Synthesis, Growth and Characterization of L-Proline Barium Chloride Monohydrate: Semiorganic Nonlinear Optical Crystal

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Abstract - Semiorganic nonlinear optical (NLO) material, L-Proline barium chloride monohydrate (LPBCM) single crystal was successfully grown from aqueous solution by Slow Evaporation Solvent Technique (SEST) at room temperature. The lattice parameters and space group were determined using single crystal XRD analysis. Powder X-ray diffraction pattern was recorded and indexed for confirmation of crystalline nature of the grown crystal. The presence of functional groups was confirmed from FTIR analysis. UV-Vis-NIR Optical transmittance spectra were recorded in wavelength region 200 - 900 nm. The thermal properties were studied by TG/DTA. Kurtz powder test shows that the crystals having NLO property. The dielectric properties of LPBCM crystal were also studied.

Keywords: Crystal growth; Barium chloride; Powder X-ray diffraction; FTIR; Second Harmonic Generation; TG/DTA; UV-Vis-NIR; Nonlinear Optical material.

I. INTRODUCTION

Tonlinear optical (NLO) materials are important in current research by the reason of its great effect in optical modulation, amplitude and phase modulation, optical switching, optical memory storage devices in the field of optoelectronic and telecommunication technologies [1-5]. The NLO material should possess large charge transfer and optical transparency with less dislocation density [6]. Semiorganic crystals which have the combined desired properties of inorganic and organic crystals [7-11]. Amino acids holding the attention for NLO applications as they possess electron donor and acceptor groups connected by extended π -electron pathways and shows large hyper polarizabilities [12]. One such amino acid is pure L-Proline and is α -amino acid, contains an amino group (NH₂), which is promising material for second harmonic generation. Lproline and metal ions doped L-proline crystals are the reputed candidates for growing semiorganic crystals [13-14]. In literature some of the L-Proline based crystals such as pure L-Proline [15], L-Proline cadmium chloride monohydrate (LPCCM) [16], L-Proline lithium chloride monohydrate (LPLCM) [17], Dichlorobis (L-Proline) zinc chloride (DBLPZ) [18], L-Proline strontium chloride (LPSCM) [19] were reported. Among these in the literature,

no work has been reported in the modification of desired properties of L-Proline by using barium chloride as dopant. In the present investigation, we report the growth and characterization of LPBCM crystal.

II. EXPERIMENTAL DETAILS

2.1 Synthesis and Growth.

The starting material was synthesized by taking Lproline and barium chloride in 1:1 stoichiometric ratio. The calculated amount of starting materials for the synthesis of LPBC salt was obtained according to the reaction,

NHCH₂CH₂CH₂CHCOOH + Bacl₂.H₂O \rightarrow

Ba (NHCH2CH2CH2CHCOOH) Cl2. H2O

The calculated amount of barium chloride was first dissolved in Millipore water of 18.2 M Ω cm resistivity. Lproline was then added to the solution slowly by stirred well using a temperature controlled magnetic stirrer about six hours to yield a homogenous mixture of solution. The purity of the synthesized salt was further improved by successive recrystallaization process. By this method good quality transparent single crystal with regular shape and size $37 \times 28 \times 3 \text{ mm}^3$ was harvested within 22 days with appropriate growth rate of 1.68 mm/day. The photograph of as grown LPBCM crystals is shown in figure 1.



Figure 1. As grown LPBCM crystals

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2.2 Solubility test

In solution growth technique selection of a solvent, which is moderately soluble, plays a major role. The solubility of LPBCM was determined for various temperatures by dissolving the solute in Millipore water in an airtight container maintained at a constant temperature with continuous stirring. The figure 2 shows the solubility curve of LPBC in aqueous solution.



Figure 2. Solubility curve of LPBCM salt

III.RESULT AND DISCUSSION

3.1 Single crystal X-ray diffraction analysis

The lattice parameter values of LPBCM crystal has been determined by single crystal X-ray diffraction analysis. From the result it has been found that LPBCM crystal belongs to orthorhombic system with space group of P2₁2₁2₁. The LPBCM crystal has a = 6.74 Å, b = 7.15 Å, c = 10.96 Å and V = 528Å³ lattice parameters.

