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Studies of L-Arginine Sodium Fluoride Crystals Grown by slow Evaporation Technique

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ABSTRACT

Solution method with slow evaporation technique was adopted to grow the single crystals of L-arginine sodium fluoride (LASF). Solubility of the sample was measured at different temperatures by gravimetric method. The micro hardness and work hardening coefficient of LASF crystal were evaluated at room temperature. Dielectric studies of the grown crystal were carried out using a multi-frequency LCR meter at various frequencies and temperatures. The relative SHG efficiency of the grown crystal of LASF was measured using Kurtz-Perry powder technique. LDT value of the sample was determined using a Nd:YAG laser and it is found to be high. Third order NLO parameters such as nonlinear refractive index, nonlinear absorption coefficient and nonlinear susceptibility of LASF crystal were determined by Z-scan technique.

KEYWORDS: Single crystal; Growth from solutions; Characterization; NLO; SHG; micro hardness; dielectric constant; LDT; Z-scan

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INTRODUCTION

An amino acid consists of a central carbon atom attached to a carboxyl group (-COOH), an amino group ($-NH_2$), a hydrogen atom, and a side group (-R), giving the general formula $R-CH-NH_2-COOH$. Amino acids are the building blocks used to make proteins and peptides. The different amino acids have interesting properties because they have a variety of structural parts which result in different polarities and solubility's. The key elements of an amino acid are carbon, hydrogen, oxygen and nitrogen. Amino acids are important in nutrition and are commonly used in food technology, Industry and Biochemistry in Industry; applications include the production of biodegradable plastics, drugs and chiral catalysts. Amino acids are crystalline solids with relatively high melting points, and most are quite soluble in water and insoluble in non-polar solvents. The amino acids which cannot be synthesized by the body and therefore need to be supplied through the diet are called essential amino acids. Arginine is one example of essential amino acid [1-, 2,3.] There are L-type, D-type and DL-type amino acids and usually L-type amino acids are the most useful in nonlinear optical (NLO) applications[4, 5, 6,7.] Here L-arginine and sodium fluoride are selected to combine to grow an NLO crystal viz., L-arginine sodium fluoride crystal. Undoped and metal doped L-arginine di-phosphate crystals have been grown and the grown crystals were characterized by XRD, FT-IR, optical absorption and NLO studied by Joseph Arul Pragasam et *al*.[8.] Saradha *et al.*, reported thermo luminescence, optical absorption, photoluminescence, FT-IR and XRD studies of orthophosphoric acid doped L-arginine crystals[9.] Monaca et al.,[10] have synthesized many complexes of L-arginine and characterized by various studies. L-arginine phosphate monohydrate crystals were grown and their characterizations were carried out by using many techniques [11,12]. The aim this work is to grow the single crystals of L-arginine sodium chloride and to characterize the harvested crystals.

GROWTH AND SOLUBILITY

AR grade chemicals of L-arginine and sodium fluoride were purchased from Merck India and they are taken in the equimolar ratio. The calculated reactants were dissolved in double distilled water and saturated solution was prepared. The solution was stirred for 3 hours at 50 ^{o}C using a hot plate magnetic stirrer. Here the solution was heated for reaction to place between L-arginine and sodium fluoride. After stirring the solution, it was cooled and filtered using good quality Whatman filter paper. The filtered solution was taken in a beaker and seed crystals were collected by spontaneous nucleation. Again the saturated solution was prepared and the seed crystals were placed in the growth vessel containing the saturated solution. The growth vessel was covered with perforated sheet and due to slow evaporation the seed crystals were grown into big-sized crystals of L-arginine sodium fluoride. A grown crystal of L-arginine sodium fluoride (LASF) is shown in the figure 1. The grown crystals are observed to be colourless and transparent. It is known that the size of a crystal depends on the amount of solute available in the saturated solution and the measurement of solubility gives the amount of solute in the 100 ml of saturated solution. The solubility of the grown crystal was measured by gravimetric method. The aqueous saturated solution of the sample was taken in a petri dish and it is warmed till the solvent evaporates. The solute deposited in the petri dish was weighed and using the weight of empty petri dish, the solubility was determined. The solubility of LASF crystal in water was found at different temperatures such as 30, 35, 40, 45, 50 and 60 ^{o}C and the plot of solubility versus temperature is presented in the figure 2. Since the solubility (S) of the sample increases as the temperature increases, the sample exhibits positive temperature coefficient of solubility. The solubility data can be fitted to a relation $S = AT^2 + BT + C$ where A, B and C are the constants, T is the temperature of the solution[13.] Since the values of solubility are moderate in the mentioned temperature range, the single crystals of LASF can be grown by both slow evaporation and slow cooling growth methods.

