Techniques and tools used for investigating the grown crystals: A review

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Abstract

The paper deals with the description of the experimental techniques employed in the characterisation of grown crystals. Apart from this, the other salient instrumentations discussed are the single crystal X-ray diffraction, thermal analyses such as TGA and DTA, Vickers hardness tester, dielectric, photoconductivity and AC/DC electrical conductivity experimental setups. These techniques have been employed for characterizing the grown crystals.

Keywords: Single crystal XRD, TGA and DTA, Vickers hardness test, Dielectric and Photoconductivity techniques.

Resumen

El trabajo estudia las diferentes técnicas, instrumentación y aplicaciones de la espectroscopia para estudiar el cristal. Aparte de esto, las otras instrumentaciones salientes discutidas son el cristal único de difracción de rayos X, análisis térmicos tales como TGA y DTA, probadores de dureza Vickers, dieléctrico, fotoconductividad y ac/dc configuraciones de conductividad. Estas técnicas han sido empleadas para la caracterización de los cristales activos NLO.

Palabras clave: Cristal único XRD, TGA y DTA, probador de dureza Vickers, dieléctricas y fotoconductividad.

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I. INTRODUCTION

An assessment technique to decide the perfection of the grown crystals is required to make rapid progress in the growth process and to improve the quality of the crystal. Post growth analysis of a crystal provides information on the process that occurred during growth. Consequently, the improvement in crystal growth can be followed from an early stage in the growth process and the route to perfection can be planned more efficiently. Characterization of a material can be defined as a complete description of its physical and chemical properties. A thorough and extensive characterization of a single crystal is very difficult, because it requires a variety of tests using a number of sophisticated instruments, an accurate analysis of the results of these tests and their confirmation. The use of instrumentation is an exciting and fascinating part of any analysis that interacts with all the areas of chemistry and with many other fields of pure and applied science. Analyses of Martian soils, the body fluids of racehorses and Olympic athletes, the engine oil of commercial and military jet aircraft, are examples of problems that require instrumental techniques. In most cases of chemical analysis, a signal is produced which reflects the chemical or physical property of a chemical system. Moreover, characterization of the grown crystals forms an integral part of the growth studies to be performed by the crystal grower. The characterization of a crystal essentially consists of an evaluation of the chemical composition, structure, defects and the study of their optical properties. The study of growth defects includes the defects such as inclusions, mechanical stress etc. The study of optical transmission and absorption of the crystal, FTIR, Kurtz powder method for SHG conversion efficiency, NLO coefficients, electro-optics coefficients and structural dependence of these properties leads to the complete understanding of the optical behaviour of the crystal.

- Crystal structure analysis by single crystal XRD using Enraf Nonius CAD4-F Diffractometer.
- Powder X-ray Analysis using STOE Model Powder X-ray diffarctometer.
- FT-IR analysis using BRUKER IFS 66V FT-IR spectrometer.
- UV spectral study to determine the transparency range using VARIAN CARRY 5E spectrophotometer.
- Kurtz powder technique employing Q-switched mode lock Nd: YAG laser to confirm NLO property.
- Study of thermal behaviour of the grown crystals using TG-DTG and DTA techniques.
- Study of microhardness of the crystals using Vickers hardness tester.

- Measurement of dielectric constant and dielectric loss studies of the grown crystals using HIOKI 3532-50 LCR HITESTER.
- Temperature dependent AC conductivity study using HIOKI 3532-50 LCR HITESTER.
- Photoconductivity study of the grown crystals using Keithley 485 Picoammeter.

II. SINGLE CRYSTAL X-RAY DIFFRACTION ANALYSIS

Single crystal X-ray diffraction is an analytical technique in which X-rays are employed to determine the actual arrangement of atoms within a crystalline specimen. Single crystal X-ray diffraction (XRD) is a non-destructive tool to analyze crystal structure of compounds, which can be grown as single crystals. XRD is employed for finding unit cell parameters, space groups, three-dimensional co-ordinates of atoms in the unit cell and mean thermal motion amplitudes of atoms in the unit cell. Single crystal X-ray diffractometer (Fig. 1) collects intensity data required for structure determination. Accurate measurements of intensities of reflections of all Miller indices within a specified reciprocal radius (usually 25°for MoK_α and 68° for CuK_α) is needed to find the structure, while unit cell parameters depend only on direction of reflections. For single-crystal work, the specimen should be smaller than cross section diameter of the beam. Larger crystals can be cut down to proper smaller crystals that contain strong diffracting elements. The single crystal X-ray diffraction analysis was performed using an Enraf Nonius CAD4-F single crystal X-ray diffractometer. The shield was equipped with graphite monochromated MoK_α radiation.

FIGURE 1. Instrumental Setup of Enraf Nonius CAD4-F Diffractometer.

Since the crystal was transparent, the single crystallinity was studied with Leica polarizing microscope. Single crystal of suitable size was cut and mounted on the X-ray goniometer. The crystal was optically centered at the sphere of confusion using the built in tele microscope. Twenty five reflections were collected from different zones of the reciprocal lattice using random search procedure. The reflections were indexed using method of short vectors followed by least square refinements. The unit cell parameters thus obtained were transformed to correct Bravais lattice.

III. POWDER X-RAY DIFFRACTION

Powder diffraction is a scientific technique using X-ray or neutron diffraction on powder or microcrystalline samples for structural characterization of materials. Ideally every possible crystalline orientation is represented equally in the sample, leading to smooth diffraction rings around the beam axis rather than the discrete Laue spots observed for single crystal diffraction. In accordance with Bragg's law each ring corresponds to a particular vector in the sample crystal with intensity proportional to the number of such planes. The machine used to perform such measurements is called a powder diffractometer.

