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Structural, Vibrational and Thermal Analysis of L-arginine Potassium Sulphate (LAKS) Crystal Having NLO Response

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ABSTRACT

A new non-linear optical potassium sulphate crystal (LAKS) has been grown from aqueous solution by the slow evaporation technique at room temperature. Orthorhombic structure has been estimated as per XRD studies. CHNS, SEM and EDAX analysis were carried out for determining the chemical composition and surface morphology. Vibrational characterization, thermal studies and linear and non-linear optical studies were also done.

Keywords: Crystal Growth, Xrd, Vibrational, Thermal And Non-Linear

I. INTRODUCTION

Among the 20 essential fundamental amino acids, L-arginine ($C_6H_{14}N_4O_2$) is widely distributed in biological substances. The α-carbon atom is attached with four groups, viz.; amino group, carboxyl group, guanidino group and hydrogen atom. Since all the carbon atoms in the L-arginine molecule are optically active, its related compounds are mostly non-centrosymmetric and exhibit second harmonic generation property. The long, linear carbon chain incorporates the character of flexibility in the l-arginine molecule. It has a catenarian structure at two ends of which carboxyl and guanidyl group form a dipole moment of about 2.4 x 10^{-8} esu. Thus l-arginine is a polar amino acid with positive guanidine group. Due to the highly basic nature of guanidine group l-arginine forms a number of salts with organic and inorganic acids viz L-arginine phosphate monohydrate, L-arginine diphosphate, L-arginine perchlorate, L-arginine nitrate, L-arginine maleate dihydrate, L-arginine formate, L-arginine acetate, L-arginine oxalate, L-arginine fluoride [1] which are interesting NLO materials.

Present work reports the growth and characterization studies of L-arginine Potassium Sulphate (LAKS) crystals synthesized for first time in our laboratory.

II. METHODS AND MATERIAL

AR grade L-arginine ($C_6H_{14}N_4O_2$) and Potassium sulphate (K_2SO_4) was used for the synthesis of L-arginine potassium sulphate (LAKS) crystals in the ratio 3:1. The crystals were obtained from aqueous solution (volume=200ml and pH=8.5) by slow evaporation method at room temperature (28°C). Optically good quality crystals of dimension 0.8 cm x 0.6 cm x 0.1cm were collected from the gel-like solution in about eight weeks of time (figure 1).

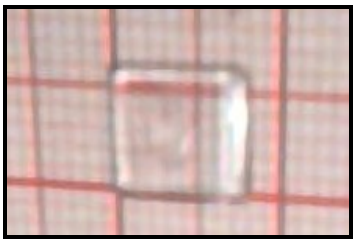

Figure 1. LAKS crystal

Since L-arginine is rich in nutrients, microbes formation is frequent during the growth of L-arginine crystals [2]. In our case the fungus formation may have been avoided as the solution was preheated to about 35°C and also the presence of sulphur in the compound may have further helped in this direction. For structure determination the crystal was subjected to powder x-ray diffraction using Panalytical Xpert MPO PRO which is highly sophisticated X-ray diffractometer system with characteristic CuK-α radiation (λ=1.5410A.U). All the major reflection lines in the XRD spectra were indexed and the unit cell parameters were calculated using the computer program POWD-interactive powder diffraction data interpretation and indexing software program. Version 2.2 (Australia). The chemical composition of the LAKS crystal was determined by CHNS analyzer (THERMO FINNIGAN, FLASH EA 1112 series). SEM and EDAX analysis was done with a scanning electron microscope (ZEISS Ultra FESEM). For identifying the various functional groups present in the grown crystals FTIR and FT-Raman spectroscopic studies were carried out. FTIR spectra were recorded in the range 4000 - 400cm^{-1} using a Nicolet MAGMA$_{550}$ FTIR spectrometer with reference to a potassium bromide pellet. FT-Raman spectra were recorded in the spectral range 4000 – 100cm^{-1} using BRUKER RFS$_{27}$: stand alone FT-Raman spectrometer. The laser source used was ND: YAG 1054nm. Thermogravimetric analysis(TGA) and Differential thermal analysis(DTA) was carried out simultaneously for determining the thermal stability of the material in the temperature range 50 - 500° C in air atmosphere at a heating rate 10° C per min. The instrument used was PERKIN ELMER, DIAMOND TG/DTA thermal analyzer. Linear optical properties of the grown crystals were studied using a Perkin Elmer model No.Lamda35 UV-Vis Spectrophotometer in the range 200nm – 1100nm. To confirm the non-linear optical property Kurtz powder SHG test was performed on the grown crystal.

