International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol. 3, No.3, pp 1373-1379, July-Sept 2011

Mechanical properties of β-Alanine doped Glycine phosphite single crystal grown by SR Method

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Abstract: The pure glycine phosphite (pure-GPI) and new β-alanine doped glycine phosphite (β-alanine-GPI) single crystals were grown from slow evaporation and Sankaranarayanan and Ramasamy (SR) method. From the β-alanine doped GPI compound the single crystals were grown. The colourless β-alanine-GPI crystal with cylindrical shape about maximum diameter of 12 mm and length of 25 mm was obtained by this method. The crystalline quality has been analyzed by X-ray diffraction methods. Meyer's index number (n) and vickers hardness value (H_v) of the crystal was calculated from vickers hardness data. The Young's modulus of the β-alanine-GPI crystal was found to be 1.535 x $10^{10}N/m^{-2}$ using Knoop microhardness (H_k) measurements. The results of all these characterizations are discussed in detail.

Keywords: Inorganic materials; Chemical synthesis; Crystal growth; Crystal structure.

INTRODUCTION

The hydrogen bonded crystal Glycine phosphite ($NH_2CH_2COOH_3PO_3$) abbreviated as GPI, and betanine phosphite crystal [$(CH_3)_3NCH_2COOH_3PO_3$] abbreviated as BPI shows ferroelectric nature with ordering of protons in their structure. In low temperature phase the proton ordering is expected along its c-axis and the spontaneous polarization is parallel to the monoclinic b-axis [1-4]. The similar situation is observed in KDP family of crystals where hydrogen bonds are perpendicular to the ferroelectric axis [5]. The GPI crystal belongs to monoclinic system with space group P21/a and cell parameters of a = 9.792 A°, b = 8.487 A° and c = 7.411 A° and β = 100.43° [6,7] and also the crystal undergoes continuous ferroelectric to para-electric phase transition at 224 K which was already reported by dielectric measurements. To understand this ferroelectric phase transition mechanism, several investigations were carried out by various research groups [8-10].

No growth details with the addition of β-alanine with GPI have been reported so far. Also the investigations on the SR method [11-18] of this crystal have not been reported yet. Hence in this paper we report a detailed surface analysis study of the SR method grown new β-alanine-GPI single crystal.

EXPERIMENTAL DETAILS

Material synthesis

The equimolar ratio of high purity glycine [NH_2CH_2COOH] (AR grade) and orthophosphorous acid [H_3PO_3] (Sigma Aldrich) were taken to synthesize Glycine phosphite (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.

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

After mixing the orthophosphorous acid and glycine in the millipore water solvent the complete dissolvation of these compounds takes place. After this dissolvation the 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. The transparent colourless solution can be 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. The temperature of the solution was decreased gradually so that we can obtain β-alanine doped GPI powder crystals. After completion of precipitation and proper filtering the β-alanine -GPI chemical powder dried form. The β-alanine-GPI synthesized salt was recrystallized several times to get purified material and good quality crystals.

By employing the slow evaporation technique, the fine single crystals of β-alanine -GPI were obtained from saturated solution[19] .

Growth of β-alanine -GPI by Sankaranarayanan and Ramasamy (SR) method

The saturated solution of β-alanine-GPI was transferred in 20 mm diameter growth ampoule. The β-alanine doped GPI single crystal having specific orientation plane of <010> was inserted into the growth ampoule. The bottom of growth ampoule consist seed mounting pad. The ring heater of 120 voltage and 1-2 mm/h translation rate was placed around the growth ampoule. The temperature around the growth ampoule was controlled by the temperature controller. The growth of seed crystal was observed and crystal was allowed to grow for required length under proper condition.

Under controlled condition, the highly transparent crystal with size of 12 mm diameter and 25 mm length were obtained with in a month. Figure 1 shows <010> ingot β-alanine -GPI single crystal grown by SR method. The highly transparent, colourless, cylindrical shape good quality crystal has been obtained by this method [19].

