing of as-grown bulk single crystals of pure and Sr(II)-doped LAM by solution growth technique and subjecting to them single crystal X-ray diffraction to confirm the cell parameter. The nature of constituents and functional groups present in the crystals were confirmed by FTIR studies. The optical, dielectric and microhardness studies of both pure and doped LAM crystals were carried out. Thermal stability of grown crystals has been analyzed with the aid of TGA, DTA and DSC. The NLO property of the title compounds was confirmed by powder technique of Kurtz and Perry.

MATERIALS AND METHODS

2.1. Solubility of LAM

The solubility test gives a key to select the best solvent and temperature to grow good quality crystals. In solution growth technique, selection of a solvent, which is moderately soluble, plays a major role. The solubility of LAM was tried for different solvents like water, acetone, ethanol and their mixtures. It is found that water is suitable to be good solvent to crystallize LAM. Hence the solubility studies for LAM in water have been performed in the temperature range between 30°C and 46°C in steps of 4°C. The measurement was performed by dissolving LAM salt in 100 ml of triply distilled water in an air tight container maintained at a constant temperature with continuous stirring. After attaining saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The same procedure was repeated for Sr(II)-doped LAM salt at different temperatures. The solubility curve for different temperatures is drawn and shown in Fig.1. As temperature increases, the solubility of both pure and doped salts is found to increase.

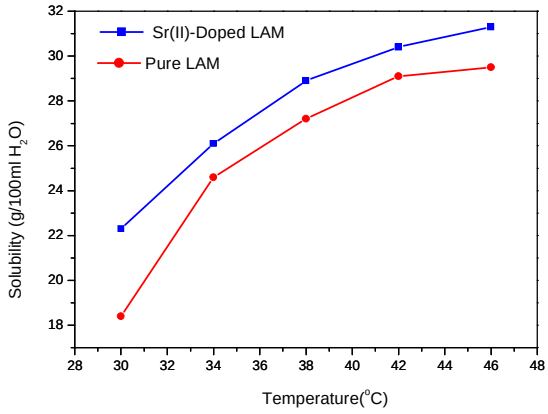

Fig.1. Solubility curve of pure and Sr(II)-doped LAM crystals.

2.2. Growth of pure and doped LAM crystals

The commercially available L-asparagine monohydrate ($C_4H_8O_3N_2.H_2O$) from HiMedia Company was purified by repeated recrystallization process using triply distilled water. Since the solubility is high (29.5 gm / 100 ml of solvent), it is easy to grown good quality single crystal of suitable size. The seed crystals were obtained after 10 days and among them the defect free and perfectly shaped ones with high transparency were used as the seed crystals for further growth experiments. The seed crystals were first seasoned in the mother solution in the mason jar crystallizer using nylon thread and then allowed to grow into bigger size. The jar was covered with perforated lid to facilitate the slow evaporation of the solvent at a constant temperature of 305 K. A good LAM transparent crystal of dimension (13.9 x 7.8 x 5.1 mm^3) was obtained in a period of 15 - 20 days. The crystal tends to grow flat and was colourless with good transparency. The photograph of the grown crystal of LAM is shown Fig 2(a). Single crystal of Sr(II)-doped LAM was grown by dissolving stoichiometric amount of L-asparagine monohydrate in 100 ml triply distilled water and then followed by addition of 10 mol % of strontium chloride to the above transparent solution under magnetic stirring. The growth experiments were carried out using the same procedure adopted in the case of pure LAM. The crystals tend to grow bigger than pure one (21.4 x 13.2 x 7.3 mm^3) and were harvested in the grown period of 25 days. Fig.2 (b) shows the photograph of Sr(II)-doped LAM single crystal.

