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Synthesis and characterization of L-arginine sodium sulphate (LANS) nanocrystals with non-linear optical response

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ABSTRACT

L- Arginine Sodium Sulphate (LANS) nanocrystals have been obtained from gel like solutions by slow evaporation technique for first time.TEM indicates the formation of nanocrystals with average particle size lying between 20-50 nm. Powder XRD studies show orthorhombic structure with lattice parameters a=5.130 A.U, b=11.680 A.U and c=8.117 A.U. The particle size of LANS nanocrystals using XRD data (Debye- Scherer relation) is found to be 56 nm and is in fair agreement with the TEM results. The chemical composition remains verified by using CHNS and EDAX Analysis. Comparative FTIR and FT-Raman spectrum confirm the presence of fundamental groups and indicates non-centro symmetric molecule. LANS nanocrystals are found to be thermally more stable than reported crystals like LADP, LAAC, LAF, LADN. UV – Vis studies indicate presence of wide transparancy window useful in optoelectonic applications and peaks below the cut off region points towards the formation of nanocrystals. Low SHG efficiency has been indicated by NLO studies. Low ac conductivity and low dielectric loss useful in photonic and NLO based devices have been noted.

Keywords: Nanocrystal, TEM, SEM, Non-linear optics, Dielectric

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INTRODUCTION

Amino acid L-arginine is seen to form a number of interesting complexes with different acids. It has attractive NLO properties which were first reported by Monaco et.al [1]. Novel properties of l-arginine phosphate (LAP) attracted the attention of large number of researchers all over the world to synthesize new materials based on l-arginine. The discovery of promising NLO properties in l-arginine phosphate monohydrate (LAP) [1], led to the interest in synthesis of crystalline salts of l-arginine and further to the work on semi-organic crystals like l-arginine H_3PO_4nanocrystals [2]. L-arginine is also adopted as carbon and nitrogen source for synthesis of N-doped carbon nanowires used in nanoelectronic devices [3]. Besides L-arginine is also one of the amino acids used as surface cappings agents for water dispersible ZnS-Mn semiconductor nanocrystals [4]. Many of the l-arginine based materials are found to have low value of dielectric constant rendering them suitable for microelectronics industries.
In the present work, nanocrystals of l-arginine sodium sulphate (LANS) were synthesized for first time and have been extensively characterized.

MATERIALS AND METHODS

LANS nanocrystalswere synthesized by slow evaporation from aqueous solution containing l-arginine ($C_6H_{14}N_4O_2$) and sodium sulphate (Na_2SO_4) in 3:1 molar ratio. The solution was preheated to 35°C for about 5 minutes. After about six weeks time the LANS nanocrystals embedded in the gel were carefully separated. These nanocrystals were subjected to transmission electron microscope(TEM) studies using PHILIPS CM_{200} operating in voltage range 20-2000kv with resolution of 2.4A.U.The solubility studies were carried out in a constant temperature water bath with a control accuracy of $\pm$ 0.05°C, using cryostat for cooling below room temperature. To measure the metastable zone width, conventional polythermal method was employed. The chemical composition of the synthesized material l-

arginine sodium sulphatenanocrystals (LANS) was estimated by CHNS analyzer (THERMO FINIGAN, FLASH 1112 SERIES). SEM and EDAX analysis was carried out using scanning electron microscope (ZEISS ULTRA FESEM). A Bruker AVANCE III 500 MHz (AV 500)multi nuclei solution NMR was employed for study of ^{1}H-NMR spectra. PanalyticalXpert PRO MPD X-ray diffractometer system with characteristic Cu-Kα radiation (λ=1.5405 A.U) was employed for XRD Studies. FTIRspectrawererecorded on NicoletMAGMA$_{550}$FTIR spectrometer using KBr pellet intherange 4000 -400 cm^{-1} andBRUKERRFS STANDALONE 27 FT-Raman Spectrometer was employed for FT-Raman analysis. ND:YAG (1054nm) laser source was used for FT-Raman studies and the spectra were recorded in the spectral range 4000-100 cm^{-1}.For TGA/DTA analysis PERKINELMER,DIAMONDTG/DTAthermalanalyzer was employed. Dielectric studies were carried out using HIOKI 3532.50 LCR Hi TESTER. UV-Vis Optical Spectra was studied using a Perkin Elmer model No.Lamda35 UV-Vis spectrophotometer. The Kurtz –Perry SHG test was performed to study the NLO response.

RESULTS AND DISCUSSION

Solubility and Metastability zone width

The solubility of LANS was determined at four different temperatures viz, 35, 40, 45 and 50^{o}C. The solubility is found to increase with rise in temperature (Figure 1). Metastable zone width is the limit of the supersaturation that can induce spontaneous nucleation. It indicates the solubility of the solution in the vicinity of the equillibrium point.Literature review shows that l-arginine based materials have positive temperature coefficient of solubility [5]. To measure the metastable zone width of LANS, conventional polythermalmethod has been suggested [6]. In case of present LANS the temperature of appearance of those very small crystallites was taken as the nucleation temperature. Metastable zone width was calculated as difference between the point of solubility and the measured point of nucleation. The metastable zone width is found to be narrow and is seen to increase with rise in temperature. The interactions of solute-solute, solute-solvent and the ionic nature of the molecules have been reported to influencethe metastable zone width [7-9].

