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A Comparative Study - Pure and Urea Doped Glycine Phosphite Single Crystals

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Abstract : Single crystals of pure glycine phosphite (pure-GPI) and urea doped glycine phosphite (UGPI) were grown by slow evaporation method and Sankaranarayanan and Ramasamy method (SR method). The transparent, colourless UGPI crystal with cylindrical shape about 20 mm diameter and 45 mm length was obtained by SR method. The crystalline quality and lattice parameters have been analyzed by single crystal, powder X-ray diffraction for both the samples. The functional groups were analyzed by the Fourier Transform Infrared Spectroscopy. The curie temperature of pure GPI and UGPI was obtained from the dielectric studies. The UGPI shows difference in curie temperature value comparing with pure GPI. The results are discussed in detail.
Keywords: Crystal growth; X-ray diffraction; FTIR; Dielectrics.

INTRODUCTION

The α-amino acid glycine gives number of inorganic materials which are having good dielectric and elastic properties. The second hydrogen bonded ferroelectric crystal of phosphorous acid with an amino acid is known as glycine phosphateCH2CH2COOH3PO3), abbreviated as GPI, and betanine phosphite crystals [(CH3)3NCH2COOH3PO3], abbreviated as BPI are related to the ordering of protons in their structure. At 224 K the GPI shows ferroelectric to paraelectric phase transition [1]. To understand the mechanism of ferroelectric to paraelectric phase transition many researchers have grown these GPI crystals [2,3].

The aim of our work was to grow the single crystals of urea-GPI (UGPI) and to compare their physical properties with pure-GPI. From saturated aqueous solutions the transparent crystals of pure GPI and urea doped GPI were grown by applying slow evaporation and Sankaranarayanan and Ramasamy method (SR method). Under optimized growth condition the colourless, transparent good quality crystals were obtained by this method.

EXPERIMENTAL PROCEDURE

Material synthesis

The equimolar ratio of high purity orthophosphorous acid [H_3PO_3] (Sigma Aldrich) and glycine [NH_2CH_2COOH] (AR grade) were taken to obtain GPI. The chemicals were weighed and mixed in millipore water solvent. The following reaction is expected to take place with the formation of the GPI.

$$NH_2CH_2COOH + H_3PO_3 \longrightarrow (NH_3CH_2COOH) \cdot H_2PO_3$$

In the millipore water solvent the orthophosphorous acid and glycine were completely dissolved. After this dissolvation, the 5 mole % of urea was added in this solution. This solution was heated upto 80°C and all the materials were dissolved completely. The transparent colourless solution was obtained. The temperature of the solution is decreased to room temperature slowly. This solution was kept in refrigerator and it was cooled to 0°C for 12 h and the solution was brought to room temperature. After complete precipitation and by doing proper filtering, the dried urea-GPI chemical powder was obtained. The urea-GPI synthesized salt was recrystallized

several times to get the purified material with good quality.

By employing the slow evaporation method, the fine crystals of UGPI were obtained from saturated solution. Pure GPI crystals were also grown similarly by slow evaporation and SR methods (the following method) without adding urea.

From slow evaporation method the change in morphology of UGPI was observed comparing with pure GPI [4] which is shown in Figure 1 and 2. The morphology of UGPI mainly consists crystal habit of {001}, {010}, {310}faces and some of other faces also which is shown in the figure.

Figure 1. UGPI crystal by slow evaporation method

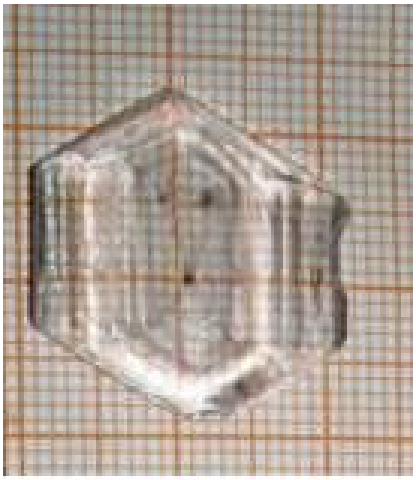
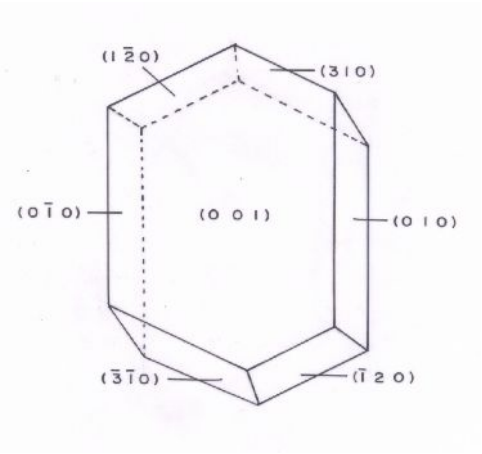
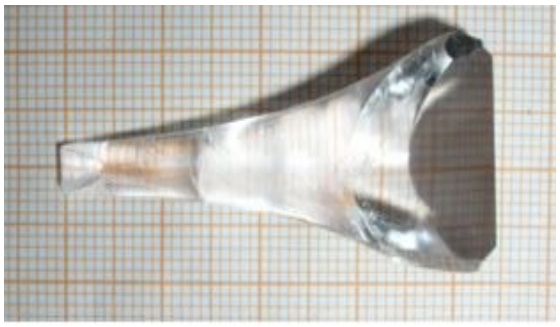


