CHAPTER 2

LITERATURE SURVEY AND CHARACTERIZATION
TOOLS AND TECHNIQUES

2.1 REVIEW OF LITERATURE

From materials point of view, the NLO materials can be broadly classified into three different categories as, inorganic, organic and semi-organic or metal organic materials. Inorganic and organic materials possess their own set of advantages and disadvantages, while in semi-organic or metal organic materials the aim is always to combine advantages of the both. All the three types of NLO materials are briefly outlined.

2.1.1 Inorganic NLO Materials

These are covalent and ionic bulk materials where the optical nonlinearity is a bulk effect. The phenomenon of SHG in inorganic materials was first reported in 1961, which led to the development of recent NLO materials such as inorganic systems, semi conductors and inorganic photorefractive crystals. Nikogosyan\textsuperscript{6} has carried out detailed survey of all NLO properties of various materials. Lithium niobate (LiNbO\textsubscript{3}), Potassium niobate (K\textsubscript{3}NbO\textsubscript{5}), Barium titanate (BaTiO\textsubscript{3}), Potassium titanyl phosphate (K\textsubscript{2}TiOPO\textsubscript{4}, KTP), Potassium dihydrogen phosphate (KH\textsubscript{2}PO\textsubscript{4}, KDP), potassium deuterium phosphate (KD*P), Ammonium dihydrogen phosphate (NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4}, ADP), Lithium iodate (LiIO\textsubscript{3}), etc., and a variety of semiconductors such as Gallium arsenide (GaAs), Cadmium sulphide (CdS), Cadmium telluride (CdTe), Zinc germanium phosphide (ZnGeP\textsubscript{2}) and Teluride (Te),
Cadmium germanium arsenide (CdGeAs₂) and Silver gallium selenide (AgGaSe₂) are appropriate infrared NLO materials.

β - Barium Borate (BBO) is an efficient NLO crystal for second, third and fourth harmonic generation of Nd: YAG lasers and best NLO crystal for fifth harmonic generations. The conversion efficiency of BBO is 70% for SHG, 60% for THG and 50% for FHG. KTP is also well-known NLO crystal with SHG coefficient about three times that of KDP. The inorganic NLO materials have some advantages like highest bulk susceptibility and compatible physical properties. On the other hand, such materials suffer from disadvantages like absorption in the visible region, poor response time and degradative photorefractive effects, low laser damage threshold (~10 MW cm⁻²) and poor optical transparency. Lithium niobate (LiNbO₃) crystals are one of the most investigated materials for widespread and promising applications in nonlinear optics, e.g., for parametric amplification and second-harmonic generation. LiNbO₃ also shows photorefractive properties, which are characterized by a change in its refractive index that result from an optically induced separation of electrons and the linear electro-optic effect. LiNbO₃ crystals are attractive due to many applications such as holographic data storage, optical information processing, phase conjugation, and wavelength filters. Borate family complexes are excellent nonlinear optical (NLO) materials, as they possess high chemical stability, damage threshold, optical quality and wide range of transparency. In particular, inorganic crystals like lithium triborate (LiB₃O₅, LBO), lithium tetraborate, beta barium borate (β-BaB₂O₄, BBO) and Potassium pentaborate tetrahydrate (KB₃) have been widely used for NLO devices in ultra-violet laser generation. The beta barium borate crystal was confirmed to be that of the low-temperature β-phase by powder X-ray diffraction and second harmonic generation. Due to its large SHG coefficient (d₂₂ = 2.22 pm/V), wide optical transmission ranges (190–3500 nm) and high damage threshold (about 50 times higher than that of
KDP), the beta barium borate as a single crystal material, has been extensively investigated for applications in the ultraviolet region. KB₅ is a desirable NLO material, which exhibits a low angular sensitivity and hence proved to be useful for type II second harmonic generation. The ultraviolet radiation generated in a lithium tetraborate (Li₂B₄O₇) crystal by Type-I walk-off compensated sum-frequency mixing (SFM) of the commonly available Nd: YAG laser radiation.