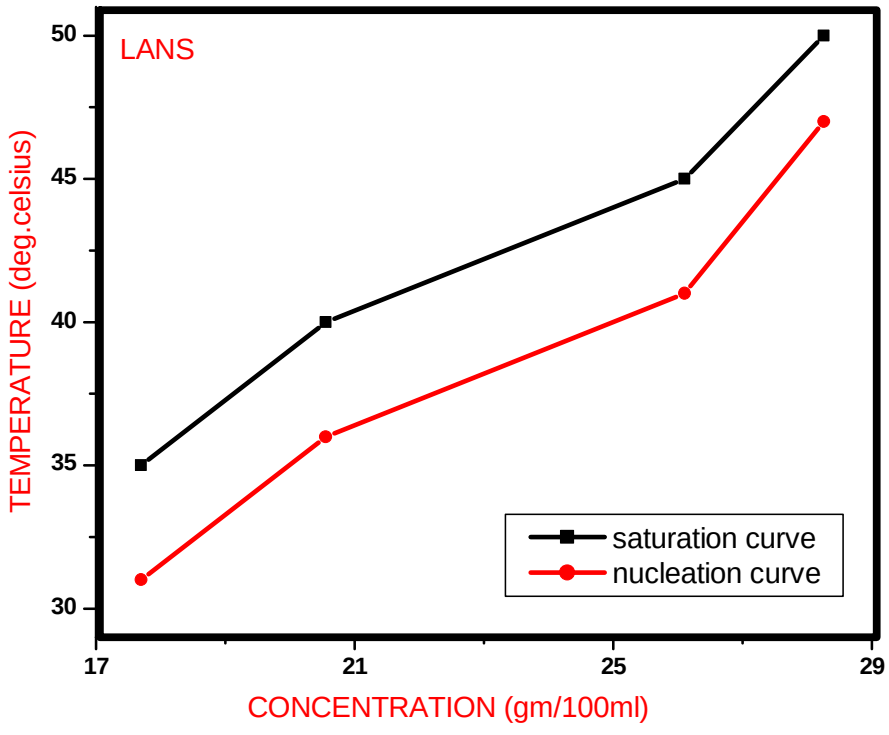

Figure 1 Solubility curve and metastable zone width of LANS nanocrystal

TEM analysis

The formation of nanocrystals took substantial time (6 Weeks) and they had to be carefully collected from the gel like remnant solution. In solution-based synthesis of nanocrystalsobtained as sols the crucial factor that imparts stability to nanocrystal is the presence of a ligand shell that may be absorbed on the surface. In the absence of this ligand shell, particles tend to aggregate to form bulk material. In an aqueous medium an electrical double layer is

formed by means of coulomb interaction between the charged ligand species. This interaction is further seen to provide a repulsive force to counter the attractive Vander Waals force between the grains [10].

TEM studies reveal the formation of nanocrystallites. Figure2shows the TEM image ofl-arginine sodium sulphate (LANS)nanocrystals. LANS nanocrystals show typical hexagonal geometry with approximate size ranging from 20-50 nm. The circular observed rings in SAED pattern suggests the nanocrystalline nature of the sample.

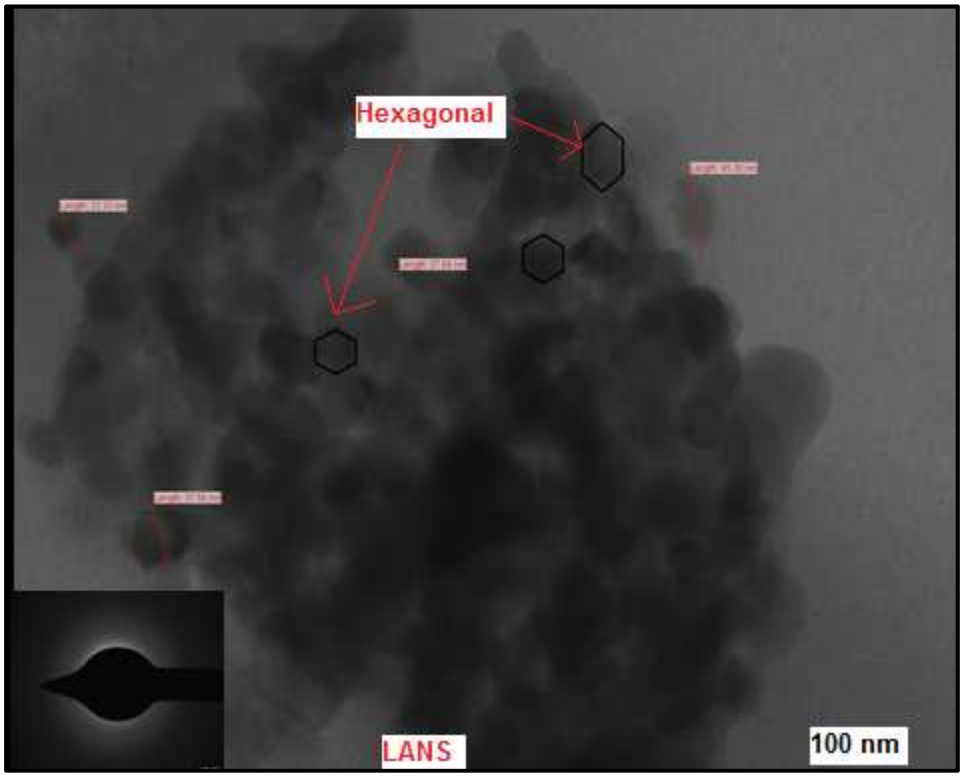

Figure 2 TEM of LANS nanocrystal

CHNS, SEM and EDAX Analysis

The chemical composition of the synthesized LANS Nanocrystals was determined by CHNS Analysis (Table 1)The oxygen and presence of other inorganic counterparts such as, sodium and sulphur has been detected in the EDAX analysis.

Table 1 Chemical composition of LANS nanocrystal

Composition (%)		
Element	Theoritical	Measured
Carbon	3.276	3.342
Hydrogen	0.637	0.652
Nitrogen	2.548	2.973
Sulphur	2.912	2.912

Very fine surface morphology is observed from SEM image of LANS nanocrystal (Figure 3). White aggregates on the edges may indicate presence of sodium in the sample. Voids if any are not visible. EDAX spectrum (Figure 4) shows peaks for sodium, oxygen and sulphur, suggesting the incorporation of sodium sulphate into the crystal lattice of l-arginine.