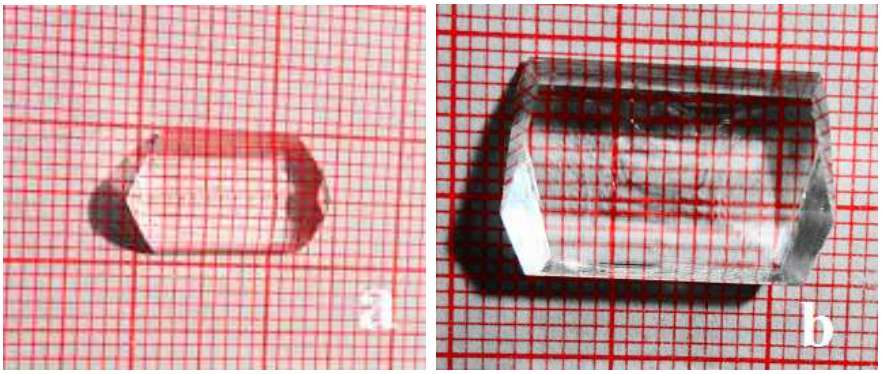

Fig. 2. Photographs of as-grown: (a) pure LAM (b) Sr(II)-doped LAM crystals

RESULTS AND DISCUSSION

3.1 Single crystal X-ray diffraction analysis

The single crystal X-ray diffraction studies of pure and Sr(II)-doped LAM single crystals were carried out using a Bruker AXS Kappa APEX II single crystal CCD diffractometer equipped with graphite-monochromated MoKα radiation (λ = 0.71073Å) at room temperature with crystal dimension of 0.35 x 0.25 x 0.15 and 0.36 x 0.23 x 0.21 mm^3. Intensity data was collected and accurate unit cell parameters were determined from the reflections of 36 frames measured in three different crystallographic zones by the method of difference vectors. The pure and doped LAM crystal crystallized in orthorhombic crystal system with space group $P2_12_12_1$. The lattice parameters are shown in Table.1. The results of the present work are in good agreement with the reported values [7]. In the case of Sr(II)-doped LAM crystals, slight variations in the lattice parameters and cell volume were observed. These variations may be attributed to the incorporation of Sr^{2+} in voids space of the LAM.

Table 1. Single crystal XRD data of pure and Sr(II)-doped LAM crystals.

Crystal Parameters	Pure LAM	Sr(II)-doped LAM
a (Å)	5.597	5.551
b (Å)	9.819	9.765
c (Å)	11.792	11.764
Volume($Å^3$)	648.05	637.67
Crystal System	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$

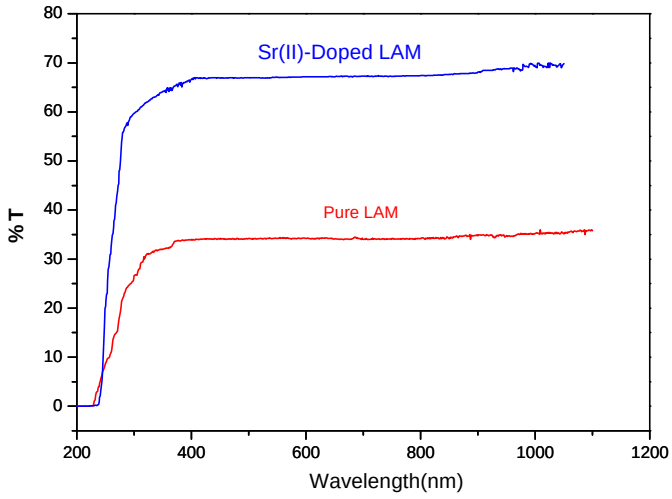

Fig.3. UV-Vis-NIR transmittance spectrum of a pure and Sr(II)-doped LAM crystal

3.2. UV-Vis-NIR spectral analysis

The UV-Vis-NIR transmission spectra of the crystals were recorded in range 200 to 1100 nm using Varian Cary 5E spectrometer. It gives limited information about the structure of the molecule because the transmittance of UV and Visible light involves promotion of the electrons in the 'σ 'and 'π 'orbital from the ground state to a higher energy state.

