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Synthesis, Growth and Structural Characterization of Semi Organic Non-Linear Optical Material: L-Arginine Doped Zinc Sulphate Heptahydrate Single Crystal

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A method of slow evaporation was adopted to grow pure semiorganic non linear L-arginine doped zinc sulphate heptahydrate single crystals. The lattice parameters of the grown crystals were found out using powder XRD pattern. The different functional bond frequencies linked within the crystals were analyzed by FT-IR spectroscopic analysis. The absorption spectrum (UV-visible) between 200-1100 nm illustrates the absorption in this range along with the absence of any combination modes above 270 nm. Further TG/DTA curves ensure the absence of lattice water and thermal stability of the grown crystals. The L-Arginine was added in 0.01, 0.03, 0.05 mole % to zinc sulphate heptahydrate and the compound salts were subjected to Kurtz powder technique technique. It was observed that the second harmonic generation efficiency of 0.03 mole % L-arginine doped zinc sulphate heptahydrate single crystal is very much higher than pure zinc sulphate heptahydrate. The Vickers's micro hardness measurements proved the mechanical stability of the grown crystals.

Keywords: L-Arginine, Zinc sulphate heptahydrate, XRD, Thermal analytical technique, Non-linear optical.

INTRODUCTION

Semiorganic non-linear optical materials have been developed to retain the merits and to overcome the shortcomings of organic compounds[1,2]. They have paid attention towards the significance of many theoretical and experimental researchers since their appreciable nonlinearity, fast response and tailor made flexibility. These non-linear optical crystalline materials have emerged as one of the most attractive fields of current research in view of their vital applications in areas *viz*., optical modulation, optical switching, optical logic, frequency shifting and optical data storage for the developing technologies in telecommunication and in proficient signal processing[3]. Furthermore, the crystallization of inorganic heptahydrate sulphates with their general formula ($RSO_4·7H_2O$, R=Mg/Ni/Zn) have become a significant field of research in various areas like medical, agricultural and chemical[4]. Gaslarite ($ZnSO_4·7H_2O$), white hydrated crystals possess wide range of applications in the field of telecommunication, solar systems for solar energy storage, coagulation bath for rayon and optical information storage devices. Zinc sulfate heptahydrate belongs to a family of non linear optical crysta[l5] which crystallizes in orthorhombic structure with tetra molecular unit cells having the space group, $P2_12_12_1$. Another area of growing necessitate is materials for birefringent, phase matched optical parametric oscillators for the generation of largely tunable mid-wave and long wave infrared radiation. An influential attention has been paid to inorganic materials showing the second order non linear effect since their higher nonlinearity. Amongst the nonlinear phenomena, frequency doubling, frequency mixing and electro optic modulations are important in the field of optical image and optical data storage[6].

The basic structure of organic non-linear optical materials is based on the π bond system due to the overlap of π orbital along with delocalization of electronic charge distribution, lead to a high mobility of electron density. Functionalization of both ends of the π bond systems with suitable electron donor and acceptor groups can enhance the asymmetric electron distribution on either or both ground end excited states, thus leading to an increased optical non-linearity[7]. The non-linear optical effects of organic molecules, possessing large second order non-linearity which are sought for potential applications in information storage. Amongst, the amino acids are the famed that occupy a vital role in the field of non-linear optical crystal growth. In particular, certain natural amino acids such as L-arginine, L-histidine, lysine and glycine *etc*., are obviously viewing non-linear optical property due to the presence of -COOH (carboxyl) and $-NH_2$ (amino) groups. In solid state, amino acids exist as dipolar ion in which -COOH group is present as carboxylate ($-COO^-$) ion and $-NH_2$ is as $-NH_3^+$ ion *i.e.*, zwitter ionic. This bipolarity of amino acids makes them ideal for non-linear optical applications. Semiorganic non-linear optical crystals formed by amino acids with inorganic materials possess the advantages of high optical nonlinearity of the organic amino acids. A series of studies on amino acid doped semiorganic compounds[5,8-9] as potential non-linear optical crystals have been reported. Organic amino acid dopants with inorganic salts are promising materials for second harmonic generation (SHG). These materials are better alternative for Kurtz powder technique crystals in all aspects. In present work we report, the synthesis, growth and structural characterization on single crystals of L-arginine doped in 0.01, 0.03, 0.05 mole % to zinc sulphate heptahydrate (LAZSH). Further, the effect of addition of L-arginine to zinc sulphate heptahydrate has been reported.