2.1.2 Organic NLO Materials

Organic materials are molecular materials that consist of chemically bonded molecular units interacting in the bulk media through weak vander waals interactions. The organic molecules which contain both conjugated bonds and acceptor group on one side and a donor group on the other side are known as nonlinear optical (NLO) materials. A typical SHG active molecule can be represented as follows:

Donor → π – conjugated system → acceptor

The π – conjugated molecules with a donor and acceptor will not display SHG activity if they possess a centre of symmetry. This symmetry requirement eliminates several materials for consideration of SHG. The π conjugated systems would be benzene, azobenzene, stilbene, tolans, biphenyl, hetrocycle, polyens, benzylidene, etc. Some acceptor groups are, for instance, NO₂, NO, CN, NH₃⁺, CF₃, COCH₃, COOH, COO⁻, etc., whereas some donor groups are NH₂, NHCH₃, FCl, Br, CH₃, COOCH₃, NHCOCH₃, and O⁻ etc.

The trade off between optical transparency and SHG efficiency is an important issue while designing devices using NLO materials. Both the second order optical nonlinearity and optical transparency are affected by the nature of conjugated bonds, length of π - conjugation and strength of electron donor/ acceptor constituents.
Nagaraja et al\textsuperscript{7} showed that benzoyl glycine (BG), an organic nonlinear crystal grown by slow evaporation from Dimethyl Formamide solution has the advantages of both the organic and inorganic NLO materials and is nondeliquescent. Owing to high nonlinear efficiency, high melting point, good chemical stability, less sublimation problems and improved hardness and cleavage properties (unlike other organic materials), benzoyl glycine is found to be a promising material for NLO applications. Lakshmana Perumal et al\textsuperscript{8} further extended the effort in synthesizing 4-methoxy benzaldehyde-N-methyl-4-stilbazolium tosylate (MBST), which is a derivative of stilbazolium tosylate and a new material having high NLO property. The Kurtz powder SHG measurements\textsuperscript{9} on MBST showed that the peak intensity is 17 times more than that of urea. Methyl p-hydroxybenzoate (p-MHB) is a para-substituted aromatic compound with a molecular formula $C_8H_8O_3$. Urea has been used in an optical parametric oscillator to generate tunable radiation throughout the visible region but intrinsic absorption and phase matchability considerations make it unsuitable for wavelengths longer than 1000 nm, as reported by Rosker et al\textsuperscript{10}. The efforts made to resolve the problems associated with urea have not been successful. The newly grown binary UNBA crystal by Rai et al\textsuperscript{11} is thermally and mechanically harder than the crystal of the parent components. It is quite transparent almost in the entire UV region and hence it can be used for producing green/blue laser light.

Amino acid crystals like L-phenylalanininium trichloroacetate (SHG efficiency 0.65 X KDP), L-arginine maleate (SHG efficiency 1.4 X KDP), L-citrulline oxalate, L-leucine (SHG efficiency 2 X Urea), L-phenylalanininium maleate (SHG efficiency 1.5 X KDP), L-histidinium maleate 1.5 hydrate, L-alanine tartrate (SHG efficiency 1.4 X KDP), Urea L-alanine acetate (SHG efficiency ~ KDP), have been grown by slow evaporation method and temperature lowering methods from aqueous solution by several workers\textsuperscript{12-19}. 
Many other organic crystals viz., m-dinitrobenzene doped urea, 2-Amino-5-nitropyridinium-toluenesulfonate, 2-Furoic acid, L-tartaric acid, β-napthol, E-5- (diethylamino)-2-(3,5-dinitrophenylimino) methyl) phenol, 2-Amino pyridinium trichloroacetate, and Chalcone derivative of (2E)-3-[4-(Methylsulfanyl)phenyl]-1-(4-nitrophenyl)prop-2-en-1-one were grown by slow evaporation and temperature lowering methods using solvents such as double distilled water and ethanol\textsuperscript{20-27}. 

