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Growth and Characterization of L Alanine Admixtured Cadmium Sulphate Crystals

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Abstract: Single crystals of L alanine admixtured cadmium sulphate were grown by slow evaporation process at room temperature. The grown compound was characterized by powder XRD analysis to confirm the crystalline nature. The cell parameters and structure of grown crystal were identified through single crystal XRD analysis. The structure of the grown crystal is monoclinic. The suitability of the crystals for optical applications was studied by UV–Vis spectroscopy which proved that the transparency of the grown crystal is 96%. Fourier transform infrared (FT-IR) spectral analysis confirmed the presence of various functional groups in the grown crystals. The mechanical property of the grown crystal was determined by Vicker's micro hardness test and it proved the soft nature of the grown crystal.

Keywords: Crystal growth, slow evaporation, powder XRD, single crystal XRD, UV–Vis, FT-IR, Vicker's micro hardness.

1. INTRODUCTION

Organic crystals have been extensively studied due to their non-linear optical (NLO) coefficients being often larger than those of inorganic materials. The basic structure of organic NLO materials is based on π bonding systems. Due to the overlap of π bonding electrons, delocalization of the charge distribution takes place, which leads to a high mobility of the electron density. The organic NLO materials play an important role in SHG, frequency mixing, electro-optic modulation, optical parametric oscillation, optical stability, etc. But most organic NLO crystals have usually poor mechanical and thermal properties and are susceptible to damage during processing. It is difficult to grow large optical quality crystals of these materials for device applications. Pure inorganic NLO materials typically have excellent mechanical and thermal properties but possess relatively modest optical nonlinearities because of the lack of extended π-electron delocalization [1,2]. Thus the research is focused on semi organic materials in order to obtain the advantages of both organic and inorganic materials.
Amino acid family crystals are playing an important role in the field of non-linear optical organic molecular crystal. Among them L-alanine (LA), with chemical formula (CH_3-CH-NH_2-COOH) is the smallest, naturally occurring chiral amino acid with a non-reactive hydrophobic methyl group (-CH_3) as a side chain. LA has the zwitterionic form (NH_3^+-C_2H_4-COO^-) both in crystal and in aqueous solution over a wide range of pH, which favours crystal hardness for device application. It belongs to the orthorhombic crystal system and the unit cell parameters are; a = 6.320 Å, b = 12.343 Å, c = 5.784 Å, α = β = γ = 90°. Recently, several new complexes incorporating the amino acid L-alanine have been crystallized and their structural, optical and thermal properties have also been investigated [3-5]. In the present study, L alanine admixtured cadmium sulphate [LACS] crystals were grown by slow evaporation solution growth technique. The crystals were characterized using PXRD, single crystal XRD, UV-Vis, FTIR and micro hardness studies.

2. MATERIALS AND METHODS

As per the estimated solubility data, saturated solution of cadmium sulphate (75 g/100 ml) and L alanine (16.72 g/100 ml) (99% purity) were prepared separately using doubly distilled water at room temperature using magnetic stirrer(REMI 1MLH). The prepared solutions were doubly filtered by Whatman No.1 filter paper and mixed in the ratio 3:1 and stirred well for 5 hours. The beaker containing the mixture was closed with a pin holed aluminium foil and kept at room temperature in a dust and vibration free environment for slow evaporation. Highly transparent, good quality LACS a single crystal of dimension 16x13x6 mm^3 were harvested on 83rd day and is shown in figure 1. Recrystallization was carried out repeatedly to enhance the purity of the crystal.

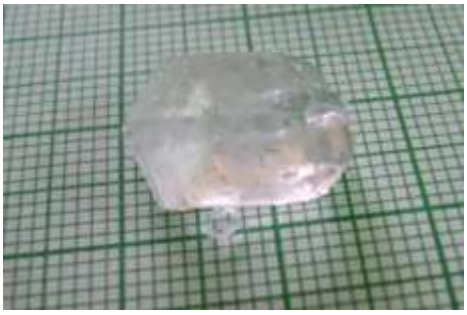

Figure 1. Photograph of LACS crystal

The expected chemical reaction is given below:

$$CdSO_4 + CH_3CH(NH_2)COOH \rightarrow NH_3^+ - CH - (CH_3) - COO^-.CdSO_4$$

3. RESULTS AND DISCUSSIONS

Various characterisation studies were carried out for the grown crystals and the results are discussed hereunder.

