Dielectric, Photoconductivity and Mechanical behaviours of L-cysteine Borate Decahydrate single crystal

Azeezaa Varsha Mohammed[1,2], Joseph Arul Pragasam Arulappan[2*] and Sunitha[3]

[1] Department of Physics, SRR Engineering college, Chennai- 603 103, India

[2] Department of Physics, Sathyabama University, Chennai- 600 119, India

[3] Department of Chemistry, Pachaiyappa's College, Chennai- 600 030, India

*Corresponding author: E.Mail: jap.azee.phy@gmail.com, Mobile: +91 9790980584

ABSTRACT

The bulk single crystal of L-cysteine Borate Decahydrate (LCBD) was grown by slow evaporation technique. The lattice parameters and crystallinity of the grown crystal were estimated by single crystal XRD. Grown crystals were found to be soft in nature (n = 1.93). The dielectric constant and dielectric loss were measured as a function of frequency and temperature for the grown crystal. Low dielectric loss at high frequency region is indicative of enhanced optical quality with lesser defects. The photoconductivity study reveals the negative photoconductivity nature of the sample.

KEY WORDS: Crystal growth, Slow Evaporation Method, Vickers Microhardness test, Dielectric Studies, Photoconductivity Studies.

1. INTRODUCTION

In the recent years, due to high speed and ease of production of photons the area of photonics has become an active area of research in view of improved telecommunications, data storage, retrieving, processing and transmission (Prasad, 1991; Munn, 1993; Bardan, 1993). The design of devices that utilize photons instead of electrons has created a need for new materials with unique nonlinear properties. Organic materials show a good efficiency of second harmonic generation. But most of the organic NLO crystals have poor mechanical and thermal stability. In order to increase the mechanical strength and thermal stability, organic compounds were added with inorganic compounds. L-cysteine was the simplest form of amino acid which reacts with other inorganic compounds to give a good mechanical and thermal stability. Amino acids were interesting organic materials for NLO applications as they contain donor carboxylic acid (COOH) group and the proton acceptor amino (NH2) group in them, known as zwitterions, which create hydrogen bonds, in the form of N–H+—O–C, which were very strong bonds. Hydrogen bonds have also been used in the possible generation of non-centrosymmetric structures, which was a prerequisite for an effective NLO crystal (Frankenbach, 1992). In the present investigation we report bulk growth, optical, mechanical and dielectric properties of L-cysteine Borate Decahydrate (LCBD) single crystals.

2. GROWTH OF LCB

L-cysteine Borate Decahydrate (LCBD) single crystal was formed in water solution containing L-cysteine and disodium tetraborate decahydrate in molar ratio 1:2 at room temperature. Calculated amount of reactants were thoroughly dissolved in water and stirred well by using magnetic stirrer to ensure homogeneous solution. The solution was then filtered using filter paper and transferred to a Petri dish. The prepared solution was allowed to evaporate at room temperature. The growth was initiated following the nucleation kinetics due to slow evaporation of the solvent. The quality of the crystal was improved by recrystallization process. After a period of 30 days, good quality of the crystal was harvested with more transparency. The grown crystal was shown in figure 1.

3. RESULTS AND DISCUSSION

3.1. Microhardness Study: Hardness was a physicochemical property that characterizes the state of the material under test and gives information on some specific features of the material such as the character of the chemical bonding. It was the resistance which the material offers to indentation by a much harder body and may be termed as a measure of the resistance against lattice destruction or permanent deformation or damage. As the hardness properties were basically related to the crystal structure of the material and the bond strength, microhardness studies have been applied to understand the plasticity of the crystals. Hardness tests were commonly carried out to determine the mechanical strength of materials and it correlates with other mechanical properties like elastic constants and yield stress (Taber, 1951). Hardness measurements can be defined as macro, micro and nano according to the forces applied and displacement obtained (Pethica, 1979). Vickers hardness method was the reliable and most common among the various methods of hardness measurement discussed above. In this method, micro indentation was made on the surface of a specimen with the help of diamond pyramidal indenter. Smith, 1923; have proposed that a pyramid be substituted for a ball in order to provide geometrical similitude under different values of load. The Vickers pyramid indenter where opposite faces contain an angle (α = 136°) was the most widely accepted pyramid indenter. A pyramid indenter was suited for hardness tests due to the following reasons (Batta Calleja, 1980): 1) The contact

pressure for a pyramid indenter is independent of indent size and 2) Pyramid indenters were less affected by elastic release than other indenters.

