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THERMAL, DIELECTRIC, AND SURFACE ANALYSIS OF NaDP DOPED GLYCINE PHOSPHITE SINGLE CRYSTALS

S. Supriya, F. Fernández-Martinez

Mechanical Engineering, Chemistry and Industrial Design Department, E.T.S.I.D.I., Technical University of Madrid, Madrid, Spain
E-mail: sciencepriya@gmail.com

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Transparent, unidirectional single crystals of sodium dihydrogen phosphate-doped glycine phosphite (NaDP—GPI) are grown by the Sankaranarayanan-Ramasamy method. The good quality crystal is obtained under controlled thermal conditions. The functional groups and melting temperature of NaDP—GPI single crystals are analysed. The phase transition temperature of NaDP—GPI is calculated from the dielectric studies. The mound-like patterns are observed on the surface of the crystal. The growth process under the controlled thermal condition was observed by optical studies. The obtained results are discussed in detail.

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The hydrogen-bonded ferroelectric single crystal of glycine phosphite (GPI) belongs to the inorganic family of crystals. Ferroelectric amino acid crystals are widely used for the fabrication of infrared detectors, piezoelectric/electrostrictive transducers, optical integrated circuits, display and optical data storage devices [1]. The GPI single crystal crystallizes from its aqueous solution and undergoes a continuous ferroelectric to paraelectric phase transition at 224 K. This single crystal belongs to a monoclinic crystal structure with the $P21/a$ space group in the paraelectric phase [2]. It is necessary to grow defect-free bulk single crystals for the fabrication of devices. In the conventional solution technique, many of the problems such as dislocations, slip bands, growth bands, liquid inclusions, low angle grain boundaries, cracks, and vacancies were observed [3]. However, in the Sankaranarayanan-Ramasamy (SR) method, the defects can be eliminated. Also this technique offers a 100 % solute-crystal efficiency. The doping effect of sodium dihydrogen phosphate (NaDP) on GPI was studied by conducting various characterization techniques such as thermal and optical analyses, and the obtained results are discussed in detail.

Experimental. As reported by S. Supriya *et al.* [4], a 5 mol% NaDP-doped GPI single crystal [5] was obtained by the SR method. The grown NaDP—GPI single crystal was transparent and unidirectional. The functional groups of NaDP—GPI samples were analysed on an Avatar 330-FTIR Thermo Nicolet spectrometer. The Zentech-1061 LCZ meter recorded the dielectric analysis of pure GPI and NaDP—GPI. The differential thermal analysis (DTA) was carried out on a SHIMADZU DT-40 simultaneous DT analyser with a heating rate of 10 °C/min. The surface of the single crystal was analyzed by a Zeiss LSM 510 confocal laser scanning microscope (CLSM). The cross profiling of a laser-scanned image was performed to assess imperfection across the growth direction of the crystal. After the initial scans, a robust Gaussian filter with a 4 μm cutoff was applied to the surface topography

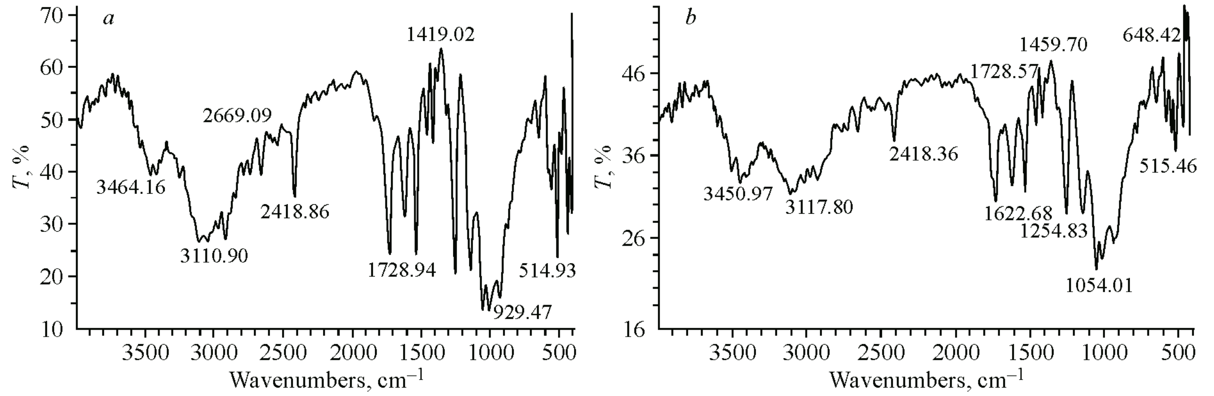

Fig. 1. Functional group analysis. FTIR data: pure GPI (*a*); NaDP—GPI (*b*)

using the mountains map topography software (Digital Surf). Surface features were then calculated from the filtered topography. Further, the crystal surface was analysed by a Nano Surf Easy Scan2 (Switzerland) atomic force microscope (AFM). The images were taken in contact mode with sharpened tetrahedral tips (OMCL-AC160TS-C2, OLYMPUS, Japan). The cantilever force constant was 42 N/m and the tip radius was 7 nm.

