Proc Indian Natn Sci Acad **79** No. 3 September 2013 pp. 423-426

Research Paper

Influence of Dopants on Vickers Microhardness of Ferroelectric Glycine Phosphite Single Crystals

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(Received 27 June 2012; Accepted 27 February 2013)

Ferroelectric Glycine Phosphite (GPI) single crystals were grown by solvent evaporation and temperature-lowering techniques from aqueous solution by doping with different materials like metals (Cr, Mn, Co, Ni, Zn, Mg, Cd), rare earth metals (Ce, Nd, La), dyes (Rhodamine B, Malachite green, Fluorescein) and amino acid (L-Proline) in the paraelectric phase. Concentration of dopants was chosen depending on the nature of dopants and quality of crystallization during the growth process. ESR, AAS, ICP, XRF and UV-Visible spectral analyses were carried out to confirm the incorporation of dopants. Lattice paramaters and structural morphology of pure and doped GPI crystals were identified by single crystal XRD studies. Vickers microhardness measurements were carried out for pure and doped GPI crystals and were subjected to the loads of 5, 10, 20, 30, 40 and 50 g with a dwell time of 10 seconds. Ferroelectric b-axis and (100) plane crystals of equal thickness were selected for the measurements. Vickers hardness number 'H_v', Meyer's index number 'n', elastic stiffness constant 'C_{11}' and yield strength 'σ_y' were calculated for pure and doped GPI crystals. Hardness number 'H_v' was found to increase with the applied load upto 20 g.

Key Words: Crystal Growth; Ferroelectric Materials; GPI; X-ray Diffraction; Microhardness; Mechanical Properties

1. Introduction

Ferroelectricity in glycine phosphite (GPI) has been reported during 1996 [1]. GPI was obtained from phosphorous acid and glycine in 1:1 molar ratio. It is one of the hydrogen bonded material crystallizing in paraelectric phase and in monoclinic structure with space group of $P2_1/a$ at room temperature [2]. GPI exhibits second order ferroelectric phase transition with the spontaneous polarization 'P_s' oriented parallel to the two-fold axis. Growth and properties of pure, urea and thiourea doped GPI crystals were investigated by several researchers [3-5]. The mechanical properties of the crystal should be evaluated so that the reliability of devices could be improved by crystal growth and device design. Hardness is the resistance offered by a material to localized plastic deformation caused by scratching or by indentation and it plays a major role in device fabrication [6]. GPI compound is capable of accommodating all categories of dopants in the interstitial spaces instead of substitution, which renders the plastic deformation and enhances the mechanical stability of the material. Mechanical stability of the material in terms of hardness increases on doping. Effect of different categories of dopants in GPI along (100) plane on microhardness values has been illustrated in the present investigation.

2. Experiment

Pure GPI material was synthesized by dissolving

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equimolar ratio of glycine [NH_2CH_2COOH] (Merk) and ortho phosphorous acid [H_3PO_3] (Siga Aldrich) with millipore water as the solvent. The synthesized material was subjected to repeated recrystallization for purification. The synthesized GPI material was doped with transition metals, rare earth metals, dyes and amino acid. Metals such as Cr^{3+}, Mn^{2+}, Co^{2+} and Ni^{2+} with 1 mol% of concentration and Zn^{2+}, Mg^{2+} and Cd^{2+} with 10 mol%, rare earths Ce^{3+}, Nd^{3+} with 0.2 mol % of concentration and 1 mol% of La^{3+} in the form of nitrates and chlorides, dyes with the concentration of 1 mol% of Rhodamine-B, 0.5 mol% of Malachite green and 0.2 mol% of Fluorescein and amino acid at 3 mo% of L-Proline were doped with pure GPI. Dopant ions are distributed homogeneously in the grown crystals. Pure and doped GPI crystals were grown by solvent evaporation as well as temperature lowering methods. Optically polished *b*-axis oriented seed crystals were used for growth of bulk crystals. During bulk crystal growth, supersaturated solution was prepared at 45°C and placed in a constant temperature bath having an accuracy of 0.01°C. Initially the cooling rate was maintained as 0.1°C/day for a week and then, it was increased to 0.2°C/day till the end of the growth period. Bulk crystals of pure and doped GPI were obtained in 30 days. Zn doped GPI crystal grown by temperature lowering technique is shown in Fig. 1. The obtained crystals were non-hygroscopic.

