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Structural and mechanical properties of diglycine perchlorate single crystals

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Good quality diglycine perchlorate (DGPCL) single crystals were grown by slow evaporation solution growth method using the combination of glycine and perchloric acid in the ratio of 2:1. Single crystal X-ray diffraction and mechanical characterization of the grown single crystals of diglycine perchlorate were analyzed in this article. Lattice parameters, space group and crytal system were found from single crystal X-ray diffraction analysis. All the cell parameters and space group are in a good agreement with the reported values. Mechanical properties, such as Vicker's microhardness number, work hardening index, standard hardness value, yield strength, fracture toughness, brittleness index and elastic stiffness constant values, were determined using Vicker's microhardness tester.

Keywords: *X-ray diffraction; work hardening coefficient; yield strength; stiffness constant*

1. Introduction

Organic materials can exhibit high nonlinear optical efficiency due to their high optical susceptibilities and large electro-optic coefficient [1]. However, those materials are mechanically weak in nature. Crystals of such materials are used in optoelectronic applications [2–4]. The hardness characteristics of the materials also play an important role in optoelectronic devices fabrication. Glycine, an aminoacid organic material, has high nonlinear optical properties [5]. To increase the hardness of the material and make it more suitable for optoelectronic devices fabrication [6], perchloric acid was mixed with glycine. Diglycine perchlorate crystalline material was grown by slow evaporation solution growth method. The study of the growth as well as XRD and microhardness characterization of diglycine perchlorate single crystals were performed and reported in this article. The sample crystals of diglycine perchlorate were subjected to structural and mechanical studies by using single crystal X-ray diffractometer and Vicker's microhardness tester. The hardness of a crystal is generally defined as its resistance to structural breakdown under applied stress. Mechanical properties, such as Vicker's microhardness number, work hardening index, standard hardness value, yield strength, fracture toughness, brittleness index and elastic stiffness constant values, give valuable information on the physical strength and deformation characteristics of a material [7]. Chemical forces in a crystal resist the motion of dislocations as it involves displacement of atoms. This hardness is an intrinsic hardness of a crystal. The hardness properties are associated with the structure of a crystal material and hardness studies are carried out to understand plasticity of the crystal [8]. Microhardness studies of various crystals using Vicker's indentor have been reported by many researchers [9, 10]. Thus, in this study, various hardness parameters were determined for diglycine perchlorate single crystal using Vicker's microhardness tester.

2. Experimental

2.1. Crystal growth

Slow evaporation solution growth method was used to grow diglycine perchlorate single crystals.

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A saturated solution of a mixture of glycine and perchloric acid in the stoichiometric ratio of 2:1 was prepared in doubly distilled water. The solution was stirred constantly for about 5 h using a magnetic stirrer. Then, the solution was filtered and kept at about 30 °C. The solution was permitted to evaporate the water slowly into the atmosphere. After 3 weeks, diglycine perchlorate-crystals were obtained from the mother solution. The collected crystals were recrystallized to get good quality highly transparent colorless diglycine perchlorate single crystals. The dimensions of the crystals are 7 mm × 4 mm × 2 mm. The photograph of a DGPCL crystal is shown in Fig. 1.

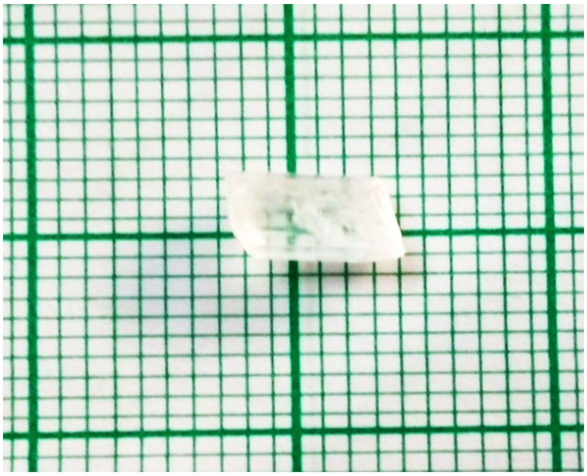

Fig. 1. DGPCL crystal.