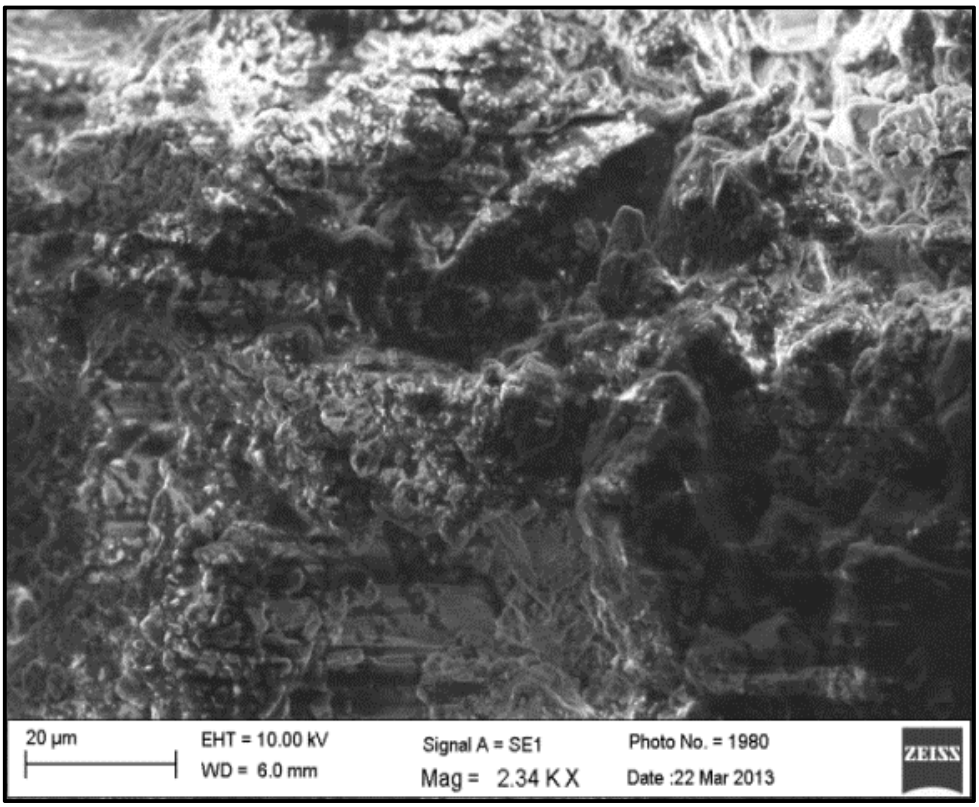

Figure 3 SEM of LANS nanocrystal

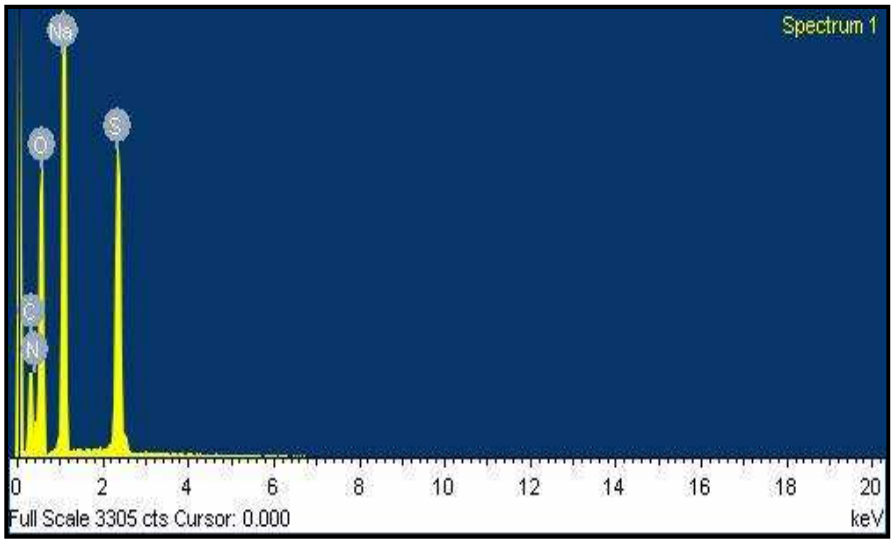

Figure 4 EDAX Spectra of LANS nanocrystal

^{1}H-NMR

^{1}H-NMR spectrum for the LANS reveals peaks near 4.7 ppm, 3.5 ppm and 1.7 ppm (figure 5). They can be assigned to HN═C─NH_2 group, ─CH─COO^- group and multiplet of methylene proton respectively[11]. Table 2 gives the details of the chemical shifts and respective assignments for LANS. Multiplet signals have been observed for γ-(CH_2) and δ-(CH_2) groups [12]. Absence due to bending of ─C─C─C─ if any which results in increase the chemical shifts of γ-(CH_2) and δ-(CH_2) have not been observed [13].