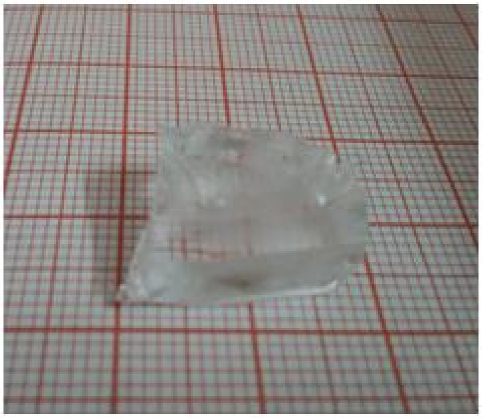

Fig. 1: A transparent and colourless crystal of LASF

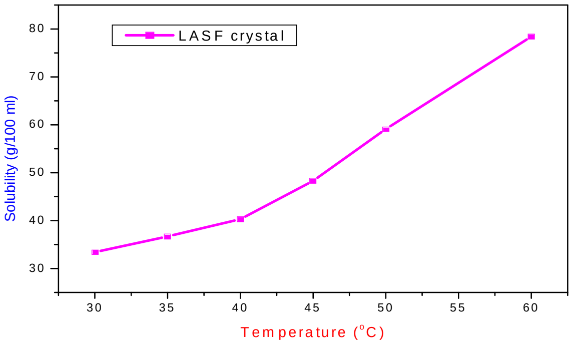

Fig.2: Solubility curve for L-arginine sodium fluoride (LASF) crystal

HARDNESS STUDIES

Hardness may be defined as the ability of a material to resist permanent indentation or deformation when in contact with an indenter under load. Generally a hardness test consists of pressing an indenter of known geometry and mechanical properties into the test material. The indenter may be spherical (Brinell test), pyramidal (Vickers and Knoop tests), or conical (Rockwell test). In the present work, Vickers micro hardness of the grown crystal was studied using SHIMADZU HMV-2T micro hardness tester. It was originally known as the 136° diamond pyramidal hardness test because of the shape of the indenter. The indentations were made on the polished crystal for the loads of 25, 50,75 and 100 g. The indentation time was kept for 10 seconds for all the loads. As the load is increased beyond this limit, cracks developed on the smooth surface due to the internal stress generated locally by the indentation. The Vickers hardness number is a number related to the applied force and the surface area of the measured unrecovered indentation produced by a pyramidal diamond indenter. The Vickers hardness number (H_v) is computed using equation $H_v = [2 P \sin(136/2)]/d^2 = (1.8544 P)/d^2$ where P is the indentation load in kg and d is the mean diagonal of indentation in mm. The calculated values of hardness number for LASF crystal are given in the figure 3. It is observed that hardness number increases with increase of the applied load. Since the hardness increases with increase of load, the crystal has reverse indentation size effect (RISE). Meyer's plot is drawn using the relation $P = a\, d^n$ where a is a constant and n is work hardening coefficient of the sample. The value of work hardening coefficient of LASF crystal was obtained from the Meyer's plot (Fig.4) and the value is 3.097. As the value of 'n' is more than 1.6, it is concluded that LASF crystal belongs to the category of soft materials[14.]

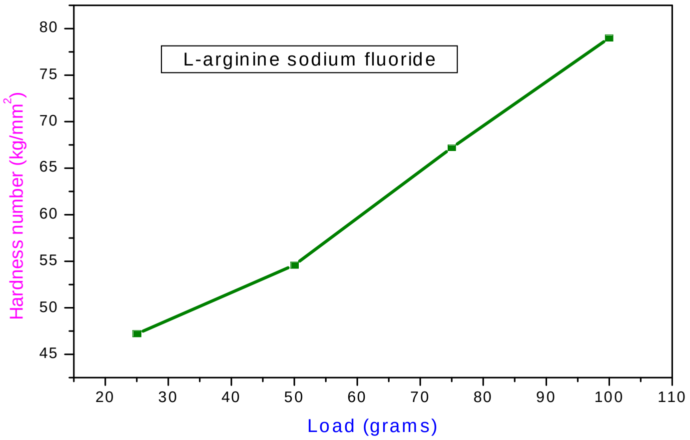

Fig.3: Plot of hardness number with the applied load for L-arginine sodium fluoride crystal

