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RESEARCH ARTICLE

STUDIES OF AMMONIUM FLUORIDE ADMIXTURED L-ASPARAGINE CRYSTALS GROWN BY SOLUTION METHOD

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ABSTRACT

Solubility is measured for L-asparagine crystals admixtured with ammonium fluoride (LAAF) at different temperatures. Single crystals of LAAF salt was grown by slow evaporation technique. Elemental analysis of the grown crystal was done by Energy Dispersive X-ray (EDX) studies. Evaluation of values of lattice parameters, optical band gap, yield strength, stiffness constant was performed for the grown crystals. Fourier Transform Infrared (FTIR) studies, Second Harmonic Generation (SHG) studies and thermal studies for LAAF crystals were carried out and the results are reported.

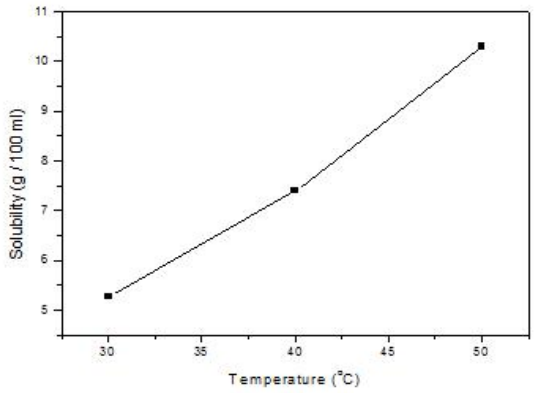
INTRODUCTION

The approach of combining the organic molecules with the inorganics has been found to be overwhelmingly successful in the recent past. Hence, recent search is concentrated on semiorganic materials due to their large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness. Semiorganic nonlinear optical materials play vital role in the field of optoelectronics and they are suitable for application in frequency conversion, optical telecommunication, image processing, optical computing, and data storage. Advances have been accounted recently in the field of nonlinear optics in the area of materials engineering and the associated optoelectronic device technologies [1,2]. L-asparagine is an amino acid used by many plants as a nitrogen reserve substance. Despite the biological interest, there is a growing interest in amino acid family of crystals as it shows lots of promise to be used in NLO devices. Being a non-centrosymmetric material it can be a second harmonic generator [3]. A survey of literature pointed out that many amino acid based crystals have been grown and characterized by many researchers already [4-7]. In this work, L-asparagine and ammonium fluoride are mixed to form L-asparagine crystals admixtured with ammonium fluoride (LAAF) and the single crystals of LAAF were grown by slow evaporation growth technique for the first time. The grown crystals of LAAF were subjected to various studies such as XRD studies, EDX studies, FTIR studies, TG/DTA studies, hardness studies and SHG studies.

MATERIALS AND METHODS

Solubility

L-asparagine admixtured with ammonium fluoride (LAAF) salt was synthesized by taking L-asparagine (99% purity) and analar grade NH_4F (98% purity) in the molar ratio of 1:1 in double distilled water. The dissolved solution was heated at 60 ^oC for the synthesis of LAAF salt. The purity of the synthesized salt was further increased by repeated re-crystallization. Initially, the temperature was maintained at 30^oC in the constant temperature bath. The re-crystallized sample of LAAF was added step by step to 50 ml of double distilled water in an air-tight container kept in the constant temperature bath and stirring was continued till a small precipitate was formed. This gave confirmation of supersaturated condition of the solution. Then 5 ml of the solution was pipetted out and taken in a petri dish and it was warmed up at 40^oC till the solvent was evaporated out. By measuring the amount of salt present in the petri dish, the solubility (in g/100 ml) of LAAF in double distilled water was determined and this method of measuring solubility is known as gravimetrical method [8]. The variation of solubility with temperature for LAAF sample is presented in the figure 1 and it is observed that the sample has positive temperature coefficient of solubility.