EXPERIMENTAL

The chemicals used were $ZnSO_4{\cdot}7H_2O$ (ZSH), L-arginine and were obtained from Sigma Aldrich (USA) without further purification. Double distilled water was used for the growth of single crystals.

Powder X-ray diffraction patterns were recorded with PANalytical powder X-ray diffractometer. The FT-IR spectra were recorded on a Shimadzu-1800S spectrophotometer with KBr pellets for solid samples. Optical absorption studies were recorded with a Hitachi U-2000 double beam spectrophotometer in the 200-1100 nm range. Thermal stabilities were recorded in dynamic nitrogen atmosphere (flow rate 20 cm^3/min) with a heating rate of 10 K/min using a Perkin Elmer (TGS-2 model) thermal analyzer.

Crystal growth: Pure zinc sulphate heptahydrate crystals were grown at low temperature from aqueous solutions[10,11]. L-arginine was added to zinc sulphate heptahydrate in 3 different concentrations *viz*., 0.01, 0.03 and 0.05 mol % to grow doped single crystals (LAZSH). The supersaturated aqueous solution of the mixture was prepared in a 100 mL beaker. The whole setup was kept in dust free area and allowed to equilibrate at ambient temperature. The period of growth ranged from 10 to 12 days, depending upon the temperature of the surroundings. Good quality optically transparent large sized crystals were selected for carrying out experiments. Photographs of the grown crystals are shown in the Fig. 1.

RESULTS AND DISCUSSION

In order to improve the quality of the grown crystals of LAZSH, they were characterized by various characterization techniques *viz*., powder XRD, FT-IR & absorption (UV-visible) spectral, thermal (TG/DTA) analysis and Vicker's micro hardness measurements. The enhancement of second harmonic generation property was confirmed by Kurtz and perry powder second harmonic generation tests.

Powder XRD analysis: The powder XRD pattern of the grown crystal was shown in Fig. 2. The obtained XRD pattern of the pure zinc sulphate heptahydrate crystal is well matched with the JCPDS data. All the observed reflection lines in XRD pattern were observed for LAZSH-0.01, 0.03 and 0.05 systems and their unit cell parameters were calculated. It is observed that LAZSH is orthorhombic structure with the space group of $P2_12_12_1$. The lattice parameter values are a, b & c and they are well agreed with the JCPDS values, shown in Table-1.

TABLE-1
UNITCELL PARAMETERS OF GROWN PURE ZINC SULPHATE HEPTAHYDRATE AND LAZSH CRYSTALS

Crystal Data	Values			
	Pure ZSH (0:1)	LAZSH (0.01:1)	LAZSH (0.03:1)	LAZSH (0.05:1)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (in A°)	11.747	11.572	11.678	11.554
b (in A°)	12.190	12.264	12.205	12.304
c (in A°)	06.769	06.829	06.765	06.765
Volume (V) (in A°)	969.33	968.24	964.43	961.88
$\alpha = \beta = \gamma$ (in °)	90	90	90	90

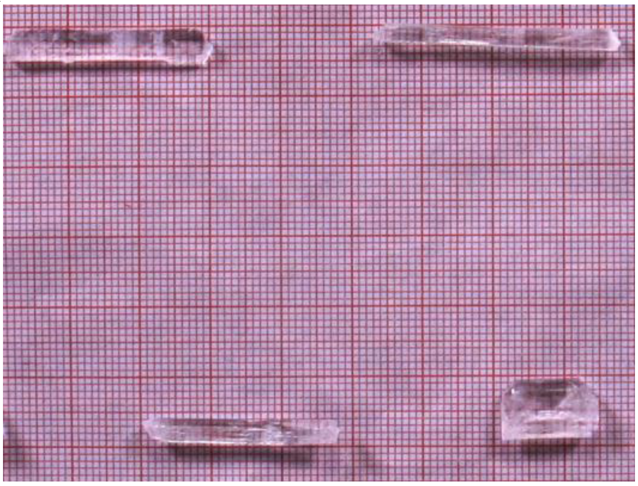


Fig. 1. Photograph of the grown single crystals (a) Pure zinc sulphate heptahydrate (0:1) (b) LAZSH (0.01:1) (c) LAZSH (0.03:1) (d) LAZSH (0.01:1)