The base of the Vickers pyramid was a square and the depth of indentation corresponds to $(1/7)^{th}$ of the indentation diagonal. Hardness was generally defined as the ratio of the load applied to the surface area of the indentation. The Vickers hardness number Hv of Diamond Pyramid Number (DPN) was defined as

$$H_v = \frac{2p\,\sin(\alpha/2)}{d^2} \qquad (1)$$

Where "α" is the apex angle of the indenter (α = 136˚). The Vickers hardness number was thus calculated using the relation,

$$H_v = \frac{1.8544}{d^2}\,Kg/mm^2 \qquad (2)$$

Where "p" is the applied load in "kg" and "d" is the diagonal length of the indentation mark in "mm". Hardness values were always measured from the observed size of the impression remaining after a loaded indenter has penetrated and has been removed from the surface. Thus, the observed hardness behaviour was the summation of a number of effects involved in the materials response to the indentation pressure during loading, in the final measurement of the residual impression. The importance of microhardness study lies in the possibilities of making an indirect estimate of mechanical characteristics of materials such as yield strength and toughness having a specific correlation with the hardness. The hardness measurements may depend upon the orientation of the indented crystals. To study the hardness anisotropy present in crystals, the crystals were initially mounted on the stage of microscope properly and indented. The initial position is 0 degree. The stage of the microscope was then rotated keeping the indenter fixed and "Hv" was measured at every 30 degrees interval till the original position. No distortion in shape of indenter will be observed with crystal orientation. When the variation of "Hv" with angular displacement was periodic, then it brings the anisotropic nature of crystals. In the present work, microhardness measurement was a general microprobe technique for assessing the bond strength, apart being a measure of bulk strength. The crystal slices were well polished with a thickness variation less than 10 μm to avoid the surface defects, which influence the hardness value strongly. Micro hardness studies were carried out at room temperature using Shimadzu HMV-2000 fitted with Vickers pyramidal indenter. The load P was varied between 10 - 50 g and the time of indentation was kept constant as 15 seconds for all trials. The diagonal lengths of indentation were measured. The variation of hardness with applied load was shown in figure 2.

The relation between log P and log d was given by Meyer's law and it was the simplest way to explain the ISE (Indentation Size Effect).

$$P = A\,d^n \qquad (3)$$

where A is a constant, P is the applied load and d is the diagonal length and the exponent 'n' is called Meyer number (or) Meyer index. Meyer index can be calculated by doing least square fit in the graph of log P versus log d shown in figure 3. According to Meyer's law, for normal ISE behavior n < 1.6, for reverse ISE behavior n > 1.6 and when n = 1.6 the hardness was independent of the test load. In the present investigation the value of n was found to be 1.93 and shows reverse ISE. If n > 1.6 then those material belongs to soft category (Onitsch, 1950; Hanneman 1941). Hence it was concluded that LCBD crystal is a soft material category.

3.2. Dielectric study: Dielectric measurement was one of the useful characterizations of electrical response of solids. A study of the dielectric properties of solids gives information about the electric field distribution within the solid. The frequency dependence of these properties gives a great insight into the materials applications. The different polarization mechanisms in solids can be understood from the study of dielectric constant as a function of frequency and temperature. Polarization "P" of a dielectric was the numerical magnitude, which describes the phenomenon of polarization of a dielectric in an external electric field. In the absence of an external electric field, each element in the volume of a dielectric has no electric moment. The action of an electric field brings the charges of the molecules of the dielectric into a certain ordered arrangement in space. The study of dielectric constant of a material gives an insight into the nature of bonding in the material. The study of the electrical and other properties of dielectrics in relation to their chemical composition and structure will lay the basis for obtaining new materials with new properties. A lot of work had been carried out on dielectric measurement for a variety of materials including ceramics and single crystals by many authors yielding valuable information (Matthias, 1951; Triebwasser, 1959; Govinda, 1975). The relative dielectric constant (ε_r) was defined as,

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_o} \qquad (4)$$

It was known that,

$$\varepsilon = \frac{Cd}{A} \qquad\qquad (5)$$

Hence,

$$C = \frac{\varepsilon_o \varepsilon_r A}{d} \qquad\qquad (6)$$

Where, 'A' is the area of the sample and 'd' is the thickness of the sample. The relative permittivity (ε_r) was usually known as permittivity. It was always greater than unity. The capacitance 'C_o' of a parallel plate condenser having a capacitance 'C' in air can be given by,

$$C = \varepsilon_r C_o \qquad\qquad (7)$$

Thus,

$$\varepsilon_r = \frac{C}{C_o} \qquad\qquad (8)$$

'ε_r' can be found by the measurement of capacitance. The dielectric constant of a substance was a property of the constituent ions. Major contributions to the dielectric constant were from,

1) The extrinsic nature of the material, 2) The electronic polarizability, 3) The ionic polarizability and 4) The deformation of the ions.

In the present work, the dielectric characteristics of the material were important to study the lattice dynamics in the crystal. Hence, the grown LCBD crystal was subjected to these studies using a HIOKI HITESTER model 3532-50 LCR meter in the frequency range from 50 Hz to 5 MHz for different temperatures. The surface of the sample was coated with silver paste for electrical contact. Figure 4 shows the plot of dielectric constant versus log frequency of the grown LCBD crystal.