Many organic crystals exhibiting third order NLO properties were also reported. Benzyl-triethylammonium bis (2-thioxo-1, 3-dichiole-4,5- dithiolato aurate (III), 4-bromo-4’ Chlorobenzylidene aniline, were structurally analyzed and reported to be third order NLO active single crystals\textsuperscript{28,29}.

In order to retain the merits and overcome the shortcomings of organic materials, some new classes of NLO crystals such as metal organic or semiorganic complex crystals have been developed. The relatively strong metal ligand bond permits the complex crystals to combine the advantages of inorganic crystals, such as good stability, with the advantages of organic crystals, such as high nonlinearity and molecular engineering features.

### 2.1.3 Semiorganic NLO Materials

Semi-organic compounds share the properties of both organic and inorganic compounds, and organo-metallic compounds. They are organic based materials in which the polarizable part is an organic molecule which is stoichiometrically bonded with an inorganic ion. The \( \pi \)-conjugated network in an organic system with large nonlinearity has significant absorption in the visible region and hence for second harmonic generation (SHG) in the blue near UV region, more transparent and less extensively delocalized organics like urea or its analogs have been considered.
Recent interest is centered on metal complexes of certain organic ligands and among them metal complexes of thiocyanate and thiourea are of special interest owing to their large nonlinearity, high laser damage threshold, low UV-cut off and good mechanical properties. An interesting class of semi-organic crystals receiving wider attention in recent past is the amino acid family which includes the analogs of L-arginine, L-histidine, L-alanine, and L-lysine etc. Among organic crystals of NLO applications, amino acids display specific features of interest such as, (i) molecular chirality, which secures acentric crystallographic structures, (ii) absence of strongly conjugated bonds leading to high transparency ranges in the visible and UV spectral regions and (iii) zwitterionic nature of the molecule, which favours crystal hardness. Amino acid can be used as a basis for synthesizing organic-inorganic compounds like L-arginine phosphate and derivatives. L-arginine phosphate monohydrate (LAP) is a new nonlinear optical (NLO) material first introduced by Chinese material scientists in 1983. LAP crystals are usually grown from aqueous solution by the temperature lowering technique. LAP crystals caught the attention of many researchers because of their high nonlinearity, wide transmission range (220-1950 nm), high conversion efficiency (38.9%) and high damage threshold. Monaco et al. formed LAP and its chemical analogs from the strongly basic amino acid and various other acids. All the compounds in this class contain an optically active carbon atom and, therefore, all of them form acentric crystals. All the crystals are optically biaxial and among them several give second harmonic signals greater than quartz. It has been reported that L-arginine fluoride (LAF) possesses high NLO coefficient next to LAP. LAF has a very strong type-I position, i.e., angularly insensitive compared to LAP, which makes LAF crystal attractive of certain cascade scheme for producing third harmonic. The amount of second harmonics generated in a powder LAF sample at 1064 nm is 5.6 times relative to a quartz standard. The efficiency of frequency doubling of L-arginine
hydrofluoride (LAHF) was 39% and was larger than KDP (22%) and LAP (33%). The growth and properties of new semiorganic nonlinear optical crystal, tetra L-lysine alanine monohydrochloride dihydrate (TLAMHCl) has been studied. The second harmonic generation (SHG) efficiency of TLAMHCl was found to be 1.2 times that of KDP.

L-histidine salts can display high NLO properties due to the presence of imidazole group in addition to amino-carboxylate. Among the L-histidine analogs, the low temperature solution grown L-histidine tetrafluoroborate (LHFB) is a promising NLO material and has superior NLO properties than LAP. The SHG intensity of L-HFB crystal is five times that of the KDP. Single crystals of L-histidinium dihydrogen orthophosphate ortho-phosphoric acid (LHP) were grown by slow evaporation technique and its SHG efficiency was found to be nearly 4 times that of KDP. The SHG efficiency of semi-organic glycine nitrate (GSN) was found to be 2 times that of KDP. Glycine forms the ferroelectric diglycine nitrate whose spectral transparency range is from 245 to 1900 nm.

