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XRD, SHG, LDT, HARDNESS, DIELECTRIC AND IMPEDANCE STUDIES OF L-CYSTEINE CRYSTALS

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Abstract

This paper deals with the characterization of L-cysteine crystals grown by slow evaporation technique using a mixed solvent of water and ethyl alcohol. The grown single crystals of L-cysteine were subjected to various studies like XRD, SHG, LDT, electrical and hardness studies. XRD study reveals that L-cysteine crystal crystallize in orthorhombic system. The mechanical stability of the sample was tested by microhardness studies. The NLO activity was checked by measuring SHG efficiency. The electrical properties were understood by measuring dielectric constant, dielectric loss and impedance. The obtained results are discussed.

1. Introduction

L-cysteine is an important compound used in a wide range of samples such as biological tissues, body fluids, food products and medicines. L-cysteine is a sulfur amino acid and contains a sulfhydryl group. When L-cysteine is exposed to air, it is oxidized to form L-cystine, which is a dimer of two L-cysteine molecules joined by a weak disulfide bond. The analysis of L-cysteine and L-cystine is essential and it can be determined by electrophoretic, chromatographic, electrochemical and spectrometric methods [1-9]. The crystal structure of L-cysteine has been analysed by XRD and neutron diffraction studies [10-11]. L-cysteine is the simplest amino acid and it has centre of chirality and is optically active. L-cysteine can exist as neutral molecule in the gas

phase and it exists as a zwitterion in solution as well as in solid state. L-cysteine crystallizes in non-centrosymmetric space group making it a potential candidate for piezoelectric and non-linear applications. L-cysteine exists as a dipolar ion in solid state in which carboxyl group is present as a carboxylate ion and amino group is present as ammonium ion. In addition, thiol group is present in aqueous solution of L-cysteine. Due to this dipolar nature, L-cysteine has a high melting point. Another added advantage of L-cysteine is the presence of chromophores namely amino group and carboxyl group which makes it transparent in the UV-visible region [12,13]. Many researchers have performed the experiments on L-cysteine family crystals and all these crystals show their suitability for their nonlinear optical properties and applications. The nonlinear optical properties of L-cysteine analogs and their complexes make them strong candidates to replace KDP for frequency conversion of infrared lasers [14-18]. Since no detailed information of NLO, hardness and electrical studies of L-cysteine crystals are found in the literature, the detailed work on L-cysteine crystal are carried out and the results are given here.

2. Crystal growth

AR grade chemical of L-cysteine was purchased commercially and saturated solution was prepared using the mixed solvent of double distilled water and ethyl alcohol in 8:2 ratio by volume. The solution was stirred well for about 2 hours using a magnetic stirrer to ensure homogeneous temperature and concentration over entire volume of the solution and filtered using a filtered paper. The filtered solution was taken in a growth vessel covered with a perforated sheet and due to slow evaporation of the solvent, the crystals were grown. To avoid the thermal fluctuations, the growth vessel was kept in a constant temperature bath (accuracy: $\pm$ 0.01 ^{o}C). It took about 25 days for the growth of L-cysteine crystals and the harvested crystals are shown in the figure 1.

Fig.1: Grown crystals of L-cysteine

3. Results and discussions

3.1 Measurement of solubility

The size of a crystal depends on the amount of the material available in the solution which in turn is decided by the solubility of the material in that solvent. Solubility is the amount of solute present in 100 ml of the saturated solution. Gravimetrical method was used to determine the solubility of L-cysteine crystal in water. 5 ml of saturated solution prepared at room temperature was taken in a petri dish and it was dried and weighed accurately. By measuring the sample deposited in the petri dish after the solution is dried, the solubility was determined at room temperature (30 ^{o}C). The same procedure was followed to determine the solubility at other temperatures. The variation of solubility with temperature is shown in figure 2. The data could be fitted to the equation S = a+bT, where S and T are the solubility expressed in g/100 ml and temperature in degree Celsius respectively and the constants can be found. It is observed that L-cysteine crystal has positive temperature coefficient of solubility and hence the solution method can be adopted to grow the crystals of L-cysteine.