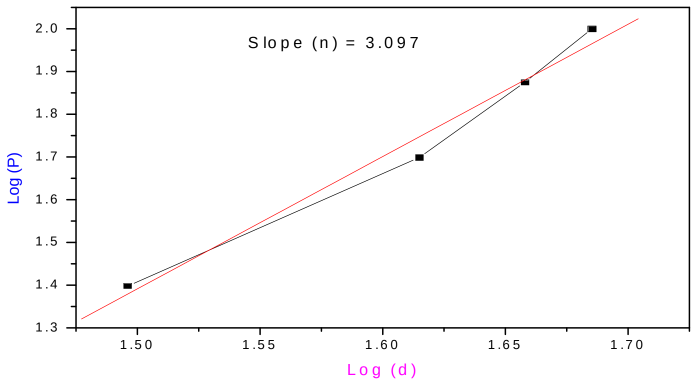

Fig.4: Meyer's plot for LASF crystal

MEASUREMENT OF LDT VALUE

Laser damage threshold (LDT) is an important factor which affects the NLO applications. The NLO crystal must be tolerance and resistance to laser damage to perform as a device for device applications. Since high optical intensities are involved in nonlinear processes, NLO materials must be able to withstand high power intensity. LDT values of grown crystal were measured using the Q-switched Nd-YAG laser of wavelength of 1064 nm and duration of the pulse is 10 ns. The laser damage threshold value depends on a number of laser parameters such as longitudinal and transverse modes. In this experiment, lens and crystal positions are fixed and the laser pulse energy was increased until a visible spot was seen at the crystal surface. The crystal is mounted on a sample holder and slightly kept away from the focal spot of the beam to avoid any possible damage. Laser operation can be controlled by Gaussian remote control back panel where the energy/volts button controls the output energy of the laser by varying the charge voltage in the flash lamp. The damage occurring on the surface of the sample is observed with the help of scattered radiation of laser from its surface. A sharp reduction in the intensity of the transmitted laser beam gives the laser damage threshold value. The LDT value was determined using the formula $P = E/\pi\tau r^2$ where E is the input energy in mJ, τ is the pulse width in ns and r is radius of the spot in mm. A good quality crystal of LASF was used as the sample in this experiment and the obtained value of LDT for the sample is 0.761 GW/cm^2. Since the LDT value of LASF crystal is more than that KDP crystal (0.21 GW/cm^2), the sample of this work is the better crystal for optical applications.

Z-SCAN STUDIES

Z-scan technique is a method for analysis of third order NLO analysis and there are two modes viz., open aperture and closed aperture Z-scan methods. Using open aperture Z-scan curve, the nonlinear absorption coefficietn can be determined and using the closed aperture Z-scan curve, the nonlinear refractive index can be calculated. Using both open aperture and closed aperture Z-scan data, the nonlinear third order susceptibility can be determined[15.] In the closed aperture method, an aperture is placed to prevent some of the light from reaching the detector. The aperture causes only the central region of the cone of light to reach the detector. The detector is sensitive to any focusing or defocusing that a sample may induce. The sample is typically placed at the focus point of the lens, and then moved along the Z-axis. Open aperture method is similar to the above method, however the aperture is removed or enlarged to allow all the light to reach the detector. In this measurement, a He–Ne laser (λ = 632.8 nm) is used as the light source. The transmitted light intensity from the sample is measured as a function of sample position in the Z-direction with respect to the focal plane either through a closed aperture or open aperture in order to resolve the nonlinear refraction and absorption coefficients. The obtained Z-scan data are given in the form of curves as shown in the figures 5 and 6. It is observed that the closed Z-scan curve is characterized by a peak followed by a valley and hence LASF crystal has negative nonlinear third order refractive index and it can be determined using the relation $n_2 = \Delta\phi / (K\, I_o\, L_{eff})$ where I_o is the intensity of the laser beam at the focus and $K = 2\pi / \lambda$ (λ is the wavelength of laser beam), L_{eff} is the effective thickness of the sample and $\Delta\phi$ is the phase shift. Using open aperture curve, the third order nonlinear absorption coefficient (β) of the sample was calculated using the relation $\boldsymbol{\beta} - \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}}$ where ΔT is the peak value or valley value at the open aperture Z-scan curve. The absolute value of third order susceptibiliy of the sample was calculated using the relation $\chi^{(3)} = [\{\text{Real part of } \chi^{(3)}\}^2 + \{\text{Imaginary part of } \chi^{(3)}\}^2]^{1/2}$ (esu). The obtained values of third order NLO parameters of LASF crystal are given in the table 1. Due to the self-defocussing nature, the sample has negative nonlinear refractive index and this property is useful in the protection of optical sensors such as night vision devices.

