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Bulk Growth and Characterization of Semiorganic Nonlinear Optical L-Alanine Cadmium Chloride Single Crystal by Modified Sankaranarayanan−Ramasamy Method

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ABSTRACT: An optically transparent bulk nonlinear optical active single crystal of L-alanine cadmium chloride was grown up to a dimension of 100 mm length and 15 mm diameter with the aid of a modified uniaxial Sankaranarayanan−Ramasamy crystal growth method along the (101) plane. The crystal was subjected to X-ray diffraction analysis to confirm that the crystal belongs to the monoclinic system. The incorporation of cadmium and chlorine in the crystal lattice was confirmed using energy dispersive X-ray analysis (EDAX). The spiral growth-steps of the crystal along the (101) plane were observed using scanning electron microscopy. The Vickers microhardness test establishes improvement of hardness along the growth axis. Prevalence of space charge polarization was enunciated by dielectric measurements along the (101) plane for different temperatures 308, 328, 348 and 368 K.

Introduction

In recent years, efforts have been made on amino acid mixed organic and inorganic complex crystals due to their enhanced chemical stability, laser damage threshold and nonlinear optical properties that have been considered for photonic applications. Series of semiorganic amino acid crystals were reported for photonic applications due to their high nonlinear optical properties.[1–6] These enhanced properties of amino acids are due to the presence of a proton donor carboxyl acid (−COO) group and the proton acceptor amino ($-NH_2$) groups. In the solid state, these exist as dipolar ions in which carboxyl group is present as carboxylate ion. Due to this dipolar nature, amino acids have physical properties which make them ideal candidates for NLO applications.[7] Recently, Sankaranarayanan and Ramasamy have used an uniaxial solution crystallization method to grow organic and semiorganic materials for device fabrication.[8–10] This method is advantageous due to the low temperature involved in the growth which is applicable for amino acid crystals that decompose at or below the melting point. This method gains 100% solute−crystal conversion efficiency and free from microbial growth which mainly alters the growth of amino acid crystals.[11,12] L-Alanine cadmium chloride (LACC) is a novel semiorganic amino acid crystal possessing a monoclinic system with space group *C*2 leading to a noncentrosymmetric structure.[13] These crystals acquire nonlinear optical properties with a second harmonic efficiency of about 1.5 times that of KDP.[14] In the present work, a large dimension crystal of L-alanine cadmium chloride (LACC) was grown by a modified Sankaranarayanan−Ramasamy (SR) method. The grown crystal was subjected to X-ray diffraction analysis, EDAX spectral analysis, optical absorption studies and characterization such as microhardness, SEM analysis and dielectric studies along the (101) plane.

Experimental Setup and Crystal Growth

Synthesis and Selection of Seed. Starting materials of L-alanine (Merck) and cadmium chloride monohydrated (Merck) of equimolar ratio were dissolved in deionized water to synthesize L-alanine cadmium chloride salt. The obtained homogeneous mixture was evaporated below an optimum temperature of 60 °C in a water bath to get a white crystalline sample of LACC. This sample was used for the growth of LACC seeds by a slow evaporation technique under a constant temperature of 35 °C. The seed crystals of LACC were obtained within a week with perfect external morphology. The plane 101 was selected for the uniaxial growth morphology and is shown in Figure 1, obtained from single crystal XRD analysis.

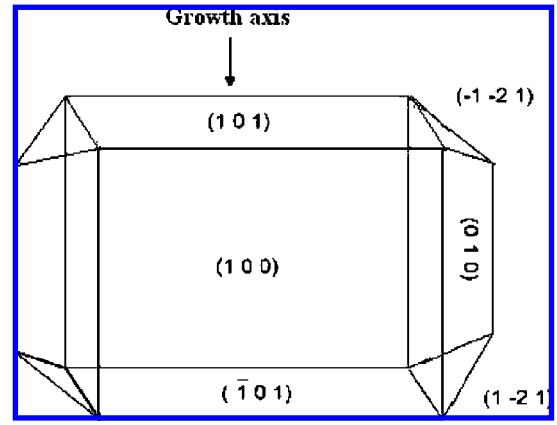

Figure 1. Morphology of L-alanine cadmium chloride crystal.