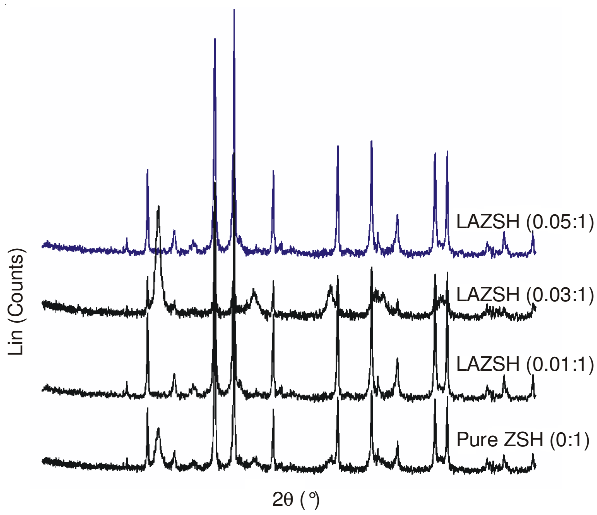


Fig. 2. PXRD pattern of the grown crystals (a) pure zinc sulphate heptahydrate (0:1) (b) LAZSH (0.01:1) (c) LAZSH (0.03:1) (d) LAZSH (0.05:1)

FT-IR spectra: Crushed powder of the crystal systems zinc sulphate heptahydrate and LAZSH-0.01, 0.03 and 0.05 were pelletized using KBr separately. The spectra were recorded in the 4000-400 cm^{-1} wavenumber region. The IR spectra are shown in Fig. 3 and the corresponding frequency assignments are given in Table-2. The above assignment agrees with those of the reported values. The spectra of L-arginine doped zinc sulphate heptahydrate displays nearly similar features as those of zinc sulphate heptahydrate. The δ(N-H) and υ(O-H) vibrations are clearly seen as intense broad envelope in the higher energy region with maxima at 3277 and 3444, 3402 cm^{-1}, respectively.

TABLE-2
IR SPECTRAL DATA (cm^{-1}) OF GROWN PURE ZINC SULPHATE HEPTAHYDRATE AND LAZSH CRYSTALS

Wave number (cm^{-1})	Band assignments
3444, 3402	υ(O–H) stretching vibrations
3277, 3063	δ(N–H)
1453, 1382/1357 & 1326	υ(–CH_2) in-plane bending/scissoring, bending & wagging
2973, 2880	υ(C–H) stretching vibrations
1684, 1655	υ(C=O) of (–COO^-) stretching vibrations
1651	υ(COO^-)$_{as}$ /δ(NH_3^+)$_{as}$ bending vibrations
1423	υ(COO^-)$_s$ /δ(NH_3^+)$_s$ bending vibrations
2010	Torsional oscillation and symmetrical bending of (NH_3^+)
777	υ(COO^-) scissoring mode
555, 532	Torsional oscillation of (NH_3^+)
1104, 981, 613	Free –(SO_4^{2-}) vibration
1089.7, 983.6, 461	–(SO_4^{2-}) vibration