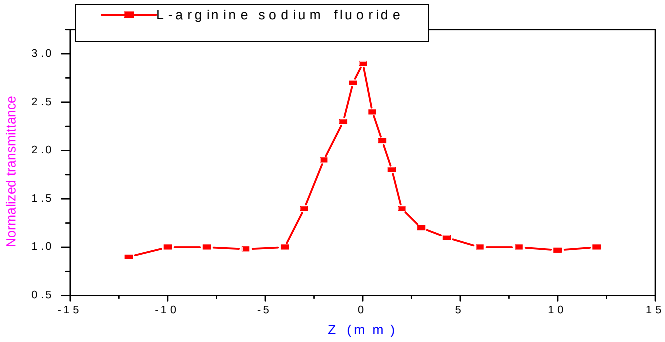

Fig.5: Open aperture Z-scan curve for L-arginine sodium fluoride crystal

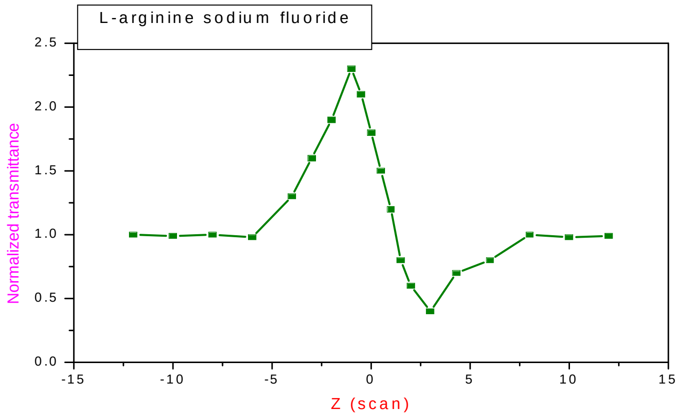

Fig.6: Closed aperture Z-scan curve for L-arginine sodium fluoride crystal

Table 1: The values of third order NLO parameters of LASF crystal

S.No.	**For Z-scan measurement**	**Values**
1.	Wavelength of laser	632.8 nm
2.	Power of the laser	5 mW
3.	Focal length of convex lens used	30 mm
4.	Nonlinear absorption coefficient (β)	9.822 x10^{-5} m/W
5.	Nonlinear refractive index (n_2)	- 8.730 x 10^{-11} m^2/W
6.	Absolute value of nonlinear susceptibility	9.025 x 10^{-7}esu

MEASUREMENT OF DIELECTRIC PARAMETERS

The dielectric parameters like dielectric constant and dielectric loss of LASF crystal were measured using HIOKI 3532-50 LCR HITESTER in the frequency region 1 kHz to 1 MHz. A good quality and transparent grown crystal of LASF was selected and used for the dielectric measurement. For good ohmic contact, opposite faces of the sample crystal were painted with good quality silver paste. The dielectric constant and the dielectric loss were measured for various frequencies under the temperature range 30-75 ^{o}C. The variations of dielectric constant and dielectric loss of LASF crystal with temperature at different frequency values are shown in the figures 7 and 8. From the results, it is observed that as the temperature increases, the value of dielectric constant increases and it decreases with increase of frequency. The high value of dielectric constant at low frequency region is due space charge polarization and due to loss of polarization in the high frequency region, the dielectric constant decreases. The same behaviour is also noticed in the case of dielectric loss of the sample. It is found that the dielectric loss factor is low for the sample and hence the lower value of dielectric constant at higher frequencies is a suitable parameter for the enhancement of SHG coefficient and this is called as the Miller's rule [16, 17].

