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Unidirectional growth of β-Alanine doped GPI Single Crystal and its Surface analysis using Etching, SEM, AFM and Laser damage threshold studies

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Abstract: The β-alanine doped glycine phosphite (β-alanine-GPI) single crystals were grown from Sankaranarayanan and Ramasamy (SR) method. The colourless β-alanine-GPI crystal with cylindrical shape about 15 mm diameter and 49 mm length was obtained by this method. The single crystal, powder X-ray diffraction and optical studies were carried out for β-alanine doped GPI and these results were discussed in detail. Comparing with pure GPI the single crystal X-ray diffraction shows changes in unit cell parameter values due to incorporation of β-alanine in glycine phosphite. The surface analysis of the crystals was analyzed by using optical microscope, Scanning Electron Micrograph (SEM) and Atomic Force Microscope (AFM). The laser damage threshold value of β-alanine-GPI was compared with pure GPI.
Keywords: Chemical synthesis; Crystal growth; Electron micrograph; Laser damage.

INTRODUCTION

The α-amino acid glycine family crystal like triglycine sulphate (TGS), triglycine selenate (TGSe), triglycine fluoberyllate (TGFBe), etc shows interesting dielectric and elastic properties [1-8]. Among these, glycine phosphite ($NH_2CH_2COOH_3PO_3$), abbreviated as GPI is a recently developed crystal which is composed of phosphorous acid and glycine. The GPI crystal belongs to monoclinic system with space group of P21/a. The GPI shows phase transition temperature T_c around 224°K and its cell dimensions are a = 9.792 A°, b = 8.487 A° and c = 7.411 A° and β = 100.43°. Several microscopic and macroscopic properties of GPI have been investigated already [9-18].

However, No investigations of β-alanine doped GPI with equimolar ratio of glycine and orthophosphorous acid by slow cooling technique has been reported yet. Hence in this paper we investigate detailed study of 5 mole % β-alanine doped with GPI crystal by SR method.

EXPERIMENTAL PROCEDURE

Material synthesis

Glycine phosphite was synthesized by dissolving equimolar ratio of high purity glycine [NH_2CH_2COOH] (AR grade) and orthophosphorous acid [H_3PO_3] (Sigma Aldrich), in millipore water. The following reaction is expected to take place with the formation of the title compound.

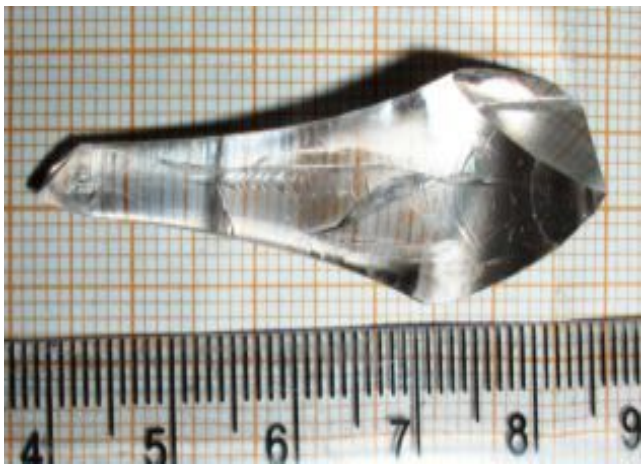
$$NH_2CH_2COOH + H_3PO_3 \longrightarrow (NH_3CH_2COOH) \cdot H_2PO_3$$

After complete dissolution of these compounds, 5 mole % of β-alanine was added as a dopant material in this solution. This solution was heated upto 80°C, so that the all the materials were dissolved completely and obtained transparent solution. The temperature of the solution was allowed to decrease continuously till it reaches the room temperature and then the solution was kept in refrigerator at 0°C for the formation of β-alanine added GPI material. The prepared β-alanine-GPI material was dried after completion of precipitation and proper filtering. To get purified material and good quality crystals, the β-alanine-GPI synthesized salt was recrystallized three times. By employing the slow evaporation technique, the fine seed crystals of β-alanine-GPI were harvested from saturated solution [19].

Growth of β-alanine -GPI by SR method

The β-alanine-GPI crystal which is obtained from slow evaporation technique is inserted to the growth ampoule which contains saturated solution. The growth ampoule is made out of glass and consisting seed mounting pad at the bottom. The crystal was allowed to grow for required length under proper condition. The growth of crystal was clearly observed because of the transparent nature of solution [19].