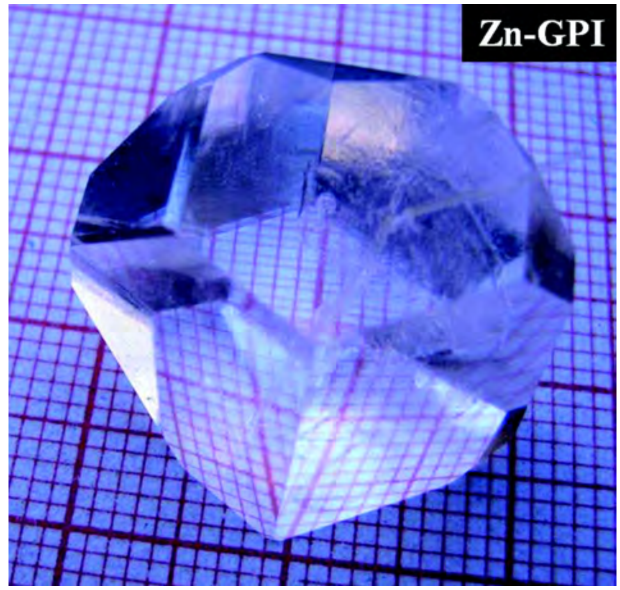

Fig. 1: Zn doped GPI crystal grown by temperature lowering technique

3. Results and Discussion

Single crystal X-ray diffraction analysis was carried out for pure and doped GPI crystals using ENRAF NONIUS CAD 4 single crystal X-ray diffractometer with MoK_α (λ = 0.717Å) radiation. The crystals of pure and doped GPI crystals have well developed facets in its morphology. Crystal slabs of all doped crystals cut along ferroelectric b-axis with one of the prominent planes (100) of equal thickness were selected for the hardness measurements. Vickers microhardness measurements were carried out for pure and doped GPI crystals using MVH-1 (METATECH) Microhardness tester. Crystals of dimension 8 x 6 x 2 mm^3 were subjected to the loads of 5, 10, 20, 30, 40 and 50 g with dwell time of 10 seconds. Vickers hardness values were calculated using the relation

$$H_V = \frac{2P\sin\frac{136^0}{2}}{d^2} = 1.8544\frac{P}{d^2}kg/mm^2 \qquad (1)$$

where H_V = Vickers hardness, P = load in kg and d = Arithmetic mean of the two diagonals, d_1 and d_2 in mm.

The trend of microhardness vs load plots (Fig. 2 a&b) show that the curves are not smooth. The hardness increases with the load up to 20 g for pure and all doped GPI crystals, which corresponds to work hardening of the crystal [7]. The plots of H_v *vs* load also satisfy the indentation size effect (ISE), i.e. decrease in H_v with increase in load in higher load region (above 20 g of load). The maximum values of H_v for pure and doped GPI crystals are presented in Table1. The value of H_V increases on doping because dopant ions enter into the lattice and hinder the formation of dislocation. Above 20 g load, plastic flow causes crack formation and hence reduces the hardness [8]. Elastic stiffness constant (C_{11}) was calculated from Wooster's empirical relation $C_{11} = H^{7/4}$ for pure and doped GPI crystals using [9] and tabulated in Table 1.

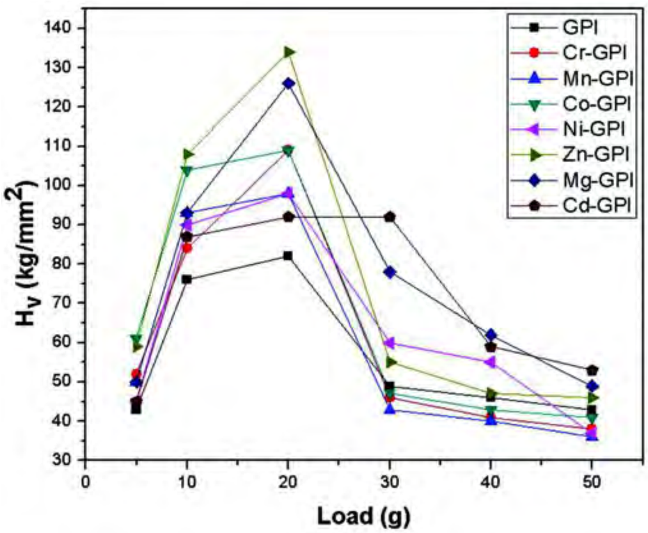

Fig. 2: (a) Hardness *vs* load plot for metals doped GPI crystals

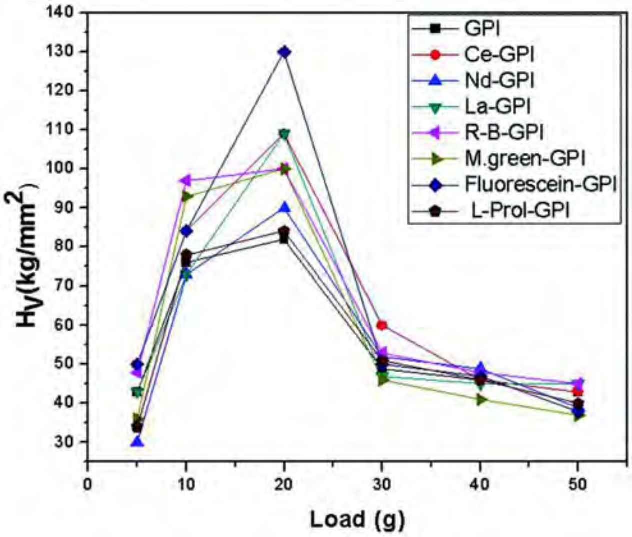

Fig. 2: (b) Hardness *vs* load plot for rare earth metals, dyes and amino acid doped GPI crystals

The relation between applied load and size of indentation was given by Meyer's law $P = k_1 d^n$ [10], where 'k_1' is the material constant and 'n' is the Meyer's index.

