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STUDIES ON MECHANICAL AND ELECTRICAL PROPERTIES OF NLO ACTIVE L-GLYCINE SINGLE CRYSTAL

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Abstract. L-glycine single crystals were grown by slow evaporation technique. The crystals are subjected to microhardness studies and the variation of the microhardness with the applied load is studied. Microhardness studies revealed that the hardness of the grown crystal increases with an increase in load. Meyer's index number n was calculated and found that the material belongs to soft material category. The dielectric measurements are carried out and the nature of variation of dielectric constant and dielectric loss in the frequency range of 50 Hz to 5 MHz at different temperatures (30 ºC, 60 ºC, 90 ºC, 120 ºC, and 150 ºC) is studied and reported. Further, electronic properties, such as valence electron plasma energy, Penn gap, Fermi energy and electronic polarizability of the grown crystal have been estimated. Photoconductivity measurements carried out on the grown crystal reveal the negative photoconducting nature.

1. Introduction

In last several years there has been considerable interest in growth and characterization of nonlinear optical materials (NLO) due to their important contribution in areas of optical modulation, optical switching, optical logic, frequency shifting and optical data storage. Several attempts have been made for exploration of nonlinear optical materials which found various applications in optoelectronics [1, 2]. The complexes of amino acids and salts are promising materials for optical second harmonic generation (SHG) as they tend to combine the advantages of organic amino acids with those of the inorganic acids. Glycine is a simple amino acid which has three polymeric crystalline forms α, β and γ. There are two types of glycine groups such as glycinium ions and zwitter ion. The zwitterionic structure of glycine is useful for its optical activity [3]. Aminoacids are interesting materials for NLO application as they contain proton donar carboxyl acid (COO^-) group and the proton acceptor amino (NH_2) group in them [4]. In the present study, bulk single crystals of L-glycine were grown and hence attempts are made to characterize the grown crystal by microhardness, dielectric and photoconductivity studies. Some of the electronic properties, such as valance electron plasma energy, Penn gap, Fermi energy and electronic polarizability of the grown crystal were calculated.

2. Experimental procedure

Single crystals of L-Glycine were grown by dissolving L-Glycine in double distilled water and stirred well for about two hours to get saturation solution. Deionised water was used as solvent and on repeated recrystallization; bright and optically transparent single crystals were harvested in about two weeks. Of the many crystals grown, good quality single crystals were chosen for various characterizations.

3. Microhardness studies

Microhardness studies for the grown L-glycine single crystal were performed at room temperature to determine microhardness number. Vickers hardness indentations were made on the flat polished face of the crystal for loads 10, 20, 30, 40, and 50 g using Vickers hardness tester fitted with Vickers diamond intender and attached to an incident light microscope. The lengths of the two diagonals of the indentations were measured and the Vickers hardness number was calculated using the formula,

$$H_v = 1.8544P/d^2, \tag{1}$$

where Hv is the Vickers hardness number in kg mm^{-2}, P is the intender load in kg and d is the diagonal length of the impression in mm. The variation of Hv with applied load is shown in Fig.1. It is evident from the plot that the microhardness of the crystal increases with increasing load. By plotting log P versus log d, the value of the work hardening coefficient n was found to be 2.33. According to Onitsch, $1.0 \leq n \leq 1.6$ for hard materials and n >1.6 for soft materials [5]. Hence, it is concluded that L-glycine is a soft material.

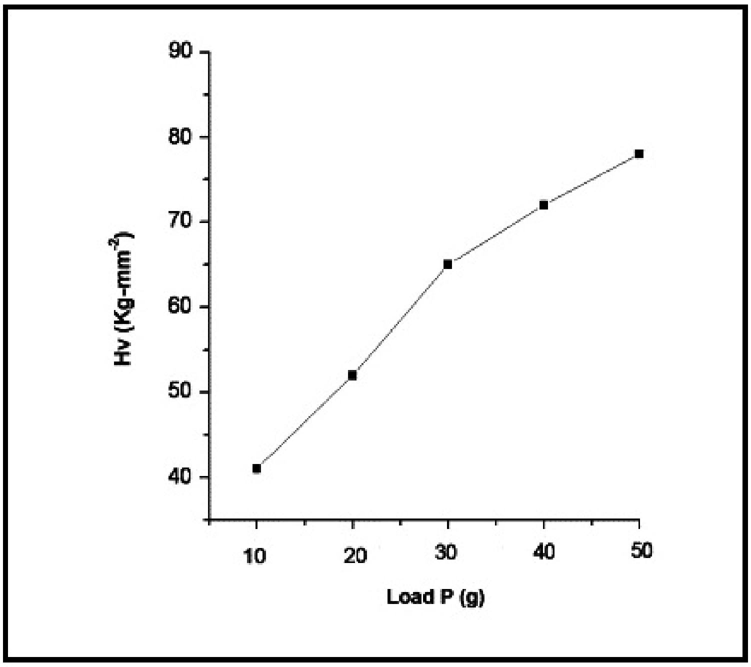

Fig. 1. Variation of hardness number *Hv* with Load P.

