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Effect of β-Alanine on Glycine phosphite Single Crystal grown by SR Method

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Abstract: The β-alanine doped glycine phosphite (β-alanine-GPI) single crystals were grown from slow evaporation and Sankaranarayanan and Ramasamy (SR) method. The colourless β-alanine-GPI crystal with cylindrical shape about 22 mm diameter and 43 mm length was obtained by this method. The single crystal, powder X-ray diffraction and high-resolution X-ray diffraction studies were carried out for β-alanine doped GPI and the results analyzed with pure-GPI. The functional groups and optical properties of β-alanine-GPI were studied by Fourier transform infrared (FTIR) spectroscopy and UV-visible spectroscopy respectively. The results of all these characterizations are discussed in detail.
Keywords: Ferroelectrics; Chemical synthesis; Crystal growth; Phase transitions.

INTRODUCTION

Glycine phosphite (GPI) is a representative hydrogen-bonded compound. In crystal structure the infinite chains of hydrogen-bonded phosphite anions are directed along the crystallographic c-axis. Crystal with this aminoacid compound exhibit structural phase transition of ferroelectric phase. The GPI shows second order ferroelectric-paraelectric phase transition with curie temperature, T_c around 224°K and the structure of GPI determined at room temperature is monoclinic (space group P21/a) with cell dimensions of, a = 9.792 A°, b = 8.487 A° and c = 7.411 A° and β = 100.43° [1].

The Sankaranarayanan and Ramasamy (SR) method is one of the latest unidirectional crystal growth method which offers large size and good quality crystals. It is very simple method which does not give problems like thermal decompositions and microbial growth. The major advantage of this method is, it gives high growth rate during growth process and it gives nearly 100 % solute-crystal efficiency. Also it is possible to grow the defect free transparent bulk single crystals along a particular axis [2].

No growth and characterization details with an addition of β-alanine in GPI have been reported and compared with pure-GPI so far. The aim of our work was to grow the single crystals of β-alanine-GPI and to compare their physical properties with pure-GPI. From saturated aqueous solutions the transparent crystals of pure GPI and β-alanine-GPI were grown by applying slow evaporation and SR method. Under optimized growth condition the colourless, transparent good quality crystals were obtained by this method.

EXPERIMENTAL PROCEDURE

Material synthesis

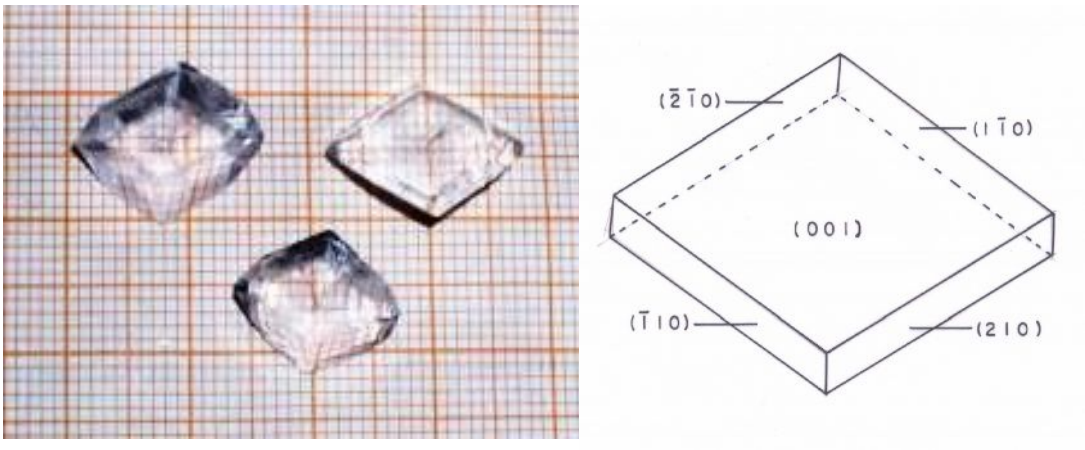
The equimolar ratio of high purity orthophosphorous acid [H_3PO_3] (Sigma Aldrich) and glycine [NH_2CH_2COOH] (AR grade) were taken to obtain GPI. The chemicals were weighed and mixed in millipore water solvent. The following reaction is expected to take place with the formation of the GPI.