Crystal growth

The saturated solution of the re-crystallized salt of LAAF was prepared in accordance with the solubility data. The calculated

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amounts of the reactants were thoroughly dissolved in double distilled water and stirred well for about 1 h using a magnetic stirrer to ensure homogeneous concentration over entire volume of the solution. The solution was filtered and transferred to crystal growth vessels and crystallization was allowed to take place in a constant temperature bath (accuracy $\pm$ 0.01 ^{o}C) by slow evaporation method. Some seeds obtained from spontaneous nucleation were placed in the growth vessels to obtain big-sized crystals. The harvested crystals of LAAF are shown in the figure 2. It is observed that the grown crystal is transparent, colourless and it is well formed with sharp edges. The dimensions of the crystal are noticed to be 8 x 5 x 3] ^{3}

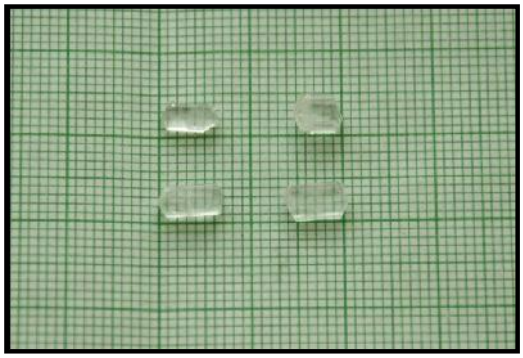

Figure 2 Harvested crystals of LAAF

Characterization after growth of crystals

EDX studies

Energy Dispersive X-ray (EDX) technique a chemical microanalysis method used in conjunction with scanning electron microscopy (SEM). This technique detects X-rays emitted from the sample during bombardment by an electron beam to characterize the elemental composition of the sample. The data generated by EDX analysis consist of spectra showing peaks corresponding to the elements making up the true composition of the sample being analyzed. When the sample is bombarded by the SEM's electron beam, electrons are ejected from the atoms comprising the sample's surface. The resulting electron vacancies are filled by electrons from a higher state and an X-ray is emitted to balance the energy difference between the two electrons states. The X-ray energy is characteristic of the element from which it was emitted. The spectrum of X-ray energy versus counts is evaluated to determine the elemental composition of the sample. The sample X-ray energy values from the EDX spectrum are compared with known characteristic X-ray energy values to determine the presence of an element in the sample. In the present study, EDX studies were performed using the EDX detector (Hitachi model S-3000H scanning electron microscope). The EDX spectrum for the grown LAAF crystal is presented in the figure 3. Using this spectrum, the elements such as carbon, nitrogen, fluorine and oxygen present in the sample are identified.

XRD studies

The grown LAAF crystal analyzed by single crystal XRD studies to confirm the crystallinity and also to estimate the lattice parameters by employing Bruker-Nonious MACH3/CAD4 single X-ray diffractometer. From single crystal X-ray diffraction data, it is observed that the LAAF crystal belongs to orthorhombic in structure with the lattice parameters a=5.601(4) Å, b=9.853(2) Å, c=11.815(1) Å, $\alpha=\beta=\gamma=90°$ and V =651(3) Å^3.