3.2 Powder X-Ray diffraction analysis

The powder of LPBCM crystal has been subjected to powder X-ray diffraction analysis. The sample was scanned over the range of 10° to 80° at a scan rate of 2° /minute and the powder X-ray diffraction pattern has been recorded. Various planes of LPBC crystal have been identified and indexed, by using the 'index' software, as shown in Figure 3.



Figure 3. Powder X-ray diffraction pattern of LPBCM crystal

The crystalline nature of the material has been established by the well defined peaks as shown in Figure 3.

3.3 Fourier Transform Infrared (FTIR) spectral analysis

The LPBCM crystal FTIR spectral analysis is shown in Figure 4. The lack of strong IR band at 1700 cm⁻¹ clearly illustrates the existence of the COO⁻ ion in zwitterionic form [20]. The presence of all functional groups has been confirmed from FTIR spectrum [21]. The wave numbers and their corresponding assignments have been given in Table 1.



Figure 4. FTIR spectrum of LPBCM crystal

Table 1.

Band assignments of FTIR spectra for LPBCM crystal

Wavenumber (cm ⁻¹)	Assignments
3853	O-H Stretching
3746	O-H Stretching
3461	O-H Stretching
3392	O-H Stretching
3244	C-H Stretching
3174	N-H Stretching vibration
3062	C-H asym. Stretching (alephatic)
2978	C-H symmetric stretching
2323	$C \equiv N$ Stretching
2097	$C \equiv C$ Stretching
1609	NH ₂ scissoring
1456	COO ⁻ symmetric stretching
1379	$\mathrm{NH_2^+}$ wagging

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1205	In plane bending of C-H and OH of COOH
1083	C-C stretching vibration
681	COO ⁻ Wagging
588	C-C-CN bending

3.4 Optical transmission spectral analysis

The study of the optical transmission range of the grown crystal has been carried out in the spectral range 200 to 900 nm as shown in Figure 5. The LPBCM crystal has the lower cut-off wavelength at 208 nm and 94% transmission in the UV region.



Figure 5 .UV-Vis transmission spectra of LPBCM crystal

3.5 NLO test

The powder NLO measurement has been carried out for LPBCM by Kurtz and perry technique using Nd:YAG laser with 1064 nm radiation. The output of grown crystal show a NLO efficiency of about 0.61 times that of KDP.

3.6 Dielectric Studies

The dielectric constant is one of the basic electrical properties of solids [22]. The variation of dielectric constant with log of frequency for LPBCM crystal at different temperatures has been shown in Figure 6 (a). The dielectric constant has high values in the lower frequency region and then decreases with increasing applied frequency. Generally it is also observed that the dielectric constant increases slowly with increasing temperature at lower frequency region. Further, the dielectric constant decreases with increase in frequencies for all the temperatures.



Figure 6 (a). Variation of dielectric constant with log frequency of the applied field for LPBCM crystal



Figure 6 (b). Variation of dielectric loss with log frequency of the applied field for LPBCM crystal

At 35 °C the dielectric constant of LPBCM has high value (ie., 267) in the low frequency range (ie., 50 Hz). The variation in dielectric loss with frequency within the temperature range 35 °C to 95 °C is shown in Figure 6 (b). At low temperature (35 °C), the dielectric loss has a low value of 0.34 at high frequency 5 MHz, which increases continuously with temperature (0.09 at 95 °C). At 35 °C the dielectric loss of LPBC has high value (ie., 10.3) in the low frequency range (ie., 50 Hz). The low value of dielectric loss at high frequency for LPBC crystal suggests that the sample possess enhanced optical quality with fewer defects and this parameter is of vital importance for NLO materials in their application [23].

3.7 Thermal analysis

The thermal methods, the most widely used techniques are the thermo gravimetric (TG) and differential thermal analysis (DTA) which find extensive use in all fields of inorganic and organic chemistry, metallurgy, mineralogy and many other areas. The TG-DTA curves

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recorded for the LPBCM is shown in Figure 7.From the TG curve, there is a weight loss at 99.8 °C. The sharp endothermic peak around 136 °C is assigned to melting point of the LPBCM. The exothermic peaks are good agreement with TG trace.