Tris (glycine) calcium (II) dichloride, bimetallic thiocyanate crystals of Cadmium mercury thiocyanate, Zinc cadmium thiocyanate, Manganese mercury thiocyanate, deuterated L-arginine trifluoroacetate, L-alanine lithium chloride, L-arginine hydrochloride, L-arginine hydrofluoride, Glycine potassium nitrate, Zinc guanidinium phosphate, Lithium sulfate monohydrate, Thiosemicarbazide cadmium chloride monohydrate and Potassium borosuccinate were grown by slow evaporation and unidirectional methods and were reported to be NLO active and identified as potential candidates for NLO applications.

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2.2 CHARACTERIZATION TOOLS AND TECHNIQUES

The advent of sophisticated instruments employing non-destructive techniques has enabled the researchers to carry out spectral measurements, structure determination and chemical analysis of new materials. The aim of this section is to present a comprehensive description on the techniques that are followed to characterize the crystal samples in the present research work.

The single crystals chosen for the present investigation were subjected to the following studies:

- Collection of XRD data by Single crystal X-ray diffraction analysis.
- CHNS and EDAX analysis to determine the qualitative and quantitative analysis of the elements in the crystals.
- FTIR spectral analysis to confirm the various functional groups present in the compound.
- UV-VIS-NIR analysis for the detection of the transparency region and cut-off wavelength.
- Thermal analysis to study the thermal stability and crystal texture.
- Hardness studies to assess the mechanical stability of the material.
- Dielectric measurements to investigate the dielectric response of the crystal with varying frequency.
- A.C. impedance spectroscopy to explore the piezoelectric properties of the crystals.
- Photoconductivity studies to determine the nature (positive/negative) of photoconductivity in the crystals.
- Laser damage threshold studies to determine the resistance provided by the crystal to the laser beam.
- Second Harmonic Generation (SHG) test to verify the nonlinear response of the crystal to incident coherent light.
2.3 SINGLE CRYSTAL X-RAY DIFFRACTION ANALYSIS

Single crystal X-Ray Diffraction (Single crystal XRD) is a non-destructive analytical technique which provides detailed information about the molecular structure, atomic coordinates, bond lengths, bond angles, unit cell dimensions, molecular orientation, and packing of molecules in single crystals. Directly related is single-crystal refinement, where the data generated from the X-ray analysis is interpreted and refined to obtain the crystal structure. Single crystal X-ray diffractometer collects intensity data required for structure determination. Only single crystals can be analysed. Non-crystalline samples (amorphous) cannot be analysed. The size of the crystal should be of the order of a few mm$^3$.

Accurate measurements of intensities of reflections of all Miller indices within a specified reciprocal radius (usually 25° for MoK$_\alpha$ and 68° for CuK$_\alpha$) 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 the cross sectional diameter of the beam. Larger crystals can be cut down to proper size and smaller crystals may be suitable if they contain strongly diffracting elements.

The monochromatic X-rays incident on a plane of single crystal at an angle $\theta$ is diffracted according to Bragg's relation $^{42}$ represented in equation (2.1):

$$2d \sin \theta = n \lambda \quad (2.1)$$

Where‘d’ is the interplanar spacing of the incident plane, ‘$\lambda$’ is the wavelength of X-rays and ‘n’ is a positive integer. The intensity of the diffracted rays depends on the arrangement and nature of atoms in the crystal. Collection of intensities of a full set of planes in the crystal contains the complete structural information about the molecule. Fourier transformation techniques are used to
determine the exact coordinates of atoms in the unit cell from this data. With the set of X-ray diffraction data collected, unit cell parameters, space groups, molecular structure of the crystalline solids and Miller indexing the different faces of the crystal are possible. Space group tells us the symmetry with which the molecules are arranged within the unit cell. All the geometrical features of molecules (bond distance, bond angles, torsion angles between bonds, dihedral angles between planes etc.,) may be obtained from coordinates. The schematic representation of the single crystal XRD is shown in Figure 2.1.