A nonlinear optical material can be of practical use only if it has a wide transparency window. Fig.3 shows the transmittance spectrum of pure and doped LAM crystal. The lower cut-off wavelength is found to be at 230 nm and 236 nm for pure and Sr(II)-doped LAM respectively. It is clear that LAM crystal has good optical transparency in the complete UV-Vis region and optical transparency of Sr(II)-doped LAM crystal increases the percentage of transmission. This confirms the incorporation of the metal dopant [13]. In the visible region, the crystal is highly transparent and it could be used for optoelectronic application [14].

3.3 FTIR analysis

The recorded FTIR spectrum of pure and Sr(II)-doped LAM were recorded on Perkin-Elmer FTIR spectrometer using KBr pellet in the range 4000 - 450 cm^{-1}. The FTIR Spectra of both the pure and doped LAM crystals are shown in Fig.4 (a) and (b) respectively. A peak appeared at 3447 cm^{-1} indicating the presence of O-H stretching vibration. The intense and fairly sharp band at 3382 cm^{-1} should be assigned to the NH_2 stretching vibration. The appearance of the broad band at 3110 cm^{-1} can only be due to the NH_3 stretching vibration confirming the zwitter ion structure of the molecule. The CH_2 symmetric stretching vibration is observed in 2952 cm^{-1}. The band at 1643 cm^{-1} is attributed to NH_3 deformation vibration in FT-IR spectrum. The peaks obtained at 1428 cm^{-1} is due to symmetric vibrations of COO^-. Other characteristic vibrations establishing the identity of the functional groups present in the compounds are represented in Table.2. The FTIR Spectra of both the pure and doped LAM confirm the structural aspects of pure compounds. Although the spectrum of Sr(II)-doped LAM provides similar features as that of pure LAM, there is slight shifting observed suggesting that it may be due to the incorporation of Sr^{2+} ions in the lattice of LAM.

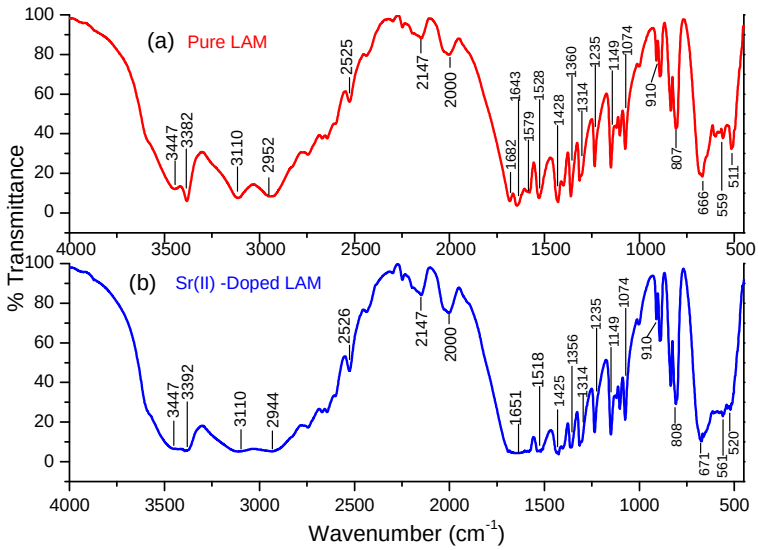

Fig.4. FTIR spectrum of (a) pure LAM (b) Sr(II)-doped LAM

Table 2. FTIR spectral assignments of pure and Sr(II)-doped LAM

Wave number (cm^{-1})		Vibrational Assignments
Pure LAM	Sr(II)-doped LAM	
3447	3447	O-H stretching
3382	3392	NH_2 stretching
3110	3110	NH_3^+ stretching
2952	2944	C-H stretching
2000	2000	N-H stretching
1643	1651	NH_3^+ deformation
1528	1518	NH_2 bending
1428	1425	COO^- sym. stretching
1360	1356	CH bending
1314	1314	CH_2 wagging
1235	1235	NH_2 rocking
1149	1149	NH_3^+ rocking
1074	1074	C-N stretching
910	910	CH_2 rocking
807	808	C-C stretching
666	663	H_2O rocking
511	520	C-N torsion