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

In the millipore water solvent the orthophosphorous acid and glycine were completely dissolved. After this dissolvation, the 5 mole % of β-alanine 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. Afterwards the solution was kept in room temperature. After complete precipitation and by doing proper filtering, the dried β-alanine -GPI chemical powder was obtained. To get purified material with good quality the β-alanine -GPI synthesized salt was recrystallized several times. The fine crystals of β-alanine-GPI were obtained from saturated solution by applying slow evaporation method.

The morphology of pure-GPI consists crystal habit of {011}, {010},{100},{110},{111} and {211} faces [3]. Figure 1 shows single crystals and morphology of β-alanine-GPI (by slow evaporation method) which consists crystal habit of {001}, {210} faces with some of other faces.

Figure 1. β-alanine-GPI single crystal by slow evaporation method and its morphology



Growth of β-alanine -GPI by SR method

Figure 2. β-alanine-GPI crystal by SR method

The β-alanine-GPI crystal which is obtained from slow evaporation technique is inserted to the growth ampoule. The growth ampoule contains saturated solution. This ampoule is made out of glass and it is consisting seed mounting pad at the bottom. Under controlled condition the crystal was allowed to grow for required length. The growth of crystal was clearly observed because of the transparent nature of solution.

Figure 2 shows the colourless, cylindrical shape, good quality unidirectional β-alanine-GPI single crystal with size of 22 mm diameter and 43 mm length.

CHARACTERIZATION STUDIES

The single crystal X-ray diffraction analysis (by using ENRAF NONIUS CAD4 diffractometer) was carried out for the grown crystals. The powder samples of pure and β-alanine doped GPI have been analyzed by using Rich seifort (model 2002) X-ray diffractometer. The high-resolution X-ray diffraction (HRXRD) curves have been recorded for both the crystal specimens by employing the multicrystal X-ray diffractometer with MoKα_1 radiation designed and developed at National Physical Laboratory. The FTIR spectra of pure and β-alanine-GPI were recorded in the range of 400-4000 cm^{-1}. To confirm the functional groups of pure and β-alanine-GPI by KBr pellet method the Avatar 330 FTIR thermo Nicolet spectrometer has been used. The UV-visible absorption and transmission spectrum was recorded on a HITACHI model U-2800 double beam spectro - photometer in the wavelength range of 200 to 900 nm.

RESULTS AND DISCUSSION

Single crystal X-ray diffraction analysis

The lattice parameters of β-alanine doped GPI were analyzed by single crystal X-ray diffraction analysis. On comparison it is seen that the lattice parameters of β-alanine GPI are slightly higher than that of pure GPI. The unit cell parameters obtained are a = 9.804A°, b = 8.498A°, c = 7.456A°, α = γ = 90° and β = 100.83°. The single crystal X-ray diffraction analysis exhibits monoclinic crystal system [4].

Powder X-ray diffraction analysis

To confirm the crystal structure, the powder samples have been analyzed by powder X-ray diffraction. The powder samples were subjected to intense X-rays of 1.5418 A° (CuKα) at a scan speed of 1° per minute. Figure 3 shows the powder X-ray diffraction pattern of monoclinic structure of pure GPI and β-alanine-GPI. The X-ray diffraction pattern which we obtained for β-alanine-GPI is compared with reported data of pure GPI. Comparing with pure GPI there is missing of some peaks and also increase in intensity of peaks is clearly visible due to addition of β-alanine with GPI [4].