4. Dielectric properties

The dielectric characteristics of the material are important to study the lattice dynamics in the crystal. Hence, the grown L-glycine single crystal was subjected to dielectric studies using LCR meter and HIOCKI 3532-50 LCR HITESTER instrument. The cut and polished single crystal of L-glycine was used for dielectric studies. The surface of the sample was electroded with silver paste for electrical contact. The experiment was carried out for the frequencies from 50 Hz to 5 MHz with the different temperatures 30 ºC, 60 ºC, 90 ºC, 120 ºC, and 150 ºC respectively. In organic crystal, the dielectric response is good in the lower frequency region; hence, the experiments were carried out in the lower frequency region only. The dielectric constant ε_r was calculated using the relation:

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A} \tag{2}$$

which C is the capacitance, d is the thickness of the crystal, ε_o is the vacuum dielectric constant and A is the area of the crystal. The dielectric loss was calculated using the relation:

$$\varepsilon'' = \varepsilon_r D, \tag{3}$$

where D is the dissipation factor. It is observed from the plot (Fig. 2) that the dielectric constant decreases exponentially with increasing frequency and then attains almost a constant value in the high frequency region. It is also observed that as the temperature increases, the value of the dielectric constant also increases. The dielectric constant has a higher value at lower-frequency region and then deceases with increase in frequency and remains practically constant. The very high values of ε_r at low frequencies may be due to the presence of all the four polarizations, namely, space charge, orientational, ionic and electronic polarizations and its low value at high frequencies may be due to the loss of significance of these polarizations gradually. The increase in the dielectric constant at low frequency is attributed to the space charge polarization. The dielectric loss is also studied as a function of frequency at room temperature and at higher temperatures for L-glycine single crystals, as shown in Fig. 3. These curves suggest that the dielectic loss strongly depends on the frequency of the applied field similar to what commonly happens with the dielectric constant in the ionic system [6, 7]. The characteristic of low dielectric loss with high frequency for given sample suggests that the sample possess good optical quality with lesser defects and this parameter is of vital importance for nonlinear optical materials in their application [8].

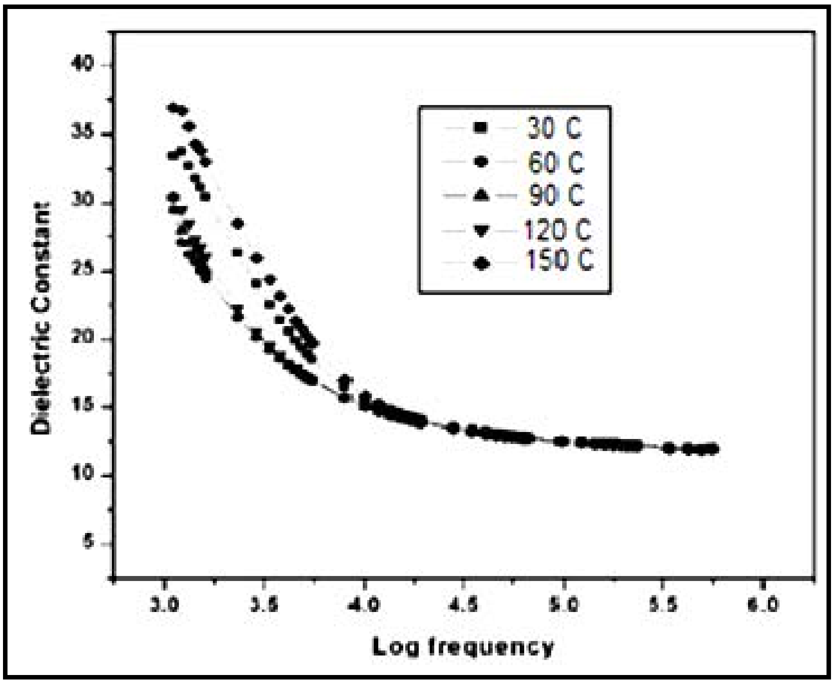

Fig. 2. Variation of dielectric constant with frequency.