Figure 2. Morphology of UGPI crystal



Growth of UGPI by SR method

Figure 3. UGPI crystal by SR method



The saturated solution of UGPI was transferred in 20 mm diameter growth ampoule. The UGPI crystal (which we obtained by slow evaporation method) having specific orientation plane of <010> was inserted into the growth ampoule. The bottom of growth ampoule consist seed mounting pad. The temperature around the growth ampoule was controlled by the temperature controller.
Under controlled condition, the highly transparent crystal with size of 20 mm diameter and 45 mm length were obtained with in a month. Figure 3 shows <010> ingot NaOH-GPI single crystal grown by SR method.

CHARACTERIZATION STUDIES

The grown crystals of pure GPI and UGPI were confirmed by single crystal X-ray diffraction analysis using ENRAF NONIUS CAD4 diffractometer. The powder samples have been analyzed by using Rich seifort (model 2002) X-ray diffractometer. The functional groups were confirmed by KBr pellet method, for this the Avatar 330 FTIR thermo Nicolet spectrometer has been used. The dielectric analysis of both the samples was recorded by Zentech- 1061 LCZ meter.

RESULTS AND DISCUSSION

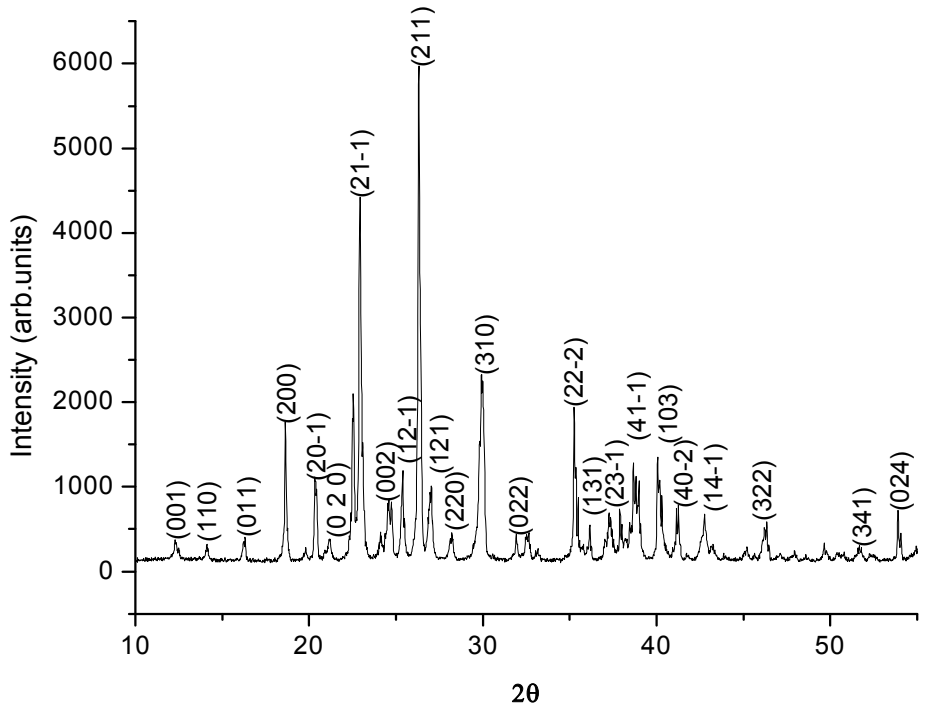
Single crystal X-ray diffraction

The lattice parameters value of UGPI was calculated by single crystal X-ray diffraction using ENRAF NONIUS CAD4 diffractometer. The unit cell parameters obtained are a = 9.183A°, b = 8.077A°, c = 7.091A°, $\alpha = \gamma = 90°$ and $\beta = 100.06°$. The single crystal X-ray diffraction analysis exhibits that it belongs to monoclinic crystal system.