3. Results and discussion

3.1. Single crystal X-ray diffraction study

The single crystal X-ray diffraction analysis of diglycine perchloratecrystal was carried out with MoKα (λ = 0.71073 Å) radiation. The lattice parameters were measured as a = 8.743 Å, b = 14.916 Å, c = 19.453 Å, α = 99.256°, β = 93.017° and γ = 106.280°. The data authenticate that the crystal belongs to triclinic crystal system and its space group is P1. The volume of unit cell, V = 2394.812 Å^3. The values obtained from a single crystal X-ray diffraction analysis of diglycine perchlorate single crystal are very well matching with the reported values [11].

3.2. Mechanical studies

Mechanical properties are essential for the fabrication of optoelectronic devices. Microhardness studies were conducted on diglycine perchlorate single crystal specimen, grown by slow evaporation method, using Leitz Wetzlar microhardness tester with Vicker's diamond pyramidal indentor. The indentations were made for various loads of 25 g, 50 g and 100 g at a constant indentation time interval of 25 s.

3.2.1. Vicker's hardness number H_v

For various loads, the values of Vicker's hardness number H_v were calculated by the relation:

$$H_v = \frac{1.8544P}{d^2}\ \mathrm{kg/mm^2} \tag{1}$$

where P is the applied load in kg and d is the mean diagonal length of the indentor impression in mm. Fig. 2 shows the variation of Vicker's hardness number H_v with the applied load P. It is observed that the hardness number H_v increases with the increasing load which is termed as reverse indentation size effect (ISE). Thus, the material is suitable for device fabrication [12].

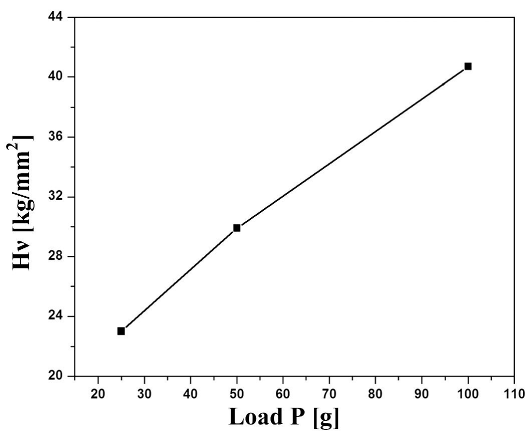

Fig. 2. Plot of H_v versus load P.

3.2.2. Meyer work hardening coefficient

According to Meyer hardness analysis, the relation between load P and indentation length d is given by [13]:

$$P = k_1 d^n \tag{2}$$

where P is the applied load, d is the observed mean diagonal length of indentation and n is the Meyer microhardenning index or work hardening coefficient. The above equation can be rewritten as follows:

$$logP = logk_1 + logd^n \tag{3}$$

or

$$logP = logk_1 + nlogd \tag{4}$$

The Meyer microhardening index n was determined from the slope of the curve drawn between logd (d in μm) and logP (P in g) as shown in Fig. 3. The standard hardness $k_1 = 15.49 \times 10^{-3}$ kg/m was determined from the Y-axis intercept.

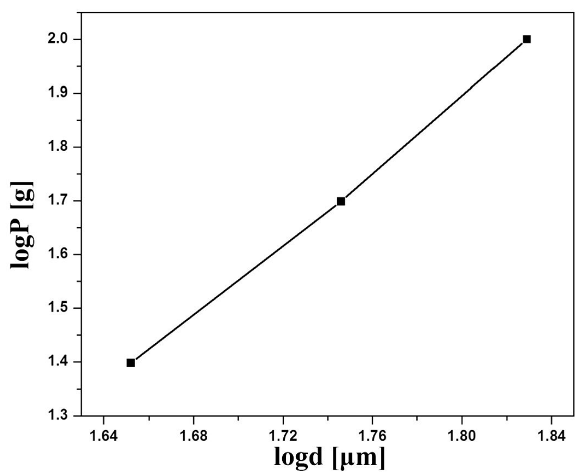

Fig. 3. Plot of logP versus logd.

According to Onitsch [14], for hard materials n lies between 1 and 1.6 and it is higher than 1.6 for soft materials. The value of work hardening coefficient n of diglycine perchlorate single crystal was found to be 3.40, which shows that the material is a soft material. After removal of applied load, the material takes some interval of time to revert to the elastic mode. Therefore, a correction of x is included to the observed value d. The Kick law is given by:

$$P = k_2(d+x)^2 \tag{5}$$

Substituting the value of P, we get:

$$k_1 d^n = k_2(d+x)^2 \tag{6}$$

$$d^n = \left(\frac{k_2}{k_1}\right)(d+x)^2 \tag{7}$$

$$d^{n/2} = \left(\frac{k_2}{k_1}\right)^{1/2}(d+x) \tag{8}$$

or

$$d^{n/2} = \left(\frac{k_2}{k_1}\right)^{1/2} d + \left(\frac{k_2}{k_1}\right)^{1/2} x \tag{9}$$

Fig. 4 shows the curve drawn between d and $d^{n/2}$. The slope and the intercept were calculated from the graph. By substituting the value of k_1, k_2 was determined which is equal to 48.64×10^{-9} kg/m. From the intercept, the correction value $x = 10.031 \times 10^{-3}$ has been calculated.

