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Dielectric and structural studies on sulphamic acid (SA) single crystal

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Abstract

Sulphamic acid single crystal of the size 14 × 8 × 6 mm^3 has been grown by slow cooling solution growth method at 35.5 °C. Fermi resonance vibrations of N–S stretching and SO_3 rocking have been observed from micro-Raman analysis. Different shapes of etch patterns have been observed for etchants like water, ethanol and HCl for different etching periods. The dielectric constant and dielectric loss have been measured for different frequencies at different temperatures.

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1. Introduction

Most of the nonlinear optical materials are currently used in the fabrication of passive and active photonic devices [1,2]. Potassium dihydrogen phosphate (KDP) is widely employed as a laser frequency doubler and the Lithium Niobate ($LiNbO_3$) crystal is virtually the exclusive material of choice for electro-optic modulators. Although the crystal growing technology for these materials is highly developed and their nonlinear optical susceptibilities are sufficient for most of the current photonic applications, they have features that are less than desirable. One such feature is the relatively slow optical switching time characteristic of photorefractive and ferroelectric inorganic crystals. Hence, new nonlinear optical materials are needed to extend the range of photonic applications. For any device fabrication in the electronic industry pure and defectless single crystals are needed.

In this point of view, the sulphamic acid (SA) single crystal was grown by slow cooling solution growth method. Sulphamic acid is a strong inorganic acid, while mixing it with water it exhibits zwitterionic form [3]. There are only few reports available on the growth of SA single crystal [4–7]. Attempts were made to grow good quality single crystal of sulphamic acid. The grown crystal was characterized by using micro-Raman, etching and dielectric studies.

2. Growth of sulphamic acid single crystal

The recrystallised material of sulphamic acid was dissolved in deionised water in accordance with solubility data (30 g/100 ml at 40 °C) and sulphamic acid solution was prepared at 40 °C. The prepared solution was filtered using Whatman filter paper (0.22 μm). The filtered solution was allowed for slow evaporation. The seed crystals were harvested from the

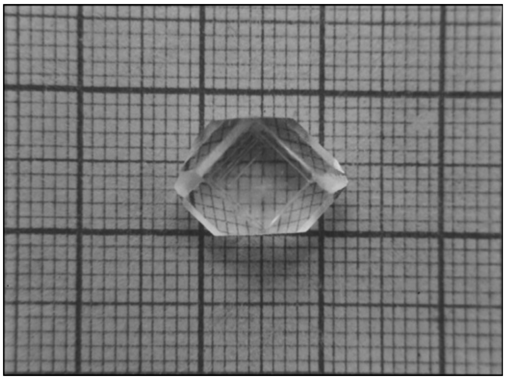

Fig. 1. Sulphamic acid single crystal.

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sulphamic acid solution and defect free crystal was selected as a seed crystal for bulk growth. For bulk crystal growth, the saturated solution was prepared at 40 °C and the seed crystal with well defined morphology was hanging in the solution. The growth experiment was carried out in a constant temperature bath of controlling accuracy ±0.01 °C. The temperature of the solution was reduced from 40 °C at the cooling rate of 0.1 K to 0.5 K/day. The growth was achieved at 35.5 °C. The bulk single crystal of sulphamic acid of size $14 \times 8 \times 6$ mm^3 was harvested after two weeks (Fig. 1).

3. Characterization studies on sulphamic acid single crystal

The grown sulphamic acid crystal was subjected to micro-Raman spectral studies. The etch-pit formation and growth mechanism were identified from the chemical etching studies. The dielectric studies were carried out on the grown sulphamic acid single crystal.

3.1. Micro-Raman studies on SA crystal

The micro-Raman spectrum of the solution grown SA single was recorded using Jobin Yuon-spex U 1000 model Raman spectrometer. The excitation source used in the experiment was 514.5 nm radiation from the Argon ion laser. A liquid nitrogen cooled charge coupled device system was employed to record the spectra. The exciting power striking the sample was about 100 mW. The slits were set for 1 cm^{-1} area. The micro-Raman spectra of SA are shown in Fig. 2a–d. The internal vibrations of SA were recorded in the Raman frequency range 300 cm^{-1}–3200 cm^{-1}. The frequency region 2800 cm^{-1}–3186 cm^{-1} is due to NH$_3^+$ stretching vibration which confirms the zwitterionic nature of SA crystal. Also this broadened peak confirms the hydrogen bonding in the grown crystal. The N–H asymmetric stretching mode vibrations are observed at 3186 cm^{-1} and also N–H symmetric stretching vibrations are observed at 3071 cm^{-1} and 3119 cm^{-1}. The rocking mode vibrations of NH$_3^+$, are observed at 1016 cm^{-1}. The N–H…S, hydrogen bonding is assigned at 1228 cm^{-1} [8]. And the peak at 2870 cm^{-1} is due to N–H..O vibration because SA contains five N–H..O vibrations in structure. The band at 1278 cm^{-1} represents SO$_3$ degenerate stretching vibration. The SO$_3$ symmetric stretching overtone was observed at 1068 cm^{-1}. Fermi resonance frequency vibrations are observed for N–S stretching at 682 cm^{-1} and overtone of SO$_3$ rocking around 694 cm^{-1} [6]. The bands at 353 cm^{-1} and 556 cm^{-1} are assigned for SO$_3$ rocking and deformation vibration modes, respectively. The deformation of NH$_3^+$ was observed at 1456 cm^{-1} and 1535 cm^{-1}.