III. RESULTS AND DISCUSSION

X-ray diffraction studies

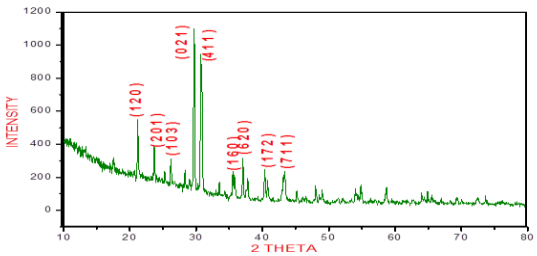

Figure 2. XRD of LAKS crystal

Powder XRD studies of grown LAKS crystal confirms the single phase formation with orthorhombic symmetry. The estimated crystal parameter are a=17.614A°, b=8.661A°, c=4.183 A° with unit cell volume=632.87A°^{3}. The intense xrd peak were recorded at 29.70° C with maximum intensity of 1107 on (0 2 1) plane (figure 2).

CHNS, SEM and EDAX Analysis

The chemical composition of the synthesized crystal was determined by CHNS analysis. The approximate empirical formula is thus established as $C_3H_{10}N_4.K_2SO_4$ for the crystal. SEM images of figure 3 shows layers with formation of crystallites sprinkled over the surface layers. Voids are clearly visible making the surface uneven. Crystalline formations of aggregates have been noted. EDAX spectrum shows peaks for potassium, oxygen and sulphur, suggesting thereby that the potassium sulphate has formed salt with l-arginine.

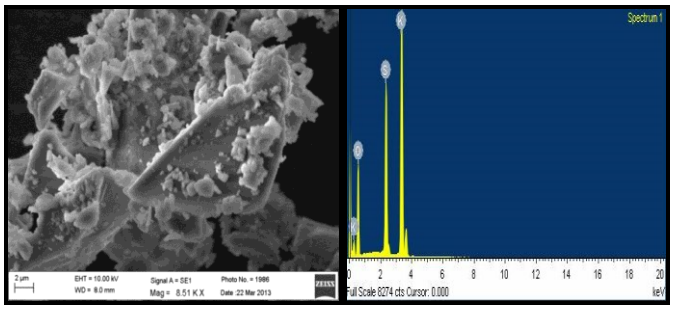

Figure 3. SEM and EDAX analysis of LAKS crystal

FT-IR and FT-Raman Analysis

An attempt has been made to correlate the IR and Raman peaks and discuss the vibrational spectra of LAKS system (figure 4). It reveals that in the crystalline state, the l-arginine molecule is deprotonated at the carboxyl group (1605.22cm^{-1}) [1, 3 4] and protonated at the guanidyl and amino groups (1682.56cm^{-1}) [5,6]. An extensive system of hydrogen bonding extends throughout the molecule leads to deformation of stretching frequencies of NH_3^+ and COO^- groups. Hence, LAKS crystal consists of an arginine molecule in the ionized form and a sulphate ion (982.06cm^{-1}, 983.42cm^{-1}). Lack of any strong IR band at 1700cm^{-1} clearly indicates the existence of the COO^- ion in zwitterionic form. In the high frequency region there is broad band between 3700-2700cm^{-1}. In this broad band there are peaks at 3347.76cm^{-1} due to N-H stretching vibrations of amino group and 2955.42cm^{-1}, 2934.56cm^{-1}, 2870.90cm^{-1} due to C-H stretching vibrations of amino group. The protonation of amino group attached to α- carbon atom can be proved because of the bands at 1558.87cm^{-1}(NH_3^+ symmetric deformation) at 1682.56cm^{-1}(NH_3^+ asymmetric deformation). The bands at 2085.10cm^{-1} is due to the combination of NH_3^+ deformation and NH_3^+ torsion and is a very good indicator band for the identification of the charged NH_3^+ group. And a band at 454.31cm^{-1} is due to NH_3^+ torsion mode. The numbers of IR bands arise due to the presence of the charged NH_3^+ group confirm the protonation of the amino group in the LAKS crystal. Symmetry stretching of SO_4 group appears at 1114.47cm^{-1}, 1106.80cm^{-1}. The frequency bands observed at 617.27cm^{-1}, 619.28cm^{-1} are assigned as asymmetric bending of the SO_4 groups. No bands above 3500cm^{-1} indicates the absence of water molecule in the crystal which also remains confirmed from the thermal study. Raman spectra are seen to be active in region up to about 1100cm^{-1}. Most of the IR and Raman peaks in region between 600cm^{-1} to 1100cm^{-1} show one to one match indicating non-centrosymmetric nature.