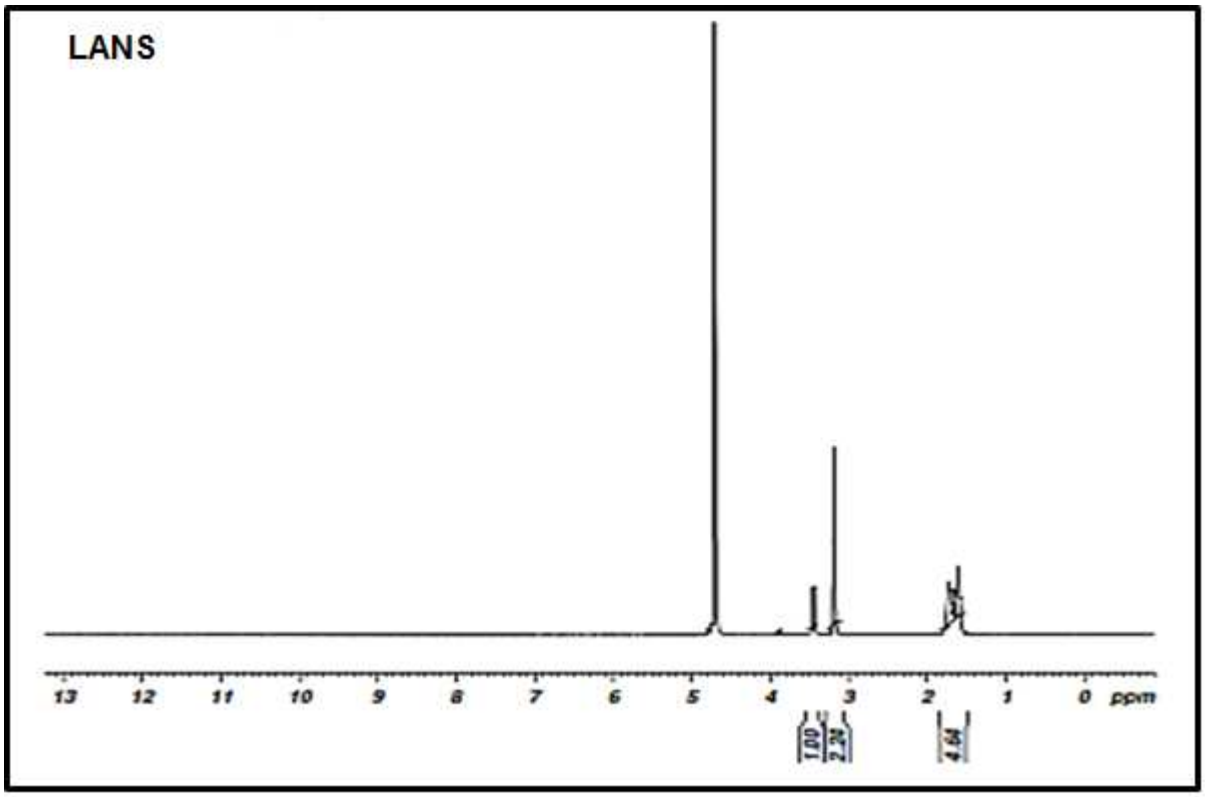

Figure 5 ^{1}H-NMR of LANS nanocrystal

Table 2 ^{1}H-NMR chemical shifts of LANS nanocrystals

	ξ(HN═C─NH_2)	α(─CH─COO)	δ(CH_2)	β(CH_2)	γ(CH_2)
LANS	4.7	3.4	3.2	1.7	1.6

Powder X-ray Diffraction studies

Rapid powder XRD studies confirm the orthorhombic structure for LANS nanocrystals like l-arginine diphosphate [14] and l-arginine perchlorate [15]. The peaks were analysed by using POWD- Interactive powder diffraction data interpretation and indexing software program, Version 2.2 (Australia). The XRD profile is shown in Figure 6. The lattice parameters were found to be a=5.130 A.U, b=11.680 A. and c=8.117 A.U with unit cell volume of about 485(A.U)^3. Highest intensity peaks were observed at 18.88° and 32.01° corresponding to (1 1 0) and (1 2 2) planes respectively. The particle size could be estimated with the help of Debye Scherer's equation D =(0.9 λ)/ β Cos θ whereD is the average crystalline size, λis the X-ray wavelength (1.5410 A°) of CuK_α, β is the full width at half maximum (FWHM) of the diffraction peaks and θ is the Bragg's angle.

