Spectroscopic, optical, thermal and mechanical properties of L–asparagine potassium chloride – A semiorganic crystal

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A new semiorganic crystal, L-asparagine potassium chloride (LAPC) has grown by slow evaporation technique. The crystals were subjected to various characterized techniques. Powder x-ray diffraction (PXRD) analysis confirms the crystalline nature. The presence of various functional groups was identified by FTIR spectroscopic technique. UV–Vis spectrum indicates that the crystal has good transmittance in the entire visible region. The grown crystal was thermally stable up to 103 ºC as determined by TG/DTA studies and mechanical stability was measured by Vicker's microhardness test. The powder Second Harmonic generation test was studied by modified Kurtz–Perry method using Nd:YAG laser with fundamental wavelength of 1064 nm.

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1. Introduction

The fast development of optoelectronics field necessitates the new and efficient of nonlinear optical (NLO) materials for second harmonic generation used in optoelectronic applications such as optical communication and optical data storage etc. The second order optical effect is concerned in both inorganic and organic materials. In this concern, the inorganic materials show the good mechanical and thermal stability with high transparency range, but their second order coefficient are limited. The organic crystals exhibit higher second order nonlinear coefficient, but poor in thermal and mechanical behavior and it is not suitable for many device applications [1-3]. For theses difficulty, optically active amino acids of crystalline are combined with inorganic host favorable for good thermal and mechanical properties with high nonlinear optical coefficient such as L–histidine chloride monohydrate [4], L–alanine cadmium chloride [5] and L–asparagine monohydrate [6] are already reported. In the present investigation on semiorganic crystal of L–asparagine potassium chloride is grown successfully and the crystals were subjected various characterization such as CHNS analysis, PXRD, FTIR, UV-Vis, TG/DTA, microhardness test and powder SHG test.

2. Experimental details

The starting materials were highly pure and growth process was carried out in aqueous solution. L–asparagine potassium chloride has been synthesized by taking in a 2:1 stoichiometric ratio. The crystal was synthesized according to the following Eq. (1).

$$2[C_4H_8N_2O_3.H_2O] + KCl \text{ ---------> } K(C_4H_8N_2O_3.H_2O)_2Cl \quad \text{(L-asparagine potassium chloride)} \qquad (1)$$

The calculated amount of potassium chloride was first dissolved in deionized water. Then L–asparagine was added to the solution slowly. The solution was agitated with a magnetic stirring device and filtered after complete dissolution of the starting materials. The prepared solution was left standby for 26–29 days at room temperature. Thereby colorless and highly transparent crystals were obtained and shown in Fig. 1.

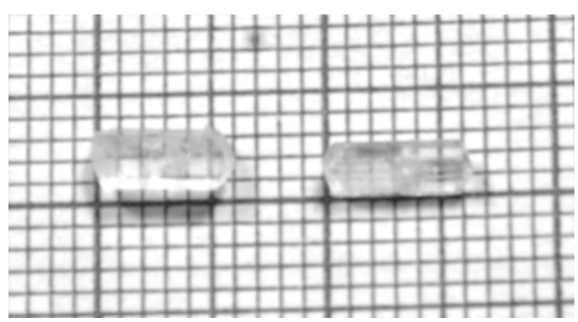

Fig. 1. As-grown LAPC crystals.

3. Results and discussion

3.1. CHNS analysis

The CHNS elemental analysis was carried out of LAPC crystals using by Elementar Vario EL III CHNS analyzer. The result of the elemental analysis shows that the compounds contain the following percentage of elements: C=42.99% (42.89%), H=10.53% (9.01%) and N=25.12% (25.01%). The micro analysis of the LAPC crystalline material shows good agreement with the calculated values.

3.2. Powder XRD analysis

Crystalline nature and purity have been studied by using powder XRD analysis and the fine crystalline powder was subjected to powder X-ray diffraction by using (Bruker AXS D8 Advance powder diffractometer with Cu, Wavelength 1.5406Å) were used. The sample was scanned in the reflection mode in the 2θ range 10–80°. All the observed prominent peaks in XRD patterns were shown in Fig. 2. The results of well defined diffraction peaks at specific 2θ angles show the purity and better crystallinity [7].

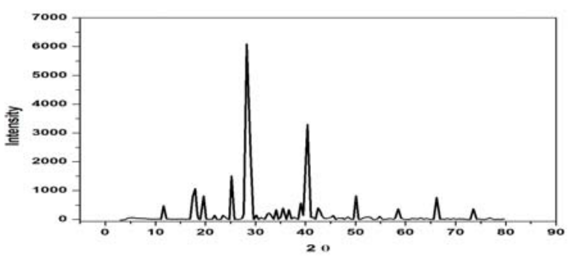

Fig. 2. Powder XRD patterns of LAPC crystals.

3.3. FTIR studies

The FTIR spectrum of LAPC crystal is shown in Fig. 3. A broad peak at 3443 cm^{-1} is assigned due to the presence of asymmetric stretching vibration of NH_3^+ group. The broad and higher intensity band in the energy region at 3382 cm^{-1} is assigned due to NH stretch of NH_2 vibration of molecule. A peak at 2949 cm^{-1} is due to the CH_2 vibration. The peaks are assigned at 1644 and 1528 cm^{-1} due to the asymmetric and symmetric stretching of NH_3^+ group [8]. C–H and N–H symmetric stretching are observed at 2742 and 2525 cm^{-1} respectively. An intensity peak at 1073 cm^{-1} is due to C–N stretching mode of vibration. The CH_2 bending and rocking vibrations of amino acid are observed at 1359 and 892 cm^{-1} respectively. The C–C and COO^- group of carboxylic are assigned at 1234 and 1149 cm^{-1} respectively. A peak is observed at 559 cm^{-1}due to presence of COO^- rocking vibration [9]. The broadened bands of the spectra in the doped crystals were the clear notification of the presence of the amino acid.

