

Growth and characterization of non-linear optical (NLO) material

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Introduction:

In the past three decades, extensive theoretical and experimental investigations of the non-linear optical (NLO) properties of materials have attracted much attention because of their potential applications in the emerging optoelectronic technology [1, 2]. Recently there have been extensive efforts to develop new organic, inorganic and semi-organic NLO crystals. Semi organic materials possess several advantages compared with the traditional inorganic NLO materials like ADP, KDP, KTP, such as large second harmonic conversion efficiency, birefringence and dispersion of refractive index, which are finding increasing use in the development of new photonic devices. In search for the new NLO materials, aromatic compounds with donor and acceptor substituent are extensively studied [3]. A number of crystals with large non-linear coefficients have been reported [4]. This interest has been fuelled by the possibility of using them in the technological devices.

The complexes of amino acids and salts are promising materials for optical second harmonic generation as they tend to combine the advantages of organic amino acids with those of the inorganic acids/salts. Among the amino acids, all except glycine, are characterized by chiral carbons, a proton-donating carboxyl (-COOH) group and the proton-accepting amino (-NH₂) group. Thus, L-argine, L-histidine and L-alanine have been exploited for the formation of salts with different organic/inorganic acids. However, the compounds of L-alanine have been much less explored. Hence, the effect of KI with L-alanine has been studied by the synthesis and characterization of a semi-organic NLO compound, L-alanine potassium iodide (L-AKI). In the present communication, we report the effect of KI on the synthesis and growth of L-AKI single crystals. The crystal structure of L-alanine has been reported by Vijayan et al [5]. The grown crystals were characterized by single crystal XRD, FTIR, FT-RAMAN, Optical transmittance and NLO studies.

Material synthesis:

L-AKI crystals were grown from the aqueous solution using the slow solvent evaporation solution growth technique at room temperature. The commercially procured AR grade L-alanine and potassium iodide supplied by MERCK, India were taken in 1:1 stoichiometric ratios as the starting materials to synthesis of the title compound. The calculated amount of these materials was dissolved in doubly deionised water with vigorous stirring by using magnetic stirrer. The filtered supersaturated solution was slowly allowed to evaporate at room temperature. Good quality single crystal was harvested after a month and is shown in Fig. 1.

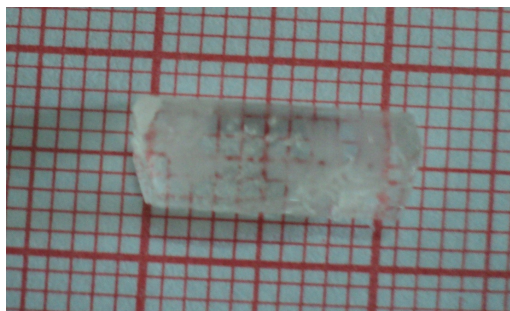


Fig. 1. Photograph of grown L-AKI crystal

Characterization:

Single Crystal XRD:

The grown L-AKI crystal was subjected to single crystal XRD studies using Oxford Diffraction Xcalibur Eos Gemini diffractometer with graphite-monochromated Mo $K\alpha$ radiation with the wavelength of 0.71073 Å. The cell parameters obtain for the grown crystals are $a = 5.7996$ Å, $b = 6.0383$ Å, $c = 12.3858$ Å, $\alpha = \beta = \gamma = 90^\circ$ and volume = 433.75 Å³. The L-AKI belongs to orthorhombic crystal structure with the space group $P2_12_12_1$.

FT-IR studies:

Fourier transform infrared spectrum (FT-IR) of L-AKI crystal was recorded with a Perkin – Elmer spectrophotometer in the range 450 – 4000 cm⁻¹ following KBr pellet technique. It provides useful information regarding the molecular structure of the compound. The characteristic transmission peaks of infrared spectrum are shown in Fig. 2.