Growth Assembly. The modified version of the Sankaranarayanan−Ramasamy growth setup is shown in Figure 2. In this growth setup a ring heater was replaced by assemblies of alternating 40 W filament lamps. A vertical bottom-seed ampule placed along the axis of the growth assembly was rotated 90°/s using a stepper motor for maintaining steady temperature around the ampule. The temperature gradient was adjusted according to the requirement by varying the spacing between the lamps which are facing opposite alternately. The seed-fitted ampule was filled with saturated solution of the synthesized salt, prepared at 35 °C. The temperature at the top of the ampule was maintained at 45 °C using a temperature controller setup for the evaporation of the saturated solution. A constant temperature of 35 °C using a controlling unit was maintained in the outer surface of the growth setup. The temperature gradient makes the concentration gradient maximum at the

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Figure 2. Crystal growth assembly.

Figure 3. Photograph of as grown crystal of LACC.

bottom and minimum at the top of the ampule for avoiding the spurious nucleation along the length of the ampule. The growth rate of the crystal was found to be 5 mm per day. Crystals of 100 mm length and 15 mm diameter have been grown successfully within a period of 20 days. The grown crystal shows a cylindrical morphology as that of the growth vessel. A photograph of the grown crystal is shown in Figure 3.

Results and Discussion

X-ray Diffraction Analysis. The powder X-ray diffraction spectrum of the grown crystal of LACC was recorded on a REICH SIEFERT X-ray diffraction instrument using Cu Kα (1.540 Å) radiation. The sample was scanned for a 2θ range 10−70° at a scan rate of 1°/min. The X-ray diffraction spectrum is shown in Figure 4. The material crystallizes in the monoclinic system with space group $C2$, and the cell parameters are a = 16.250(4) Å, b = 7.262(1) Å, c = 7.997(2) Å, $\alpha = \gamma = 90.0°$ and β = 116.31(1)°, which is in good agreement with the reported value.[13] The obtained single crystal XRD and powder X-ray diffraction parameters are presented in Table 1. The calculated (*hkl*) planes satisfy the general reflection condition of space group observed from the structure determination of the crystal.

UV−Visible Absorption Spectral Studies. The UV−visible absorption spectrum of the LACC crystal was recorded in the wavelength region 200−1500 nm using a VARIAN CARY 5E UV−vis−NIR spectrophotometer, and the obtained spectrum is shown in Figure 5. When the absorbance is monitored from longer to shorter wavelength, the absorption is found to be moderately low in the visible region and near IR region of the spectrum. This is the most desirable property of materials possessing NLO activity. The crystal is highly transparent in

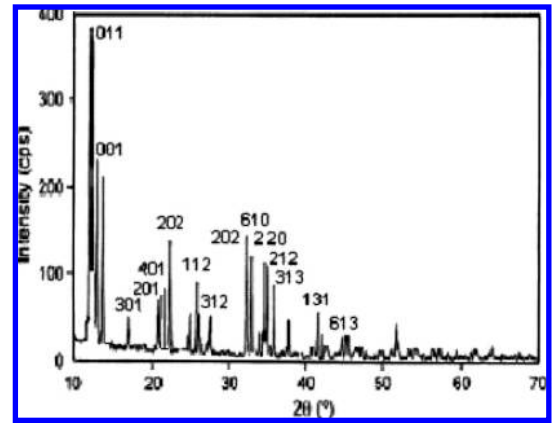

Figure 4. The powder X-ray diffraction pattern of LACC crystal.

Table 1. Unit Cell Parameters of L-Alanine Cadmium Chloride Single Crystal

		single crystal XRD	
unit cell params	powder XRD	present work	ref 13
a (Å)	16.250 (4)	16.258 (6)	16.240 (2)
b (Å)	7.262 (1)	7.268 (12)	7.272 (1)
c (Å)	7.997 (4)	7.998 (8)	7.987 (2)
vol (Å)	845.3 (5)	846.5 (6)	844.7 (2)
β (deg)	116.31 (1)	116.39 (4)	116.44 (1)

the entire UV, visible and near IR region. The UV cutoff wavelength in which the transmittance falls to zero is found to be 240 nm.