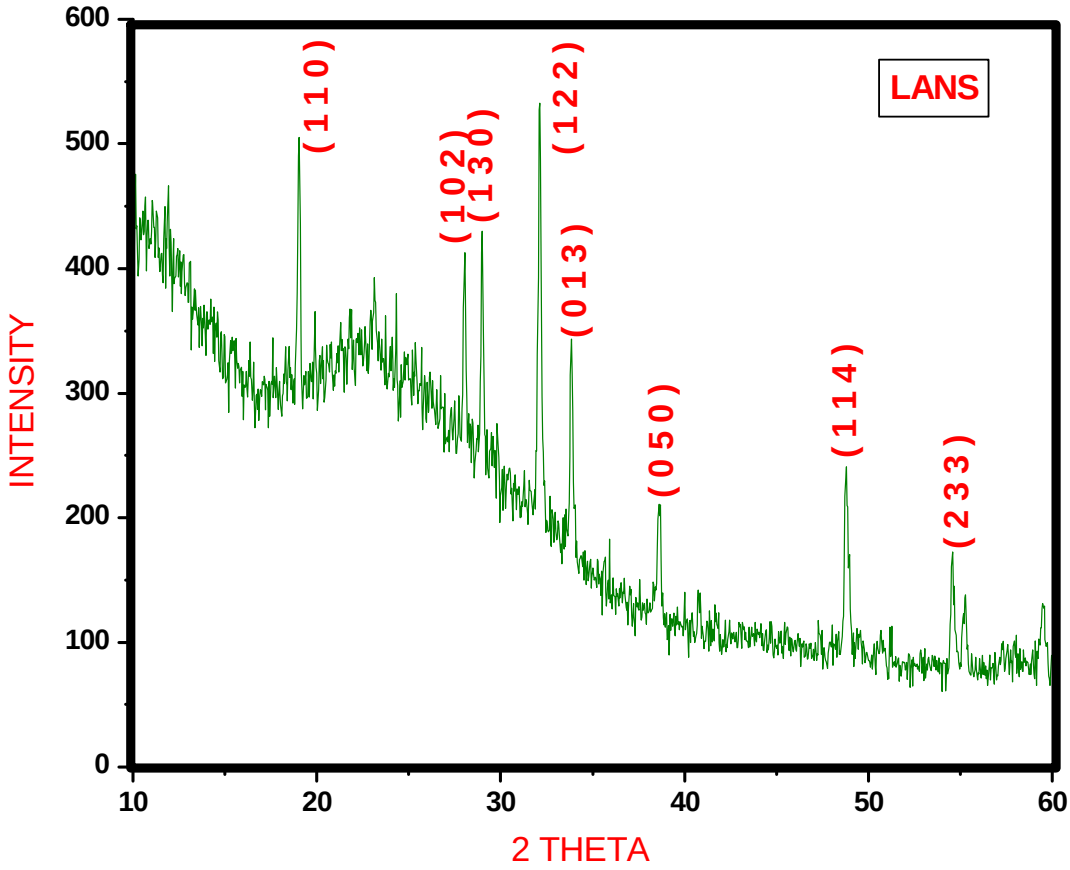

Figure 6 XRD Profile of LANS nanocrystal

The particle size of LANS Nanocrystals was found to be 56 nm using the (1 2 2) plane which is in fair agreement with the TEM results.

FTIR and FT-Raman Analysis

An attempt has been made to correlate the IR and Raman peaks of LANS nanocrystals. It reveals the presence of amino, carboxyl and sulphate groups in the molecule.

Table 3 Comparative Chart of FTIR and FT Raman band assignments of LANS nanocrystals

Wavenumber (cm^{-1})		
IR	**RAMAN**	**Band assignments**
	149.93	Lattice vibrations
	451.41	Rocking COO^-
616.36	621.05	Rocking COO^-
	992.79	Symmetric bending of SO_4
1118.45	1100.98	Symmetric bending of SO_4
	1152.98	NH_2 wagging
	1309.94	Twisting vibration of CH_2 group
1476.08	1439.71	O-H stretching
1593.87		NH^{3+} symmetric deformation
1630.81		Asymmetric stretching of COO^-group
1674.6		NH^{3+} asymmetric deformation
2106.34		Combination of NH^{3+} deformation andNH^{3+} torsion
2180.34		Combination of NH^{3+} deformation andNH^{3+} torsion
2238.66		Combination of NH^{3+} deformation andNH^{3+} torsion
2954.69	2935.63	Aliphatic C-H stretching
3190.39		N-H stretching
3371.69		N-H stretching
3780.3		O-H stretching