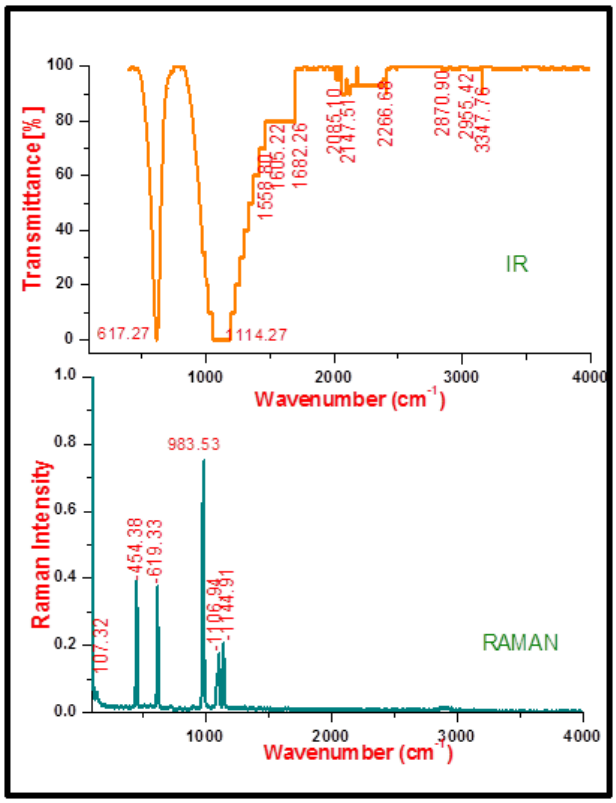

Figure 4. IR and RAMAN spectra of LAKS crystal

Thermal Analysis

From the TGA curve of LAKS crystal (figure 5), it is observed that the material starts decomposing above 210°C. No weight loss up till 200°C indicates the absence of any physically absorbed or lattice water in the grown crystal [7]. Absence of water molecule is infact responsible for the long range stability of the grown crystals and is also evident from FTIR and FT-Raman studies. The DTA curve shows endothermic broad curve. Thus the grown crystal are highly stable as compared to LAP(111°C), L-ADP(173.9°C),

LAHClBr(92°C), LA-HCl(70°C), LAHBr(110°C), LAF(200°C) and LAAC(200°C).

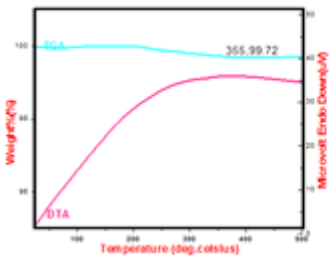

Figure 5. TGA and DTA curve of LAKS crystal

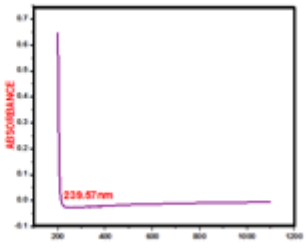

Figure 6. UV-VIS spectrum of LAKS crystal

Linear and Non-linear optical Studies

The optical absorption spectrum of LAKS crystals of figure 6 shows a sharp UV cut-off at 239.57nm and the absorption is nearly zero in the entire visible region. The observed cut-off wavelength is may be due to weak n-π transitions in carboxylate ($-COO^-$) or guanidyl ($NHC(NH_2)^-$) ions. Wide transparency window makes the material useful for NLO studies. To check the nonlinear optical property of the grown crystal, Kurtz and Perry technique was used [8]. A high intensity Nd:YAG laser (λ = 1064nm) with a pulse duration of 10ns and beam energy 24mJ per pulse was passed through the powdered sample. The generation of second harmonic was confirmed by the emission of green radiation. SHG efficiency of LAKS is found to be 0.39 times that of KDP crystal.

IV. CONCLUSION

Optically good quality crystals of l-arginine potassium sulphate (LAKS) have been grown from aqueous solution by slow evaporation technique in about eight weeks. XRD studies confirm the crystalline nature with orthorhombic structure. SEM and EDAX analysis confirms the presence of potassium and sulphur in the crystal lattice of l-arginine. The study of FTIR and FT-Raman spectrum confirms the presence of amino, carboxyl and sulphate group in grown crystal. Thermal analysis revealed that the compounds are thermally stable upto 210°C. Linear optical property study revealed a good transparency of 100%. Kurtz powder SHG test confirmed the non-linear optical behaviour of the LAKS crystals

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