Figure 3. Powder X-ray diffraction pattern of pure and β-alanine doped GPI

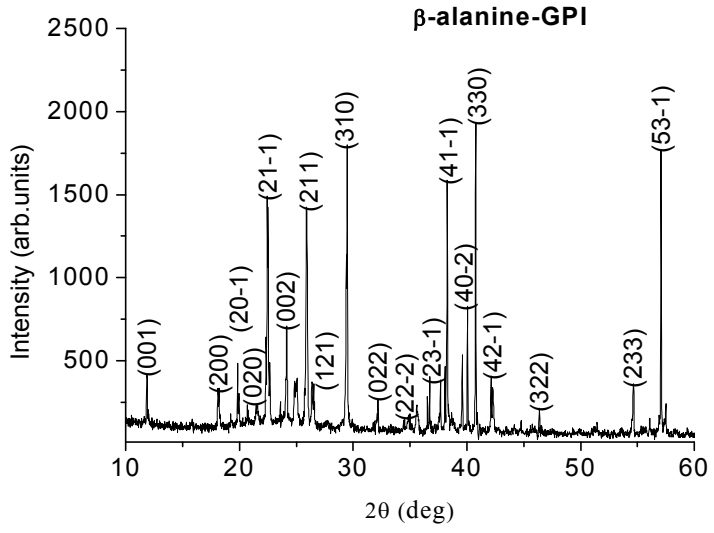
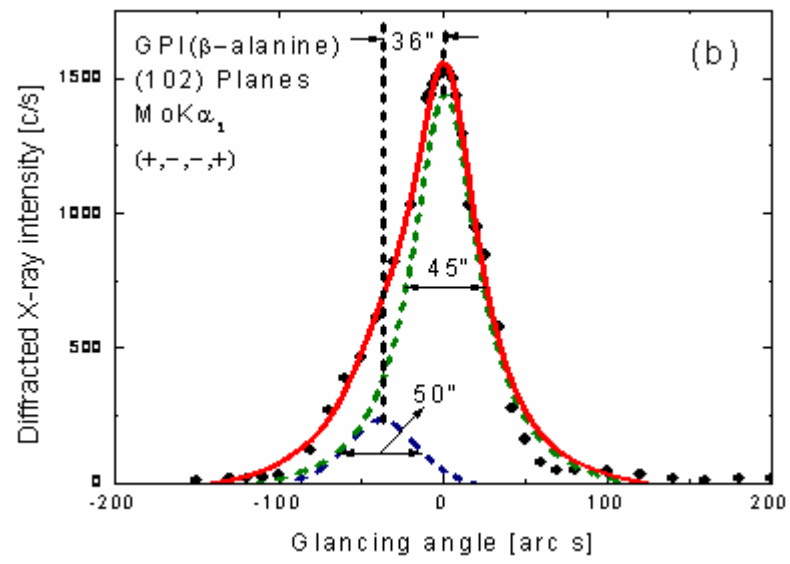


Figure 4. HRXRD of β-alanine-GPI



High resolution X-ray diffraction analysis (HRXRD)

Figure. 4 shows the high-resolution X-ray diffraction curves (DCs) recorded for typical β-alanine-GPI single crystal specimens using (102) diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer using $MoK\alpha_1$ radiation. Both the curves have similar features. The solid line (convoluted curve) is well fitted with the experimental points represented by the filled circles. On deconvolution of the curves, it is clear that both the DCs contain an additional peak. The additional peak depicts an internal structural very low angle (tilt angle ≤ 1 arc min) boundary [5,6] characterized by a tilt angle, α [misorientation angle (please see the inset in the figure) between the two crystalline regions on both sides of the structural grain boundary] and these tilt angles respectively for pure and β-alanine-GPI single crystals are 28 and 36 arc s.

The FWHM (full width at half maximum) of the main peak and the very low angle boundary for pure GPI are respectively 44 and 30 arc s and that of β-alanine-GPI single crystal are 45 and 50 arc s. Though the specimens contain a very low angle boundary, the relatively low angular spread of around 200 arc s of the diffraction curves and the low FWHM values show that the crystalline perfection is reasonably good. The affect of such very low angle boundaries may not be very significant in many device applications, but for applications like phase matching, it is better to know these minute details regarding crystalline perfection. Thermal fluctuations or mechanical disturbances during the growth process could be responsible for the observed very low angle boundary in both pure and β-alanine-GPI single crystals.

FTIR studies

The Fourier transform infrared spectra of pure GPI and β-alanine-GPI are shown in Figure 5. The IR spectral data of β-alanine-GPI is compared with that of pure GPI. The pure GPI values of our sample are matching with the reported data [7]. From the Figure 5 and Table 1, it is seen that there is an increase in symmetric bending vibrations and decrease in antisymmetric stretching vibrations of COO- in the case of β-alanine-GPI. Comparing with pure GPI, increase in rocking vibrations of COO- has been observed in β-alanine-GPI. Also decrease in rocking vibrations and increase in symmetric stretching vibrations of NH^{3+} have been observed in β-alanine-GPI. All these features confirm the incorporation of β-alanine in glycine phosphite compound.