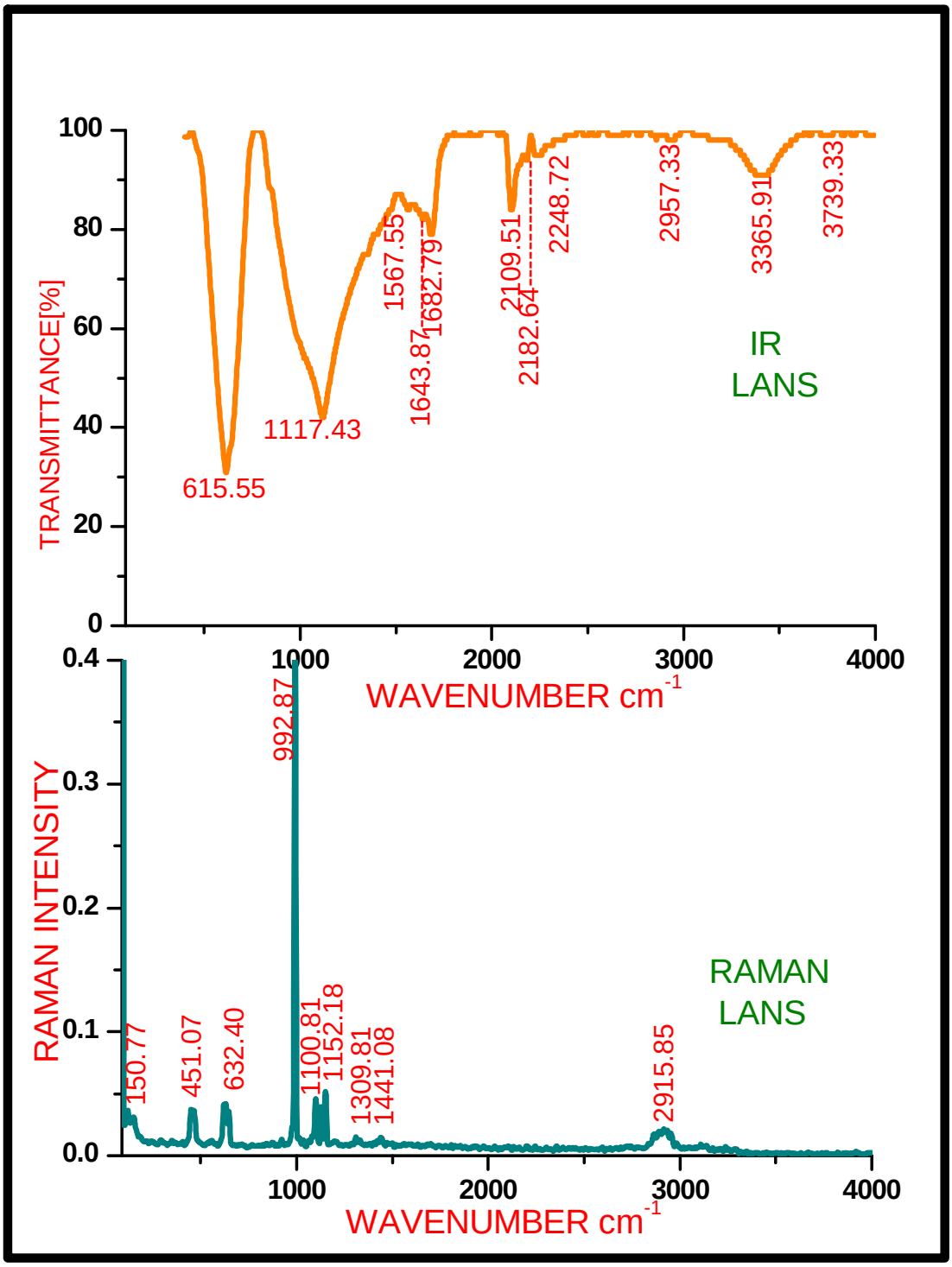

Figure 7 FTIR and FT-Raman spectra of LANS nanocrystal

Raman bands at 451.41cm^{-1}and IR bands at 1630.81 cm^{-1} for LANS are due to rocking and asymmetric stretching of COO^- groups. NH^{3+} symmetric and asymmetric deformation appears at 1593.87 cm^{-1}, 1674.60 cm^{-1} respectively in the IR spectrum [16, 17] and are found to be very weak in Raman spectra. The presence of C-H bands is indicated by the absorption at 2954.69 cm^{-1} in IR and by 2935.63 cm^{-1}in RAMAN. The presence of N-H stretching is indicated by the IR bands lying at 3190.39 cm^{-1} and 3371.63 cm^{-1}. The NH_2 wagging is observed at 1152.98 cm^{-1}. Symmetric stretching of SO_4 group has been observed at 1118.45cm^{-1}, 992.79cm^{-1} and 1100.81cm^{-1} [9, 18]. Absence of peaks above 3400 cm^{-1}indicates absence of water molecule in the crystal lattice. Fig.7 shows

comparative profile of FTIR and FT-Raman spectra of LANS nanocrystals and the comparative assignments are given in table 3.

TGA/DTA Analysis

Thermogravimetricanalysis(TGA)andDifferentialthermalanalysis(DTA)wascarriedoutsimultaneouslyfordetermining thethermalstabilityofthematerialinthetemperaturerange 50-500^{o}C in air atmosphere at the rate of 10^{o}C per minute. The combined TGA and DTA profile of LANS nanocrystals is shown in figure 8.

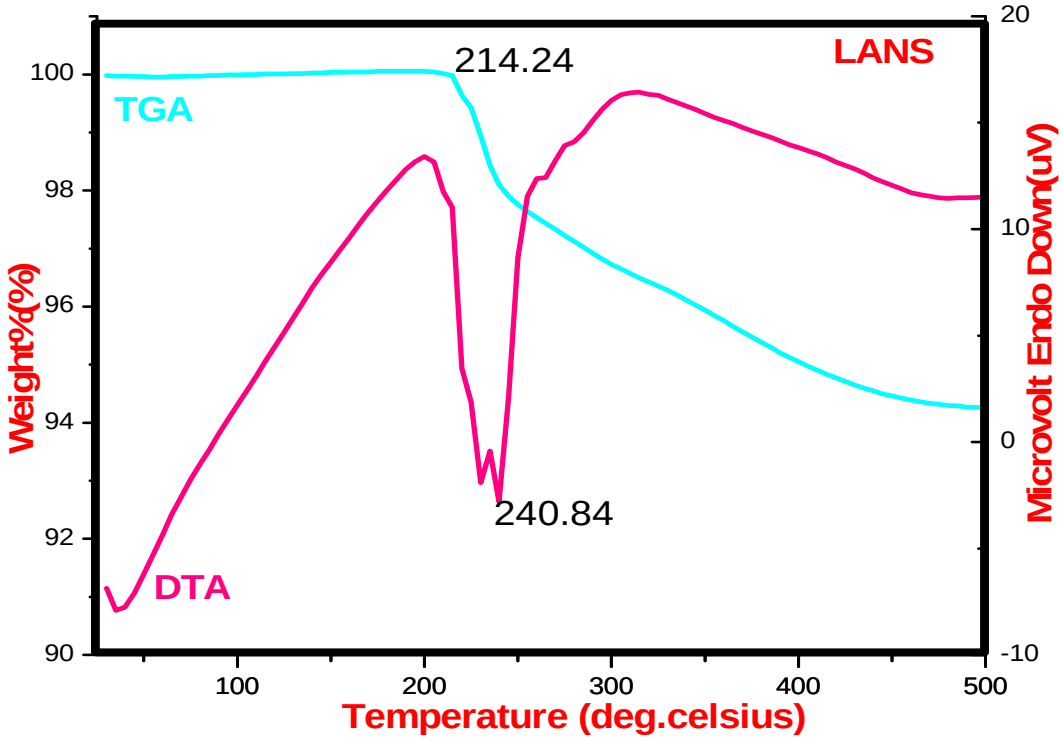

Figure 8 TGA/DTA Profile of LANS nanocrystal

From the TGA curve an initial weight loss at 46.51°C and there after the nanocrystal is stable upto 211.70°C with a further small weight loss of about 6.5% uptill 500°C. No weight loss up till 200°C in LANS indicates the absence of any physically adsorbed water molecule. Absence of water molecule is in fact responsible for the long range stability of the synthesized nanocrystals and is also evident from FTIR and FT-Raman studies. The DTA curves shows an exothermic peak at 229.0^{o}C for LANS mostly coincides with the initial weight loss, as seen in TGA trace. Thus the LANS nanocrystal are highly stable as compared to LAP(111^{o}C), L-ADP(173.9^{o}C), LAHClBr (92^{o}C), LA-HCl (70^{o}C), LAHBr (110^{o}C), LAF (200^{o}C) and LAAC (200^{o}C) [19].