Scanning Electron Microscopy (SEM) Analysis. The morphology of the growth surface was observed by a scanning electron microscopy (SEM) using a JSM-253 SEM analyzer. The obtained micrograph of the LACC crystal, scanned by a magnification 500×, is shown in Figure 6. From the micrograph, it is observed that the growth surface shows screw dislocation which confirms the spiral growth-steps of the crystal along the (101) plane of the LACC crystal.[16,17]

Energy Dispersive X-ray Analysis (EDAX). An elemental analysis was carried out for LACC by employing the energy dispersive X-ray analysis (EDAX) in order to confirm the composition of cadmium and chlorine radicals in the crystal. Figure 7 illustrates the EDAX spectrum of LACC crystals recorded on a keV x delta class I microanalyzer attached to a JEOL (JSM-253, SEM), which suggest the percentage of cadmium and chlorine present in the crystal lattice of the LACC single crystal.

Microhardness Studies. The microhardness measurements were carried out with the load range from 25 to 200 g on growth

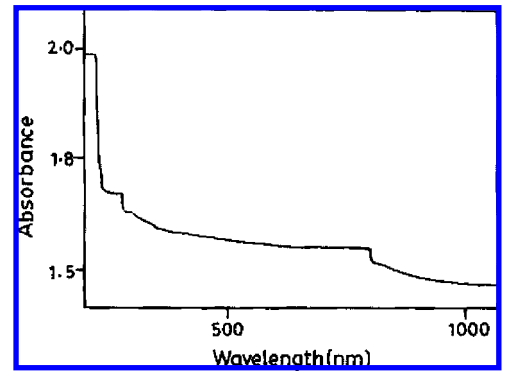

Figure 5. UV absorption spectrum of LACC crystal.

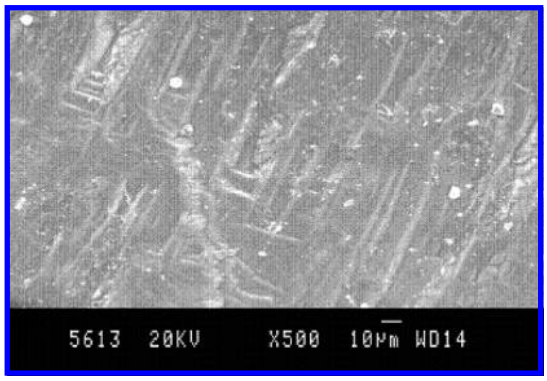

Figure 6. SEM micrograph of the title crystal.

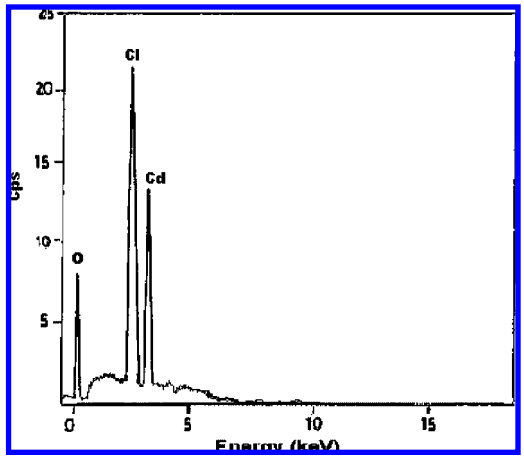

Figure 7. EDAX spectrum of LACC crystal.

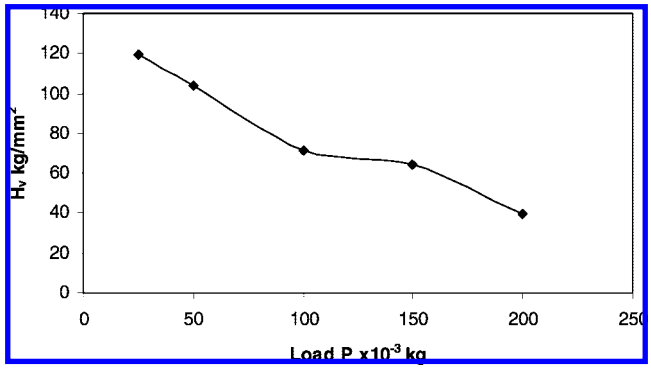

Figure 8. Variation of H_v with load P.