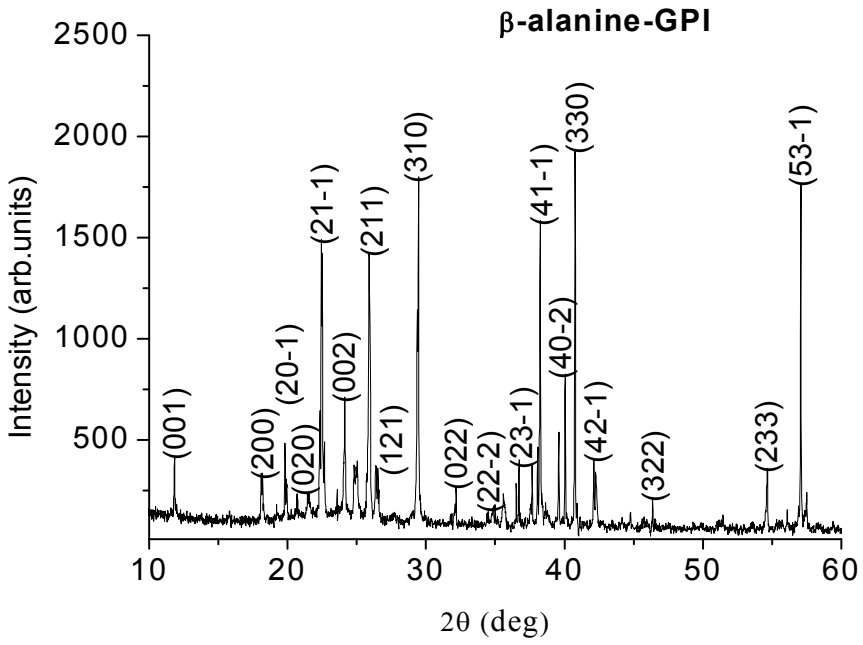
Figure 1. β-alanine-GPI crystal by SR method



Under controlled condition, the highly transparent crystal was obtained by SR method which is shown in figure 1. The colourless, cylindrical shape, good quality unidirectional β-alanine doped GPI single crystal with size of 15 mm diameter and 49 mm length was obtained by SR method.

Powder X-ray diffraction analysis

Figure 2. Powder X-ray diffraction pattern of β-alanine doped GPI



CHARACTERIZATION STUDIES

Single crystal X-ray diffraction analysis

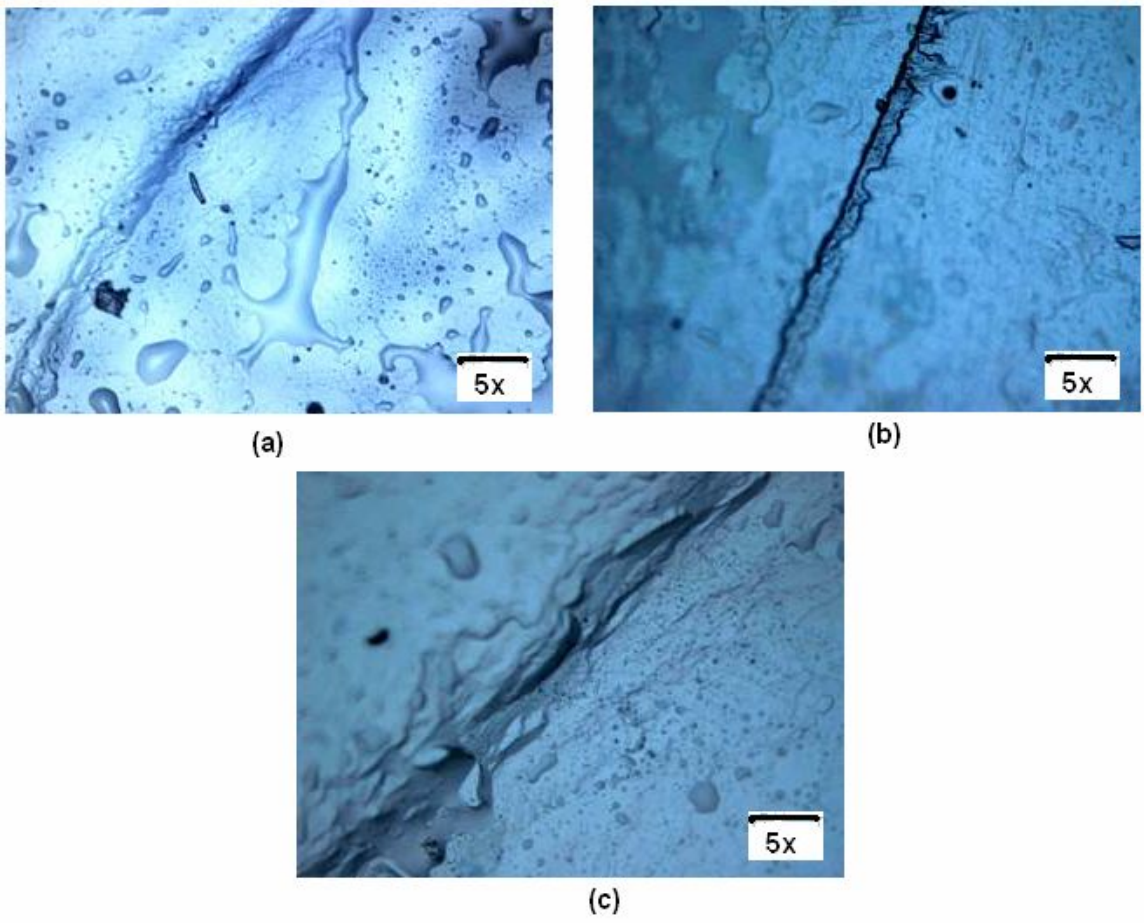
The lattice parameters of β-alanine-GPI were calculated by single crystal X-ray diffraction using ENRAF NONIUS CAD4 diffractometer. The unit cell parameters obtained are a = 9.804A°, b = 8.498A°, c = 7.456A°, α = γ = 90° and β = 100.83°. The single crystal X-ray diffraction analysis exhibits monoclinic crystal system. On comparison with already reported data pure GPI, it is seen that the lattice parameters of β-alanine doped GPI are slightly higher than that of pure GPI [20].