The NH₂ group of L-alanine is protonated by the COOH group, giving rise to NH₃⁺ and COO⁻ groups. L-AKI compound shows absorption peak at 1623 cm⁻¹ indicating the presence of primary amino group. The peak observed at 3083 cm⁻¹ corresponding to asymmetric stretching mode of NH₃⁺. The CH₃ bending modes are assigned to the peaks at 1360 and 1507 cm⁻¹. The peak at 1404 cm⁻¹ is assigned to symmetrical stretching of the –COO⁻ group. C-OH stretch and O-H bend of the COOH group are observed at 1228 and 1309 cm⁻¹, respectively [6]. The different frequencies of the fundamental vibration of the grown crystal are shown in Table 1.

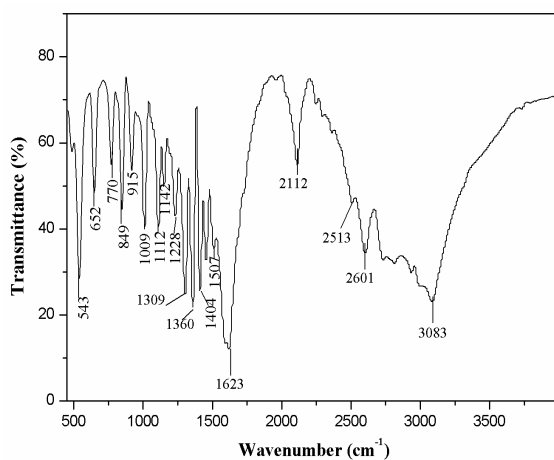


Fig. 2. FT-IR spectrum of L-AKI

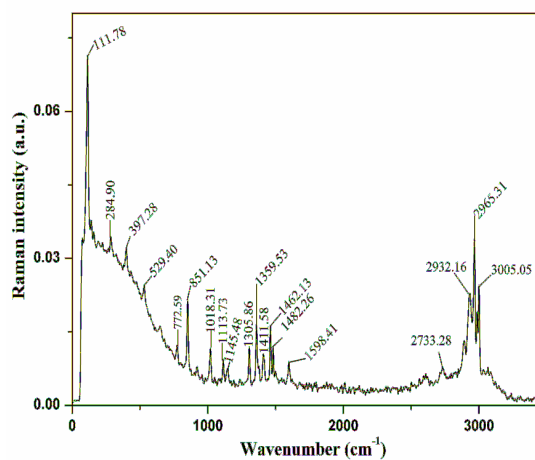


Fig. 3. FT-Raman spectrum of L-AKI

FT-RAMAN spectral analysis:

FT-Raman spectrum was recorder for L-AKI single crystal using a Bruker RFS 27 spectrophotometer. The spectrum was recorded in the 100 – 3500 cm^{-1} Stokes region using 1064 nm wavelength of an Nd: YAG laser for excitation operating at 200 mW power. The recorded spectrum is shown in Fig. 3. The FT-Raman spectrum of the grown crystal was broadly analysed in the three regions namely, lower wavenumber region (below 1000 cm^{-1}), medium wavenumber region (2000 – 1000 cm^{-1}) and higher wavenumber region (3500 – 2000 cm^{-1}), respectively. On the investigation of the absorption bands below 1000 cm^{-1} , -COO^- rocking, -COO^- wagging, C-C stretching and -CH_2 rocking are identified. In the medium wavenumber region (2000 – 1000 cm^{-1}), the presence of -COO^- , -NH_3^+ stretching vibration forms, which indicates the zwitterionic structure of L-alanine cation. High wavenumber region (3500 – 2000 cm^{-1}) contains -NH_2 , -NH_3^+ , and -CH_2 stretching vibration and combination of them [5, 8].

L-Alanine [7]	L-Alanine Cadmium Chloride [2]	Present work	Assignment of vibrations
540	548	543	-COO^-
	633	652	-COO^-
771	766	770	-COO^-
852	850	849	CCN
918	927	915	CCN
1015	1012	1009	CH_3
1113	1111	1112	NH_3^+
1148	1187	1142	CCN
		1228	
		1309	
1355	1348	1360	CH_3
1412	1421	1404	-COO^-
1455	1460	1507	CH_3
1623	1606	1623	NH_3^+
		2112	
		2513	
		2601	
	3076	3083	NH_3^+