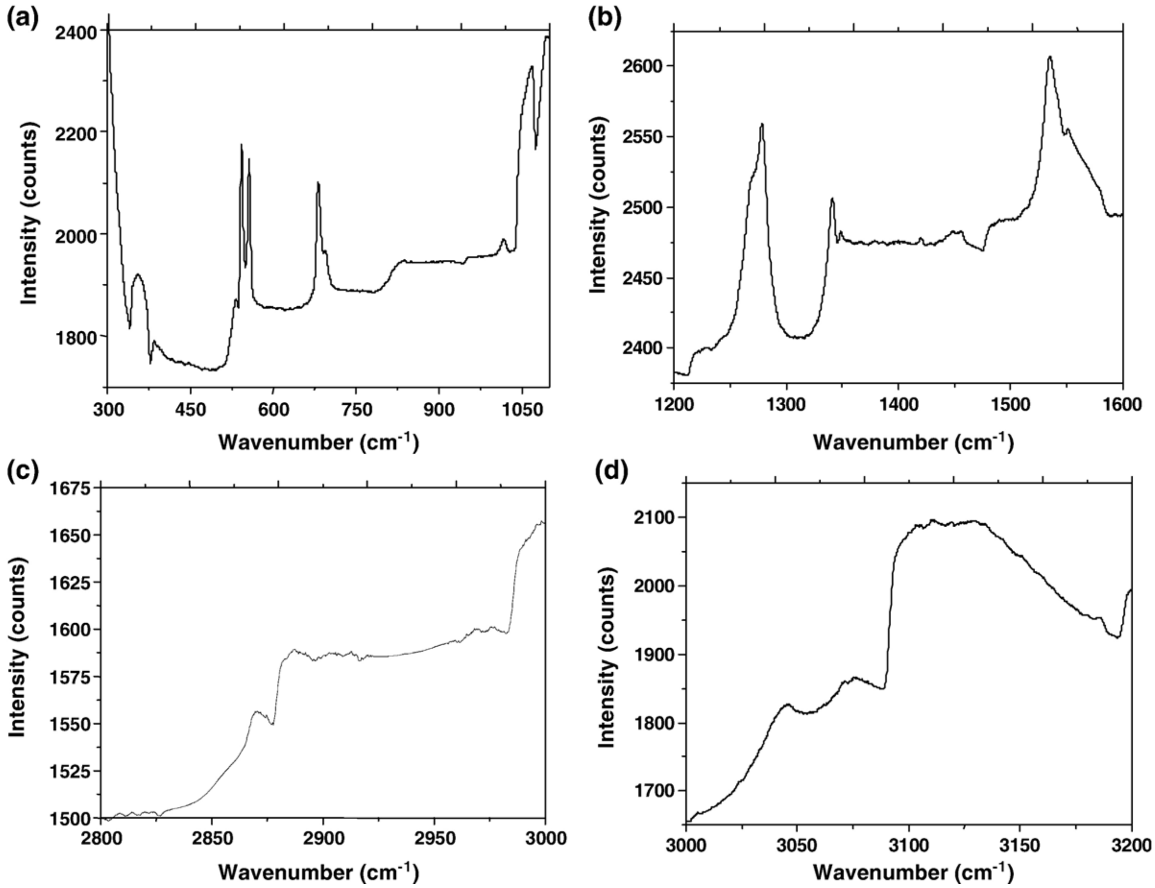

Fig. 2. (a) and (b) Micro-Raman spectra of SA single crystal in the frequency range of 300–1100 cm^{-1} and 1200–1600 cm^{-1}, respectively. (c) and (d) Micro-Raman spectra of SA crystal in the frequency range of 2800–3000 cm^{-1} and 3000–3200 cm^{-1}, respectively.