plane (101) using the Vickers hardness tester (LEITZ WETZLER) fitted with a diamond pyramidal indenter and attached to an incident light microscope in order to confirm the mechanical strength of the LACC crystal along the growth axis. The Vickers microhardness number was calculated using relation 1,

$$H_v = \left(\frac{1.8544P}{d^2}\right) \quad (1)$$

where P is the indenter load and d is the diagonal length of the impression. Figure 8 shows the variation of P versus Vickers hardness number (H_v) for LACC. It is evident from the plot that the Vickers microhardness number of LACC decreases with the applied load. According to Meyer's law, the relation connecting the applied load is given by eq 2,

$$P = k_1 d^n \quad (2)$$

where n is the Meyer index or work hardening exponent and k is the constant for a given material. The hardness number H_v decreases with the load and the value of the Meyer index or the work hardening coefficient (n) was determined from Figure 9, the slope of log P versus log d, is estimated to be 1.132, which is less than 2 establishing the crystal to be a hard material. Low work hardening coefficient shows less dislocation in the grown crystal since work hardening coefficient is caused by the dislocations present in the crystal.[18,19]

Dielectric Studies. The dielectric constant and the dielectric loss of the LACC crystals were studied at four different temperatures (308, 328, 348 and 368 K) using a HIOKI 3532 LCR HITESTER instrument in the frequency region 50 Hz to 5 MHz. Figure 10 shows the plot of dielectric constant (ϵ_r) versus log frequency. The dielectric constant is high in the lower frequency region, and then it decreases with the applied frequency. The very high value of ϵ_r at low frequencies may be due to the presence of all four polarizations, namely, space charge, orientation, electronic and ionic polarization, and it is a low value at higher frequencies, which may be due to the loss of significance of these polarizations gradually. From the plot, it is also observed that dielectric constant increases with increase in temperature. This is attributed to the presence of space charge polarization near the grain boundary interfaces which depends on the purity and perfection of the sample.[20] The variation of dielectric loss with frequency is shown in Figure 11. The characteristic low dielectric loss with high frequency for a given sample suggests that the sample possesses enhanced

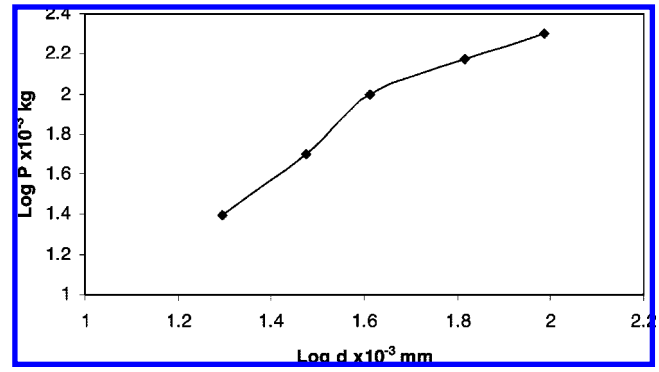

Figure 9. Plot of log P versus log d.

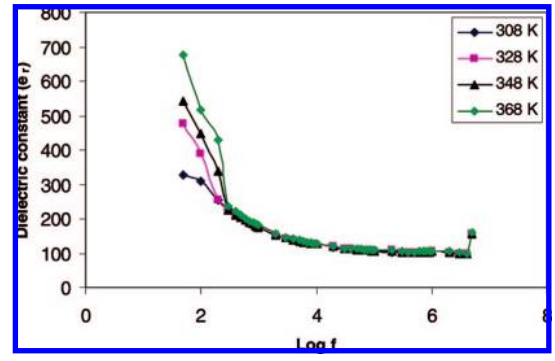

Figure 10. Variation of dielectric constant with frequency.

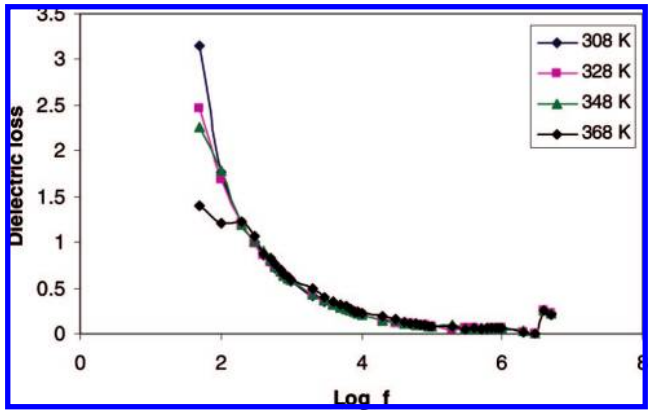

Figure 11. Variation of dielectric loss with frequency.