IV. FOURIER TRANSFORM INFRARED (FT-IR) ANALYSIS

A. Introduction

Fourier Transform Spectroscopy is a simple mathematical technique to resolve a complex wave into its frequency components. The conventional IR spectrometers are not of much use for the far IR region, as the sources are weak and the detectors are insensitive. FT-IR has made this energy-limited region more accessible. It has also made the mid–infrared ($4000\text{-}400cm^{-1}$) more useful. In the Fourier transform spectrometer, a time domain plot is converted into a frequency domain spectrum. The actual calculation of the Fourier transform of such systems is done by means of high – speed computers.

B. Experimental setup

The FT-IR spectrometer consists of an infrared source, a sample chamber with a provision for holding solids, liquids and gases, monochromator, a detector and a recorder, which are integrated with a computer. At present, all commercially available infrared spectrophotometers employ reflection gratings rather than prisms as dispersing elements. Interferometric multiplex instruments employing the Fourier transform are now finding more general applications in both qualitative and quantitative infrared measurements. The interference pattern is obtained from a two–beam interferometer, as the path difference between the two beams is altered, then Fourier transformed output gives rise to the spectrum. The schematic diagram of a FT-IR spectrometer is shown in Fig. 2. Solid samples are dispersed in KBr or polyethylene pellets depending on the region of interest. This instrument has resolution of $0.1cm^{-1}$. Signal averaging, signal enhancement, baseline correction and other spectra manipulations are possible with multitasking OPUS software on the dedicated PC/AT 486. Spectra are plotted on a HP plotter and data can be printed. Recording of IR spectra of solid sample is more difficult because the particles reflect and scatter the incident radiation and therefore transmittance is always low. A few milligrams of the sample are ground together in an agate or mullite mortar with about 100 times the quantity of a material (KBr) transparent to the infrared. The grounded powder is palletized in proper form suitable for IR transmission work.

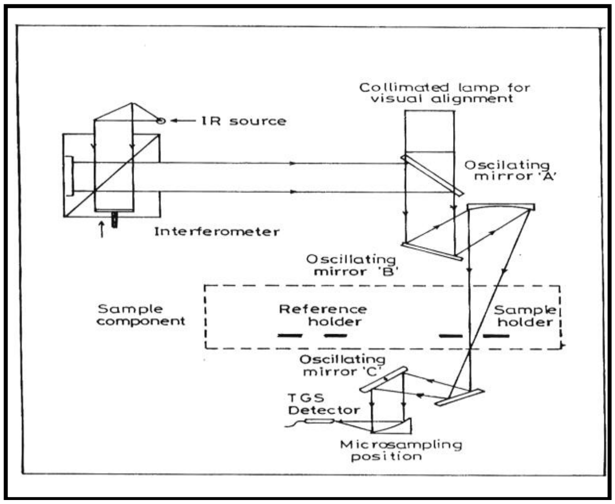

FIGURE 2. Schematic diagram of a FT-IR spectrometer.

V. UV-Vis-NIR SPECTROSCOPY

The experimental arrangement of Varian Cary 5E UV-Vis-NIR Spectrophotometer is shown in Fig. 3. UV-Vis-NIR spectroscopy might be defined as the measurement of the absorption or emission of radiation associated with changes in the spatial distribution of electrons in atoms and molecules. In practice, the electrons involved are usually the outer valence or bonding electrons, which can be excited by the absorption of UV or visible or near IR radiation.

A. Electronic energy levels and electronic transitions

Absorption of ultraviolet radiation by a molecule leads to electronic excitation among various energy levels within the molecule. The transitions generally occur in between a bonding or lone-pair orbital and an unoccupied non-bonding or anti-bonding orbital. The σ orbitals, involved in forming σ bonds, are the lowest energy occupied molecular orbitals. The π-orbitals lie at somewhat higher energy and the orbitals holding the unshared electron pairs (non-bonding orbitals) lie at even higher energy levels than the π-orbitals. The unoccupied or anti-bonding orbitals (π^* and σ^*) are the orbitals of highest energy. The probability for electronic transitions determines the intensity of spectral lines. There must be large overlap between the vibrational states in the initial and the final electronic states to have a large absorption cross-section, or high probability that the molecule will absorb/emit radiation. Electronic transitions are possible for a wide range of vibrational levels within the initial and final electronic states. Saturated hydrocarbons and compounds containing only alkyl groups, alcohol groups and ether groups are transparent in the region 200-1000nm. Such compounds are useful as solvents for making solutions of the specimen to study in this region. An isolated functional group not in conjugation with any other group is said to be a chromophore if it exhibits absorption of a characteristic nature in the ultraviolet or visible region. If a series of compounds has the same functional group and no complicating factors are present, all of them will generally absorb at very nearly the same wavelength. Thus, it is readily seen that the spectrum of a compound, when correlated with data from the literature for known compounds, can be a very valuable aid in determining the functional groups present in the molecule.

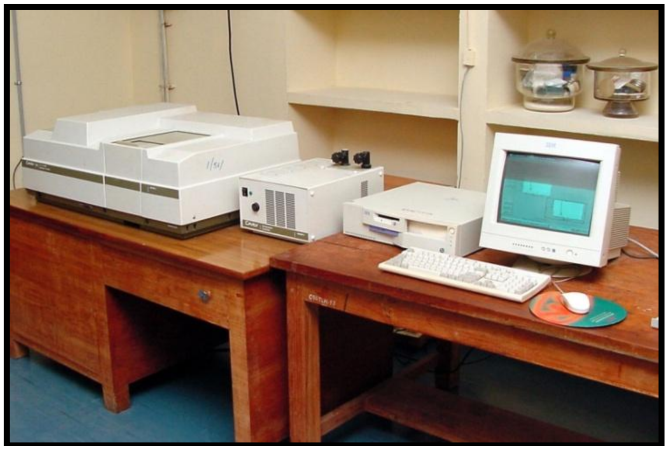

FIGURE 3. Experimental arrangement of Varian Cary 5E UV-Vis-NIR Spectrophotometer.