3.1. Powder X-ray diffraction analysis

In order to confirm the structure of the grown crystal, powder X-ray diffraction was recorded at a wavelength of radiation λ=1.540598 Å (Cu) using reflection scan mode. Finely crushed powder of the sample was scanned over the range of 10-80° at the scan rate of 1°/minute. The X-ray diffractogram is shown in figure 2.

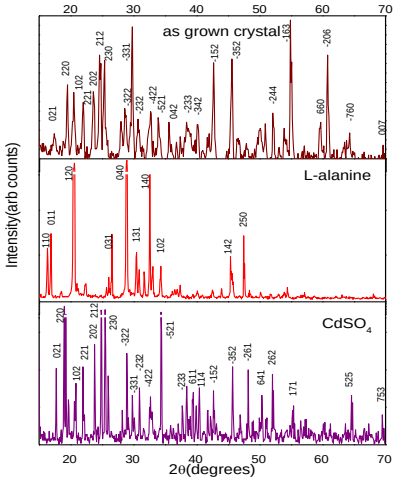

Figure. 2 Powder X-ray diffraction patterns of the grown crystals

The well defined sharp Bragg's peaks at specific 2θ angles in the spectra of grown crystals show high crystalline nature of the compound. PXRD pattern of the grown crystal contains some new peaks, in addition to the peaks of parent material which may be due to the presence of L alanine.

3.2. Single crystal X-ray Diffraction analysis

As grown crystal had been subjected to single crystal XRD employing a Bruker AXS diffractometer using MoKα radiation (λ = 0.71073Å). The single crystal XRD revealed that the crystal belonged to monoclinic system. The lattice parameter values were compared with the parent material and are shown in Table 1.The results of the present work are in good agreement with the reported values [6]. As grown crystal possessed the same crystal system as that of parent crystal but there is a tiny change in lattice constant values and cell volume.

Table 1. Cell parameters of the grown crystals

Cell parameters	L alanine	Cadmium sulphate	LACS
a(A°)	6.032	14.780	14.823
b(A°)	12.343	11.870	11.909
c(A°)	5.784	9.440	9.461
α=β	90^0	90^0	90°
γ	90°	97.31^0	97.47°
Cell volume (A^{o3})	430.09	1642.68	1656.1
Crystal System	Ortho rhombic	Mono clinic	Mono clinic

3.3. Optical transmittance spectral analysis

For optical applications, the material considered must be transparent in the entire visible region [7]. Optical transmission spectrum was recorded on PerkinElmer UV Win Lab Lambda 900 spectrophotometer in the wavelength range 200 and 800 nm as shown in figure 3.

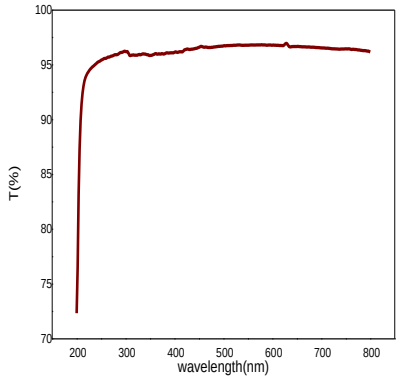

Figure 3. UV-Visible spectrum of LACS crystal

The crystal showed a good transmittance in UV and in the entire visible region, suggesting the suitability of the material for NLO applications. The cut off wave length is found to be around 217 nm. The transparency of the grown crystal is 96.08%. The band gap energy of the grown crystal is 5.7eV.

3.4. FT-IR analysis

The Fourier transform infrared spectrum of LACS was recorded in between the region 400 cm^{-1} and 4000 cm^{-1} and is shown in Figure 4.