![Schematic of 4-Circle diffractometer, the angles between the incident ray, the detector and the sample](http://serc.carleton.edu)

Specific applications of single-crystal diffraction include:

- New mineral identification, crystal solution and refinement.
- Determination of unit cell, bond-lengths, bond-angles and site-ordering.
- Characterization of cation-anion coordination.
- Variations in crystal lattice with chemistry.
• With specialized chambers, structures of high pressure and/or temperature phases can be determined.
• Determination of crystal-chemical vs. environmental control on mineral chemistry.
• Powder patterns can also be derived from single-crystals by using specialized cameras.

In the present study, the single crystal X-ray diffraction analysis was performed using **Bruker Kappa Apex II** single crystal X-ray Diffractometer, with MoKα radiation of wavelength $\lambda = 0.7107\text{Å}$ (Figure 2.2).

![Figure 2.2 Instrumental set up of Bruker Kappa Apex II single crystal X-ray Diffractometer.](image-url)
2.4 CHNS ANALYZER

Elemental analyzer technique determines the presence of the elements like carbon, nitrogen, hydrogen and sulphur in a given sample and gives the result as percentage amount of these against the total weight. Most of the organic compounds are made up of these three elements and oxygen; hence after determining these three elements the percentage weight of oxygen can be easily calculated.

This is an important study when it comes to a newly synthesized compound to prove its exact composition. Solid samples weighing from less than 1 mg up to 200 mg are packed in tin boats. The principle of the instrumentation is that the substance under study is combusted under oxygen stream in a furnace at high temperatures (1000 °C). In the combustion process, carbon is converted to carbon dioxide; hydrogen to water; nitrogen to nitrogen gas/oxides of nitrogen and sulphur to sulphur dioxide. That is, the end product of the combustion would be mostly the oxides of the concerned elements in the form of gases. These are then separated and carried to the detector using inert gases helium or argon. Schematic diagram of an automatic C, H, and N analyzer is shown in Figure 2.3.
The Vario EL III-Germany CHNS analyser was used in the present study. Samples must be non-fluorinated, non-explosive, about 10-30 mg for solid sample or 25ml for liquid sample (depending on the components).

2.5 ENERGY DISPERSIVE X-RAY ANALYSIS (EDAX)

It is a technique used for identifying the elemental composition of the specimen. The EDAX analysis system works as an integrated feature of a scanning electron microscope (SEM), and cannot operate on its own without the latter. During EDAX analysis, the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the specimen atoms' own electrons, knocking some of them off in the process. The EDAX spectrum is a plot of intensity of X-rays vs. energy of the emitted X-rays. An EDAX spectrum normally displays peaks corresponding to the energy levels for which the most X-rays have been received. Each of these peaks is unique to an atom, and therefore corresponds
to a single element. The higher the intensity of peak in a spectrum, the more concentrated is the element in the specimen.

In the present study the EDAX measurements were performed by using JEOL Model JED – 2300 Energy Dispersive X-ray (EDAX) Microanalysis system attached to a JEOL JSM-6390LV scanning electron microscope (SEM) with a low vacuum resolution of 4 nm.

2.6 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Infrared spectroscopy is a very useful technique for characterization of materials that gives information about the composition and the structure of molecules. IR spectra originate in transitions between two vibrational levels of a molecule in the electronic ground state and are usually observed as absorption spectra in the infrared region. For a molecule to present infrared absorption bands it is needed that it has a permanent dipole moment.