VI. NLO TEST – KURTZ POWDER SHG METHOD

A. Introduction

Recent interest is focused on to find the materials which have suitable nonlinear optical properties for use as the active media in efficient second harmonic generators, tunable parametric oscillators and broadband electro-optic modulators. Kurtz and Perry [1] proposed a powder SHG method for comprehensive analysis of the second order nonlinearity. Employing this technique, Kurtz [2] surveyed a very large number of compounds.

B. Experimental setup

The nonlinear optical property of the single crystals can be tested by passing the output of Nd:YAG Quanta ray laser. The schematic of the experimental setup used for SHG studies is shown in the Fig. 4. A Q-switched, mode locked Nd:YAG laser was used to generate about 6mJ/pulse at the 1064nm fundamental radiation. This laser can be operated in two modes. In the single shot mode the laser emits a single 8ns pulse.

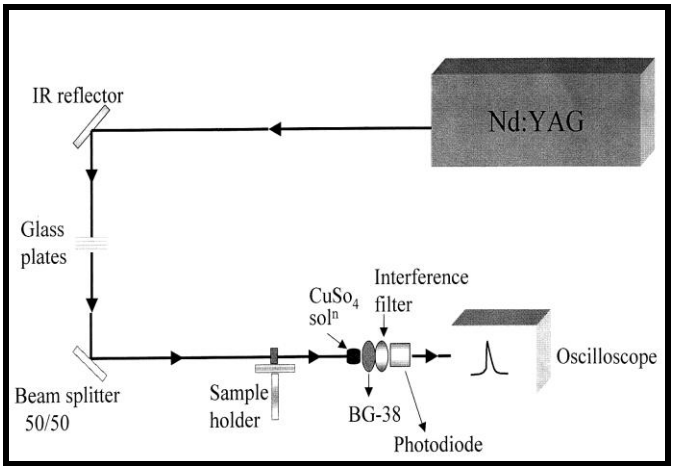

FIGURE 4. Schematic experimental setup for SHG efficiency measurement.

In the multi shot mode the laser produces a continuous train of 8ns pulses at a repetition rate of 10Hz. In the present study, a single shot mode of 8ns laser pulse with a spot radius of 1mm was used. This experimental setup used a mirror and a 50/50 beam splitter (BS) to generate a beam with pulse energies about 6.2mJ. The input laser beam was passed through an IR reflector and then directed on the micro crystalline powdered sample packed in a capillary tube of a diameter 0.154mm. The light emitted by the sample was measured by the photodiode detector and oscilloscope assembly.

VII. THERMAL STUDIES

A. Introduction

Recent trends indicate that thermal analysis has become an established method in the study of the thermal behaviour of materials and finds widespread applications in diverse industrial and research fields. Thermal analysis is a general term, which covers a group of related techniques in which the temperature dependence of the parameters of any physical property of a substance is measured. Thermal studies not only provide valuable information on the thermal stability of the compounds and the decompositions products but also provide an insight into their mode of decomposition.

B. Thermoanalytical methods

Thermoanalytical methods involve the measurement of various properties of materials subjected to dynamically changing environments under predetermined conditions of heating rate, temperature range and gaseous atmosphere or vacuum. Among the thermal methods, the most widely used techniques are TG, DTA and DSC which find extensive use in all fields of inorganic and organic chemistry, metallurgy, mineralogy and many other areas. In many cases, the use of a single Thermoanalytical technique may not provide sufficient information to solve the problem on hand and hence the use of other thermal techniques, either independently or simultaneously for complementary information becomes necessary. For example, both differential thermal analysis (DTA) and thermogravimetry (TG) are widely used in studies involving physicochemical changes accompanied by variation in the heat content and the weight of the material.

C. Differential thermal analysis

Differential thermal analysis (DTA) though, often considered an adjunct to TG is, in fact, far more versatile and yields data of a considerably more fundamental nature. The technique is simple as it involves the measurement of the temperature difference between the sample and an inert reference materials, as both are subjected to identical thermal regimes, in an environment heated or cooled at a constant rate. The origin of the temperature difference in the sample lies in the energy difference between the products and the reactants or between the two phases of a substance. This energy difference is manifested as enthalpic changes- either exothermic or endothermic. The differential thermal curve would be parallel to the temperature (time) axis till the sample undergoes any physical or chemical change of state. However, as soon as the sample has reached the temperature of this change of state, the additional heat flux reaching the sample will not increase the sample temperature at the same rate as that of the reference and the differential signal appear as a peak. The differential signal would return to the base line only after the change of state of the sample is completed and the temperature becomes equal to that of the reference material. The thermal effects are observed as peaks whose sequence, sign (endothermic or exothermic), magnitude and shape reflect the physical or chemical changes that take place. Since any change in the chemical or physical state of a substance is accompanied by changes in energy which are manifested as heat changes, the DTA method is applicable to all the studies listed for TG and also to phase transformations including polymerization, phase equilibria and chemical reactions.

C.1. Instrumentation

The DTA apparatus consists of a furnace for heating the sample and reference in an identical environment, linear temperature-programmer controller, sample holder, differential temperature detector with preamplifier and a recorder.

