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Studies of L-asparagine crystals admixtured with ammonium chloride (LAAC) grown by solution method

KEYWORDS

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ABSTRACT *L-asparagine crystals admixtured with ammonium chloride (LAAC) were grown by slow evaporation technique at room temperature (32 °C). The grown crystals were found to be transparent, colourless and well-shaped. Single crystal XRD studies were carried out to analyze the structural properties of the grown sample. UV-visible studies were performed to find the band gap and transparency. EDAX spectrum was recorded to identify the elements present in the grown crystal. SHG study reveals the NLO activity of the sample. The mechanical strength of the grown crystal was checked by microhardness test.*

1. Introduction

Many efforts are being made recently to combine amino acids with different acids and salts to synthesize the useful nonlinear optical (NLO) materials and these materials are of great interest because of their significant impact on laser technology, optical communication and optical data storage and optical data processing etc [1,2]. L-asparagine is an amino acid and some L-asparagine complexes such as L asparagine potassium chloride, L-asparagine-L-tartaric acid, L-asparaginium picrate, L-asparaginium nitrate and L-asparagine cadmium bromide have already been reported in the literature [3-7]. The aim of this work is to grow single crystals of L-asparagine admixtured with ammonium chloride (LAAC) by slow evaporation solution growth technique and to characterize the grown crystals by various studies such as structural, transmittance studies, SHG, microhardness and EDAX studies.

2. Synthesis and growth

The complex viz. L-asparagine admixtured with ammonium chloride (LAAC) was formed by taking the AR grade of L-asparagine (99% purity) and AR grade of ammonium chloride (98% purity) in the molar ratio 2:1. The calculated amounts of the chemicals were dissolved in de-ionized water and stirred well using a magnetic stirrer for about 2 hours. The solution was heated until the synthesized salt of LAAC was obtained. During the synthesis, temperature of the solution was maintained at 50°C in order to avoid the oxidation of the sample. The purity of the synthesized salt was improved by repeated re-crystallization. The solubility study was performed for the twice re-crystallized of LAAC salt in de-ionized water by gravimetrical method [8]. In accordance with the solubility data, the saturated solution of LAAC was prepared at 30 °C in a 250 ml beaker and stirred well using a magnetic stirrer for about 2 hours. Then the solution was filtered using a Whatmann filter paper. After filtering, the beaker was loaded in the constant temperature bath and temperature was maintained at 30 °C. Seed crystals were kept in the saturated solution to harvest the crystals of LAAC after a growth period of 25-30 days. The grown crystals of ammonium chloride admixtured L-asparagine (LAAC) are displayed in the figure 1.

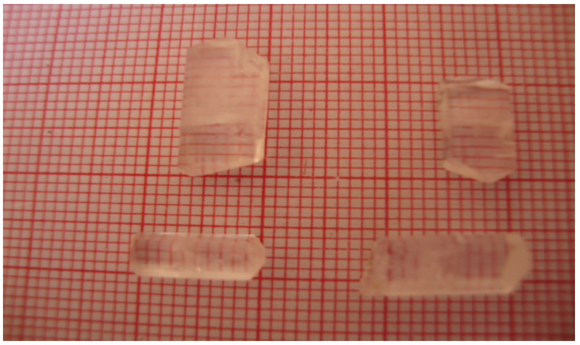

Fig.1: The grown crystals of ammonium chloride admixtured L-asparagine (LAAC) crystals

3. Single crystal X-ray diffraction (XRD) studies

Single crystal X-ray diffraction (XRD) study of the grown crystals were carried out using a single crystal CCD diffractometer and the intensity data was collected and accurate unit cell parameters were determined from the reflections. The obtained single crystal XRD data are provided in the table 1. For the comparison purpose, the XRD data of pure L-asparagine crystals are also given in the table. It is observed from the results that the grown crystals crystallize in orthorhombic system with space group $P2_12_12_1$. The number of molecules per unit cell is found to be 4. It is noticed that the volume of the unit cell of LAAC crystal is more than that of pure L-asparagine crystal.

Table 1: XRD data for pure and ammonium chloride admixured L-asparagine crystals

Crystal parameters	Pure L-asparagine[9]	Ammonium chloride admixtured L-asparagine
a (Å)	5.589(1)	5.621(3)
b (Å)	9.831(3)	9.850(2)
c (Å)	11.810(4)	11.813(1)
α	90°	90°
β	90°	90°
γ	90°	90°
Crystal system	Orthorhombic	Orthorhombic

Crystal parameters	Pure L-asparagine[9]	Ammonium chloride admixtured L-asparagine
Space group	P212121	P212121
Volume (Å3)	648.90	657.1
Z	4	4

4. Transmittance studies

The transparency was checked by carrying out UV-visible spectral studies for both pure and ammonium chloride admixtured L-asparagine crystals. The recorded transmittance spectra are displayed in the figure 2. It is observed that the transparency of ammonium chloride admixtured L-asparagine crystal is slightly more in the visible region and the magnitude of energy band gap of pure L-asparagine and ammonium chloride admixtured L-asparagine crystals are almost the same. Using the formula $E_g = 1240 / \lambda$ (here λ is in nanometre), the band gap energy was calculated. The optical band gap is slightly increased when L-asparagine crystals were grown in the ammonium chloride solution. The cut-off wavelength values for pure and LAAC samples were found to be 227 and 223 nm and corresponding energy gap values are 5.46 eV and 5.56 eV respectively.