Hence,

$$\log P = \log k_1 + n \log d \qquad (2)$$

The plot of log P against log d for all crystals give a straight line which is in good agreement with Meyer's law. The slope of the graph yields the value of 'n'. This was determined for pure and doped GPI crystals and presented in Table 1. Comparing equation (1) and Meyer's law, one can get

$$H_V = 1.8544 k_1 d^{n-2}$$

or

$$H_V = 1.8544 k_1^{\frac{2}{n}} P^{\left(1-\frac{2}{n}\right)}$$

or

$$H_V = bP^{(n-2)/n} \qquad (3)$$

where $b = 1.8544 k_1^{\frac{2}{n}}$ is a constant [11]. The above equation (3) represents that H_V increases with increase

Table l: Mechanical properties of pure and doped GPI crystals

Crystal	Maximum value of 'H_V' (kg/mm^2)	Meyer's index 'n'	Stiffness constant 'C_{11}' (MPa)	Yield strength 'σ_y' (MPa)
GPI	82	1.94	2234.47	27.33
Cr-GPI	109	1.88	3677.02	36.33
Mn-GPI	98	1.84	3052.43	32.67
Co-GPI	109	1.74	3677.02	36.33
Ni-GPI	98	1.92	3052.43	32.67
Zn-GPI	134	1.69	5277.56	44.67
Mg-GPI	126	1.81	4738.58	42.00
Cd-GPI	92	1.95	2732.93	30.67
Ce-GPI	109	1.73	3677.02	36.33
Nd-GPI	90	1.65	2629.81	30.00
La-GPI	109	1.96	3677.02	36.33
R.B-GPI	100	1.88	3162.28	33.33
M.green-GPI	100	1.97	3162.28	33.33
Fluorescein -GPI	130	1.88	5004.96	43.33
L.Prol-GPI	84	1.98	2330.71	28.00

of *P* which corresponds to normal Indentation Size Effect (ISE). Meyer's index 'n' is a measure of ISE, if the hardness is independent of load, then, $n = 2$. If the hardness increases when the applied load decreases, $n < 2$. If the hardness decreases when the applied load decreases, $n > 2$. Deviations from $n = 2$ are the measure of ISE and in a specific case will be a measure of microstructural variations, surface layers, mechano-chemical effects etc. [12] for certain materials. According to Onitsch [13] and Hanneman [14], '*n*' should lie between 1 and 1.6 for hard materials and above 1.6 for softer ones. Meyer's index '*n*' was calculated for pure and doped GPI crystals and is presented in Table 1. The '*n*' value observed in the present study was more than 1.6 for pure and doped GPI crystals suggesting that all crystals are relatively soft materials.

Yield strength can be calculated from hardness values for Meyer's index $n > 2$ using the following relation.

$$\sigma_y = \frac{H_V}{2.9}\left[1-(n-2)\right]\left\{\frac{12.5(n-2)}{1-(n-2)}\right\}^{n-2} \qquad (4)$$

If $n < 2$, the above equation is reduced to $H_v / 3$ [15]. Since '*n*', being less than 2 for pure and doped GPI crystals. Equation $\sigma_y = H_v/3$ is applied and yield strength was calculated and presented in Table 1.

4. Conclusions

The maximum value of Vickers microhardness H_v for pure and doped GPI crystals lie in the range of 82-134 kg/mm^2 for (100) face under the application of load in the range of 5-50 g. Among the dopants, Zn and 1 mol% L-proline doped GPI shows the higher hardness number of 134 kg/mm^2 at 20 g of load and 133 kg/mm^2 at 10 g of load respectively, which indicates that dopants significantly enhance the mechanical properties of pure GPI. The variation of H_v satisfies the trend of normal ISE i.e., H_v decrease with increase of load above 20 g for all crystals except L-Proline doped GPI. This type of variation of H_v is in good agreement with Meyer's law. Meyer's index '*n*' was more than 1.6 for pure and doped GPI crystals, suggesting that crystals are relatively soft materials. Elastic stiffness constant C_{11} gives the idea of tightness of bonding between the neighbouring atoms. C_{11} was found to be in the range of 2234.47-5277.56 MPa for pure and doped GPI crystals. Yield strength for pure and doped GPI crystals was found to be in the range of 27.33-44.67 MPa.

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