D. Thermogravimetry

Thermogravimetry is a technique in which the mass of a substance is measured as a function of temperature or time while the substance is subjected to a controlled temperature program. The curve obtained in a thermogravimetric analysis is called a thermogram (TG) and its first derivative is called a derivative thermogram (DTG).

D.1. Instrumentation

Modern commercial TG instrument consists of

- A sensitive analytical balance.
- A temperature programmable furnace.
- A purge gas system for providing suitable gas atmosphere.
- A microprocessor for instrument control, data acquisition and display.

The null–point weighing mechanism is employed since the sample remains in the same zone of furnace irrespective of changes in mass. The furnace is normally an electrical resistive heater and the temperature range for most of the furnace is from ambient to 1000–2000°C. The rate of heat exchange between the furnace and the sample depends upon the heating rate which influences the TG curve in a number of ways. A slower rate gives a better resolution of the closely lying steps, while the faster heating rate merges such steps. One of the objectives of TG and DTA is to delineate as accurately as possible the various temperatures associated with the thermal behaviour of a given substance, *i.e.*, temperature of decomposition, stability range of an intermediate compound and the temperature at which the reaction is complete.

VIII. MICROHARDNESS STUDIES

Hardness is an important factor in the choice of ceramics for abrasives, bearings, tool bits, wear resistance coatings etc. Hardness is a measure of resistance against lattice destruction or the resistance offered to permanent deformation or damage measurement of hardness is a non-destructive testing method to determine the mechanical behaviour of the materials. As pointed out by Shaw [3], the term hardness is having different meanings to different people depending upon their area of interest. For example, it is the resistance to penetration to a metallurgist, the resistance to cutting to a machinist, the resistance to wear and tear to a lubrication engineer and a measure of flow of stress to a design engineer. All these actions are related to the plastic stress of the material. For hard and brittle materials, the hardness test has proved to be a valuable technique in the general study of plastic deformation [4].

The hardness depends not only on the properties of the materials under test but also largely on the conditions of measurement. Microhardness tests have been applied to fine components of clock and instrument mechanisms, thin metal strip, foils, wires, metallic fibers, thin galvanic coatings, artificial oxide films, etc., as well as the thin surface layers of metals which change their properties as a result of mechanical treatment (Machining), rolling, friction and other effects. The microhardness method is widely used for studying the individual structural constituent elements of metallic alloys, minerals, glasses, enamels and artificial abrasives.

A. Methods of Hardness Test

Hardness of a material can be measured by

i. Static indentation test.
ii. Dynamic indentation test.
iii. Scratch test.
iv. Rebound test.
v. Abrasion test.

In static indentation test, a steady load is applied to an indentor which may be in the form of hardened steel ball or diamond pyramid. After making a clear impression on the material, the hardness is calculated from the area or depth of indentation produced. The indentor is made from a very hard material so as to prevent its deformation by the test material. In this test, the indentor is pressed perpendicularly into the surface of the test sample by means of an applied load. Using the data of the applied load and cross-sectional area or depth of the indentation, an empirical hardness number can be calculated. This method is followed in Breinell, Meyer, Vickers, Knoop and Rockwell tests [5, 6, 7]. The microhardness measurements were carried out using Vickers hardness method and the details are outlined below.

B. Vickers test

Vickers test is said to be a more reliable method of hardness measurement. In order to get similar geometrical impression under varying loads, Smith and Sand land [8] have suggested that a pyramid be substituted for a ball. The Vickers hardness test method consists of indenting the test material with a diamond indentor, in the form of a right pyramid with a square base and an angle of 136° between opposite faces subjected to a load of 1 to 100kg (Fig. 5). The base of the Vickers pyramid is a square and the depth of indentation corresponds to $1/7^{th}$ of the indentation diagonal. The longitudinal and transverse diagonals will be in the ratio 7:1. The full load was normally applied for 10 to 15 seconds. The two diagonals of the indentation left in the surface of the material after removal of the load were measured using a microscope and their average was calculated. The area of the sloping surface of the indentation was calculated.

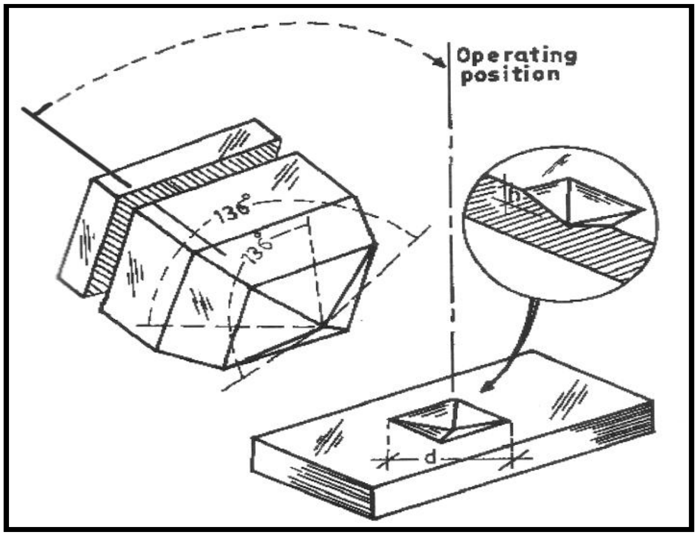

FIGURE 5. Vickers hardness test.

The Vickers hardness is the quotient obtained by dividing the kg load by the square mm area of indentation.

$$H_V = \frac{2p\sin\frac{136}{2}}{d^2}$$

$$= 1.852\frac{P}{d^2}\, kg/mm^2 or MPa, \qquad (1)$$

where H_V = Vickers hardness number
P = load in kg.
d = arithmetic mean of the two diagonals.