The infrared spectrum can be divided into two regions, one called the functional group region and the other the fingerprint region. The functional group region is generally considered to range from 4000 cm\(^{-1}\) to 1500 cm\(^{-1}\) and all frequencies below 1500 cm\(^{-1}\) are considered characteristics of the fingerprint region. The fingerprint region involves molecular vibrations, usually bending motions which are characteristic of the entire molecule or large fragments of the molecule. Thus these are used for identification of the material. The functional group region tends to include motions, generally stretching vibrations, which are more localised and characteristic of the typical functional groups, found in organic molecules. While these bands are not very useful in confirming identity, they do provide some very useful information about the nature of the components that make up the molecule.

Fourier-transform infrared (FTIR) spectroscopy is based on the idea of the interference of radiation between two beams to yield an interferogram.
The latter is a signal produced as a function of the change of path length between the two beams. The two domains of distance and frequency are interconvertible by the mathematical method of Fourier-transformation.

The FTIR spectrometer consists of an infrared source: globar and mercury vapour lamp, a sample chamber with a provision for holding solids, liquids and gases, monochromator, a detector and a recorder, which are integrated with a computer.

An interferometer chamber comprising of KBr and Mylar beam splitters is followed by a sample chamber and detector. The schematic diagram of a FTIR spectrometer is shown in Figure 2.4. The spectrometer works under vacuum condition. Solid samples are dispersed in KBr or polyethylene pellets depending on the region of interest. Spectra are plotted on a HP plotter and data can be printed. Three different techniques are employed commonly in recording such spectra. For solid compounds, that are insoluble in the usual solvents, a convenient sampling method is the Pressed Pellet Technique. A few milligrams of the sample are ground together in an agate or mullite mortar with about 100 times the quantity of a material (the matrix) transparent to the infrared. The usual material is KBr, although other compounds such as CsI, TlBr and Polyethylene are used in special circumstances.

Some of the general uses of FTIR spectra are:

- Identification of all types of organic and many types of inorganic compounds.
- Determination of functional groups in organic materials.
- Determination of the molecular composition of surfaces.
- Identification of chromatographic effluents.
- Quantitative determination of compounds in mixtures.
• Determination of molecular conformation (structural isomers) and stereochemistry (geometrical isomers).
• Determination of molecular orientation (polymers and solutions).

In the present investigation, the infrared spectrum of the grown crystals was analyzed in the region between 400 and 4000 cm\(^{-1}\) with **Perkin Elmer FTIR spectrometer model SPECTRUM RXI** with a resolution of 4 cm\(^{-1}\), using KBr pellet technique.

### 2.7 UV–Vis-NIR SPECTROSCOPY

Ultraviolet-visible spectroscopy is also known as electronic spectroscopy. Ultraviolet (200-400 nm) and visible (400-800 nm) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface.

Ultraviolet and visible light are energetic enough to promote outer (valence) electrons to higher energy levels. Valence electrons are found in three types of electron orbitals namely ‘\(\sigma\)’ bonding orbitals, ‘\(\pi\)’ bonding orbitals and non-bonding orbitals (n-lone pair electrons). Sigma ‘\(\sigma\)’ bonding orbitals tend to be lower in energy than ‘\(\pi\)’ bonding orbitals, which in turn are lower in energy than non-bonding orbitals. The unoccupied or anti bonding orbitals (\(\pi^*\) and \(\sigma^*\)) are the orbitals of highest energy. An energy level diagram showing electronic transitions is depicted in Figure 2.4. Of the six transitions outlined, only the two lowest energy ones (\(n \rightarrow \pi^*\)) and (\(\pi \rightarrow \pi^*\)) are achieved by the energies available in the 200 to 800 nm spectrum. As a rule, energetically favored electron promotion will be from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) and the resulting species is called an excited state.

In particular, absorption bands results from transitions (\(\pi \rightarrow \pi^*\)) and
(n → π*) π-orbitals and lone pairs (n - non-bonding) are important and so UV-Vis spectroscopy is of most use for identifying conjugated systems which tend to have stronger absorptions. Absorption bands can also arise from certain molecules where the energy required for removing an electron from one atom and placing it on another falls within the UV/Vis region. This process is known as a charge transfer excitation. Molecules with the ability to exhibit the above types of electronic transitions are said to possess chromophores. 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. The most common are (C=C) and (C=O) which exhibits (π → π*) and (n → π*) transitions respectively.