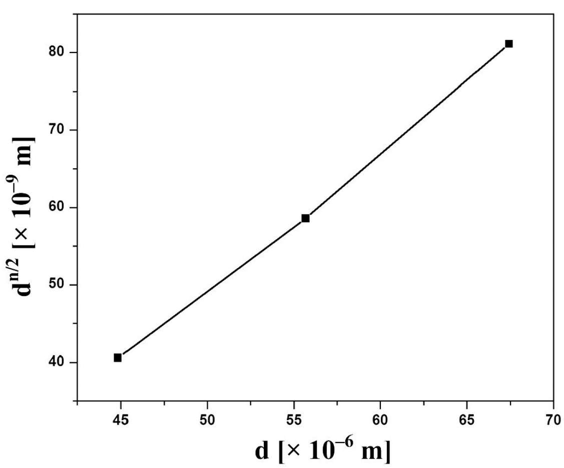

Fig. 4. Plot of $d^{n/2}$ versus d.

3.2.3. Fracture toughness K_C

Fracture toughness is a property which describes the ability of a material to resist fracture. It is one of the most important characteristics of any material for design applications. Fracture toughness gives the information necessary to estimate the fracture resistance of brittle materials.

The fracture toughness K_C is given by the relation [15]:

$$K_c = \frac{P}{\beta C^{3/2}} \tag{10}$$

where C is the crack length measured from the centre of the indentation mark to the crack tip, P is the applied load and β is the geometrical constant which depends upon the indentation geometry. For the Vicker's indentor, $\beta = 7$. The fracture toughness K_C values of diglycine perchlorate material were obtained from the above formula for different loads and tabulated in Table 1.

Table 1. Fracture toughness of diglycine perchlorate

Load P [g]	Fracture toughness K_C [$\times 10^4$ kg/m$^{-3/2}$]
25	3.364
50	4.863
100	7.296

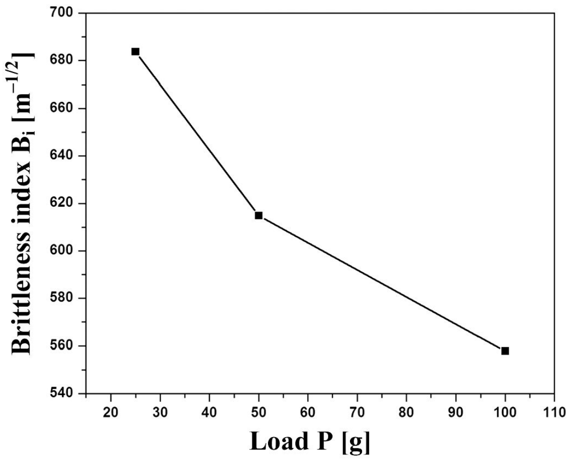

Fig. 5. Plot of B_i versus P.

3.2.4. Brittleness index B_i

Brittleness is an important property of a material which determines the material's fracture without any appreciable deformation. It is expressed in terms of brittleness index. The brittleness index B_i of diglycine perchloratecrystal was calculated for various loads by the following relation [16]:

$$B_i = \frac{H_v}{K_c} \tag{11}$$

Fig. 5 shows the plot drawn between load P and brittleness index B_i, which shows the decrease in the brittleness index B_i with the increase in load P. Table 2 gives the calculated values of the brittleness index.

Table 2. Brittleness index of diglycine perchlorate.