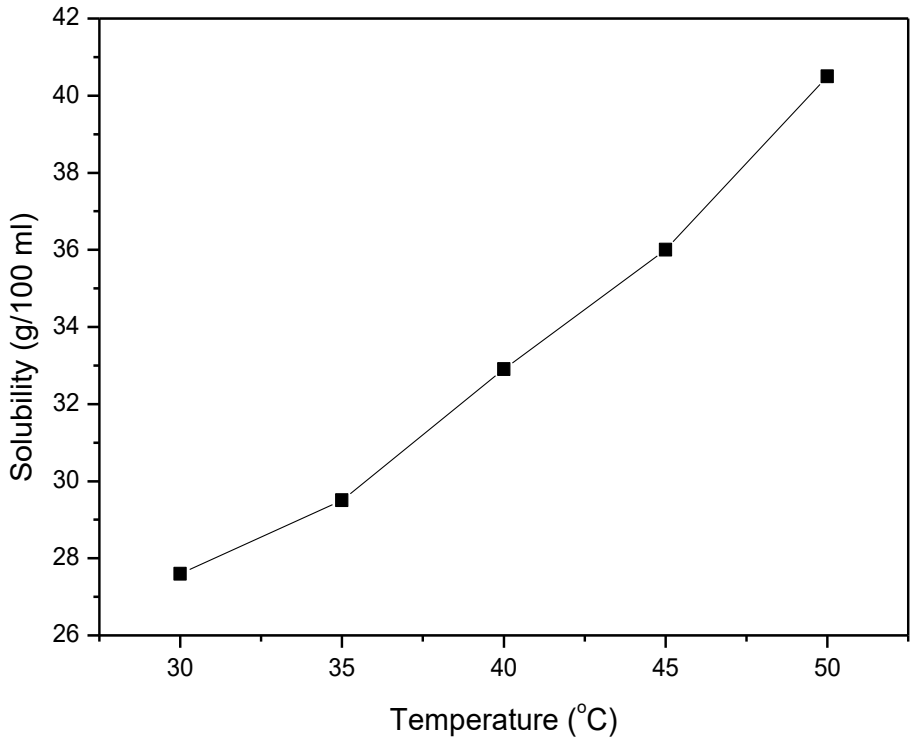

Fig.2: Solubility curve for L-cysteine crystal

3.2 Finding the lattice parameters by XRD method

Single crystal X-ray diffraction study was carried out using Bruker Kappa Apex II X-ray diffractometer with M_oK_α radiation to determine the lattice parameters of L-cysteine crystal. The unit cell parameters obtained are a = 5.427(3) Å, b = 8.109(5) Å, c = 12.152(4) Å, α = γ = β = 90º, and volume of the unit cell (V) = 534.78(2) Å^3. Hence, the sample exhibits orthorhombic crystal system with space group of $P2_12_12_1$. The obtained results in this work are found to be in good agreement with the reported values [10].

3.3 Measurement of hardness

The hardness of a material is calculated from the measured value of indentation diagonal length (d) produced by an applied load. The mean diagonal length of the indentation was measured using a LEITZ microhardness tester, fitted with a Vickers diamond pyramidal indenter. The well polished crystal was placed

on the platform of Vickers microhardness tester and the loads of different magnitudes were applied in a fixed interval of time of 10 seconds. Vickers microhardness values were calculated by using the formula $H_v = 1.8544\ P/d^2$ kg/mm^2 where P is the applied load in kg, d is the mean diagonal length of the indentation in mm and 1.8544 is a constant of a geometrical fraction for the diamond pyramidal indenter. The plot of hardness number versus the applied load is presented in the figure 3. The grown crystals exhibit the reverse indentation size effect (RISE), in which the hardness value increases with the increasing of load. At small loads, indenter penetrated only surface layers of the wafer and the penetration effect was pronounced. However, when the depth of penetration was increased, the inner layers played prominent role that resulted in the impressing of indenter more and more hard [19].