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 2 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. The observed results are in good agreement with the reported results [21].

Etching studies- Optical microscope

The chemical etching was carried out to analyze the surface of SR method grown single crystal of alanine doped GPI. The crystal was subjected in water for 5, 10 and 15s. Afterwards it was wiped with filter paper and its surface was analyzed under optical microscope. The figure 3 (a), (b) and (c) shows etching with water in 5,10 and 15 s respectively. In all the figures the low angle grains boundary and pits are clearly visible. The low angle grain boundaries occurred may be due to segregation of impurities on the surface of the crystal [22]. The inclusions are of various shapes and sizes also been observed in Figure 3 (a), (b) and (c).

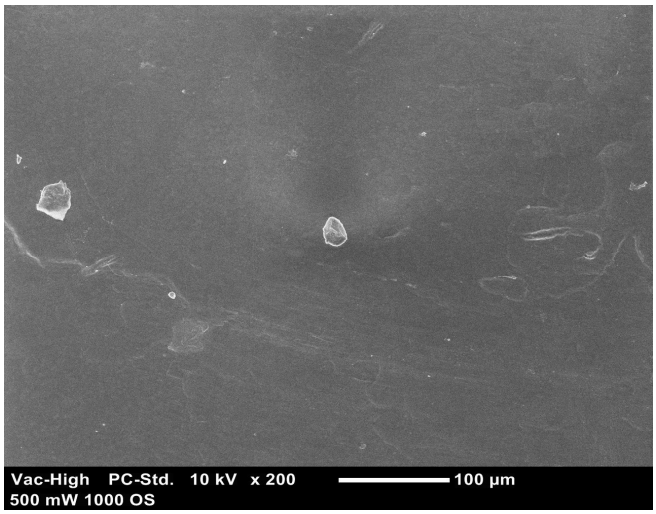
Figure 3. Etching studies (a) Surface of β-alanine -GPI crystal after 5 s etching, (b) Surface after 10 s etching (c) Surface after 15 s etching



Scanning Electron Micrograph analysis (SEM)

SEM photograph along <100> plane was recorded. Figure 4 shows SEM micrograph of surface of β-alanine-GPI crystal which is grown by SR method. It is observed from figure that the surface of β-alanine-GPI appears with one or two microcrystals and pits [22].