Powder X-ray diffraction analysis

The powder samples of UGPI have been analyzed by powder X-ray diffraction to confirm the quality of crystal. Figure 4 shows the powder X-ray diffraction pattern of monoclinic structure of UGPI. From the UGPI pattern, there is a change in the intensity of diffraction peaks and also missing of some peaks can be observed comparing with pure GPI. The observed results are in good agreement with the reported results [5].

Figure 4. Powder X-ray diffraction pattern of UGPI.



FTIR studies

The Fourier transform infrared spectra of UGPI are compared with the reported data of pure GPI [6]. From the obtained data, it is seen that there is an increase in symmetric bending vibrations (1419.82 cm^{-1}) and decrease in antisymmetric stretching vibrations of COO- (1533.92 cm^{-1}) in the case of UGPI. Also increase in rocking vibrations (427.88 cm^{-1}) and and symmetric stretching vibrations of NH^{3+}(1460.88 cm^{-1}) have been observed in UGPI [6]. All these features confirm the incorporation of Urea in GPI.

Dielectric studies

The good quality crystal of pure GPI (size of 4 x 2 x 2 mm) and UGPI (size of 3 x 2 x 1 mm^3) were polished well using alumina powder and paraffin oil to study the dielectric property. The silver paste was applied on both the opposite surfaces of the crystals which acted as electrodes and dielectric response is measured for the frequency of 1000 KHz for the pure GPI and urea doped GPI. The temperature is controlled from 205 to 300 K by using computer controlled Keithley nano voltmeter with relay arrangement up to accuracy of 0.1 K. Measurements are recorded and the almost similar variation was observed for other frequencies also for the both the samples. So the graph is plotted for 1000 KHz only.

It has been reported that for the pure GPI, the measured value of dielectric constant is at the transition temperature of 224 K for a frequency value of 10 KHz [6]. But for the frequency value of 1000 KHz we found that the phase transition temperature of pure GPI is at 231.10 K and the UGPI's phase transition temperature was compared with this value. The curie temperature of UGPI was found at 234.50 K. The Figure 5 shows the dielectric constant values and the phase transition temperature of pure GPI and urea doped GPI. The UGPI shows high curie temperature value comparing with pure GPI. This result confirms the presence of urea in glycine phosphite.

CONCLUSION

The good quality UGPI crystal was grown by SR method. The crystalline quality was analyzed by single crystal and powder X-ray diffraction. The functional groups were confirmed from FTIR spectroscopy. The curie temperature of NaOH-GPI was found from dielectric studies and it is compared with pure GPI. The phase transition temperature of UGPI at 234.50 K for 1000 KHz gives new result, which has been not reported so far.

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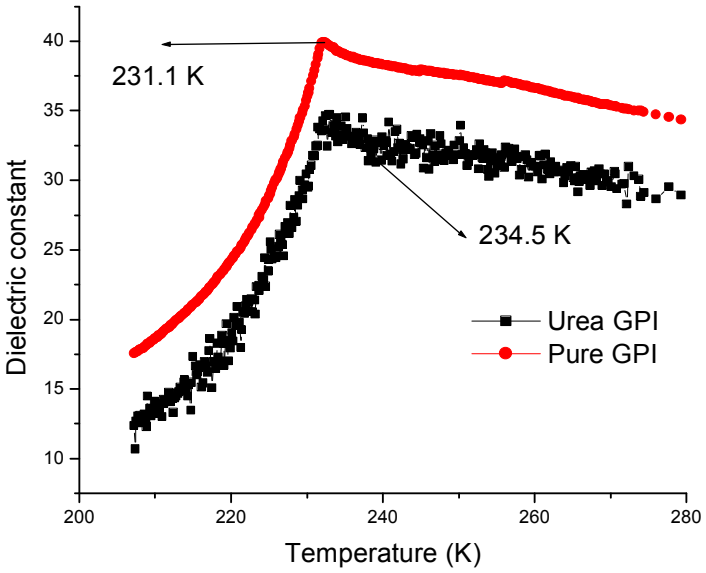
Figure 5. Dielectric constant with temperature



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