Figure 7. TG-DTA Curves of LPBCM crystal

IV. CONCLUSION

Synthesis, growth and characteristics of LPBCM crystal were studied. The LPBCM crystal was grown from aqueous solution by SEST method at room temperature. The single crystal XRD was recorded, that reveals LPBCM crystal belongs to orthorhombic and possesses $P2_12_12_1$ space group. The powder X-ray diffraction pattern of LPBC crystal was recorded and indexed that reveals the high degree crystalline perfection. The presence of functional groups in the grown LPBCM crystal has been confirmed by FTIR analysis. The optical transmission spectrum has been recorded in the wavelength region between 200 nm and 900 nm. The NLO study was carried out and it reveals the LPBCM crystal has 0.61NLO efficiency than that of KDP. The thermal properties have been studied by obtaining **TG-DTA** curves. The electrical properties were also studied by dielectric constant studies. The high values of dielectric constant in the doped crystal than pure crystal indicated that the doping of barium is highly useful for NLO applications.

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REFERENCES

- D. S. Chemla, J. Zyss, Eds, 'Nonlinear optical properties of organic molecules and crystals', Academic press; New York (1987).
- [2] P. N. Prasad, D. J. Williams, 'Introduction to Nonlinear optical effects in Molecules and Polymers', Wiley-Interscience; New York (1991).
- [3] R. F. Belt, G. Gashurov and Y. S. Liu, Laser Focus, Vol.10, pp.110 (1985).
- [4] R. S. Calark, Photonics Spectra, Vol.22, pp.135 (1988).
- [5] R. J. Gambino, Bull Mater. Res. Soc, Vol.15, pp.20 (1990).
- [6] R. Rajasekaran, P.M. Ushashree, R.Jayavel, P. Ramasamy, J. Cryst. Growth, Vol.229, pp.563-567 (2001).
- P. A. Franken, A. Hill, C. W. Peters,
 G. Weinrich, Phys. Rev. Lett, Vol.7, pp.118 (1961).
- [8] A. Kandasamy, R. Siddeswaran, R. Mohan P.Murugakoothan, P. Suresh kumar, Cryst. Growth & Design, Vol.7, pp.183-186 (2007).
- [9] Reena Ittyachan, P. Sagayaraj. J. Cryst. Growth, Vol.249, pp.557 (2003).
- [10] K. V. Rajendran, D. Jayaraman, R. Jayavel, P. Ramasamy, J. Cryst. Growth, Vol.255, pp.361 (2003).
- [11] A. Ben Ahmed, H. Feki, Y. Abid,
 - H. Boughzala, A. Mlayah, J. Mol. Struct, Vol.888, pp.180 (2008).
- [12] B. Narayanamoolya, S. M. Dharmaprakash, J. Cryst. Growth, Vol.290, pp.498-503 (2006).
- [13] P. Jagdish, N. P. Rajesh, J. Optoelect & Advanced mater, Vol.13 (8), pp.962-966 (2011).
- S. A. Martin Britto Dhas, S. Natarajan,
 G. Bhagavannarayana, J. Cryst. Growth, Vol.310, pp.3535 (2008).
- [15] G. Anantha Babu, P. Ramasamy, Mater. Chem. Phys, Vol.113, pp.727 (2009).
- [16] N. Sakthivel and P. M. Anbarasan, International Journal of Current Research, Vol.3 (11), pp.386-389 (2011).
- [17] J. Thomas Joseph Prakash, S.Kumararaman, Materials letters, Vol.62, pp.4097-4099 (2008).
- [18] T. Uma Devi, N. Lawrence, R. Ramesh Babu, S. Selvanayagam, Helen Stoeckli-Evans and K. Ramamurthi, Cryst. Growth & Design, Vol.9 (3), pp.1370-1374 (2009).
- [19] D. Kalaiselvi, R. Jayavel, Optoelect & Adv. Mater.-rapid communications, Vol.5 (1), pp.58-62 (2011).
- [20] A. M. Petrosyan, R. P. Sukiasyan, S. S. Terzyan H.A.Karapetyan, R.S.Feigelson, J. Crystal Growth, Vol.213, pp.103 (2000).
- [21] K.Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination compounds, Wiley, New York, 1978.
- [22] P.V.Dhanraj, N.P. Rajesh, C.K. Mahadevan, G. Bhagavannarayana, Physica B 404, 2009.
- [23] C. Balarew, R. Duhlew, J. Sold State Chem, Vol.55, pp.1, 1984.