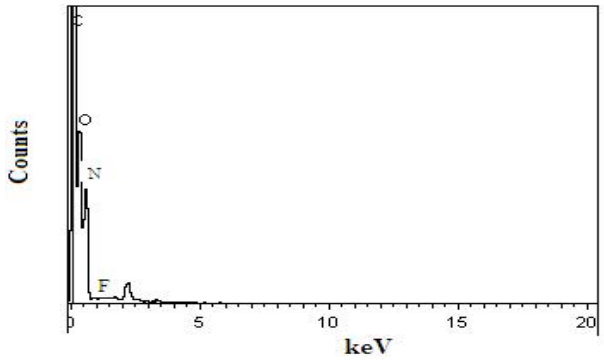

Figure 3 EDX spectrum for LAAF crystal

Microhardness, Yield strength and Stiffness constant

Microhardness studies find wide applications in the study of material properties of solids. Hardness testing has been widely used to study the strength and deformation in materials. Hardness is defined as the ratio of the load applied to the surface area of the indentation. The method of measuring hardness is not dependent on a single physical property but may involve both the elastic and plastic deformation characteristics such as work hardening coefficient, tensile strength, stiffness constant and elastic modulus etc. Vickers microhardness test is found to be the most suitable (among various types of hardness measurements available) for the measurement of microhardness of crystals. Hardness measurement is to performed on a limited area with small damage to the area being measured and must yield extremely reliable results. A hardness tester fitted with a diamond pyramidal indenter attached to an incident light microscope is used for this study. Microhardness analysis was carried out using Vickers microhardness tester fitted with a diamond indenter. A good quality LAAF crystal was placed on the platform of the Vickers microhardness tester and loads of different magnitudes were applied for a fixed interval of 10 seconds. The hardness number was calculated using the equation H_v 1.8544 P/d^2 kg /mm^2 where P is the applied load in kg and d is the diagonal length of the indentation impression in millimeter [9]. The plot between hardness number (H_v) and load (P) LAAF crystals are shown in Figure 4. It is observed that Vickers hardness number of all the crystals increases gradually with increase in load and above 100 g cracks develop on the smooth surface of the crystal due to release of the internal stresses generated locally by indentation. A plot obtained between log P against log d gives a straight line which is derived from the Mayer's law, the relation connecting the applied load is given by $P = a\, d^n$. Here, n is the Mayer's index or work hardening coefficient that has been calculated from the slope of the straight line from the figure 5. The value of n for LAAF crystal is found to be 3. According to Onitsch [10], if n is greater than 1.6, the material belongs to the category of soft materials. In the present study the work hardening coefficient of grown LAAF crystal is greater than 1.6 and hence it is a soft material. The microhardness is related to yield strength (σ_y) by the equation $Hv = 3\sigma_y$ and the first order elastic stiffness constant (C_{11}) is related to the microhardness by the equation $\log C_{11} = (7/4) \log H_v$ [11, 12] . The load dependence of yield strength and

stiffness constant are given in the figures 6 and 7 and it is observed that the values of yield strength and stiffness constant increase with the applied load on the crystal.

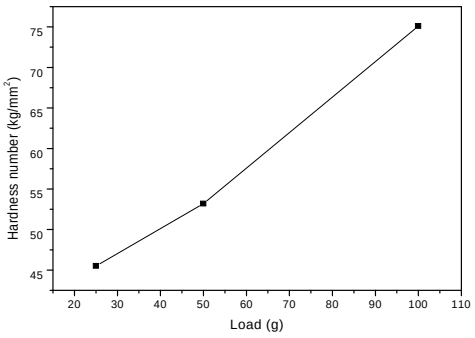

Figure 4 Dependence of microhardness with load for LAAF crystal

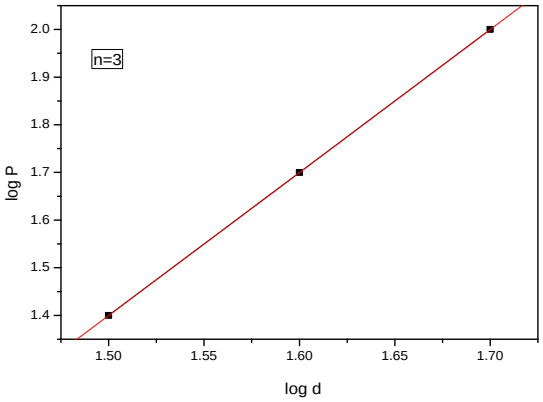

Figure 5 Plot of log P versus log d for LAAF crystal

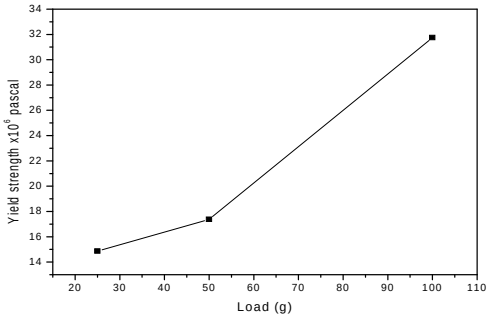

Figure 6 Variation of yield strength with load for LAAF crystal

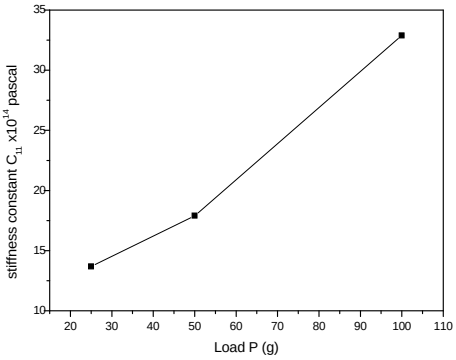

Figure 7 Variation of stiffness constant with load for LAAF crystal

Linear optical studies

UV-visible spectral study may be assisted in understanding the electronic structure of the optical band gap of the crystal and the study of the absorption edge is vital in connection with the theory of electronic structure. UV-visible transmittance spectrum for the grown LAAF crystal was recorded in the region 190-1100 nm using a Varian Cary 5E UV-Vis-NIR spectrophotometer and it is presented in the figure 8. It is observed from the result that the sample has transmittance and no absorbance in the entire visible region and hence this material is suitable for NLO applications. The lower cut-off wavelength corresponds to the fundamental absorption and it occurs at 235 nm. Absorption in the near ultraviolet region arises from electronic transitions associated within the sample. Using the formula E_g = 1240 / λ (nm), the band gap is calculated to be 5.276 eV for the grown LAAF sample.