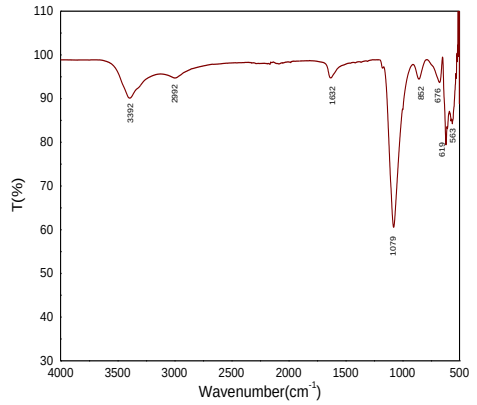

Figure 4. FTIR spectrum of LACS crystal

Observed bands along with their vibrational assignments have been tabulated in Table 2.

Table 2. FTIR spectral data of LACS crystal

Wave number in cm^{-1}	Band assignment
3392	OH/NH_2 stretching
2992	C-H stretching in CH_3
1632	NH_2 scissoring
1079	$SO^2{}_4{}^-$, C-N
852	C-H out of plane bending vibrations
676	O-C=O in plane deformation
563	COO^- rocking

The peaks at 3392 and 1632 cm^{-1} correspond to NH_2. The frequency observed at 676 and 563 cm^{-1} can be attributed to COOH vibrations. The peaks at 2992 and 852 cm^{-1} confirm the presence of C-H group. The peak at 1079 cm^{-1} indicates the possibility of C-N stretch and sulphate ion. O-H stretching is proved by the occurrence of the peak at 3392 cm^{-1} [6-10].

3.5. Micro hardness studies

The hardness of the crystals depends on type of chemical bonding, lattice energy, Debye temperature, heat of formation and inter atomic spacing, which may differ along the crystallographic directions. Micro hardness test provides useful information about the mechanical properties like elastic constants, yield strength, resistance, pressure etc., of the materials. Vickers hardness test is the most common and reliable method for hardness measurement of solid surfaces [11]. The micro hardness of the grown crystals was measured using a Shimadzu Micro hardness Tester with a diamond indenter. In the present work, well polished crystal was mounted on a platform of the micro hardness tester and indentations were made on the grown crystals for three loads 25, 50 and 100 g and indentation time given was 10 seconds. The length of the two diagonals of diamond indenter was measured and the average was found out. For a particular load, at least two well defined indentations were considered and the average value (d) was calculated.

Vicker's hardness number was determined using the expression

$$H_V = 1.8544\frac{P}{d^2}$$

where, 'P' is the applied load, 'd' is the average diagonal length of the indentation marks and the result is plotted (Figure. 5). From the graph, the hardness value increased with the increasing load and hence the grown crystal exhibited the reverse indentation size effect (RISE).

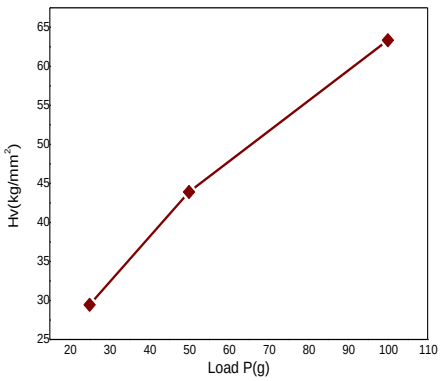

Figure 5. Variation of H_v Vs load

According to the Meyer's law, the relation between the load and size of indentation is $P=k_1d^n$, where 'k_1' is the material constant, 'n' is the Meyer's index or work hardening coefficient. The above relation showed that H_V should increase with load if $n > 2$ and decrease with load when $n < 2$. The plot of log P against log d is shown in figure. 6 which gave a straight line (after least square fitting). The slope of the line (Meyer's index n) was 4.42. According to Onitsch and Hanneman, 'n' should lie between 1 and 1.6 for hard materials and should be above 1.6 for softer materials and hence the sample is a soft material. The higher hardness value of crystal

appeared to be due to the absence of liquid inclusions and higher stress required to form dislocations [12,13].