The dielectric constant has high values in the lower frequency region and then it decreases with the increase in frequency. The very high value of dielectric constant at low frequencies may be due to the presence of all the four polarizations, namely, space charge, orientational, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of these significant polarizations gradually. From the plot, it was also observed that dielectric constant increases with an increase in temperature and this was attributed to the presence of space charge polarization near the grain boundary interfaces, which depends on the purity and perfection of the sample (Smyth, 1965). The variations of dielectric loss with frequency of the grown LCBD crystal was shown in figure 5. The characteristics of low dielectric loss with high frequency for the sample suggest that it possesses enhanced optical quality with lesser defects and this parameter was of vital importance for nonlinear optical applications (Balarew, 1984). This behaviour was useful for the fabrication of microelectronic and nonlinear optical devices.

3.3. Photoconductivity study: Photoconductivity studies have been carried out using the Keithley 485 picoammeter instrument. The dark current was recorded by keeping the crystal unexposed to any radiation. Figure 6 shows the variation of both the dark current and photocurrent with applied field at different levels of illumination for LCBD crystal. The required current was noted for varying applied fields. It was seen from the plots that both dark current and photocurrent of the sample increase linearly with the applied field. The dark current was seen to be higher than the photocurrent for the same applied field, which was termed as negative photoconductivity. The negative photoconductivity exhibited by the sample may be due to the reduction in the number of charge carriers in the presence of radiation. The decrease in the mobile charge carriers during negative photoconductivity can be explained by the Stockmann model (Joshi, 1990). The negative photoconductivity in a solid was due to the decrease in the number of charge carriers or their lifetime, in the presence of radiation (Bube, 1981). For a negative photoconductor, the forbidden gap holds two energy levels in which one was placed between the Fermi level and the conduction band while the other was located close to the valence band. The second state has a higher capture cross-section for electrons and holes. As it captures electrons from the conduction band and holes from the valence band, the number of charge carriers in the conduction band gets reduced and the current decreases in the presence of radiation.

4. CONCLUSION

The single crystal of L-cysteine Borate Decahydrate (LCBD) has been grown by slow evaporation technique. The grown LCBD crystal was a relatively soft material from the investigations of microhardness. The dielectric constant and dielectric loss have been studied as a function of frequency at different temperatures. The characteristics of low dielectric loss for the sample suggest that it possesses enhanced optical quality with lesser defects and this parameter was of vital significance for nonlinear optical applications. Photoconductivity investigations reveal the

negative photoconducting nature of the title material. However, this material can be used in photonic and optoelectronic devices which have more stability.

REFERENCES

Balarew C, Duhlew R, Application of the Hard and Soft Acids and Bases Concept to Explain Ligand Coordination in Double Salt Structures, Journal of Solid State Chemistry, 55, 1984, 1-6. http://dx.doi.org/10.1016/0022-4596(84)90240-8

Bardan J, Hierle R, Perigaud A, Zyss J, Williams DJ, Nonlinear Optical Properties of Organic Molecules and Polymeric Materials, Vol. 223 of ACS Series. American Chemical Society, Washington, 1993.

Batta Calleja FJ, Rueda DR, Poster RS, Mead WT, New Aspects of the Microhardness of Ultra Oriented Polyethiline, Journal of Material Science, 15, 1980, 762-765.

Bube RH, Photoconductivity of solids, Wiley, Newyork, 1981.

Frankenbach GM, Etter MC, Chemistry of Materials, 4, 1992, 272-278. http://dx.doi.org/10.1039/CS9942300283

Govinda S, Rao KV, Dielectric Properties of Single Crystals of Al2O3 and Al2O3 Doped with Chromium and Vanadium, Physica Status Solidi (A), 27, 1975, 639-644. http://dx.doi.org/10.1002/pssa.2210270237

Hanneman M, Metall Manchu, 23, 1941, 135.

Joshi VN, Photoconductivity, Marcel Deckker, Newyork, 1990.

Matthias BT, Remeika JP, Dielectric Properties of Sodium and Potassium Niobate, Physical Review, 82, 1951, 727-729. http://dx.doi.org/10.1103/PhysRev.82.727

Munn RW, C.N. Ironside, Principles and Applications of Nonlinear Optical Materials. Chapman and Hall, London, 1993. http://dx.doi.org/10.1007/978-94-011-2158-3

Onitsch E M, Microscope, 95, 1950, 12.

Pethica JB, Taber D, Contact of Characterized Metal Surface at Very Low Loads: Deformation and Adhesion, Surface Science, 89, 182-190 (1979). http://dx.doi.org/10.1016/0039-6028(79)90606-X

Prasad PN, Williams DJ, Introduction to Nonlinear Optical Effects in Molecules and Polymers. John Wiley & Sons, Newyork, 1991.

Smith RL, Sandland GE, An Accurate Method of Determining the Hardness of Metals with Reference to those of a High Degree of Hardness, Proceedings of the Institution of Mechanical Engineers, 1, 1923, 623-641.

Smyth CP, Dielectric Behavior and Structure, McGraw-Hill, Newyork, 1965.

Taber D, The Hardness of Materials, Clarendon Press, Oxford, 1951.

Triebwasser S, Study of Ferroelectric Transitions of Solid-Solution Single Crystals of KNbO3-KTaO3, Physical Review, 114, 1959, 63-70. http://dx.doi.org/10.1103/PhysRev.114.63