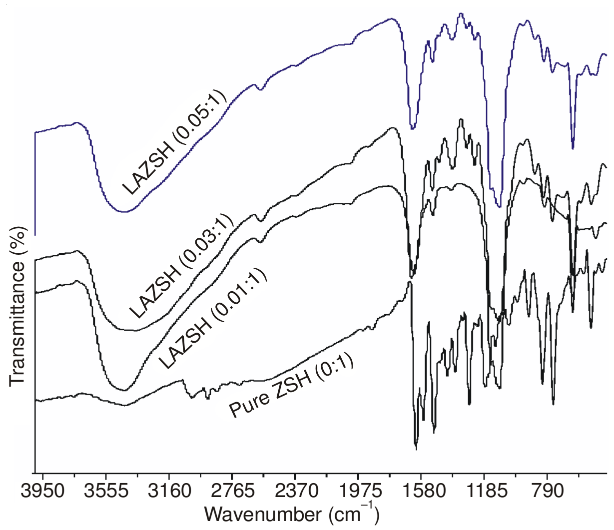


Fig. 3. FT-IR Spectra of grown pure zinc sulphate heptahydrate and LAZSH crystals

The υ(C-H) vibrations are seen at 2973 and 2880 cm^{-1}, respectively. Additionally, there are some hyperfine structural bands in the lower region which are assigned to hydrogen bonding of -NH and -OH groups. Some peaks are at 1651 cm^{-1} and which are responsible to υ(COO^-)$_{as}$ and δ(NH_3^+)$_{as}$ ions. Further some additional peaks which are positioned at 1491 and 1423 cm^{-1} for υ(COO^-)$_s$ and δ(NH_3^+)$_s$ ions, respectively. The υ(-CH_2) bending vibrational peaks[12] are seen at 1453, 1382, 1357 and 1326 cm^{-1}. A free SO_4^{2-} ion has four fundamental vibrations, namely a non degenerate at 981 cm^{-1} ($υ_1$), a doubly degenerate at 613 cm^{-1} ($υ_2$) and triply degenerate mode of vibrations at 1104 cm^{-1} ($υ_3$ and $υ_4$), respectively. Now the peaks were observed at 1089.7 ($υ_3$ and $υ_4$), 461 ($υ_2$), 983.6 cm^{-1} ($υ_1$) and were attributed to the triply, doubly and non degenerate symmetric stretching mode of vibrations for (SO_4^{2-}) ions. Thus, there is a clear indication of the presence of L-arginine in the zinc sulphate heptahydrate crystal lattice.

Optical absorption studies (UV-visible): The transmission ranges of the grown samples were illustrated by UV-visible spectral analysis which has been carried out in the wave length range 200-1100 nm. The recorded spectra are shown in Fig. 4. In the present study, it was found that all the grown crystals are highly transparent in the entire UV-visible and near IR region. The large transmission in the entire visible region enables it to be a good candidate for electro optic and non-linear optical applications. L-arginine addition decreases the absorbance in the case of zinc sulphate heptahydrate single crystals. The low cut off wavelength and the large transmittance window are the most desirable properties of the crystals used for non-linear optical applications.