Theoretical calculations shows that the high frequency dielectric constant is explicitly dependent on the valence electron Plasmon energy, an average energy gap referred to as the Penn gap and the Fermi energy. The Penn gap is determined by fitting the dielectric constant with the Plasmon energy [9].

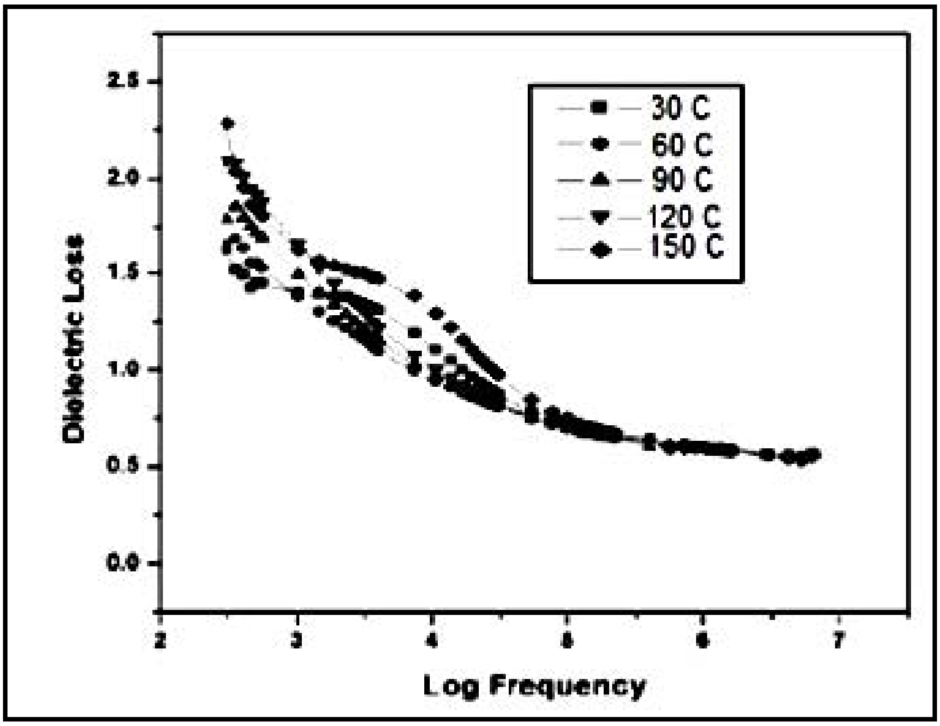

Fig. 3. Variation of different loss with frequency.

The valence electron plasma energy, $\hbar\omega_p$, is calculated using the relation:

$$\hbar\omega_P = 28.8\left(\frac{Z\rho}{M}\right)^{1/2}, \tag{4}$$

$$E_P = \frac{\hbar\omega_P}{(\varepsilon_\infty - 1)^{1/2}}. \tag{5}$$

Plasma energy are the Penn gap and the Fermi energy [9] given by

$$E_F = 0.2948(\hbar\omega_P)^{4/3}. \tag{6}$$

Then we obtained electronic polarizability α using the relation [10, 11]:

$$\alpha = \left[\frac{(\hbar\omega_P)^2 S_0}{(\hbar\omega_P)^2 S_0 + 3E_P^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} cm^3, \tag{7}$$

where S_0 is a constant given by

$$S_0 = 1 - \left[\frac{E_P}{4E_F}\right] + \frac{1}{3}\left[\frac{E_P}{4E_F}\right]^2. \tag{8}$$

The value of α obtained from equation (7) closely matches with that obtained using Clausius-Mossotti relation,

$$\alpha = \frac{3}{4}\frac{M}{\pi N_a \rho}\left[\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right]. \tag{8}$$

All the above parameters as estimated are shown in Table 1.

Table 1. Electronic properties of L-glycine single crystal.

Parameters	Value
Plasma energy ($h\omega_p$)	23.10 eV
Penn gap (E_p)	6.17 eV
Fermi Energy (E_F)	19.19 eV
Electronic polarizability (Penn analysis)	1.498×10^{-23} cm^3
Electronic polarizability (using CM relation)	1.523×10^{-23} cm^3

5. Photoconductivity property

Photoconductivity studies were carried out at room temperature for L-glycine single crystals, using Keithley 485 picoammeter. The dark current was recorded for the samples by keeping them unexposed to any radiation. The light from the halogen lamp (100 W) containing iodine vapour is focused on the respective samples and the photo currents of the samples were measured. The DC inputs were increased in steps and the photo currents were measured. Fig. 4. shows the variation of both dark current (I_d) and photocurrent (I_p) with applied field. It is seen from the plots that both I_d and I_p of the sample increase linearly with applied field. It is observed from the plot that the dark current is always higher than the photo current, thus confirming the negative photoconductivity nature of the material [12, 13].