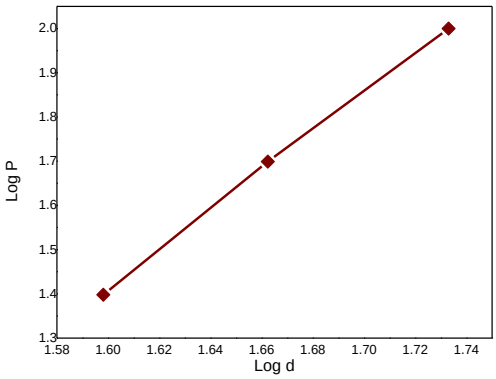

Figure 6. Variation of load Vs indentation length

Yield strength is the important property for the device fabrication and it is the maximum stress that can be developed in a material without causing plastic deformation. Since n is found to be more than 2, yield strength of the material can be found out using the relation,

$$\text{Yield strength } \sigma_y = \frac{H_V}{3}(0.1)^{n-2}$$

The yield strength for different loads is listed in table. 3 and it was observed that yield strength increased with load. Hence the grown crystal had relatively high mechanical strength.

Elastic stiffness constant (C_{11}) was calculated by Wooster's empirical relation as

$$C_{11} = H_V^{7/4}$$

Stiffness constant for different loads calculated from Vickers hardness values are given in table. 3. From the table, it was clear that the stiffness constant increased with increase of load. Hence the high value of C_{11} indicated that the binding forces between the ions are quite strong [14]. The higher the hardness values, greater was the stress required to form dislocation, thus confirming greater crystalline perfection.

Table 3. Variation of hardness number, yield strength and stiffness constant with load

Load P (gm)	Hardness number Hv	Yield strength σ_y (M Pa)	Stiffness constant C_{11} (x10^{14}Pa)
25	29.45	1.82	3.72
50	43.90	8.16	7.49
100	63.35	11.78	14.22

4. CONCLUSION

Good optical quality single crystals of L alanine admixtured cadmium sulphate were grown by slow evaporation solution growth method at room temperature. Powder XRD pattern confirms the crystalline nature of the grown compound. Single crystal XRD study established the crystal system of the grown crystal as monoclinic. From UV-Visible transmission spectra, it is clear that the width of the transmission window is high. This property can be used for frequency doubling and other optical applications. The presence of various functional groups stand confirmed from FT IR spectrum. Vicker's micro hardness study revealed the softness of the grown crystals and the variation of hardness coefficient, yield strength and stiffness constant with load. Hence the grown crystals are suitable for optoelectronic applications.

5. ACKNOWLEDGEMENT

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REFERENCES

[1] P. Hemalatha, V. Veeravazhuthi, J. Mallika, Sa.K. Narayandass and D. Mangalaraj, Cryst. Res. Technol. 41, 8, 775 – 779 (2006).

[2]P.Hemalatha,V.Veeravazhuthi,.Chandramohan, Journal of Crystal Growth 311 (2009) 4317–4322.

[3] Ferdousi Akhtar and Jiban Podder, Journal of Crystallization Process and Technology (2011) 1, 18-25.

[4] S. Masilamani, A. Mohamed Musthafa and P. Krishnamurthi, Arabian Journal of Chemistry, Available online 14 (June 2014) 1-5.

[5] M. Senthilkumar and C. Ramachandraraja, Optik, 124, 12 (2013) 1269–1272.

[6] G. Rajadurai, A. Puhal Raj and S. Pari, Archives of Applied Science Research, (2013) 5 (3):247-253

[7] M. Lawrence, J. FelicitaVimala, International Journal of Engineering Science and Innovative Technology, Vol. 4, 2, 210-214 (2015)

[8] G. Ramasamy and Subbiah Meenakshisundaram, Journal of Crystal Growth, 377 (2013) 197–202

[9] G.G. Muley, M.N. Rode and B.H. Pawar, Acta Physica Polonica A, Vol. 116, 6, (2009)

[10] K.Seethalakshmi and S.Perumal, Recent Research in Science and Technology (2012) 4(6):13-16

[11] G. Ganesh, A. Ramadoss, P.S. Kannan and A. Subbiah Pandi, Scholars Research Library Der Pharma Chemica, Vol.3, 4, 433-439 (2011)

[12] Y. Wang, D.F. Eaton, Chemical Physics Letters, Vol.120, 441-443 (1985)

[13] K.Gayathri, P.Krishnan, P.R.Rajkumar and G.Anbazhakan, Bulletin of Material Science, Vol. 37, 7, 1589-1595, (2014)

[14] O. Sahin, O. Uzun, U. Kolemen, N. Ucar, Materials Characterization Vol. 58, 2, 197-204 (2007)