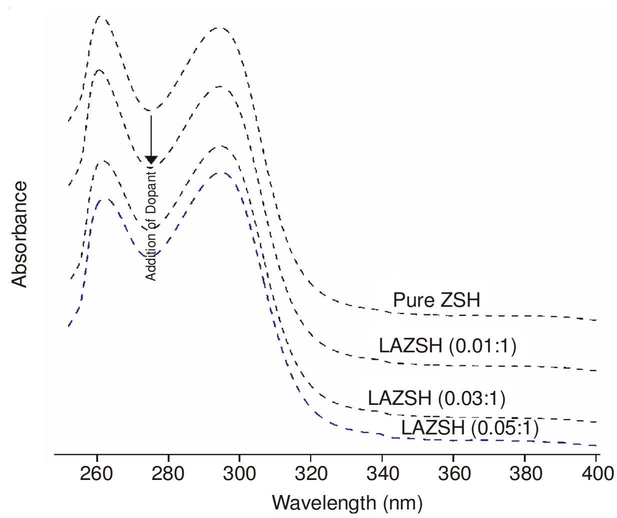
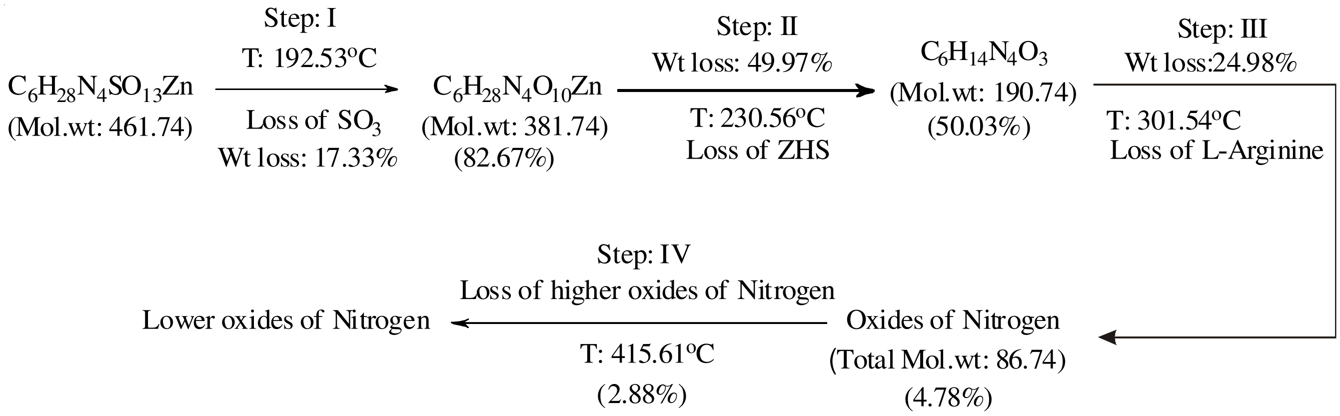


Fig. 4. UV-visible spectrum of zinc sulphate heptahydrate and L-arginine doped zinc sulphate heptahydrate crystals

Thermal analytical technique: The weight loss and thermal stability of the samples were analyzed at a heating rate of 25 °C/min for temperature range 50 to 900 °C in nitrogen inert atmosphere. The recorded thermograms are shown in **Scheme-I**. It reveals that in the case of L-arginine doped zinc sulphate heptahydrate crystals, the weight loss about 49.97 % takes place in the region 230.56 °C and 24.98 % at 301.54 °C. There is no weight loss upto 190 °C, ensuring the absence of lattice water in the crystal structures. The first weight loss is due to organic compound evaporation and liberation of volatile substances like oxides of sulphur and the second and third weight loss are due to decomposition of both the compounds[13]. The sharpness of the endothermic peak has been observed at 230.56 °C for pure zinc sulphate heptahydrate crystal and at 301.54 °C for L-arginine doped zinc sulphate heptahydrate crystal. It is evident that the doped crystal is more stable than pure ZTS crystal and the grown crystals are stable upto 240 °C and are best suitable for non-linear optical applications.



Scheme-I: Representation of TG/DTA Analysis of LAZSH Crystals

Non-linear optical Studies

Second harmonic generation efficiency measurement: The second harmonic generation behaviour of the grown crystal was determined by Kurtz powder technique[14]. The sample was grounded into fine powder and tightly packed in a micro capillary tube. The crystal was illuminated using Nd:YAG pulsed laser emitting a fundamental wavelength of 1064 nm, pulse energy 3 mJ/pulse with 8 ns and repetition rate 10 HZ was allowed to strike the crystals separately. The emission of green radiation from the sample ascertains the second harmonic generation property of all these grown crystals. The amplitude of the green radiation is found to be increased when the concentration of L-arginine is increased. Kurtz powder technique was used as the reference material and second harmonic generation relative efficiency of the pure zinc sulphate heptahydrate and doped crystals (0.01, 0.03, 0.05 mole %) were found to be good.

Vicker's microhardness measurement: It is observed that in all the grown crystals, the hardness value increases with increasing load and by increasing the dopants concentration. This is attributed to the fact that the dopant incorporated to the zinc sulphate heptahydrate lattice probably enhances the strength of the bonding with the host molecules. The Meyer's equation relates the load P and indentation diagonal length. The Meyer's index number was calculated by the equation , where k is the material constant; P is the load and n is the Meyer's index. The value of n is calculated by plotting *versus* and it is shown in the Fig. 5.