CHARACTERIZATION STUDIES

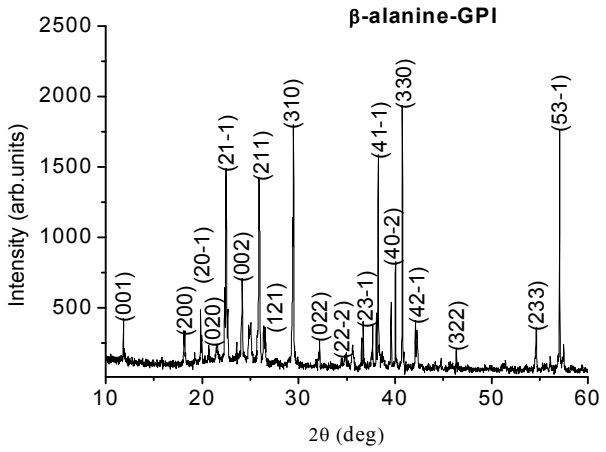
Single crystal X-ray diffraction analysis

The single crystal X-ray diffraction analysis (by using ENRAF NONIUS CAD4 diffractometer) was carried out for the grown crystals. The lattice parameters of pure and β-alanine doped GPI were calculated by single crystal X-ray diffraction analysis. On comparison it is seen that the lattice parameters of β-alanine GPI are slightly higher than [(a = 9.804, b = 8.498, c = 7.456 (A^0)] pure GPI [19].

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

Powder X-ray diffraction analysis

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



To confirm the crystal structure, the powder samples have been analyzed by (using Rich seifort (model 2002) X-ray diffractometer) powder X-ray diffractometer. 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 [19].

Microhardness studies

The crack free crystal having approximate dimensions of 3 x 3 x 2 mm^3 (β-alanine -GPI), with flat and smooth faces, were chosen for vicker's and knoop's indentation test.

Vicker's microhardness

The Vicker's microhardness measurements were done for different forces (10, 25 and 50 gms) for β-alanine - GPI crystal. For a load after 50 g, the cracks started developing around the indentation mark. The graph was plotted between Vicker's hardness number (H_v) Vs applied load (P) which is shown in the figure 3.

Figure 3. Plot of Vickers hardness number (H_v) V_s load (P)