Results and discussion. The Fourier transform infrared (FTIR) spectra of NaDP—GPI are compared with those of pure GPI. The functional groups of the NaDP—GPI sample were analyzed by the potassium bromide (KBr) pellet method. Due to a small percentage of the dopant no major changes were observed. Comparing with pure GPI, a minor shift in the range of hydrogen bonds (3450.97 cm^{-1}, 3117.08 cm^{-1}) was observed in NaDP—GPI. A comparison of the FTIR data for pure GPI and NaDP—GPI (Fig. 1, *a*, *b*) shows an increase in symmetric bending vibrations (1459.70 cm^{-1}); antisymmetric stretching vibrations (1622.68 cm^{-1}) of COO^- and rocking vibrations at 515.46, 648.4 cm^{-1} were observed. At 1254.83 cm^{-1} and 1054.01 cm^{-1} a decrease in symmetric bending vibrations and rocking vibrations of NH^{3+} was observed respectively [6, 7]. The characteristics observed in the FTIR studies confirm the incorporation of the NaDP compound into GPI.

The dielectric constants and the phase transition temperature of pure GPI and NaDP-doped GPI were analyzed (Fig. 2). The well-grown NaDP—GPI crystal (size = 3×2×2 mm) was polished using alumina powder and paraffin oil to study the dielectric property. The silver paste was applied on both opposite surfaces of the single crystal which acted as electrodes and the dielectric property was measured with a frequency of 1000 KHz. Using a computer-controlled Keithley nano voltmeter with relay arrangement (up to an accuracy of 0.1 K), the temperature was controlled from 205 to 320 K. The

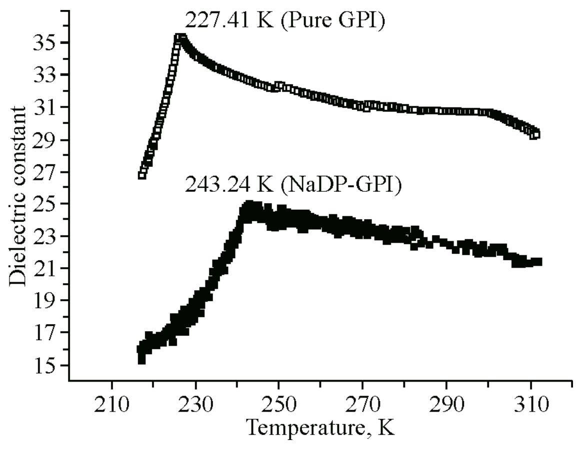

Fig. 2. Dielectric studies

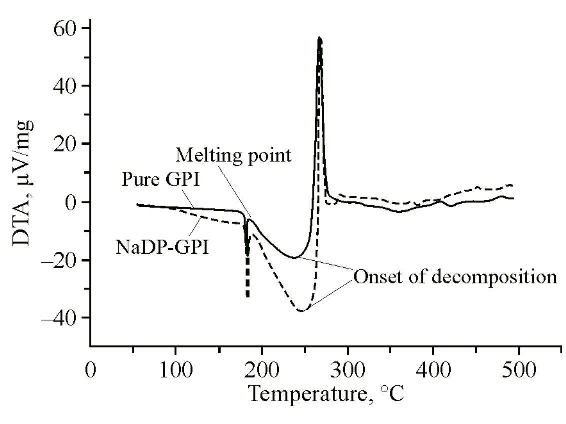

Fig. 3. Thermal analysis-DTA curve

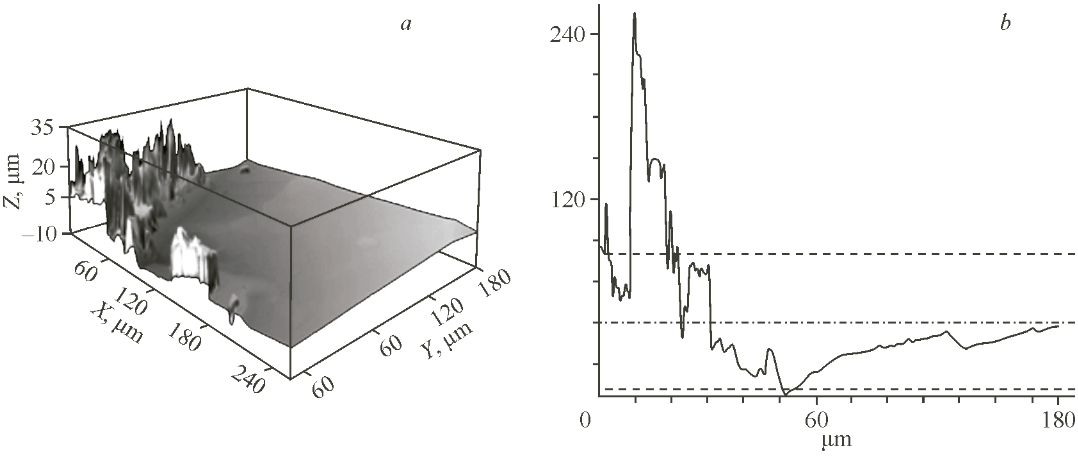

Fig. 4. Surface 3D image (*a*) and cross profiling plot of a NaDP—GPI single crystal (*b*)

dielectric responses were recorded and the almost similar variation was observed. It has been reported that for pure GPI, for a frequency value of 10 KHz, the dielectric constant is at the transition temperature of 224 K [8].