When the mean diagonal of the indentation has been determined, the Vickers hardness number can be calculated from the above formula. Several different loading settings give practically identical hardness numbers on uniform material, which is much better than the arbitrary changing of scale with the other hardness testing methods. The advantages of the Vickers hardness test are that extremely accurate readings can be taken, and just one type of indentor is used for all types of metals and surface treatments.

C. Correlation of microhardness with other properties

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 correlation of the indentation hardness with other physical properties has been investigated by several workers. Even though the mechanism of deformation during indentation is clearly not understood, hardness testing provides useful information concerning the mechanical behaviour of solids. As an example, the hardness H_V is related to the yield stress (Y in kg/mm^2) by

$$H_V = 2.8Y \qquad (2)$$

It is found experimentally (Wyatt and Dew Hughes 1974) [3] that the best fit is given by

$$H_V = 3Y \qquad (3)$$

Based on the analysis of results of hardness, Kick suggested the relation between applied load P and indentation length d as

$$P = Kd^n \qquad (4)$$

where K and ‘n’ are constants for a given material. Further, Kick’s analysis for hardness, postulated a constant value of n = 2 for all indentors and for all geometrically similar impression. However, one of the drawbacks in the relation is that n usually has a value less than 2, particularly in the low load region and hence the relation has not received complete acceptance. If n is less than 2, the hardness number increases with decreasing load, and if n is greater than 2, it decreases with decreasing load. The constant n is usually called as work hardening coefficient. The value of n can be determined from the slope of the log p versus log d plot.

IX. DIELECTRIC STUDIES

The useful method of characterization of electrical response is the dielectric measurement. A study of the dielectric properties of solids gives an electric field distribution within solid. The frequency dependence of these properties gives great insight into the materials applications. The range of measurement depends on the properties and the materials of interest. From a study of dielectric constant as a function of frequency, temperature etc., the different polarization mechanism in solids such as atomic polarization of the dipoles, space charge polarization etc., can be understood.

A. Experimental

Suitably cut and polished samples (with known dimensions) are subjected to dielectric studies using HIOKI 3532-50 HITESTER LCR meter (Fig. 6) with a conventional four terminal sample holder for investigations involving temperature variations and a conventional two terminal sample holder (Westphal) for only ambient conditions. The samples are prepared and mounted between the copper platforms and electrodes. In order to ensure good electrical contract between the crystal and the ensure that the silver paint does not spread to the sides of the crystal. The capacitance and the dissipation factor of the parallel plate capacitor formed by the copper plate and electrode having the sample as a dielectric medium are measured. The dielectric constant and dielectric loss are calculated using the Eqs.5 and 8 respectively. The measurements are made at frequencies ranging from 50Hz to 5MHz.

B. Dielectric constant

One of the most important parameters widely used is the relative dielectric constant or relative permittivity [9]. The dielectric constant of a material may be defined as the ratio of the field strength in vacuum to that in the material for the same distribution of charge. The dielectric constant of a substance is a property of the constituent ions.

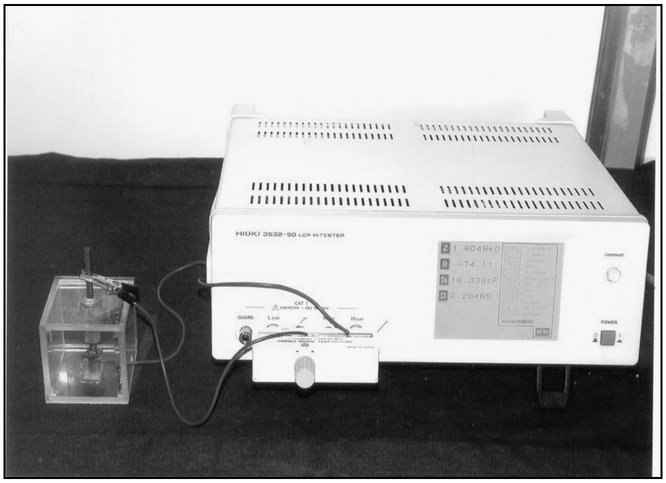

FIGURE 6. Photograph of HIOKI 3532-50 LCR HITESTER.

In general, if electrode effects are neglected the four major components contributing to the dielectric constant are:

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

The relative dielectric constant or relative permittivity can be defined as,

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}. \tag{5}$$

We know that

$$\varepsilon = \frac{Cd}{A}. \tag{6}$$

Thus we have

$$C = \varepsilon_r \varepsilon_0 A/d\,, \tag{7}$$

where A is the area of the sample, d is the thickness of the sample. The relative permittivity (ε_r) is usually known as dielectric constant. It is always greater than unity. Suppose a parallel plate condenser has a capacitance of C_0 in air then its capacitance when the space between the plates is filled by a medium of dielectric constant ε_r is given by,

$$C = \varepsilon_r C_0\,, \tag{8}$$

ε_r can be found out from the measurement of capacitance. The dielectric constant in any direction of the medium can be considered as a measure of electrostatic binding strength between the ions in the direction. The higher the dielectric constant, the lower the electrostatic binding and hence higher is the lattice energy.

C. Dielectric loss

When a dielectric is subjected to an alternating electric field, the electric field strength changes as,

$$E = E_0 \cos \omega t\,. \tag{9}$$

The induced current in the dielectrics does not change exactly with the applied voltage. The current is found to lead the potential in phase. In a similar way the electrical displacement is also not in phase with respect to E.