Conclusion

Pure zinc sulphate heptahydrate and L-arginine doped zinc sulphate heptahydrate [LAZSH (0.01:1), LAZSH (0.03:1), LAZSH (0.05:1)] single crystals have been grown by slow evaporation method at ambient temperature and water is the solvent. The lattice parameters have been found out by powder

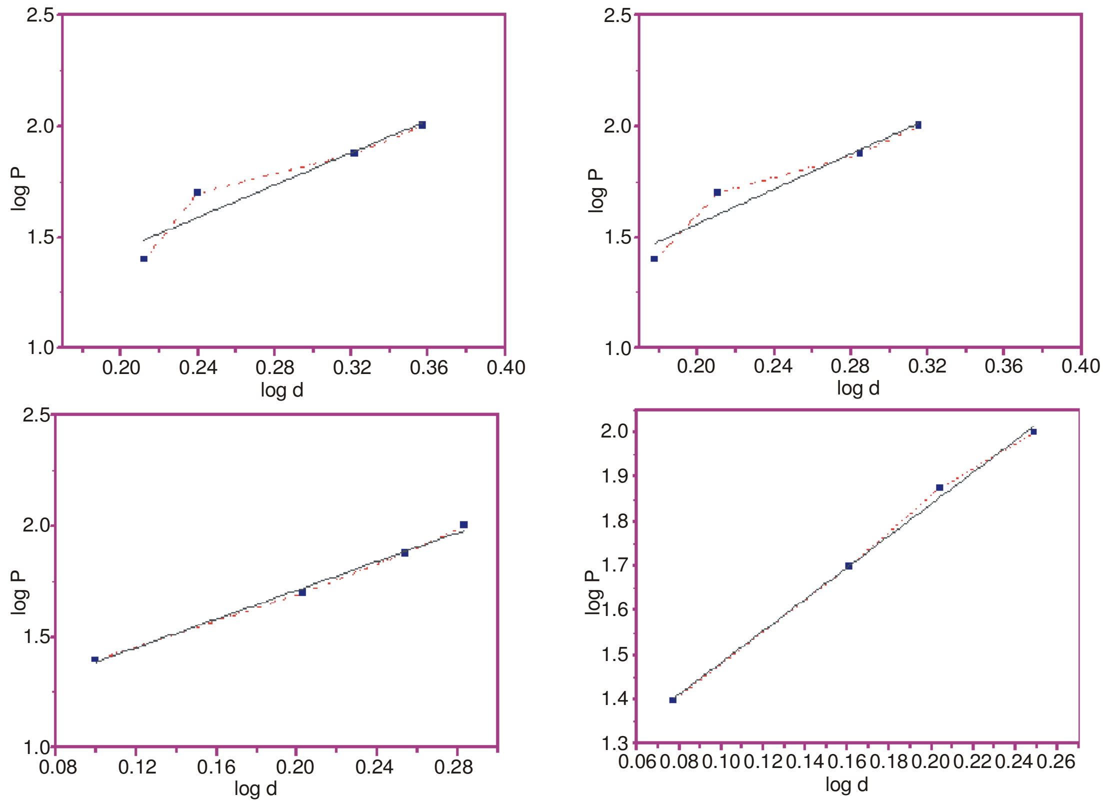


Fig. 5. log P vs. log for grown crystals (a) pure ZSH (0:1) (b) LAZSH (0.01:1) (c) LAZSH (0.03:1) (d) LAZSH (0.05:1)

XRD technique. The FT-IR spectra in the range 4000-400 make known to the various functional groups present in the grown crystals. The optical absorption by UV-visible is less between 300-1100 nm which illustrates the absence of any overtone modes above 270 nm. TG/DTA analysis shows that all the doped crystals are stable upto 301.54 °C. The Vicker's micro-hardness measurement proved the mechanical stability of the grown crystals is much harder than the pure zinc sulphate heptahydrate crystals. The studies on non-linear optical property confirm the second harmonic generation conversion efficiency of the crystals to be better than Kurtz powder technique.

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