Dielectric Studies

For understanding internal polarization dielectric studies of grown LANS nanocrystals was carried out. Figure 9 shows the frequency response of dielectric constant (ϵ^{I}) and dielectric loss (ϵ^{II}) of LANS nanocrystal in the range 1 KHz to 5 KHz.It is observed that ϵ^{I} decreases with increase in frequency and becomes very low to become constant at high frequencies. All the four polarizations viz., ionic, dipolar, electronic and space charge which are active in low frequency region are responsible for high value of ϵ^{I} at low frequency. At high frequency, due to the inertia of molecules and ions, ionic and dipolar contributions decreases, thereby decreasing the value of ϵ^{I}[20, 21].A linear nature is seen in graph of log(dielectric loss) Vs log(frequency) (figure 9) .Using straight line approximation, the slope turns out to be -1.6966 which indicates deviation from dc conduction [22]. The deviation of slope from unity at low frequencies may be due to space charge effects [22]. Weak dielectric relaxation peaks are found near 1MHz (figure 9).Materials with low dielectric constant at high frequencies can find applications in photonic and NLO devices. The decrease in dielectric loss(ϵ^{II}) with increase in frequency is also observed. This can be attributed to the perturbation of the phonon system by the electric field. The energy transferred to the phonons gets dissipated in the form of heat [23]. Low value of dielectric loss suggests that the grown material has optical property.

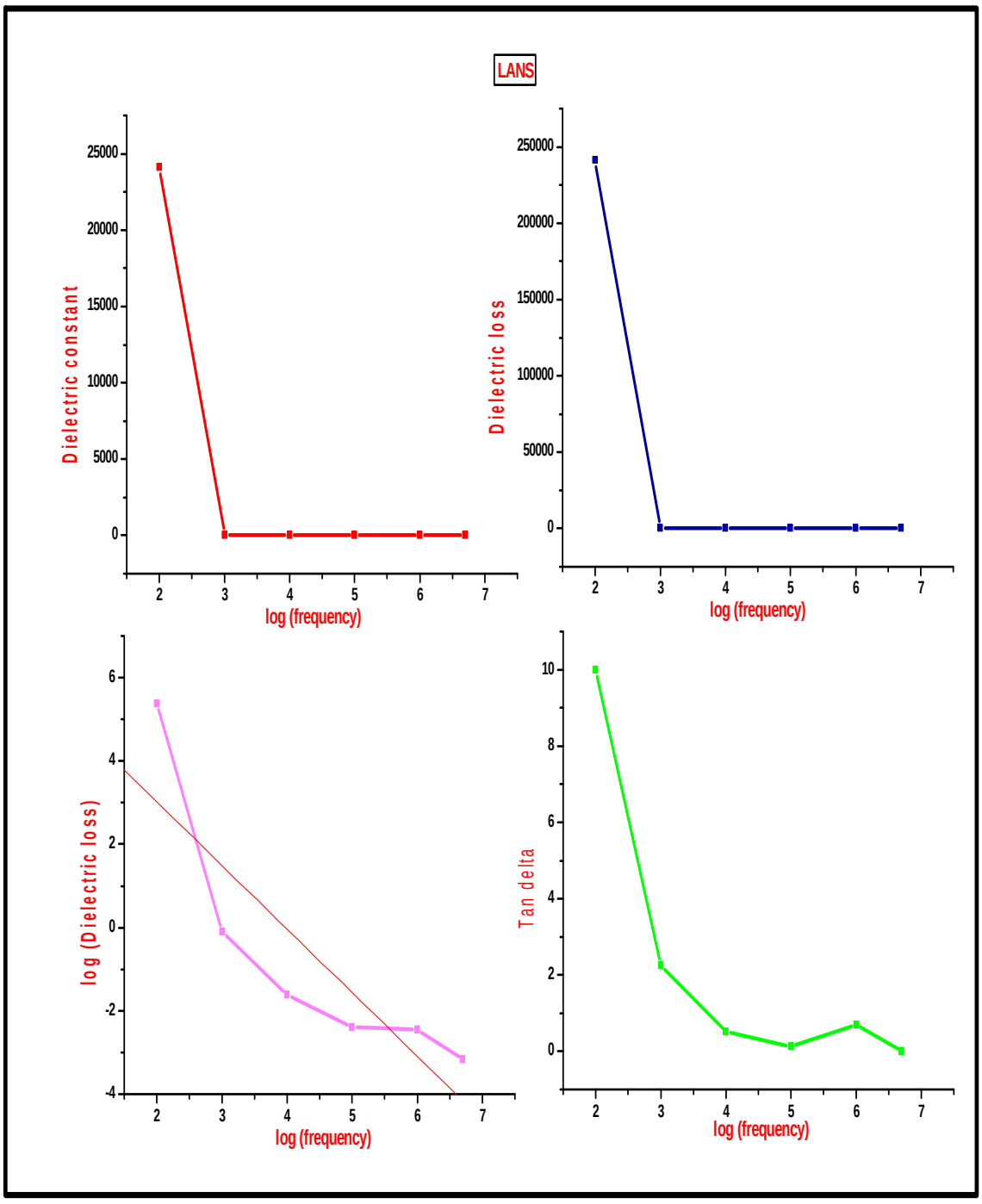

Figure 9 Dielectric Graphs of LANS nanocrystal

Linear and Non-linear Optical Studies

100% transmission (nearly zero absorption) after the cut-off wavelength of 240.50 nm with energy band gap of5.16 eV is evident from UV spectrum (Figure 10).As per the literature review, laser heated pedestal growth of the crystalline fibres of KDP doped with l-arginine phosphate (LAP) show such 100% transmission. Pure LAP and l-arginine trifluoroacetate (LATF) show 85% transmission [24, 25]. This high transmission indicates that LANS nanocrystal possess less number of defects. The observed cut-off is may be due to weak n-π transitions in carboxylate ($-COO^-$) or guanidyl ($NHC(NH_2)^-$) ions. [25] Recently Paredes et al [2] reported the NLO property of l-arginine H_3PO_4nanocrystal.