3.4. ICP elemental analysis

ICP (Inductively Coupled Plasma) is an emission spectrophotometric technique, based on the fact that excited electrons emit energy at a given wavelength as they return to ground state. The fundamental characteristic of this process is that each element emits energy at specific wavelengths peculiar to its chemical character. This technique is used to find qualitative and quantitative determination of strontium present in the LAM crystal. The result shows that the amount of strontium present in the sample was determined as 26.7 ppm for strontium wavelength of 407.771 nm. From the obtained results, it has been confirmed that the concentration of strontium concentration are present in the sample. It is also confirmed that Sr^{2+} ions have entered into the crystal lattice of L-asparagine monohydrate.

3.5. Dielectric analysis

The dielectric study of pure and Sr(II)-doped LAM single crystals were carried out using HIOKI 3532-50 LCR HITESTER and a conventional two terminal sample holder. In order to ensure good electrical conduct between the crystal and the electrodes, silver paint was applied to the surfaces of the crystals. Dielectric measurements were made in the frequency range 50 Hz to 5 MHz at room temperature. Fig.5, shows the variation of dielectric constant (ε_r) as a function of frequency of pure LAM and Sr(II)-doped LAM crystals. It is observed that the dielectric constant has higher values in the lower frequency region and then it decreases with applied frequency. The very high value of ε_r at low frequencies may be due to the presence of all the four polarizations namely space charge, orientational, electronic and ionic polarization. The low value of ε_r at higher frequencies may be due to the loss of significance of these polarization gradually. Similarly, the variation of dielectric loss with frequency is shown in the Fig.6. In the case of Sr(II)-doped LAM the same trend is observed with reference to pure LAM. However it is marginally altered in the dielectric nature of pure LAM, which may be due to the incorporation of metal dopant. It is confirmed that the grown crystals possesses enhanced optical quality with fewer defects, and this parameter is of vital importance for various second harmonic generation applications [15, 16,].