Now the expression for D becomes,

$$D = D_0 \cos(\omega t - \delta)$$

$$D = D_0 \cos \omega t \cos \delta + D_0 \sin \omega t \sin \delta\,. \tag{10}$$

The factor sin δ is a measure of the energy absorbed by dielectrics. It is known that in a capacitor the dielectrics usually have a resistance R and impedance Z that are related to the phase angle. Assuming R to be very large,

$$\sin \delta \approx \tan \delta = 1/\omega RC\,. \tag{11}$$

The factor tan δ is referred to as the dielectric loss.

D. Dielectric constant and alternating fields

When measured in alternating electric fields, the dielectric constant is found as a function of frequency. This is due to the different response times of the permanent dipoles (if any), ions and/or electrons towards the applied alternating field.

As a consequence, with increasing frequency, the dielectric constant decreases in steps. At high enough frequencies, only the electronic polarisability contributes to the polarization and hence, the dielectric constant attains a constant, but small value.

At this stage, the (high frequency) dielectric constant becomes equal to the square of the refractive index of the material. Considerable work had been carried out on dielectric measurements including ceramics and single crystals by several authors yielding valuable information [10, 11, 12, 13, 14, 15, 16].

The dielectric constant is extremely low for low concentration of thiourea doped KDP, in comparison of higher concentration thiourea doped KDP. This provides an added advantage for high frequency modulation [17]. L-alanine acetate was found to show low dielectric constant, due to less number of dipoles per unit volume; as a result it had minimum loss as compared to the material having high dielectric constant [18]. Crystals with high dielectric constant led to power dissipation [19].

In the temperature range 30 < T < 160°C, the dielectric constant of holmium tartrate trihydrate is practically temperature independent, other tartrate salts also have been reported to shows this type of behavior [20, 21] but the occurrence of the peak at 250 °C suggests a phase transition in holmium tartrate trihydrate crystal at 250°C [22]. Dielectric behavior of $HgCl_2$: 2KCl. H_2O single crystals along two different directions in the radio frequency region were measured [23]. The dielectric behavior of Mn-Zn ferrite was found to increase with sintering temperature due to the cooperation between rotational and orientational polarization [24]. The system $AgBr\text{-}PbI_2\text{-}Ag_2O\text{-}B_2O_3$ system behaves as a superionic conductor because of its high dielectric constant at higher temperature [25].

X. CONDUCTIVITY

Material's conductivity depends on its overall characteristics, such as its chemical composition, purity and crystal structure. Measurements taken with continuous currents provide only total conductivity. However, simultaneous information on conductivity and on the material's electrode interface effects can be partially offset by impedance measurements. Impedance measurements are a flexible tool for electrical characterization of materials. The compacted pellet (diameter 8mm) of the sample is dried at 100°C for a few hours before being used in the experiment. In the present study, electric ohmic contacts were made using air drying silver paint on the opposite faces. Electrical measurements were taken in the frequency range 20 Hz to 1MHz using HIOKI 3532-50 LCR HITESTER. A chromel-Alumel thermocouple was employed to record the sample temperature. A 30 minute interval was used prior to thermal stabilization after each measuring temperature. All the measurements were carried out in atmospheric air.

A. Principle and theory of AC conductivity

A capacitor when charged under AC voltage will have some loss current due to ohmic resistance or impedance by heat absorption. If Q be the charge in coulombs due to a potential difference of V volts between two plates of a condenser of area, A, and inter-plate distance d, then a.c. conductivity (σ_{ac}) due to a.c. voltage is given by the relation

$$\sigma_{ac} = \frac{J}{\vec{E}}. \qquad (12)$$

J is the current density and $\vec{E}$ is the electric field strength vector.

But the electric field vector, $\vec{E} = \vec{D}/\varepsilon$, where $\vec{D}$ is the displacement field vector of the dipole charges and ε is the complex permittivity of the material. For a parallel plate capacitor the electric field intensity ($\vec{E}$) is the ratio of potential difference between the plates of the capacitor to the inter-plate distance, *i.e*.

$$\vec{E} = V/d \qquad (13)$$

Since the current density $J = (1/A)dQ/dt$, where Q is given by

$$Q = V\varepsilon A/d$$

Therefore,

$$J = (1/A)dQ/dt = \frac{d(V\varepsilon/d)}{dt} = \varepsilon/d.dV/dt \qquad (14)$$

Therefore,

$$J = (\varepsilon/d)dV/dt \qquad (15)$$

Substituting for $\vec{E}$ and J in (12)

$$\sigma_{ac} = J/\vec{E} = \varepsilon j\omega$$

Since ε is a complex quantity

$$\sigma_{ac} = (\varepsilon' - j\varepsilon'')j\omega = \varepsilon' j\omega + \omega\varepsilon'' \qquad (16)$$

In order that the AC conductivity may be a real quantity, the term containing j has to be neglected. Hence,

$$\sigma_{ac} = \omega\varepsilon'' \qquad (17)$$

In any dielectric material, there will be power loss because of the work done to overcome the frictional damping forces encountered by the dipoles during their rotation. If an AC field is considered, then in an ideal case the charging current I_C will be 90° out of phase with the voltage. But in most of the capacitors due to the absorption of electrical energy some loss current, I_L will also be produced, which will be in phase with the voltage. Charging current, I_C, and loss current, I_L, will make angles δ and θ, respectively with the total current, I, passing through the capacitor. The loss current is represented by sinδ of the total current, I. Generally, sin δ is called the loss factor but when δ is small then sin δ = δ = tan δ. But the two components ε' and ε'' of the complex dielectric constant, ε, will be frequency dependent and is given by

$$\varepsilon'(\omega) = D_0 \cos\delta / \vec{E}_0 \qquad (18)$$

$$\varepsilon''(\omega) = D_0 \sin\delta / \vec{E}_0 \qquad (19)$$

Since the displacement vector in a time varying field will not be in phase with $\vec{E}$ there will be a phase difference δ between them. From (18) and (19), we have