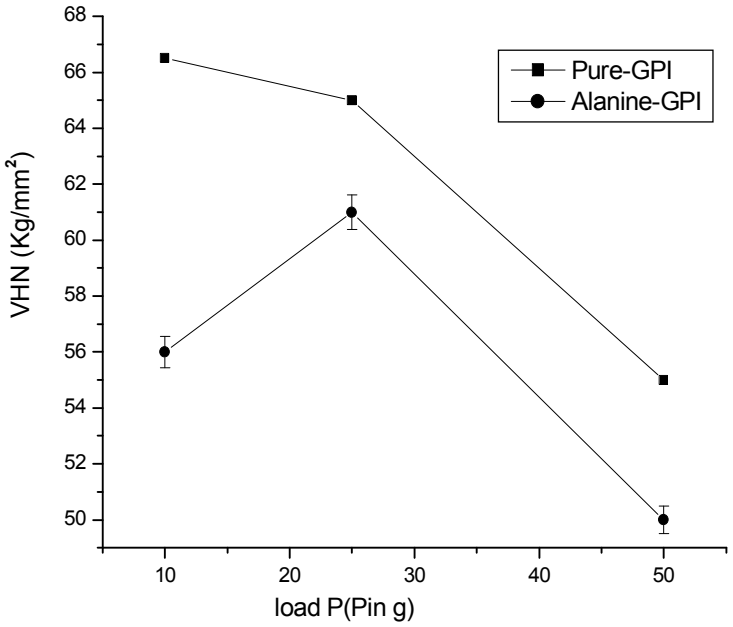


Figure 4. Plot of log P V_s log d

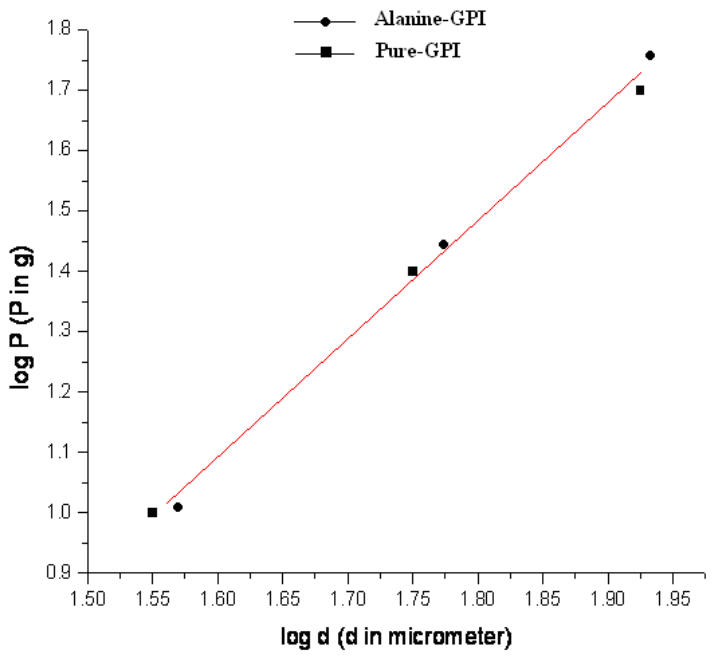


Figure 4 explains the relation between log P Vs log d fitting data before cracking after least square fitting gives the straight line graph for pure and β-alanine doped GPI. The β-alanine-GPI Vicker's hardness value is decreased comparing with pure GPI.

The value of (Meyers index number) n is found from the slope of the graph and it was found to be 1.610 for β-alanine -GPI which shows harder than pure GPI. The value of β-alanine -GPI shows that it belongs to soft material category [20].

Knoop microhardness

For this crystal also beyond the 50 gms of load the hardness measurement could not be carried out. From this measurement it was observed that the load increased upto 50 g, the knoop microhardness number decreases with load.

Figure 5 shows the photograph of the indentation mark of knoop microhardness which was performed in the surface of the β-alanine -GPI crystal. The graph was plotted against knoop hardness (H_k) Vs load (P) for pure and β-alanine doped GPI figure 6.