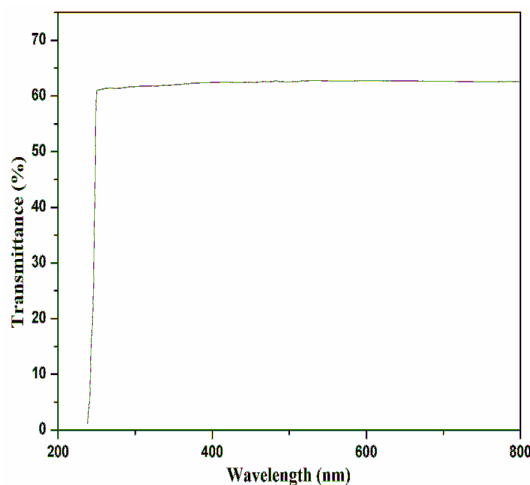


Fig. 4. Optical transmittance spectrum of L-AKI

Table 1. Frequencies of the fundamental vibrations of L-AKI

Optical studies:

The optical transmittance spectrum of the grown crystal was recorded in the wavelength range 200 – 800 nm using a Perkin – Elmer Lamda 935 UV-vis-NIR spectrometer. The recorded spectrum is shown in Fig 4. The crystal shows a good transmittance in the entire visible region, which enables it to be a good material for optoelectronic applications. From the UV-visible spectrum, it is clear that the lower cut-off wavelength 244 nm combined with the very good transparency makes the useful of this material for optoelectronic and non-linear optical applications.

SHG test:

Kurtz-Perry powder technique [9] is the most widely used and is a preliminary tool to identify the second harmonic generation signal from the crystal with non-centrosymmetric crystal structure. The crystal was made into a

homogeneous powder of particles and then packed in a micro capillary tube of uniform bore. This sample was illuminated using Spectra Physics Quanta – Ray Nd: YAG laser with the first harmonic output of 1064 nm pulse width of 8 ns with a repetition rate of 10 Hz. The second harmonic signal generated in the crystal was confirmed from the emission of green radiation of wavelength 532 nm. Hence, the grown crystal can be useful in the fabrication of NLO materials.

Conclusions:

Semi-organic non-linear optical crystal L-AKI has been grown by the slow solvent evaporation technique from aqueous solution of L- alanine and potassium iodide at room temperature. The grown crystal was confirmed by single crystal XRD analysis which shows that the crystal belongs to orthorhombic system with the space group $P2_12_12_1$. The various functional groups present in the crystal were identified using FT-IR and FT-RAMAN studies. The optical transmittance studies of the grown crystal reveals that the crystal has good transparency in the entire visible region. The SHG efficiency was tested by using Kurtz powder technique. All the results indicate that the title crystal is a suitable candidate for the LASER and NLO applications.

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References:

1. D. R. Askeland, P. P. Rhule, *The Science and Engineering of Materials*, Thomson (2003).
2. S. Dhanuskodi, K. Vasantha, P. A. Angeli Mory, *Spectrochim. Acta Part A* **66**, 637-642 (2007).
3. D. Kalaiselvi, R. Jayavel, *Optoelectron. Adv. Mater.* **4**, 1400-1403 (2010).
4. M. Esthaku Peter, P. Ramasamy, *J. Cryst. Growth* **312**, 1952-1956 (2010).
5. N. Vijayan, S. Rajasekaran, G. Bhagavannarayana, R. Ramesh Babu, R. Gopalakrishnan, M. Palanichamy, P. Ramasamy, *Cryst. Growth Des.* **6**, 2441-2445 (2006).
6. R. Mohan Kumar, D. Rajan Babu, D. Jayaraman, R. Jayavel, K. Kitamura, *J. Cryst. Growth* **275**, 1935-1939 (2005).
7. K. Nakamoto, *IR Spectra of Inorganic and Coordination Compounds*, 2nd ed. New York: Wiley Interscience, (1978).
8. Z. H. Sun, W. T. Yu, X. F. Cheng, X. G. Wang, G. H. Zhang, G. Yu, H. L. Fan, D. Xu, *Opt. Mater.* **30**, 1001-1006 (2008).
9. S. K. Kurtz, T. T. Perry, *J. Appl. Phys.* **39**, 3798-3813 (1968).