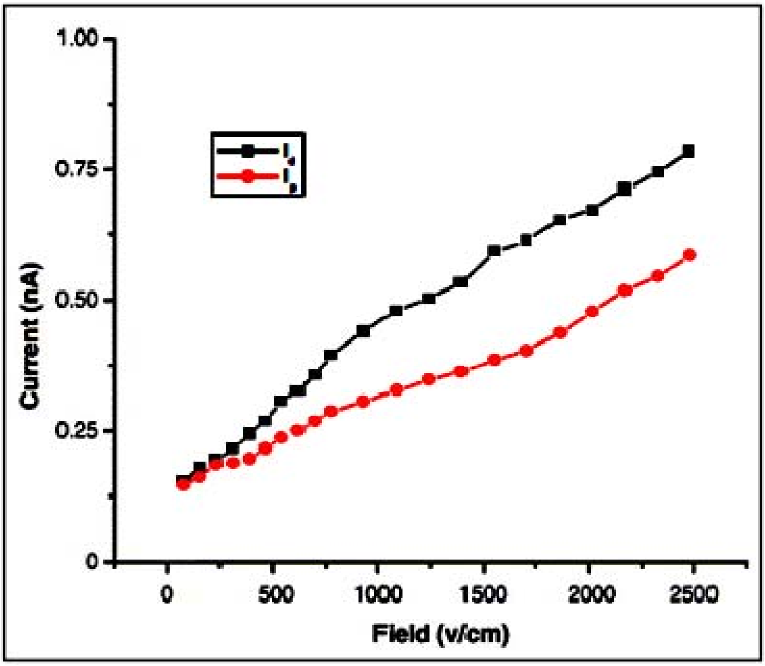

Fig. 4. Field dependence of photo and dark conductivity.

6. Conclusions

Single crystals of L-glycine were grown by slow evaporation technique. The mechanical behavior is studied by Vickers hardness method. From microhardness test, it is observed that hardness number H_v increases with the increase in load and the value of Meyer index number or the work hardening coefficient *n* was calculated as 2.33, which is greater than 2 establishing that the crystal to be a soft material. Dielectric measurements were carried to analyse the dielectric constant and dielectric loss at different frequencies and different temperatures. The characteristics of low dielectric loss for the sample suggest that it possesses enhanced optical quality with lesser defects and this parameter is of vital significance for nonlinear optical applications. Some electronic properties like plasma energy, Penn gap, Fermi energy and electronic polarizability of the crystal have been calculated. Photoconductivity investigations reveal the negative photoconducting nature of the L-glycine material.

References

[1] Yun Zhang, Hua Li, Bin Li, Yunxia Che, Jimin Zheng // *Mater. Chem. Phys*. **108** (2008) 192.
[2] Shankang Gao, Weijun Chen, Guimel Wang, Jianzhong Chen // *J. Cryst. Growth* **297** (2006) 361.
[3] Xia Yang, Jie Lu, Xiu-Juan Wang, Chi- Bun Ching // *J. Cryst. Growth* **310** (2008) 604.
[4] Tapati Mallik, Tanusree Kar // *J. Cryst. Growth* **285** (2005) 178.
[5] S. Mukerji, T. Kar // *Cryst. Res. Technol*. **34** (1999) 1323.
[6] K.V. Rao, A. Smakula // *J. Appl. Phys*. **37** (1966) 319.
[7] K.V. Rao, A. Smakula // *J. Appl. Phys.* **36** (1965) 2031.
[8] Christo Balarew, Rumen Duhlev // *J. Solid State Chem*. **55** (**1**) (1984) 1.
[9] N.M. Ravindra, R.P. Bharadwaj, K. Sunil Kumar, V.K. Srivastava// *Infrared Phys*. **21** (1981) 369.
[10] N.M. Ravindra,V.K. Srivastava // *Infrared Phys*. **20** (1980) 67.
[11] D.R. Penn // *Phys. Rev.* **128** (1962) 2093.
[12] R.H. Bube, *Photoconductivity of Solids (*Wiley, New York, 1981).
[13] V.N. Joshi, *Photoconductivity (*Marcel Dekker, New York, 1990).