Load P [g]	Brittleness index B_i [m$^{-1/2}$]
25	683.71
50	614.85
100	557.84

3.2.5. Yield strength σ_v

The microhardness value correlates with other mechanical properties such as yield strength σ_v and elastic stiffness constant C_{11}. Yield strength of a material is the maximum value of stress that can be developed in the material without causing plastic deformation or change in shape. A material having high yield strength can withstand high stress without permanent deformation. The yield strength is an important property for engineering structural design and device fabrication, which can be calculated by the relation [17]:

$$\sigma_v = \frac{H_v}{2.9}\left\{[1-(n-2)]\left[\frac{12.5(n-2)}{(1-(n-2))}\right]^{n-2}\right\} \tag{12}$$

where H_v is the hardness number and n is the microhardenig index. The yield strengths of diglycine perchlorate material for different loads were determined and tabulated in Table 3. Fig. 6 shows a graph plotted between load P and yield strength σ_v which shows the variation of σ_v with the varying load P.

Table 3. Yield strength of diglycine perchlorate.

Load P [g]	Yield strength σ_v [$\times 10^4$ MPa]
25	2.723
50	3.539
100	4.820

3.2.6. Elastic stiffness constant C_{11}

The elastic stiffness constant C_{11} of a material determines the nature of tightness of the bonding

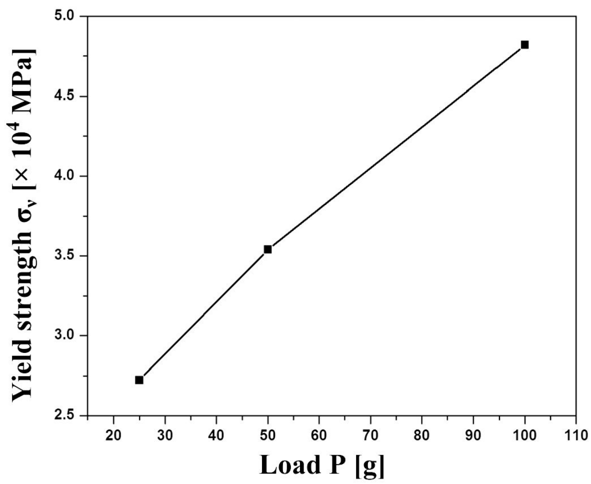

Fig. 6. Plot of σ_v versus load P.

between adjacent atoms. Stiffness is rigidity of a material determining the the extent to which it resists deformation at an applied force. The complementary concept is flexibility. The higher is the stiffness the lesser is the flexibility. The C_{11} for different loads has been determined using Wooster empirical formula [18]:

$$C_{11} = H_v^{7/4} \tag{13}$$

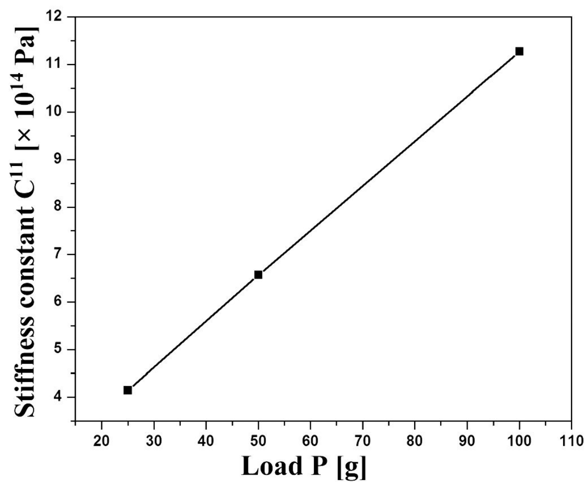

Fig. 7. Plot of C_{11} versus load P.

Fig. 7 shows a curve drawn between load P and C_{11}. It shows an increase in stiffness constant with an increase in load. High values (Table 4) of C_{11} indicate that the binding forces between the atoms and ions of diglycine perchlorateare are quite strong [19].

Table 4. Elastic stiffness constant of diglycine perchlorate.

Load P [g]	Stiffness constant C_{11} [× 10^{14} Pa]
25	4.15
50	6.57
100	11.27

4. Conclusions

Optically high quality diglycine perchloratesingle crystals were grown by slow evaporation solution growth method. The single crystal X-ray diffraction analysis of diglycine perchloratecrystal showed that the crystal data are in a good agreement with the reported values. Mechanical properties, such as Vicker's microhardness number, work hardening coefficient, yield strength, elastic stiffness constant, brittleness index, standard hardness and fracture toughness values, were determined using Vicker's microhardness tester. It was observed that the hardness number increases with increasing load, termed as reverse ISE. The value of work hardening coefficient n was determined as 3.40 which shows that the title crystal is a soft material. The high value of the stiffness constant indicates that the binding forces between atoms are quite strong. Hence, the material is suitable for optoelectronic devices fabrication.

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