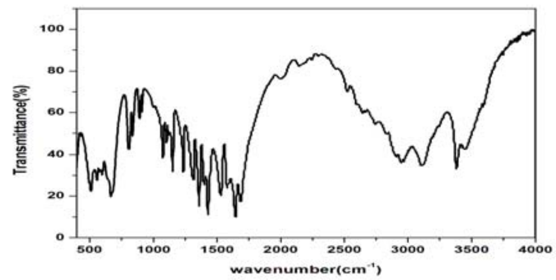

Fig. 3. FTIR Spectrum of LAPC crystals.

3.4. UV-Vis studies

The optical transmission range of crystal was observed in between wavelength 200 and 1000 nm with scanning speed of 200 nm/min using Varian, Cary 5000 instrument. Transmittance nature of LAPC crystal is found to be in the entire visible region is a desirous property for this material for NLO applications. From the spectrum it is evident that LAPC crystal has lower UV cut off of 205 nm, which makes it a very potential material for blue light emission [10]. A graph of transmission Vs wavelength (nm) is shown in Fig. 4.

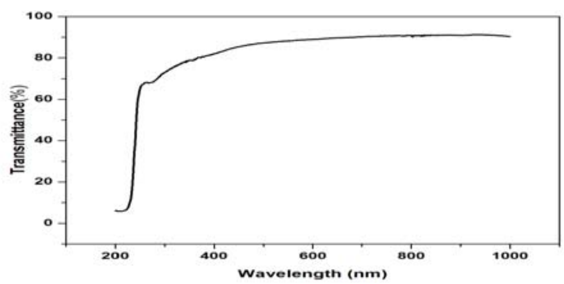

Fig. 4. Optical transmittance spectrum of LAPC crystals.

3.5. Thermal analysis

The thermal behavior of grown sample was studied by using TA instrument Q600 SDT and Q20 DSC model. To determine the melting point and thermal stability of grown crystal is shown in Fig. 5. TG curve show that there was a weight loss of about 32.78% in the temperature 103–360 ºC due to the liberation of volatile substances. From the DTA curve, there are sharp endothermic peaks at 103 ºC, 241 ºC and 360 ºC correspond to the melting point of the crystal and the peaks are well coincide with the TG trace. Hence, the crystal does not have any isomorphic transition below its first stage of decomposition at 103 ºC. According to DSC curve, the decomposition peaks are exactly matches with DTA trace [11]. Hence the material can be exploited to NLO applications up to its melting point.

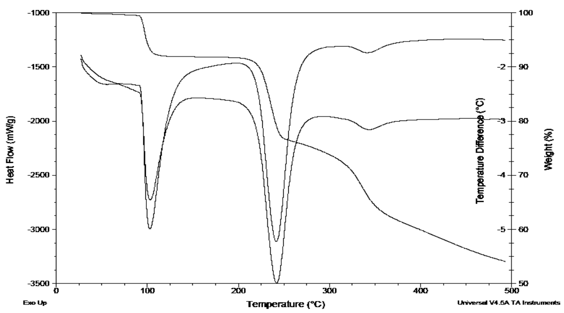

Fig. 5. TG/DTA and DSC Curve of LAPC crystals.

3.6. Microhardness test

The microhardness test was carried out to determine the mechanical strength of the grown crystal using HMT 2T, SHIMADZU, Vicker's microhardness tester. The mechanical strength of the grown crystal is shown in Fig. 6. The static indentations were made at room temperature with a constant indentation time of 15 s for all indentations. The indentation marks were made on the surfaces by varying load such as 25, 50 and 100g. Vicker's microhardness number was determined by using Hv=1.8544 P/d^2 kg/mm^2. The maximum hardness number was found about 105.5 kg/mm^2 with the load up to 100g and higher load cracks developed in the material [12]. This may be due to the release of internal stresses generated locally by indentation.

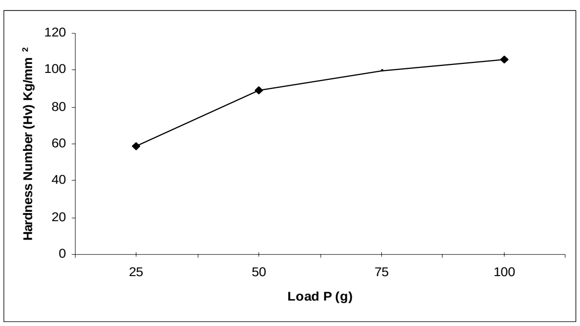

Fig. 6. Microhardness of LAPC crystals.

3.7. Powder SHG test

Nonlinear optical property of the crystal was determined by the modified version of powder technique developed by Kurtz and Perry [13]. The crystal was ground into fine powder and packed in the micro capillary tube. A Q-switched Nd:YAG laser with wavelength of 1064 nm has been used. The input pulse energy of 1.9 mJ/S, pulse width 8ns and repetition rate 10Hz is used. The present result shows that SHG conversion efficiency of KDP is 19 mV and for LAPC is 2.1 mV.

4. Conclusion

L-asparagine potassium chloride, a new semiorganic material has been synthesized by slow evaporation technique at room temperature. The elemental analysis confirms stoichiometric ratio. The sharp well defined Bragg's peaks confirm the crystalline nature of the materials. The FTIR analysis verified all the functional groups and molecular strength of the crystal. The thermal analysis indicated that crystals are stable up to 103 ºC, suggesting that it has good thermal stability. From the micro hardness investigations, the grown crystal has minimum surface hardness about 105.5 kg/mm^2. The NLO property of grown crystal was studied by using Kurtz-Perry powder technique.

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