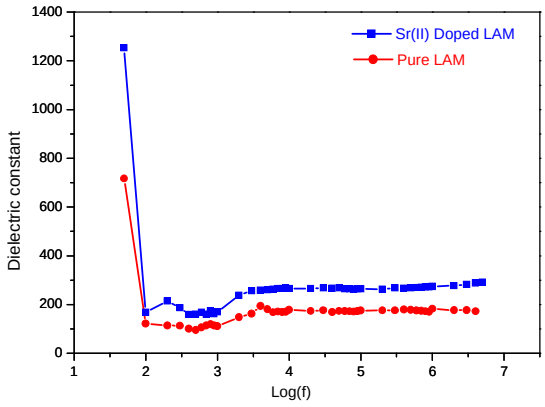

Fig.5. Dielectric constant of a pure and Sr(II)-doped LAM crystals

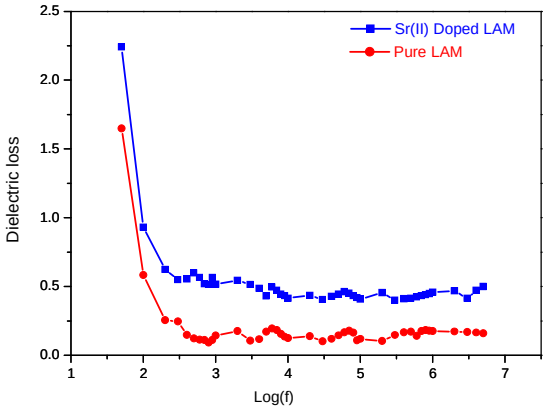

Fig.6. Dielectric Loss of a pure and Sr(II)-doped LAM crystals

3.6. Thermal analysis

The Thermo gravimetric analysis (TGA) / Differential Thermal Analysis (DTA) and Differential Scanning Calorimetric (DSC) analysis of pure and Sr(II)-doped LAM crystals were performed in the temperature range 20 to 800 ^{o}C using SDT Q600 V20.9 Build 20 analyzer, under nitrogen atmosphere and a heating rate of 10 °C/min was maintained. From Fig.7 (a) for pure LAM crystal, the TGA curve shows three stages of weight loss. The first stage (between 102 and 207°C) is about 11 % due to the evaporation of adsorbed water. The second stage is between 207 and 250 °C and the third stage is between 258 and 590 °C with a weight loss of 24 % and 38 % due to the liberation of volatile substances. The remaining residue is 26 % which is upto 800 °C. From the DTA curve, there is sharp endothermic peaks at 113.45 ^{o}C is showing the thermal stability of the crystal But, in the case of Sr(II)-doped LAM crystal, the decomposition temperatures slight variation than pure LAM crystal as shown in Fig.7(b).According to DSC curve, the decomposition peaks exactly matches with DTA trace. Fig.7(C) shows DSC curve of both pure and Sr(II)-Doped LAM crystals, the curve shows that the peaks of doped LAM crystal are slightly lower in value and shifted accordingly. This supports the fact of incorporation of isovalent ion Sr^{2+} in the host crystal [17]. There is a reduction in the decomposition temperature of the doped crystal which is attributed to the decreased lattice energy caused by the addition of metal ion [18].