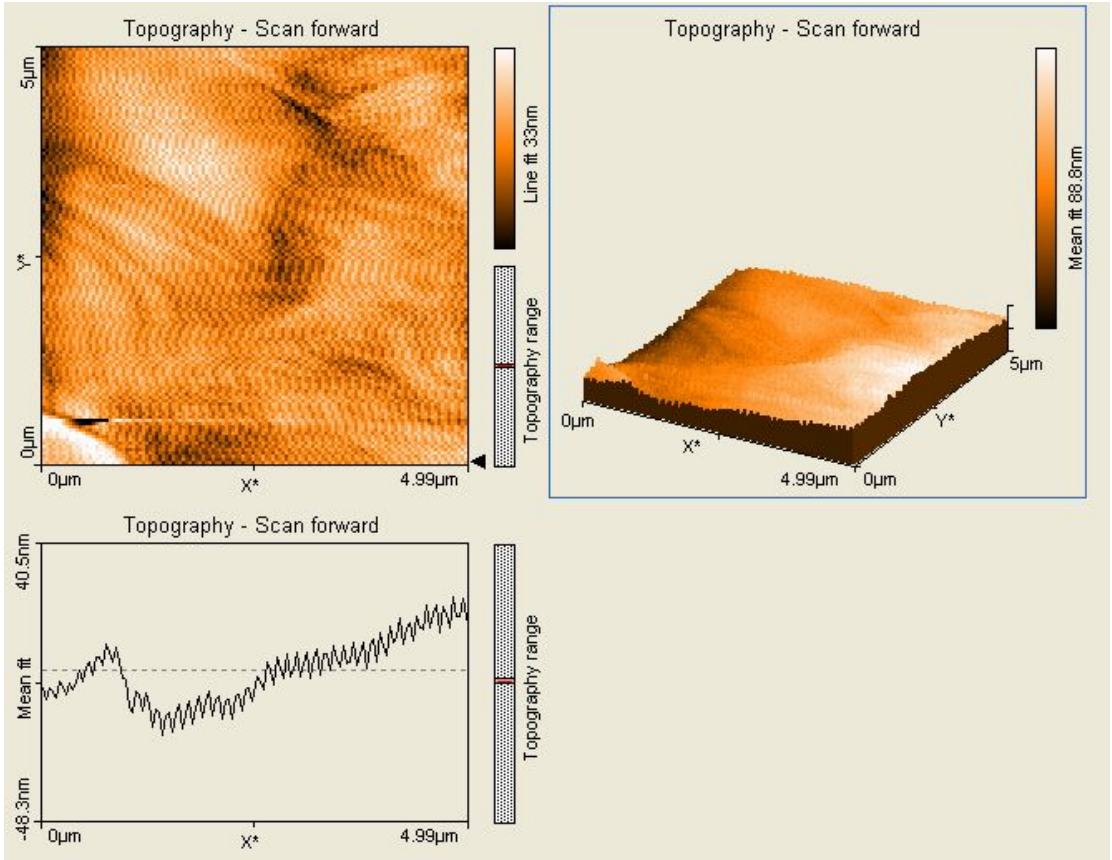
Figure 4. SEM image of β-alanine –GPI



Atomic Force Microscope (AFM)

The defects in the surface of the crystal were analyzed by atomic force microscope (AFM). Figure 5 shows AFM image of β-alanine doped GPI crystal which is grown by SR method. The AFM image of 5 µm size has been recorded. In the surface of the grown crystal, the defects have been observed. The deep hole like region in the figure confirms about the defects present in the crystal [23]. The topographical view of the surface of the crystal explains about the length and depth of the defects present in the surface of SR method grown β-alanine doped GPI crystal.

Figure 5. AFM image of β-alanine –GPI crystal



Laser Damage Thresholod (LDT)

The Nd:YAG laser beam was (532 nm radiation) passed along the {001} direction of the β-alanine doped GPI crystal. The β-alanine doped GPI crystal which is grown by SR method with 2 mm thickness was used to pass the laser beam. The laser beam of energy around 10 mJ was passed into the crystal surface. From 10 to 30 mJ energy of laser beam the crystal shows no damage for every 30 s intervals. when beam with 35 mJ was applied in the surface of the crystal, it became cracked. Figure 6 shows the cracks developed in the surface of β-alanine -GPI crystal during laser damage studies. (Image under optical microscope). The laser damage threshold (LDT) obtained on the β-alanine doped GPI was 35 mJ /cm^2 and the observed results are given in Table 1. The β-alanine doped GPI single crystal shows the LDT value which is obtained for this crystal is lower than comparing with pure GPI crystal [24]. Due to doping of β-alanine in the GPI the LDT value has been decreased. The figure 7 shows the LDT value Vs energy of the laser beam.