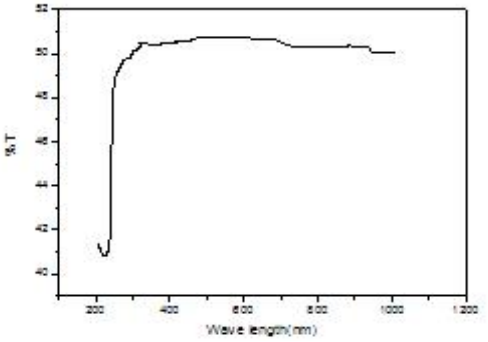

Figure 8 UV-visible spectrum for LAAF crystal

Fourier transform infrared (FTIR) analysis

To analyse the presence of functional groups in the sample, Fourier Transform Infrared (FTIR) Spectrum was recorded using a Shimadzu spectrophotometer with KBr pellet technique in the range of 4000 to 400 cm$^{-1.}$ FTIR spectrum of the grown crystals is shown in figure 9. Intense band in the range 3450 - 2900 cm^{-1} is due to stretching vibration from amino groups and OH stretching. An intense band in the range 1645 -1750 cm^{-1} is due to carbonyl stretching vibration. The complete assignments for the absorption peaks/bands of the FTIR spectrum are given in table 1.

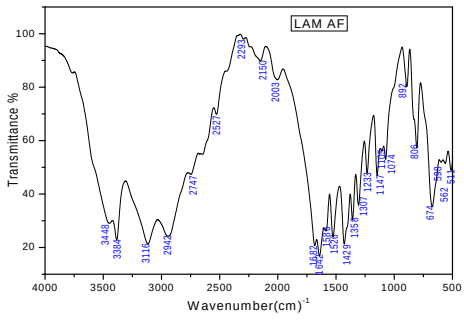

Fig.9 FTIR spectrum of LAAF crystal

Nonlinear Optical studies

Second harmonic generation (SHG) is a nonlinear optical process that results in the conversion of an input optical wave into an output wave of twice the input frequency. The light propagated through a crystalline solid, which lacks a center of symmetry, generates light at second and higher harmonics of

the applied frequency. Such frequency doubling processes are commonly used to produce green light (532 nm) from, for example, a Nd:YAG (Neodimium:Yttrium-Aluminium-Garnet) laser operating at 1064 nm. The Kurtz powder technique is a convenient method for screening large number of powdered materials for the second order NLO activity without needing to grow large single crystals. A laser is directed onto a powdered sample and the emitted light is collected, filtered and detected with a photo multiplier tube. The technique is crude in the sense that it detects a convolution of all the tensor components of second order susceptibility ($\chi^{(2)}$) and makes little attempt to account for the propagation characteristic of the beams. Since the results are particle-size dependent, great care must be taken in applying this technique quantitatively [13,14]. A Q-switched, flash lamp pumped Nd:YAG laser of power 72 mJ was used for this study. The generation of second harmonics was confirmed as the LAAF crystal is found to produce green light of halved wavelength (532 nm) when it is irradiated by fundamental wavelength (1064 nm) of Nd:YAG laser. It is observed from this study that the relative SHG efficiency for LAAF crystal is 0.87 times that of the reference KDP crystal.