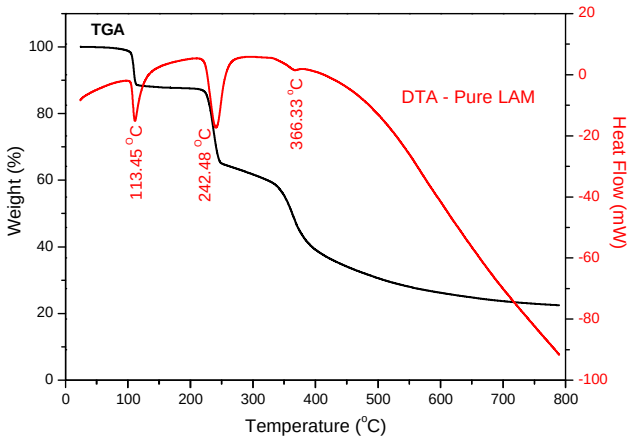

Fig. 7 (a). TG/DTA Curve of pure LAM crystal

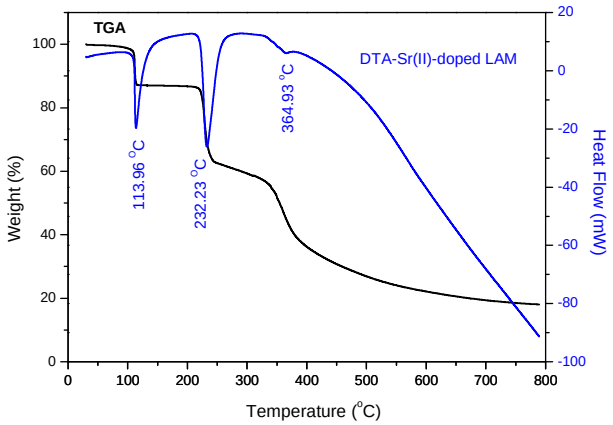

Fig.7 (b). TG/DTA Curve of Sr(II)-Doped LAM crystal

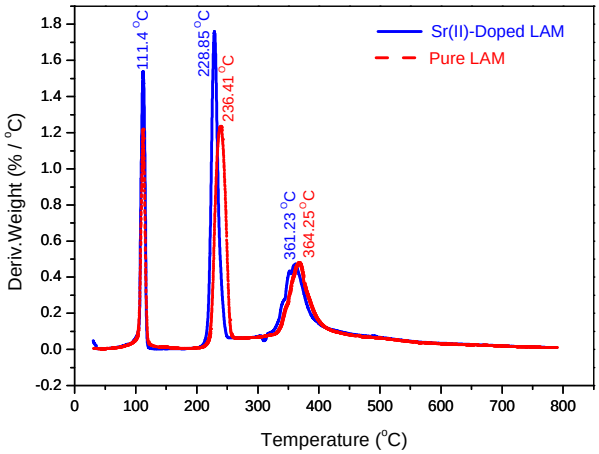

Fig. 7 (c). DSC Curve of pure and Sr(II)-Doped LAM crystals

3.7. Microhardness analysis

Mechanical properties of the pure and Sr(II)-doped LAM single crystal were studied by making indentations on the selected (011) plane using a Reichert MD 4000E ultra micro hardness tester fitted with a Vicker's diamond pyramidal indenter. The static indentations were made at room temperature with a constant indentation time of 3 s for all indentations. Vicker's microhardness number (H_v) was evaluated from the relation:

$H_{v\,=}$ 1.8544 P / d^2 (kg/mm^2)

Where 'P' is the applied load and 'd' is the mean diagonal length of the indenter impression. A plot between the load P and hardness number H_v is shown Fig.8 (a). The hardness number was found to increase with increase in applied load up to 20 g. After 20 g the hardness decreases with increasing load. Beyond the load of 30 g, the hardness value increase slightly with the load. Such behaviour were observed for both LAM crystals. The slight increase in micro hardness with increase of load could be attributed to the heaping up of material at the edges of the impression made by the diamond pyramid. Same trend also observed in Mn^{2+} doped LAM crystal [13].The H_v is found to be 103.82 and 108.72 kg/mm^2 for pure and Sr(II)-doped LAM crystal at 75 g. From the results, it is observed that the hardness of the pure LAM crystal increases when it is doped with Sr(II). This increase in the hardness value of doped sample can be attributed to the incorporation of an impurity (strontium) in the lattice of the LAM crystal. Plots of log P versus log d for the grown crystals are shown in Figure 8(b). It can be seen that log P versus log d is linear for both the crystals and the slope of the straight line gives the work hardening coefficient (n). The values of 'n' were determined to be 1.98 and 2.13 respectively. According to Onitsch, $1.0 \leq n \leq 1.6$ is for hard materials and $n > 1.6$ is for soft materials [19]. This suggests that the pure and Sr^{2+} doped LAM crystals belongs to soft material category. Because of the high mechanical strength, both crystals can be very well used for device fabrication.

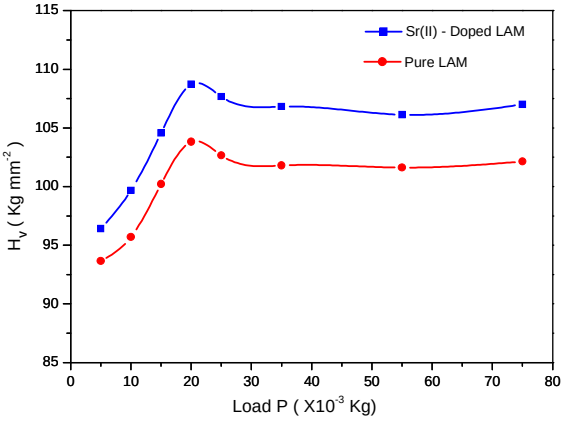

Fig.8 (a). Variation of (H_v) with load (P) for pure and Sr(II)-doped LAM crystals