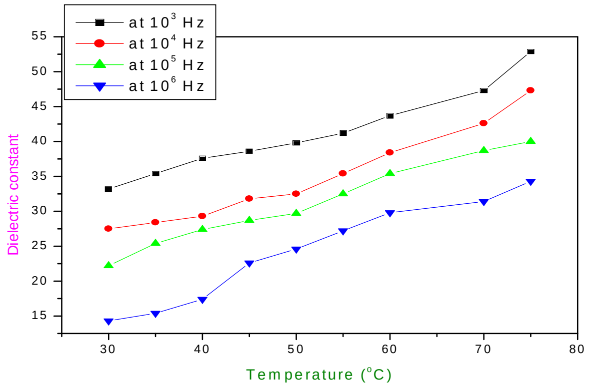

Fig.7:Variation of dielectric constant with temperature at different frequency values for LASF crystal

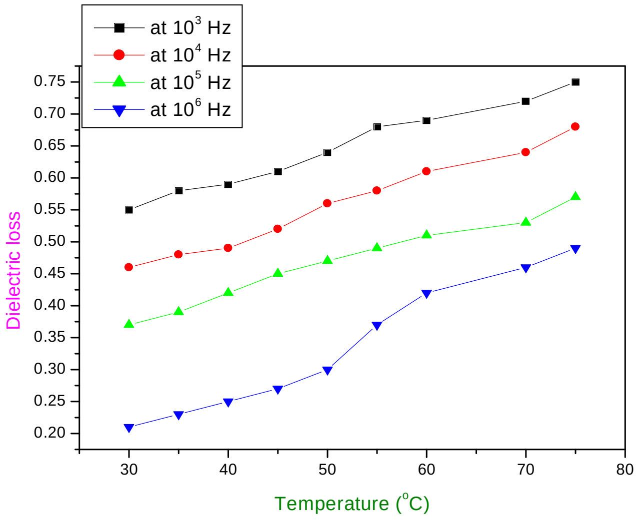

Fig.8: Variation of dielectric loss factor with temperature at different frequency values for LASF crystal

SHG STUDIES

The important second order NLO study is second harmonic generation (SHG) study and it devised by Kurtz and Perry [18]. This technique consists of a Q-switched Nd: YAG laser the output of which is filtered through 1064 nm narrow pass filter. The power of the fundamental beam is monitored by the power meter. The sample is in the form of fine powder of known grain size and pressed between two glass plates. The generated harmonic wave is passed through a 532 nm narrow pass filter and fed to other channel of the power meter. The ratio of the fundamental and harmonic intensities determines the SHG efficiency of the sample. The SHG efficiency varies with the grain size of the powdered sample. To eliminate the experimental error, potassium dihydrogen phosphate (KDP) sample of the same size is tested in the same set-up and the efficiency is evaluated as a ratio. Both the reference and test samples must have the uniform particle size of 150 to 200 microns and throughout the experiment the laser power is kept constant. To determine the essential features of second harmonic generation in thin powder layers, experiments may be conducted to measure the dependence of second harmonic intensity on the following parameters like angle between detector and direction of incident light beam, powder layer thickness, average particle size and laser beam diameter. For the present study, Q switched High Energy Nd: YAG with EPM 2000 dual channel power/energy meter was used. The laser with pulse width of 8 ns and a wavelength of 1064 nm and 10 Hz fundamental radiation is focused on the powdered microcrystalline samples. The emission of green light (532 nm) from the sample is taken as the evidence for the second harmonic generation. The calculated relative SHG efficiency of LASF crystalline powder sample is 1.41 times that of the standard KDP sample.

CONCLUSION

L-arginine sodium fluoride (LASF) crystal was prepared by taking L-arginine and sodium fluoride in 1:1 molar ratio using double distilled water as the solvent. Saturated solution was prepared and due to slow evaporation, the single crystals of LASF were grown. Solubility of the sample was found to be increasing with increase of temperature. LDT value of LASF crystal was found to be 0.761 GW/cm^2. The microhardness was determined and it is observed to be increasing with increase of the applied and work hardening coefficient of the sample was found to be 3.097. The nonlinear refractive index of LASF crystal is observed to be negative and hence the sample shows the de-focusing nature. The dielectric parameters of the grown crystal of LASF are noticed to be increasing with increase of temperature and it reveals the insulating nature of the sample.

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