Table 1 FTIR bands/peaks and their assignments for LAAF crystal

Wave number (cm^{-1})	Band assignments
3384	NH_3^+ asymmetric stretching and OH stretching
2942	NH_3^+ symmetric stretching
2293	Stretching of CH_3 vibration
2150	Combination of NH_3^+ asymmetric stretching and torsional oscillation
1642	NH_3^+ bending
1429	COO^- symmetric stretching
1358	C-C stretching
1307	CH_2 wagging
1147	NH_3^+ rocking
892	C-C-N symmetric stretching
806	C-CH_3 bending
674	N-H out-of plane bending
598	COO^- scissoring
511	COO^- rocking

Thermal studies

Thermal gravimetric analysis (TG) provides a quantitative measurement of any weight changes associated with thermally induced transitions and in the Differential Thermal analysis (DTA), the difference in the temperature between the sample and the thermally inert reference material is measured as a function of temperature. In the present work, the STD Q600 V8.3 Build 101 thermal analyzer was used to record TG/DTA thermal curves of LAAF sample. The sample was scanned at the rate of 20 ^oC_/minute in nitrogen atmosphere in the temperature range 30 -700 ^oC. The recorded thermal curves are presented in Fig. 10. From the TG curve, the thermal stability of the sample is realized up to 104 ^oC and the endothermic peak at 104 ^oC corresponds to liberation of water molecules from the lattice of LAAF crystal. The endothermic peak at 233 ^oC corresponds to the decomposition point of the sample. The endothermic peak at 361 ^oC is due to a phase transition which is unknown. 90% weight loss is noticed in the temperature range 500-700 ^oC.

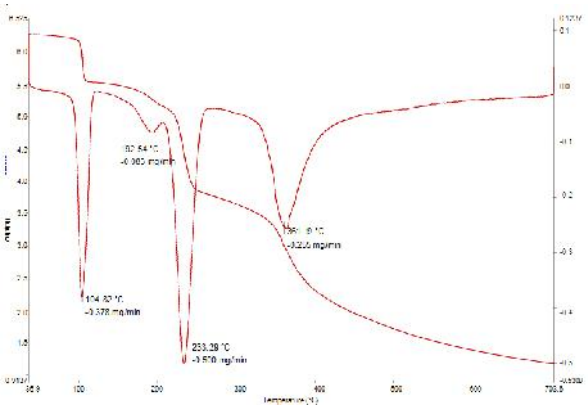

Fig.10 TG/DTA thermal curves for LAAF sample

CONCLUSION

L-asparagine crystal admixtured with ammonium fluoride (LAAF) salt was synthesized and single crystals were grown by slow evaporation solution technique. EDX and XRD studies were performed for the grown LAAF crystal to confirm the elements present and crystal structure. Microhardness studies were carried out to evaluate work hardening coefficient, yield strength and stiffness constant for sample. Optical band gap was evaluated to be is 5.276 eV. Second harmonic generation efficiency for the LAAF sample was found to be 0.87 times that of KDP sample. The sample has water molecules in the lattice of the crystal. The functional groups present in the sample were identified by FTIR spectral studies.

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References

1. A.S.I Joy sinthiya, P.Selvarajan, Ind. J. Appl. Res. 3 (2013) 521-523.
2. B Helina, P Selvarajan and A S J Lucia Rose, Physica Scripta 85 (2012) 055803.
3. *E.M.Onitsch, Mikroskopie 2(1947)131.*
4. F. Yogam *et al,* J. Therm. Anal. Calorimetry, 114 (2013) 1153-1159.
5. J. Chandrasekaran, P. Ilayabarathi, Optoelectronics Adv. Materials 5 (2011) 1325 – 1327.
6. J. Glorium Arul Raj, P. Selvarajan, S. Perumal, and N. Murali Krishnan, Mater.
7. J. Zyss, Molecular Nonlinear Optics: Materials, Physics and Devices, Academic Press, New York, 1994.
8. Manufact. Process. 26 (2011) 1254–1260.
9. P.Selvarajan, J. Glorium Arulraj, S.Peruml,J. Crystal Growth, 311 (2009) 3835–3840.
10. R. Wytt, Metal Ceramics & Polymers, Cambridge University Press,London (1974).

11. R.W.Boyd, Nonlinear Optics, 2nd Edn, Academic, Inc., San Diego (2003).
12. S. Masilamani, Optik 123 (2012) 1304–1306.
13. *S. Masilamani, K. Tamilarasan , Optik 124 (2013) 4303-4306.*
14. S.B.Monaco, L.E.Devis, S.P.Velsko, F.T.Wang, D.Eimerl, J.Crystal Growth 85(1987) 252.
15. W. A. Wooster, Widersande and Science Anwendung, Rep. Prog. Phys.1(1953) 62.

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