![Energy level diagram with electronic transitions](image)

**Figure 2.4 Energy level diagram with electronic transitions**

Samples are typically placed in a transparent cell, known as a cuvette. The sample holders (cuvettes) are the rectangular shaped quartz or glass cells of about 10 mm path length. The transmitted light radiation is received at the photomultiplier tube alternately from the reference and the sample beams. A photoelectric signal timing system is synchronized with the alternate pulses.
which permits the comparison of signals from the two beams. The difference between the two signals is recorded with the help of a motor driven pen or is interfaced with a PC-XT and stored there for easy reference. Samples in solid form, powder, pellets are dissolved in suitable solvents to form the contents of the sample cell and the solvents are taken in the reference cell.

General applications of Ultraviolet Spectroscopy

- Extent of conjugation in organic compounds.
- Distinction between conjugated and Non-conjugated compounds.
- Detection of a Chromophore in an unknown compound by comparison of its spectrum with that of a known compound.
- Identification of a chromophore (Functional Group).
- Study of strain.
- Study of Geometric Isomerism.
- Study of Tautomerism.

In the present work, the UV-Visible spectrum was recorded by Lamda 35 model Perkin-Elmer double beam UV–Vis–NIR spectrometer in the range from 190 nm to 1100 nm. The instrumental make of UV–Vis–NIR spectrometer is shown in Figure 2.5.
2.8 THERMAL STUDIES

Thermal analysis is a very essential method to study the thermal behaviour of materials and finds widespread applications in diverse industrial and research fields. It 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. 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.

Thermoanalytical analysis incorporates the following three closely related techniques:

- Thermogravimetric analysis (TGA), which involves monitoring weight while varying temperature.
- Differential thermal analysis (DTA), which involves comparing the precise temperature difference between a sample and an inert reference material, while heating both.
• Differential scanning calorimetry (DSC), similar to DTA except that electrical energy is used to restore the cooler of the two materials to the same temperature as the other. This allows direct measurement of energy changes.

These techniques are useful for determining glass points, phase changes, water of crystallization and mixtures where the components have different melting or decomposition points.

Thermogravimetric analysis (TGA) is based on the measurement of mass loss of material as a function of temperature. In thermogravimetry a continuous graph of mass change against temperature is obtained when a substance is heated at a uniform rate or kept at constant temperature. TG curve helps in revealing the extent of purity of analytical samples and in determining the mode of their transformations within specified range of temperature. The instrument used in thermogravimetry (TG) is called a thermobalance as shown in Figure 2.6.

![Figure 2.6 Block diagram of a Thermobalance](image-url)
Basic components of a typical thermobalance are listed below:

- Balance
- Furnace - heating device.
- Unit for temperature measurement and control (Programmer)
- Recorder - automatic recording unit for the mass and temperature changes

Differential thermal analysis (DTA) is a technique in which the temperature of the substance under investigation is compared with the temperature of a thermally inert material such as α-alumina and is recorded with furnace temperature as the substance is heated or cooled at a predetermined uniform rate. The schematic representation of DTA is shown in Figure 2.7.

Differential thermal analyzer consists of following basic components:

- Furnace Assembly
- Sample and reference holder with temperature detector
- Temperature programmer
- Amplifier and recorder
- Atmosphere control equipment for furnace and sample holder

The instrument measures the differential temperature of the sample as a function of temperature or time where the temperature rises at a constant linear rate.
In differential scanning calorimetry (DSC), the initial temperatures of the sample and the reference are kept same. The amount of heat that has to be supplied to the sample or reference to achieve this equivalence in temperature is constantly measured over the temperature range employed. This can be achieved by placing separate heating devices in the sample and reference chambers. This is in contrast to the DTA scheme, where both sample and reference are heated by the same source. In DSC, samples for analysis, ranging in size from 1 to 100 mg, are placed in a sealed sample container. A wide range of heating rate (0.5 to 80°C/min) can be used. DSC instruments are generally energy sensitive and detect heat evolution or absorption at rate
less than one millicalories per second. The block diagram of DSC is shown in Figure 2.8.