$$\tan\delta = \varepsilon''(\omega)/\varepsilon'(\omega). \qquad (20)$$

Substituting the value of ε'' (ω) from (16) and (19) we have

$$\sigma_{ac} = \omega \tan\delta\varepsilon'(\omega), \qquad (21)$$

where ω = *2πf* and $\varepsilon' = \varepsilon_0 \varepsilon_r$, where ε_r is the relative permittivity of the material and ε_0 the permittivity of the free space. So

$$\sigma_{ac} = 2\pi f \tan\delta\varepsilon_0 \varepsilon_r. \qquad (22)$$

This equation is used to calculate the AC conductivity using dielectric constant and tan δ at a given frequency. It is to be noted that both tan δ and ε_r were available from dielectric measurement. The plots between $\ln(\sigma_{ac})$ and 1000/T were found to be very linear. So the conductivity values can be fitted to the relation

$$\sigma_{ac} = \sigma_0 \exp\left[-\vec{E}/kT\right] \qquad (23)$$

where $\vec{E}$ is the activation energy, k the Boltzmann constant, T the absolute temperature and σ_0 the parameter depending on the material. Activation energy was estimated using the slopes of the above line plots $[\vec{E} = -(slope)k \times 1000]$.

XI. DC CONDUCTIVITY STUDIES

Although dielectrics are defined as materials which under direct voltage do not allow current to flow, in fact any dielectric has a finite and very large resistivity. There are three mechanisms of electrical conduction dielectrics (depending on the type of carriers) (a) ionic or electronic conduction (b) mol ionic or electrophoretic conduction and (c) electronic conduction. Dielectrics actually exhibit a combined conduction, especially ionic and electronic conduction. Ionic conductivity studies provide valuable information about the state of point imperfections. At any particular temperature, the Gibb's free energy of a crystal is minimum when a certain fraction of ions occupy the normal lattice. As the temperature rises, more and more defects are produced which, in turn, increases the conductivity. In the high temperature (intrinsic) region, the effect of impurity on electrical conduction will not change appreciably whereas in the low temperature (extrinsic) region the presence of impurity in the crystal increases its conductivity. The electrical conduction in dielectrics is mainly a defect controlled process in the low temperature region. The presence of impurities and vacancies mainly determine this region. The energy needed to form the defect is much larger than the energy needed for its drift. The conductivity of the crystal in the high temperature region is determined by the intrinsic defects caused by thermal fluctuations in the crystal.

Conduction in an ionic crystal is, in general, a defect controlled property. The defect concentration increases exponentially with rise of temperature and the electrical conductivity increases correspondingly. Addition of divalent impurities to the crystal influences the concentration of point defects. Processes like association, aggregation and precipitation which become important at low temperatures and higher impurity levels, in general, reduce the free point defects that are necessary for electrical conduction. Formation, migration and association of point defects are governed by characteristic activation energies. An analytical increase in the concentration of defects both through the law of mass action and charge neutrality criterion. With the usual electric field, the charge transport by electrons in ionic crystals is zero because of a large forbidden gap.

Ionic conduction occurs either through the migration of positive and negative ions in an external electric field (the ions originate either in the material in question or in interstitial impurities) or through the motion of ions in vacancies which reflects the migration of vacancies. If the sample is placed in a stationary electric field, the carriers may be considered to be contained in an enclosure bounded by the capacitor plates. As the carriers may not leave the enclosure they accumulate in the regions close to the plates which cause a concentration gradient to be formed and this gradient feeds diffusion current. At equilibrium the diffusion current density equals that of the drift current. Charge accumulation is related to the homogeneities of the material and the agglomeration of impurity ions by diffusion in the vicinity of electrodes or chemical changes in layers close to electrodes.

A. Experimental

The samples (rectangular shaped crystals) were cut parallel to the cleavage plane to the desired thickness of 1-2mm and polished using silicon carbide paper. They were annealed for two hours at 150°C to remove moisture content, if present. Opposite faces of the sample crystals were coated with good quality graphite to obtain a good ohmic contact with the electrodes. The samples were again annealed in the holder assembly at 15^{o}C before making observations. The resistance of the crystal was measured using a megohmmeter. The observations were made while cooling the sample and temperature was controlled to an accuracy of ± 1°C. The dimensions of the crystal were measured using a travelling microscope. The conductivity (σ_{dc}) of the crystal was calculated using the relation,

$$\sigma_{dc} = t / RA, \tag{24}$$

where R is the measured resistance, t is the thickness of the sample and A is the area of the face in contact with the electrode. The above procedure was used to determine the DC electrical conductivity. The general relation for the temperature variation of conductivity is given by

$$\sigma_{dc} = \sigma_0 \exp[-\vec{E} / kT] \tag{25}$$

where σ_{dc} is a constant depending on material, $\vec{E}$ the activation of energy, T the absolute temperature and k the Boltzmann's constant. The above equation may be rewritten as

$$\ln \sigma_{dc} = \ln \sigma_0 [-\vec{E} / kT] \tag{26}$$

A plot of σ_{dc} versus 1000/T gives -$\vec{E}$/k as the slope and lnσ_{dc} as the intercept. It is customary to plot lnσ_{dc} versus 1000/T, from the slope of which activation energy ($\vec{E}$) can be calculated.

XII. PHOTOCONDUCTIVITY STUDY

A. Introduction

In the recent past, advancements in the study of quantum well and superlattice structures have dramatically changed the concepts of photosensors and the field of modern photodetectors is emerging. Photodetection technology has become very important in military applications, particularly in guided weapons and communication through fiber optics. Infrared developments are based on solid state photonic devices. Further developments in these fields demand a good understanding of the basic principles of photoconductivity processes.