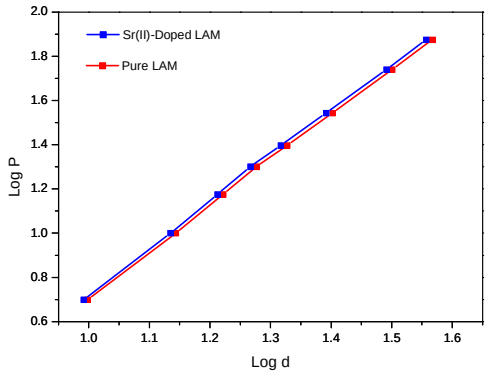

Fig.8 (b). Log d Vs log P for pure and Sr(II)-doped LAM crystals

3.8. Etching analysis

To get the preliminary idea about the quality of the grown crystals, etching technique has been employed. Etching process was done on the (011) face of the Sr(II)-doped LAM crystal with water as an etchant for 10, 20 and 30 s were carried out and are shown in Fig.9 (a),(b) and (c) respectively. Each time, surface of the crystal was observed by high magnification (4000X) REICHERT POLY VAR 2 MET microscope. The etching analysis shows predominant straight striations on the grown crystal. The size of the pit increases with the increase of etching time. The pit pattern remains the same. The observed etch pits are due to the layered grown of the crystal. This shows how the crystal would have been formed from the solution [20].

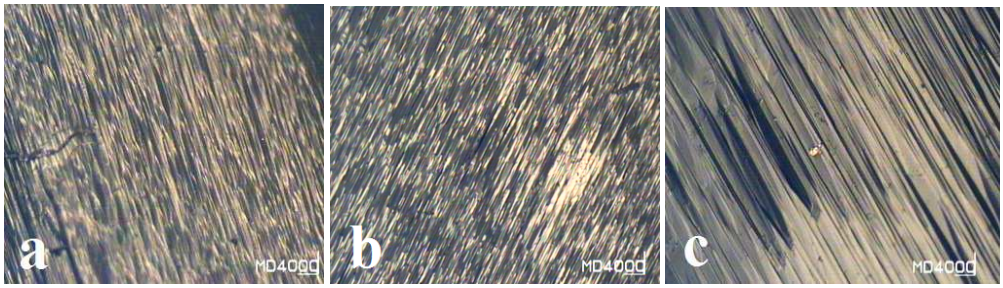

Fig. 9. Etching micrographs of Sr(II)-doped LAM (a) 10 s (b) 20 s and (c) 30 s.

3.9. Second harmonic generation (SHG) studies

The SHG efficiency was measured for the grown pure and doped LAM crystal using the Kurtz and Perry experimental technique [21]. A Q-switched Nd:YAG laser emitting a fundamental wavelength of 1064 nm was used with an input power of 0.5 J, pulse width of 8 ns repetition rate of 10 Hz. The crystals was ground in to a homogenous powder of particles and densely packed between two transparent glass slides. The second harmonic signal generated was confirmed from the emission of green radiation (λ = 532 nm) from the samples. The intensity of the green light was measured using a photomultiplier tube. The SHG efficiency of the grown crystal was found to be 2.7 mJ and 2.9 mJ were obtained for pure and Sr(II)-doped LAM respectively. A sample of powdered potassium dihydrogen phosphate (KDP) was used as the reference material in the SHG measurement. The standard KDP crystal gave a SHG signal of 8 mJ per pulse for the same input energy. From the obtained data, it is found that the SHG efficiency of the pure LAM sample is 0.33 times and that of the Sr(II)-doped LAM sample is 0.36 times of the well known KDP crystal.

CONCLUSION

The single crystals of pure and Sr(II)-doped L-asparagine monohydrate organic crystal were grown from aqueous solution by slow evaporation technique under room temperature. The grown crystals are transparent and have well defined external appearance. Single XRD studies confirm that both pure and doped LAM crystals crystallize in orthorhombic crystal structure. The UV-Vis-NIR study identified the UV cut-off wavelength of pure and doped as 230 nm and 236 nm respectively. The FTIR spectrum confirms the presence of functional groups of grown compounds. ICP elemental analysis confirms the presence of strontium in the grown crystal. The dielectric studies reveal the low dielectric constant and dielectric loss of the crystal at high frequency region. The TGA/DTA and DSC studies show that the Sr^{2+} impurity have slightly altered the thermal stability of the molecules. The micro hardness

studies indicate the soft nature of the crystals. It is interesting to note that the incorporation of dopant have slightly improved the hardness of the parent. Etching of grown Sr(II)-doped LAM crystal shows the crystalline perfection. The second harmonic generation of grown crystal were studied by using Kurtz and Perry powder technique.