Figure 5. Indentation mark of knoop's microhardness

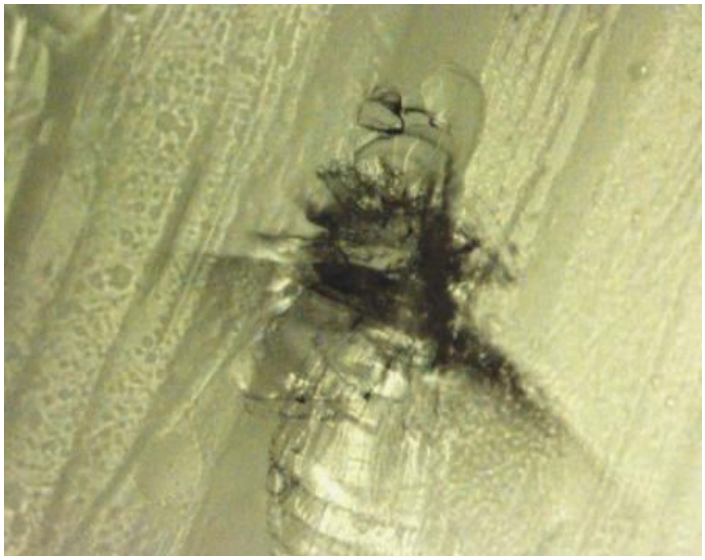


Figure 6. Variation of Knoop microhardeness with load

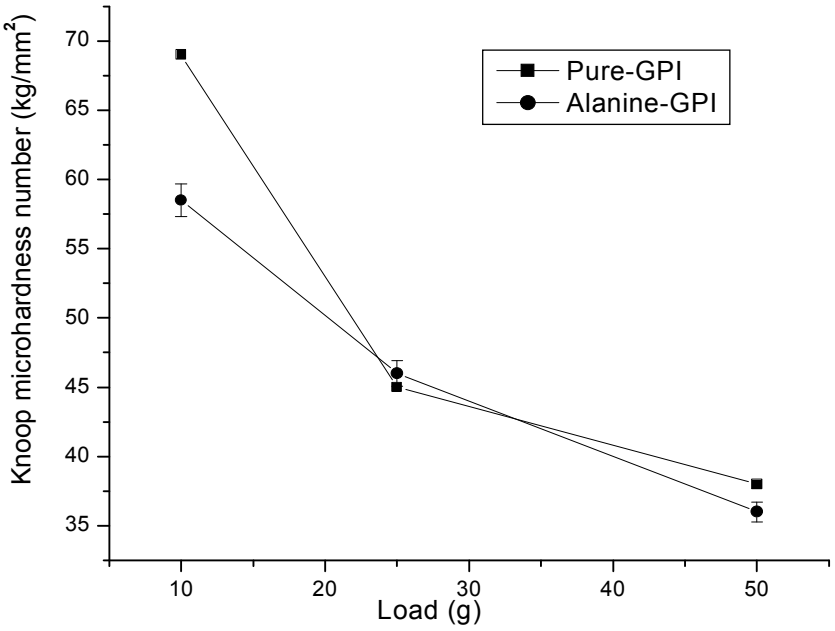
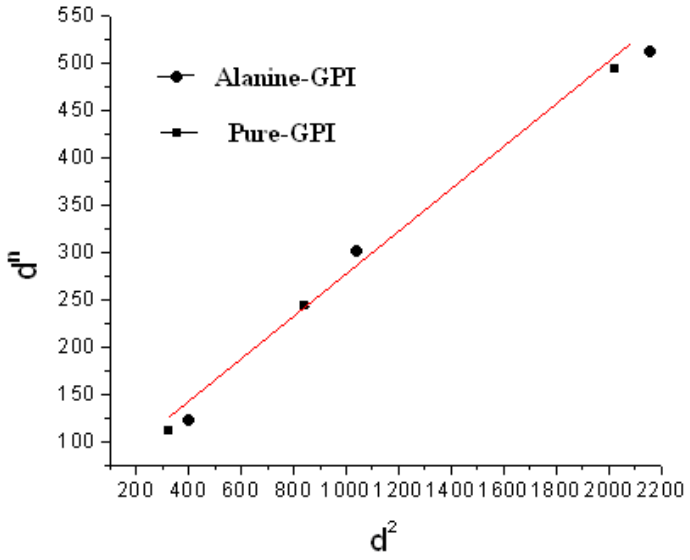


Figure 7. Plot of d^2 V_s d^n

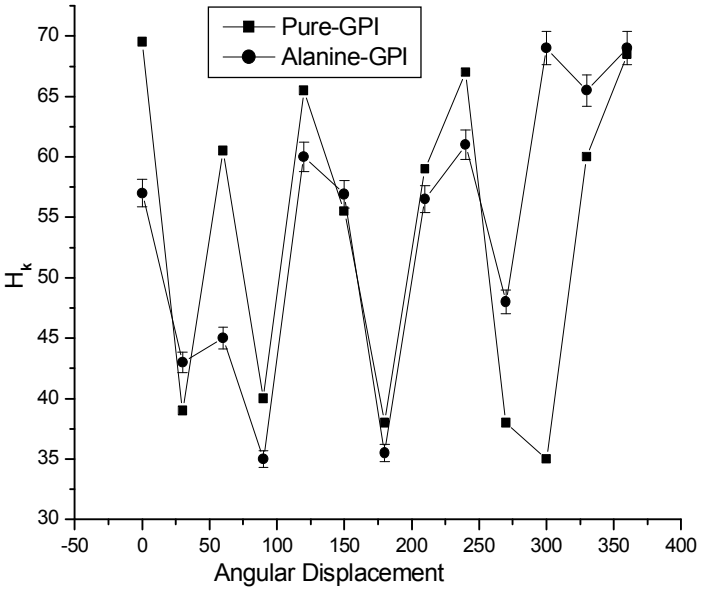


The value of d^n was calculated (for both the samples) and the graph was plotted against d^2 and d^n which gives a straight line as shown in the figure 7. For β-alanine doped GPI the Young's modulus was calculated as 1.218 x 10^{10}N/m^{-2} [21].

Anisotropy nature

To study anisotropic nature of β-alanine-GPI crystal, the microhardness was measured by varying the crystal orientation over the range of 0°– 360° insteps of 30° which is show in the figure 8. The variation in hardness number indicates the anisotropic nature of both the crystals [22].

Figure 8. Anisotropy nature



Brittleness index

The value of brittleness index number was calculated for β-alanine doped GPI. The value of K_c [23] was calculated as 0.1352 $MNm^{-3/2}$ for β-alanine doped GPI. For this crystal the B_i was found to be 4749.99 $\mu m^{-1/2}$.

CONCLUSIONS

The mechanical properties of β-alanine doped glycine phosphite were analyzed and compared with pure GPI materials. The Vickers and Knoop microhardness numbers (H_v and H_k) were calculated. It shows lower hardness, Young's modulus and Brittleness index values comparing with pure GPI. Also the variation in hardness values of these crystal exhibits anisotropic property.

ACKNOWLEDGEMENTS

Authors are thankful to management of VIT University, Vellore for constant encouragement and financial support.

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