Photoconductivity is an important property of solids by means of which the bulk conductivity of the sample changes due to incident radiation. Photoconduction includes the generation and recombination of charge carriers and their transport to the electrodes. Obviously, the thermal and hot carrier relaxation process, charge carrier statistics, effects of electrodes, and several mechanisms of recombination are involved in photoconduction. Photoconductivity, in general, is a very complex process as the mechanism involved is a complicated one. It provides valuable information about physical properties of materials and offers applications in photodetection and radiation measurements. W. Smith recorded first the photoconductivity effect in 1873 when he observed the decrease in the resistivity of selinium by the radiation shining on it. This is the first ever experimental detection of photoconductivity [26]. Einstein's theory of the photoelectric effect initiated the interpretation of the interaction of radiation with matter, particularly optical absorption, photoconductivity, the photovoltaic effect and other related phenomena. When photons of energy greater than that of the band gap of the material are incident upon a photoconductive material, electrons and holes are created in the conduction and valence bands respectively, increasing the conductivity of the sample. Also, in a doped material, the photon of slightly less energy than that of the band gap is absorbed by the impurity atom and free electron is created in the conduction band [27].

B. Photoconduction

Photoconductivity is due to the absorption of photons (either by an intrinsic process or by impurities with or without phonons), leading to the creation of free charge particles in the conduction band and/or in the valence band. Photo-absorption and hence photo-conduction takes place by one of the following mechanisms.

(i) Band-to-band transitions.
(ii) Impurity levels to band edge transitions.
(iii) Ionization of donors.
(iv) Deep level (located in the valence band) to conduction band transitions.

C. Dark conduction

Dark current I_d, is the amount of current that flows through the material or device when no radiation is incident on it. It changes with operating temperature and applied voltage, and therefore these parameters should be always mentioned.

Dark current is not a constant background current but also has fluctuations or noise. The average DC value of the current is generally mentioned as dark current.

D. Experimental

The crystal sample is well-polished and surfaces are cleaned with acetone. This is attached to a microscope slide and two electrodes of thin copper wire (0.14cm diameter) are fixed onto the specimen at some distance apart using silver paint. After this it is annealed at a temperature of 100^{o}C to perfect dryness. A DC power supply, a Keithley 485 picoammeter and the prepared sample are connected in series. The sample is covered with a black cloth to avoid exposure to any radiation. The current (dark) is measured. To measure the photoconductivity, light from a 100W halogen lamp is focused onto the sample. The current is noted for varying applied fields as before.

E. Negative photoconductivity

In few cases, it has been observed that when radiation of certain energy is incident on a photoconductor, a decrease in current is observed instead of the expected increase; this phenomenon is called “negative photoconductivity”. The variation in the mobilities of charge carriers is generally very small (here two-dimensional materials excluded) and hence can be ignored. This means that either the number of free charge carriers or their life time is substantially reduced by incident radiation. One well-accepted model due to Stockmann (Joshi 1990) is based on a two-level scheme. According to this model, the forbidden band gap contains two types of centres with energies E_1 and E_2. One type is located between the Fermi level and the conduction band, while the other is situated close to the valence band or between the Fermi level and the valence band. It is also assumed that the first type of centres have a high capture cross section for electrons and the probability of electrons being ejected to the conduction band is very low. In short, the function of these types of centers in the presence of radiation is to create holes (by accepting electrons from the valence band) but at the same time not to increase the number of free electrons. The second type of centres has a high cross-section for electrons and holes and consequently they capture electrons from the conduction band and holes from the valence band and recombine them. Thus, the net number of mobile charge carriers is reduced due to incident radiation giving rise to negative photoconductivity

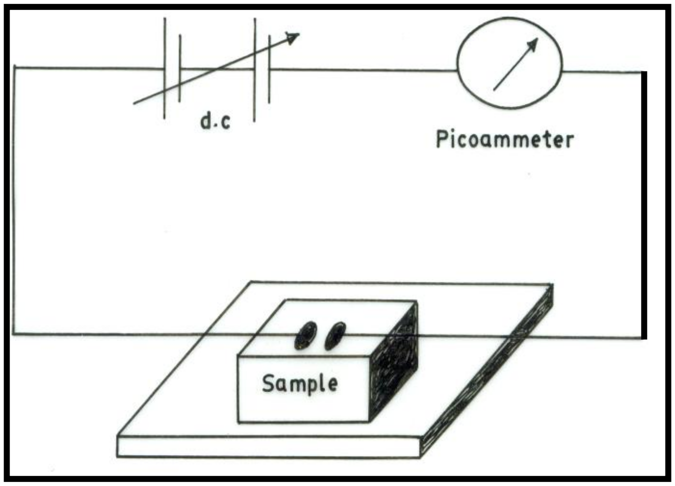

FIGURE 7. Experimental set-up for measuring photoconductivity.

XIII. CONCLUSION

Single crystals grown by the various methods need to be characterized to that assess the suitability of the crystal for various applications including NLO device application. In order to understand the behaviour of any solid material, firstly, the structural characterization is carried out. Secondly, the optical characterization helps to check the transparency window and cut-off frequency of the crystal. The presence of noncentrosymmetry and the various functional groups are confirmed by FTlR spectral analysis. Thermal characterisation of the grown crystals is done by using TGA/DTA. Second harmonic generation in the grown crystals is studied by Kurtz and Perry technique. In addition, the mechanical, dielectric, electrical and photoconductivity characterization techniques were also discussed.

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