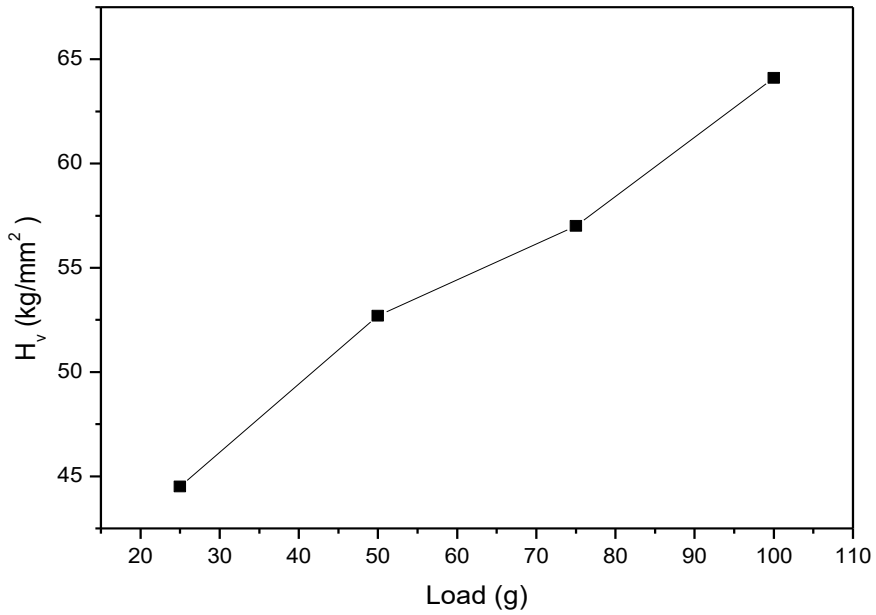

Fig.3: Variation of hardness number with the applied load for L-cysteine crystal

3.4 Measurement of SHG efficiency

Second harmonic generation (SHG) efficiency was measured by Kurtz and Perry powder technique. A high intensity Nd:YAG laser (λ = 1064 nm) with a pulse duration of 10 ns was passed through the powdered sample of L-cysteine and the emission of green radiation of wavelength 532 nm from the sample confirms SHG.

The obtained second harmonic generation signal is 8.18 mJ/pulse and the input energy used is 0.68 J/pulse. The standard potassium dihydrogen phosphate (KDP) sample gave an SHG signal of 8.8 mJ/pulse for the same input energy. Thus, it is observed that the relative SHG efficiency of L-cysteine sample is 0.93 times that of the KDP sample.

3.5 LDT characterization

Laser damage threshold (LDT) value is one of the important device related properties of NLO crystals. This involves the interaction of high power laser radiation with the matter followed by various physical, chemical, optical, thermal and other processes in the material. LDT value is the maximum permissible power that can withstand in a particular crystal and it was measured using an Nd:YAG laser (1064 nm, 18 ns pulse width). The energy of the laser beam was measured by Coherent energy/power meter (Model No. EPM 200). The LDT value was determined using the formula $P = E/\pi r^2$ where E is the energy in mJ, τ is the pulse width in ns and r is radius of the spot in mm and the value of LDT obtained for L-cysteine crystal is 0.448 GW/cm^2 .

3.6 Dielectric studies

The important electrical properties of NLO materials are dielectric constant and dielectric loss. The capacitance and dielectric loss factor (tan δ) measurements were carried out using the parallel plate capacitor method at various temperatures ranging from 30 to 90 ^{o}C using an Agilent 4284A LCR meter at different frequencies ranging from 10^2 to 10^6 Hz. Using the values of capacitance without sample and with sample of the capacitor, the dielectric constant is calculated. The dielectric loss factor can be measured directly from the LCR meter. The variations of dielectric constant and dielectric loss with frequency and with temperature for L-cysteine crystal are displayed in figures 4 and 5. The results show that both dielectric constant and loss factor decrease with frequencies and increase with increase in temperature. The high value of dielectric constant in low frequency region is attributed to space charge polarization which depends on the purity and perfection of the sample. The increase of dielectric parameters with increase of temperature is due to change of polarization, expansion of the sample and production of crystal defects. The low value of dielectric constant of the sample at high frequencies indicates that the usefulness of the grown crystal in electro-optic devices [20,21].