However, at a frequency value of 1000 KHz we found that the phase transition temperature of pure GPI was 227.41 K and the NaDP—GPI phase transition temperature was 243.24 K. NaDP—GPI shows a high Curie temperature as compared with that of pure GPI. The change in the phase transition temperature proves the presence of NaDP in glycine phosphate.

The thermal stability of pure GPI and NaDP—GPI was studied on a differential thermal analyzer (DTA). The thermal analysis graph (Fig. 3) shows the endothermic peak corresponding to the melting point and a stepwise decomposition of pure and NaDP-doped GPI. When the sample and the reference are heated to higher temperatures the melting and decomposition take place. The sample temperature increases and again decreases due to endothermic and exothermic reactions. In this process, heat is released. The DTA curve shows an increase and a decrease in the temperature ranges of pure GPI and NaDP-doped GPI. The thermal data on NaDP—GPI was compared with that for pure GPI. Minor changes have been observed in the thermal data. Both samples show the melting point at 184 °C.

The surface 3D image (Fig. 4, *a*) and the cross profiling plot (Fig. 4, *b*) of a NaDP—GPI single crystal were recorded by a confocal laser scanning microscope. The ⟨110⟩ plane of the as grown NaDP—GPI single crystal was analysed with CLSM. The mound like islands was observed on the surface of the crystal at regular intervals. The 3D image and the cross profiling plot explains the structure and the growth rate of the crystal surface respectively. The cross profiling of the image recorded a height difference of 25 microns on average with respect to the regular surface. The colony of islands suggests that there may be a minor change in the growth rate due to a temperature difference of 1° per day [9].

The surface of the NaDP GPI single crystal was analyzed by AFM. The AFM image was recorded from 0 to 10.5 μm sizes at the ⟨110⟩ plane of the crystal. The topographical view of the crystal surface is shown in Fig. 5. The tiny bright spots [9] were observed on the crystal surface. These bright spots may be due to a temperature change during the growth process and were not observed in the confocal microscope. The dark line on the surface reveals the influence of the growth process. The outer morphology shows wave-like surface structures; the height difference between the wave-like structures is about 267 nm.

Conclusions. The functional groups of the 5 mol% doped NaDP—GPI sample were analyzed by IR spectroscopy. The NaDP—GPI and pure GPI samples melt at the same temperature. The laser scanning microscopy studies reveal the growth pattern on the surface of the single crystal under the controlled thermal conditions. The presence of tiny bright spots was observed on the surface of the crystal. This may be due to the influence of the growth process. From the dielectric studies, the phase

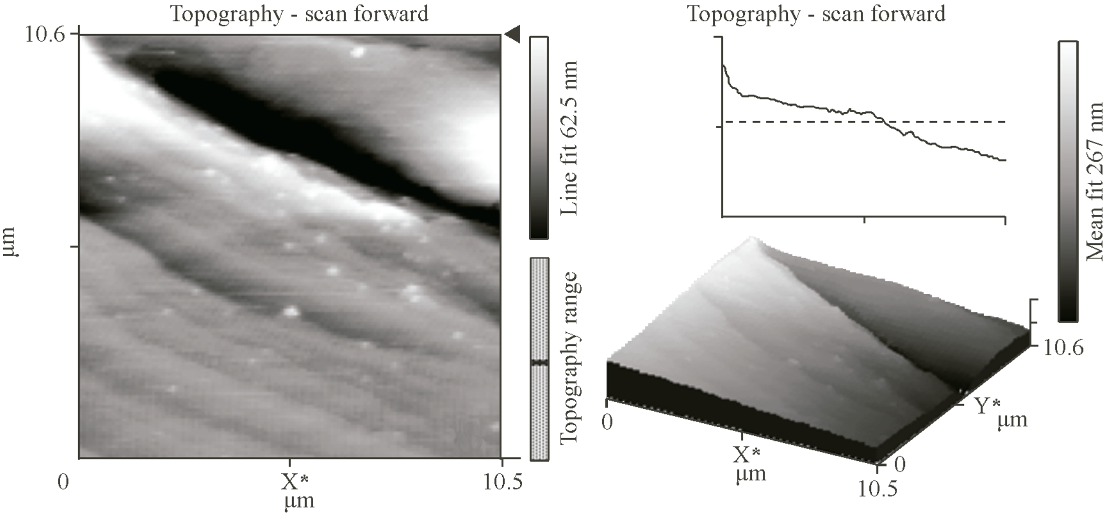

Fig. 5. AFM image recorded from the surface of the crystal

transition temperature of NaDP—GPI was calculated as 243.24 K (at 1000 KHz), which gives a new result as compared with that of the pure GPI single crystal.

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