optical quality with lesser defects, and this parameter is of vital importance for the fabrication of nonlinear optical devices.[21]

Conclusion

An optically good quality bulk single crystal of L-alanine cadmium chloride of dimension 100 mm length and 15 mm diameter was grown successfully within a period of 20 days by modified uniaxial growth of Sankaranarayanan−Ramasamy method along the (101) plane. Powder X-ray diffraction analysis confirms the lattice parameters of the grown crystal. UV absorption spectral analysis confirmed the transparency of the grown crystal with a cutoff wavelength at 240 nm. The presence of cadmium and chlorine in the crystal lattice was confirmed using energy dispersive X- ray analysis (EDAX). Scanning electron microscopy reveals the spiral growth-steps along the growth axis. The Vickers microhardness test carried along the growth axis confirmed the mechanical stability of the grown crystal with work hardening coefficient less than 2. The dielectric studies confirmed the presence of space charge polarization of the LACC crystal. From the present investigations, it is found that the LACC crystal is superior to L-alanine formate[15] due to the size, transparency and growth rate. The above characterization and the nonlinear optical properties confirm that the crystal is applicable for electro-optical device fabrications.

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References

(1) Misoguti, L.; Varela, A. T.; Nunes, F. D.; Bagnato, V. S.; Melo, J.; Mendes Filho, F. E. A.; Zilico, S. C. *Opt. Mater.* **1996**, *6*, 147–152.
(2) Kitazawa, M.; Higuchi, R.; Takahashi, M. *Appl. Phys. Lett.* **1994**, *64*, 2477–2479.
(3) Eimerl, D.; Velsko, S.; Davis, L.; Wang, F.; Loicono, G.; Kennedy, G. *IEEE J. Quantum Electron.* **1989**, *QE-25*, 179–193.
(4) Espinosa, E.; Wyneke, B.; Brehat, F.; Gerbaux, X.; Veintemillas, S.; Molins, E. *Infrared Phys. Technol.* **1997**, *38*, 449–458.
(5) Owens, C.; Bhat, K.; Wang, W. S.; Tan, A.; Aggarwal, M D.; Penn, B. G.; Frazier, D. O. *J. Cryst. Growth* **2001**, *225*, 465–469.
(6) Mohan Kumar, R.; Rajan Babu, D.; Jayaraman, D.; Jayavel, R.; Kitamura, K. *J. Cryst. Growth* **2005**, *275*, e1935−e1939.
(7) Fuchs, B. A.; Ksyn, C.; Veisko, S. P. *Appl. Opt.* **1989**, *28*, 4465–4472.
(8) Sankaranarayanan, K.; Ramasamy, P. *J. Cryst. Growth* **2005**, *280*, 467–473.
(9) Sankaranarayanan, K. *J. Cryst. Growth* **2005**, *284*, 203–208.
(10) Sankaranarayanan, K.; Ramasamy, P. *J. Cryst. Growth* **2006**, *292*, 445–448.
(11) Sankaranarayanan, K.; Ramasamy, P. *Cryst. Res. Technol.* **2006**, *41*, 225–230.
(12) Balamurugan, N.; Ramasamy, P. *Cryst. Growth Des.* **2006**, *6* (7), 1642–1644.
(13) Kathleen, I. S.; Douglas, A. K. *Acta Crystallogr. C* **1993**, *49*, 1156–1158.
(14) Dhanuskodi, S.; Vasantha, K.; Angeli Mary, P. A. *Spectrochim. Acta A* **2007**, *66*, 637–642.
(15) Justin Raj, C.; Jerome Das, S. *J. Cryst. Growth* **2007**, *304*, 191–195.
(16) Frank, F. C. *Phil. Mag.* **1951**, *42*, 1014–1021.
(17) Amelinckx, S. *Nature* **1952**, *169*, 841–842.
(18) Onitsch, E. M. *Mikroskopie* **1947**, *2*, 131–194.
(19) Jerome Das, S.; Gopinathan, R. *Cryst. Res. Technol.* **1992**, *21* (1), K17−K21.
(20) Smith, C. P. *Dielectric Behaviour and Structure*; McGraw-Hill: New York, 1965.
(21) Balarew, C.; Duhlew, R. J. *Solid Sate Chem.* **1984**, *55*, 1–6.

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