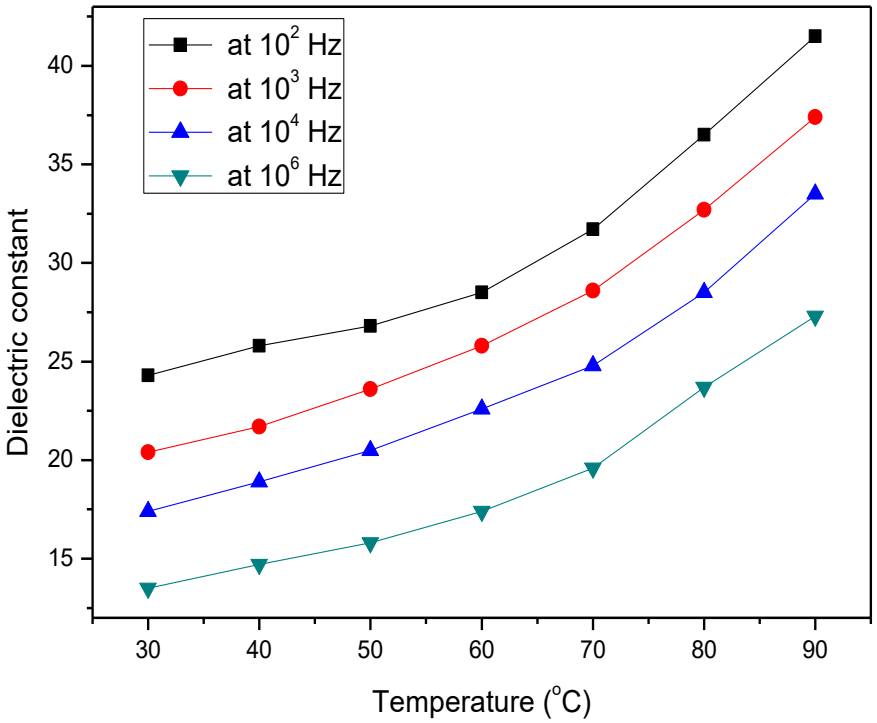

Fig.4: Plots of dielectric constant versus temperature at different frequencies for L-cysteine crystal

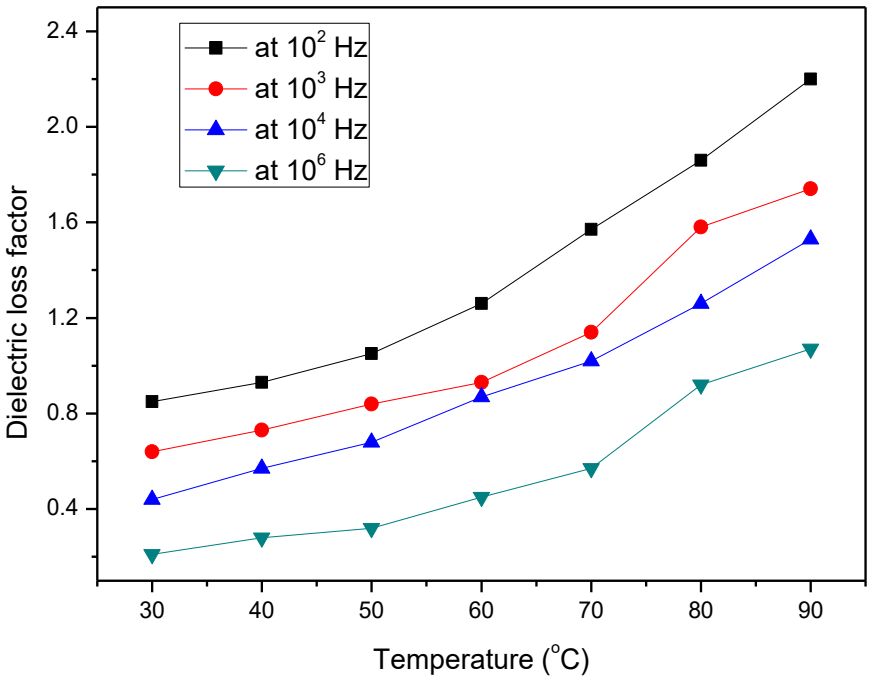

Fig.5: Plots of dielectric loss factor versus temperature at different frequencies for L-cysteine crystal

3.7 Measurement of impedance

Impedance is the quantity that opposes the current in an AC circuit. Impedance analysis was carried out for grown sample to understand the AC electrical processes that are taking place in the sample. Impedance spectroscopy is a powerful technique for the characterization of electrical behavior of NLO material. The complex impedance is written as $Z^* = Z' - jZ''$ where Z' is the real part and Z'' is the imaginary part of impedance. The complex impedance of the sample demonstrated as the sum of the single RC circuit with parallel combination. The impedance data were obtained for the samples at different frequencies and temperatures using an impedance analyzer. The diagrammatic representation of frequency dependence of real part and imaginary part of impedance at different temperatures for L-cysteine crystal are shown in the figures 6 and 7. The results show that the real part of impedance and imaginary part of impedance of the sample decreases with increase of frequency. Usually space charge polarization is responsible for higher values of impedance at low frequency region. As the temperature of the sample increases, it seems that the impedance decreases and

it indicates that the sample is an insulating type of the material. The relaxation frequency is an intrinsic property of the sample and it is independent of its geometrical factors. The plots of imaginary part of impedance versus frequency are useful for finding the relaxation frequency. Fig. 7 shows that the relaxation frequency increases as the temperature of the sample increases. The relaxation process may be due to the presence of immobile species at low temperatures and defects at higher temperatures. The shifting of relaxation frequency to the higher side in imaginary impedance plots with increasing temperature indicates the increasing energy loss in the sample [22,23].