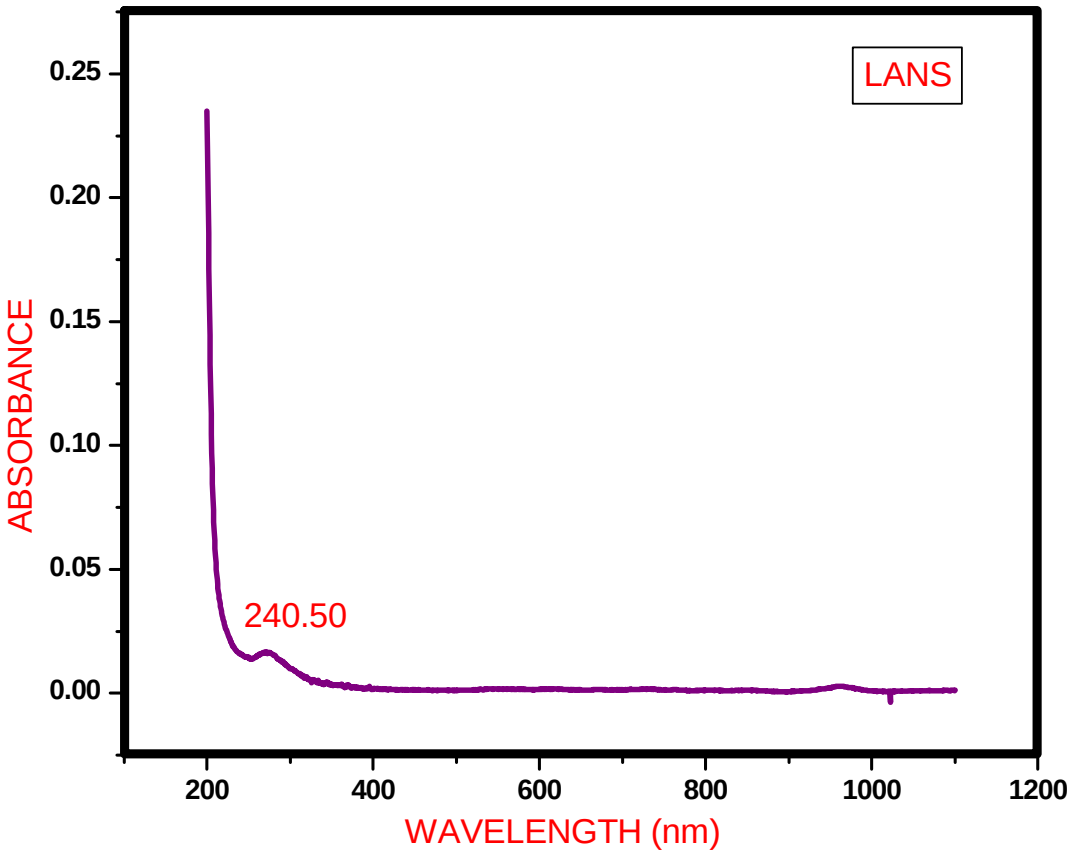

Figure 10UV-Vis spectra of LANS nanocrystal

Absence of electronic transition in the range 240.50 -1100nm suggests the newly grown LANS nanocrystals for a non-linear optical study.The sharp fall in the spectrum also indicates possible existence of third harmonic generation (THG) in the nanocrystal. To check the nonlinear optical property of the grown crystal, Kurtz and Perry technique was used [26]. A high intensity Nd-YAG laser (λ = 1064nm) with a pulse duration of 10ns and beam energy 24mJ/pulse was passed through the powdered sample of LANS nanocrystals. The observed green emission (532 nm) confirmed the presence of second harmonic generation in the sample. The SHG efficiency is found to be 0.51 times that of standard KDP crystal. Table 4 shows a comparative chart of the SHG efficiencies of reported l-arginine based materials and synthesized LANS nanocrystal.

Table 4 Comparative Chart of the SHG efficiencies of L- Arginine based Crystals

Sample	SHG efficiency with respect to KDP
L-arginine phosphate	3
L-arginine acetate	3
L-arginine trifluoroacetate	2.5
L-arginine fluoride	0.95
L-arginine dihydrofluoride	2
L-arginine hydrochloride monohydrate	0.38
L-arginine maleate	3
L-arginine maleate dehydrate	1.4
L-arginine dehydrate	0.66
LANS	0.51

CONCLUSION

LANS nanocrystals obtained from solution show assorted hexagonal geometry with evidence of rectangular, cubic and circular shapes due to varied rate of nucleation. The particle size from TEM is in fair agreement with particle size from XRD studies using Debye- Scherer relation. Solubility studies show positive temperature coefficient and LANS were found to have good solubility. Narrow metastable zone width has been observed for synthesis of LANS.

The SEM analysis of LANS show very fine surface morphology as with presence of white aggregates may indicate the unreacted elements. ^{1}H-NMR shows chemical shifts for α, β, γ, δ, and ξ hydrogen atom with multiplet signals. Single phase formation remains verified from XRD studies The LANS nanocrystals are found to be thermally more stable than LADP, LAAC, LAF, LADN, etc., owing to stronger thermal bonds present in the system. Absence of water molecule is also a probable reason for the good stability of the synthesised nanocrystals.Near one to one correspondence has been observed between the peaks of IR and RAMAN spectra confirming the non-centrosymmetric nature of the molecule. The extensive system of hydrogen bonding extends throughout the molecule leads to deformation of stretching frequencies of NH_3^+ and COO^- group. As evident from the optical absorption studies, wide optical window of the synthesized materials makes them a promising candidate for the non-linear optical applications. The peaks below the cut-off wavelength represent distinct electronic transitions which are a characteristic of formation of nanocrystals. Optical non-linearity of the grown nanocrystals has been tested by Kurtz and powder SHG technique. While ac conductivity is found to be low, deviation from dc conductivity is indicated by dielectric studies. The dielectric constant and dielectric loss are found to behave normally with applied frequency and are found to become very low at lower frequencies indicating their applications in photonic and NLO based devices.

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