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REFERENCES

[1] M.D. Aggarwal, J.Choi, W.S.Wang, K. Bhat, R.B. Lal, A.D. Shields, B.G. Penn, D.O. Frazier, *J. Crystal Growth*. 204 (**1999**) 179.
[2] H.W. Zhang, A.K. Batra, R.B. Lai, *Journal of Crystal Growth*.137 (**1994**)141.
[3] A. Joseph Arul Pragasam, S. Selavakumar, J. Madhavan, D. Prem Anand and P. Sagayaraj, *Indian J. Pure & Appl Phys*, 43 (**2005**) 463.
[4] J. Badan, R. Hierie, A. Perigaud, J.Zyss, *ACS Symp.Ser*.233 (**1983**) 81.
[5] A.F. Garito, K.D. Singer, *Laser Focus Fiberopt.Technol*.18 (**1982**) 59.
[6] P.Lund, Nitrogen Metabolism in Mammalian, *Applied Science*, *Barking* (**1981**).
[7] J.J. Verbist, M.S. Lehman, T.F. Koetzla, W.C. Hamilton, *Acta Cryst.* Vol.B 28 (**1972**) 3006.
[8] M. Ramanadham, S.K. Sikka and R. Chidambram, *Acta Cryst*. Vol.B 28 (**1972**) 3000.
[9] K. Moovendaran, Bikshandarkoil R. Srinivasan, J. Kalyana Sundar, S.A. Martin Britto Dhas and S. Natarajan, *Spectrochimica Acta Part A,Molecular and Biomolecular Spectroscopy*, Volume 92(**2012)** 388.
[10] F. Yogam, I. Vetha Potheher, A. Cyrac Peter, S. Tamilselvan, M. Vimalan and P. Sagayaraj, *Scholars Research Library*, 3 (**2011**) 267.
[11] S. Tamilselvan, X. Helan Flora, A. Cyrac Peter, M. Gulam Mohamed, C.K. Mahadevan, M. Vimalan and J. Madhavan, *Scholars Research Library*, 3 (**2011**) 235.
[12] S. Masilamani, P. Ilayabarathi, P. Maadeswaran, J. Chandrasekaran, K. Tamilarasan, *Optik* (**2011**).
[13] Mohd. Shakir, V. Ganesh, M.A. Wahab, G. Bhagavannarayana, K. Kishan Rao, *Materials Science and Engineering* B 172 (**2010**) 9.
[14] N. Vijayan, R. Ramesh babu, R.Gopalakrishan, P. Ramasamy and W.T.A. Harrision, *Journal of crystal growth* 262(**2004**) 490.
[15] Mohd. Shakir, S.K. Kushawaha, K.K. Maurya, Sumeet Kumar, M.A. Wahab and G. Bhagavannarayana, *Journal of Applied Crystallography* 43 (**2010**) 491.
[16] C. Balarew, R. Duhlew, *J.Solid State Chem*.55 (1984) 1.
[17] K. Muthu , M. Rajasekar , K. Meena , C.K. Mahadevan, SP. Meenakshisundaram, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 96 (**2012**) 825.
[18] P. Praveen Kumar, V. Manivannan, S. Tamilselvan, S. Senthil, Victor Antony Raj, P. Sagayaraj, J. Madhavan, *Optics Communications* 281 (**2008**), 2989.
[19] E. M. Onitsch , *Mikroscopic* 2 (**1947**) 131.
[20] K. Sangwal.,"Defects in Solids," North Holland Publishing Company, Netherlands, Vol.15. (**1987**).
[21] S.K. Kurtz, T.T. Perry, *J. Appl. Phys.* 39 (**1968**) 3798.