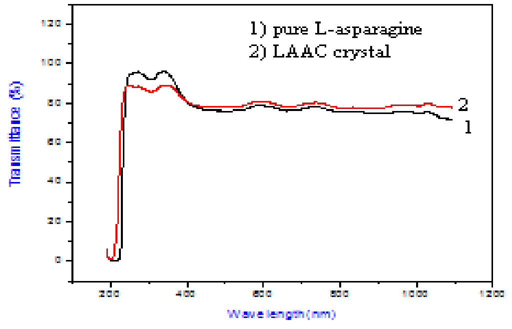

Fig. 2: UV-Visible transmittance spectra of pure L-asparagine and ammonium chloride admixtured L-asparagine (LAAC) crystals

5. Second harmonic generation (SHG) efficiency measurement

When a high intense laser light is passed onto a crystalline material, the nonlinear optical (NLO) effect is observed and it is the interaction of an electromagnetic field of high intensity laser light with the material. The second harmonic generation behavior of the powdered material was tested using the Kurtz and Perry method [10]. The grown crystal was ground into a homogenous powder and densely packed between two transparent glass slides. A Q switched Nd:YAG laser beam of wavelength 1064 nm with an input power of 0.68 J/pulse, pulse width of 6 ns and repetition rate of 10 Hz was directed on the sample. The SHG output of wavelength 532 nm (green light) was detected by the photomultiplier tube (PMT). The powdered material of potassium dihydrogen phosphate (KDP) was used in the same experiment as a reference material. SHG efficiency of the LAAC sample was found to be 0.59 times that of KDP.

6. EDAX studies

EDAX stands for Energy Dispersive Analysis by X-rays and it is a technique used for identifying the elemental composition of the specimen. The EDAX spectrum for LAAC sample is shown in the figure 3. Since the element H is a light element, it cannot be identified using the EDAX method. From the spectrum, the elements such as C, O,N and Cl were identified. When L-asparagine crystals are grown in the solution of ammonium chloride, the ions like Cl may be trapped in the interstitials of the lattice of the grown crystal and this leads to changes in the properties of L-asparagine crystals.

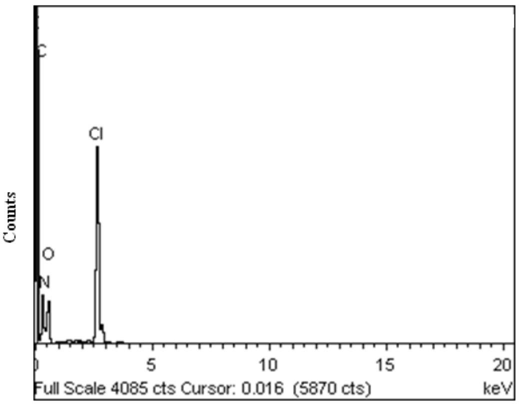

Fig.3: EDAX spectrum for ammonium chloride admixtured L-asparagine (LAAC) crystal

7. Microhardness measurement

Hardness of a material depends on different parameters such as lattice energy, Debye temperature, heat of formation and interatomic spacing. Measurement of hardness is a useful non-destructive testing method used to determine the applicability of the crystal in the device fabrication and it is one of the best methods of understanding the mechanical properties of the materials such as fracture behavior, yield strength, brittleness index and temperature of cracking etc. The microhardness studies of LAAC crystal were carried out by Vickers hardness measurement. Crystals, free from cracks, with flat and smooth surfaces were chosen for the static indentation tests. The crystal was mounted properly on the base of the microscope. Now, the selected faces were indented gently by loads varying from 25 to 75 g for a period of 10 s using Vickers diamond indenter attached to an optical microscope. The length of the two diagonals of diamond indenter was measured by a calibrated micrometer attached to the eyepiece of the microscope after unloading and the average was found out. For a particular load, at least three well defined indentations were considered and the average value (d) was measured. The Vickers hardness (H_v) numbers at different loads were calculated using the relation $H_v = 1.8544 P / d^2$ where P is the applied load in kilogram and d is the average diagonal length of the indentation marks in millimetre. The calculated values of hardness number for LAAC crystal are 101.23, 111.65 and 120.38 kg/mm^2 for the corresponding applied loads 25 g, 50 g and 75 g respectively. From the results, it is noticed that the hardness number increases with the applied load and this is due to reverse indentation size effect (RISE) [11].

8. Conclusions

Single crystals of ammonium chloride admixtured L-asparagine (LAAC) were grown by solution method. XRD studies reveal that the grown crystals crystallize in orthorhombic structure. The cut-off wavelength for the grown LAAC crystal is found to be 223 nm. The elemental composition of the grown crystal was analyzed by EDAX studies. The hardness of LAAC crystal is found to be increasing with the increase in the applied load.

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