Figure 5. FTIR spectra β-alanine doped GPI

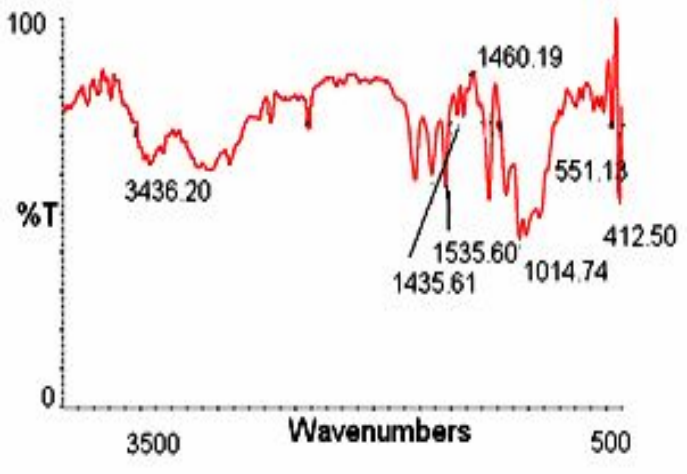
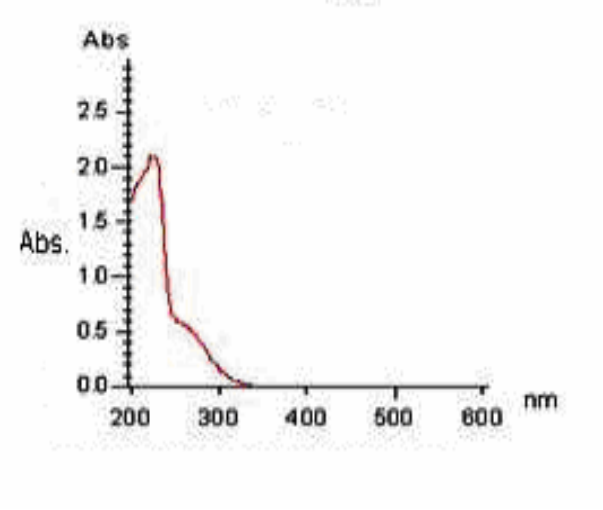


Table. 1. Comparison of the main IR Aspectral data (cm^{-1}) of pure β-alanine doped GPI.

S. no.	Assignment	pure-GPI	β-alanine-GPI
1.	υ_a (COO^-)	1620.90	1535.60
2.	δ_s (NH_3^+)	1459.09	1460.19
3.	υ_s (COO^-)	1419.02	1435.61
4.	ρ_r (NH_3^+)	1145.70	1014.74
5.	δ (COO^-)	514.93	551.13
6.	ρ_r (COO^-)	412.22	412.50

UV-visible absorption spectrum

Figure 6. UV-visible absorption spectrum



The UV-visible absorption spectrum of pure and β-alanine doped GPI were recorded in solution by using ethanol-water solvent in the ratio of 1:1. Figure 6 shows UV-visible spectrum of β-alanine doped GPI. The cutoff wavelength was visible at 250 nm and small difference is observed in case of absorption spectrum of β-alanine-GPI and there is no significant visible transmission spectrum observed from the range of 300 nm for this sample.

CONCLUSION

The comparative study of pure GPI and β-alanine doped GPI has been carried out in this work. The colourless, transparent and high quality crystals of pure and β-alanine doped glycine phosphite were grown by slow evaporation and SR method. The change in morphology has been observed for the pure and β-alanine doped GPI crystals which are obtained by slow evaporation method. The lattice parameters and crystalline quality were identified by single crystal, powder X-ray diffraction and HRXRD. Comparing with pure GPI the β-alanine doped GPI shows the increase in lattice parameter values. The crystalline perfection of both pure and β-alanine doped GPI specimens are nearly same and fairly good. The functional groups were confirmed by FTIR spectroscopy. The optical properties were observed by UV-visible spectrum analysis.

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