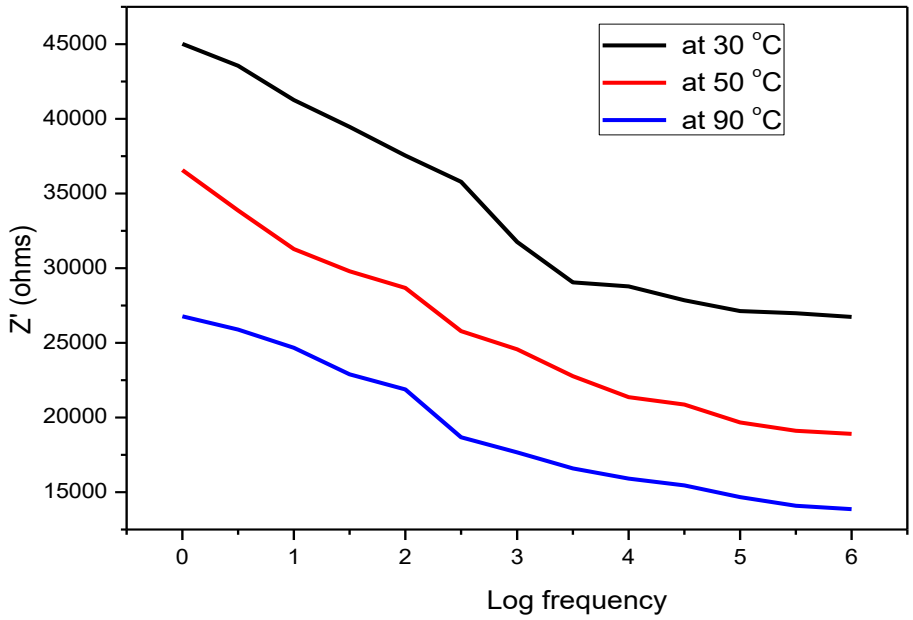

Fig.6: Plots of real part of impedance versus frequency for L-cysteine crystal at different temperature

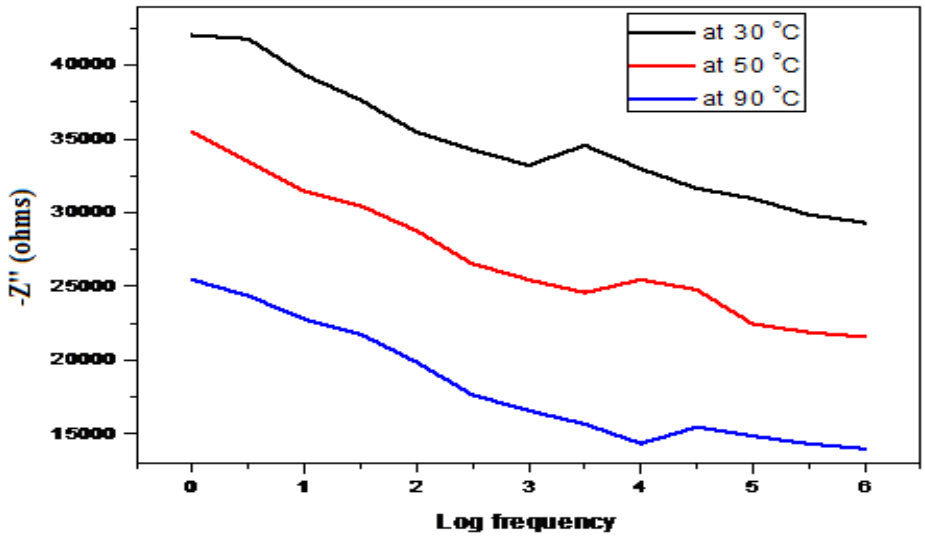

Fig.7: Plots of imaginary part of impedance versus frequency for L-cysteine crystal at different temperature

4. Conclusions

Using the mixed solvent of water and ethyl alcohol, single crystals of L-cysteine were grown by slow evaporation technique. The solubility of the sample was found to be increasing with increase of temperature. The lattice parameters were found by single crystal XRD studies. The microhardness values are observed to be increasing with increase of the applied load. LDT and SHG values of the grown sample were found out. The electrical properties of the sample were analyzed by dielectric and impedance studies.

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