Figure 6. Cracks developed in the surface of β-alanine -GPI crystal during laser damage studies. (Image under optical microscope)

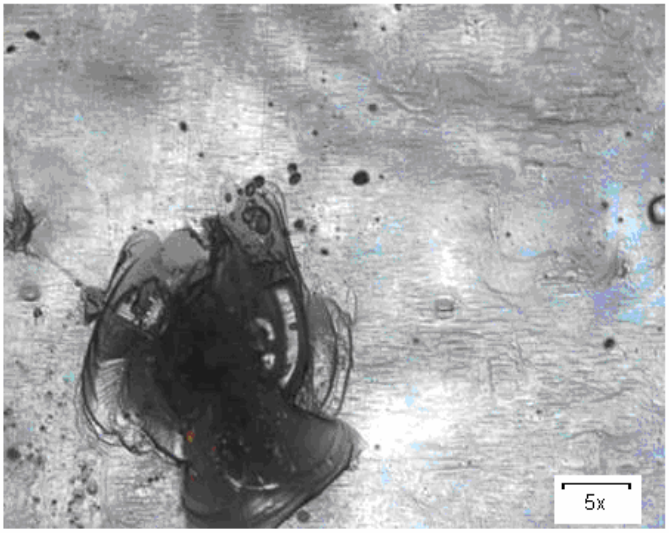


Figure 7. LDT value V$_s$ energy of β-alanine-GPI crystal

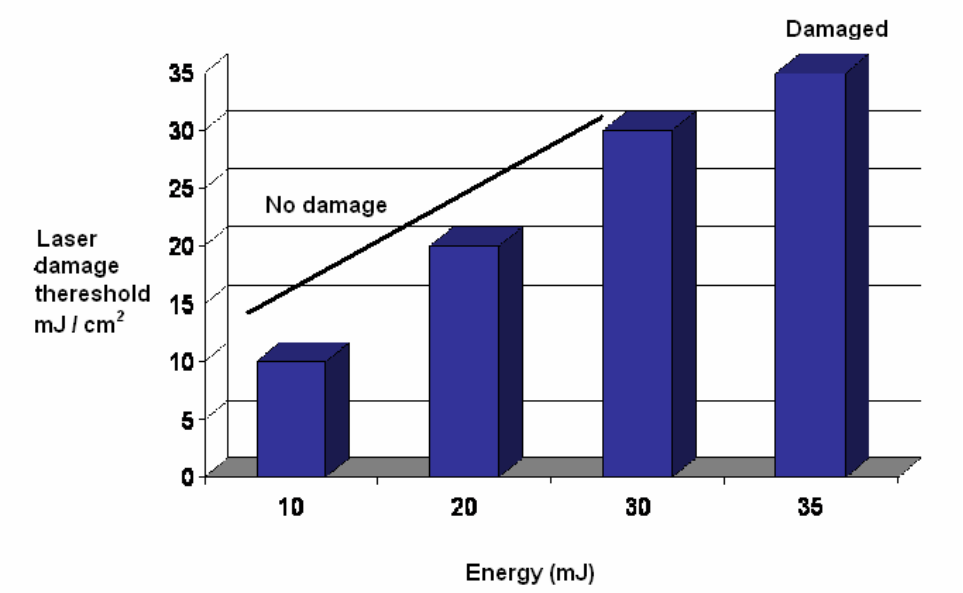


Table. 1. Laser damage threshold values of β-alanine-GPI crystal and its observations

β-alanine doped GPI by SR method			
Pulse width 7ns, Pulse rate 10Hz			
Laser pulses (Hz)	Energy (mJ)	Time (s)	Observation
30	10	30	No damage
30	20	30	No damage
30	30	30	No damage
30	35	30	Damaged

CONCLUSION

The 5 mole % of β-alanine doped glycine phosphite crystal was grown by SR method. The crystalline quality and lattice parameters were analyzed by single crystal, powder X-ray diffraction studies. The surface of β-alanine-GPI single crystal was analyzed by optical studies. The presence of microcrystals has been observed from SEM images. The defects in surface of the crystal were observed from AFM. The changes in laser damage threshold value have been observed due to doping of β-alanine in glycine phosphite.

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