![Block Diagram of DSC Instrument](image)

**Figure 2.8 Block diagram of a DSC instrument**

In the present work, thermal behaviour of the grown samples was studied by using **TG/DTA 6200 simultaneous thermal analyzer** between 32°C to 800°C at a heating rate of 20°C/min in nitrogen atmosphere and Differential scanning calorimetry (DSC) was carried out at a scanning rate of 10 K/min in nitrogen atmosphere, by **Perkin Elmer NETZSCH, DSC-204** equipment (Figure 2.9).
2.9 MICROHARDNESS STUDIES

Hardness is 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 is 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.

The most popular and simplest test is the static indentation test, wherein an indenter of specific geometry is pressed into the surface of a test specimen under a known load. A permanent impression is retained in the specimen after removal of the indenter. The hardness is calculated from the area or the depth of indentation produced. The variables are the type of indenter or load. The indenter is made up of a very hard material to prevent its deformation by the test piece, so that it can cover materials over a wide range of hardness. For this reason, either a hardness steel sphere or a diamond pyramid or cone is employed. A pyramid indenter is preferred as
geometrically similar impressions are obtained at different loads. In this static indentation test, the indenter is pressed perpendicularly to the surface of the sample by means of an applied load. By measuring the cross sectional area or depth of the indentation and knowing the applied load, empirical hardness number may be calculated.

In the dynamic indentation test, a ball or a cone (or a number of small spheres) is allowed to fall from a definite height and the hardness number is obtained from the dimensions of the indentation and the energy of impact. In this method, microindentation is made on the surface of a specimen with the help of diamond pyramidal indenter. Smith et al. 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 ($\alpha = 136^\circ$) is the most widely accepted pyramid indenter (Figure 2.10).

![Figure 2.10 Schematic description of Vickers Hardness Testing](image-url)
A pyramid indenter is suited for hardness tests due to the following reasons.

- The contact pressure for a pyramid indenter is independent of indent size.
- Pyramid indenters are less affected by elastic release than other indenters.

The base of the Vickers pyramid is a square and the depth of indentation corresponds to \(1/7\)th of the indentation diagonal. A diamond, in the form of a right pyramid with a square base and an angle of 136° between opposite faces is forced into the material subjected to a load of 1 to 100 kgf. The full load is normally applied for 10 to 15 seconds. The two diagonals, ‘\(d_1\)’ and ‘\(d_2\)’, of the indentation left in the surface of the material after removing the load are measured, and their arithmetic mean ‘\(d\)’ is calculated. The area of the sloping surface of the indentation is calculated. The Vickers hardness is the quotient obtained by dividing the kgf load by the square mm area of indentation.

The Vickers hardness number ‘\(H_v\)’ of Diamond Pyramid Number (DPN) is defined as

\[
H_v = \frac{2P \sin (\alpha/2)}{d^2}
\]  
(2.2)

Where ‘\(\alpha\)’ is the apex angle of the indenter (\(\alpha = 136^\circ\)). The Vickers hardness number is thus calculated using the relation in equation (2.3):

\[
H_v = \frac{1.8544 \, P}{d^2} \text{ kg/mm}^2
\]  
(2.3)

Where ‘\(P\)’ is the applied load in kg and ‘\(d\)’ is the diagonal length of the indentation mark in mm. Standard designation of Vickers hardness is usually given with load and duration values: 450VHN/30/20 means a 450 Vickers hardness value measured under a load of 30kg for duration of 20 sec.
The data obtained for ‘P’ and ‘d’ can be analysed by Meyers’ relation in equation (2.4):

\[ P = k_1 d^n \]  \hspace{1cm} (2.4)

Where ‘k₁’ and ‘n’ are constants for the material. The constant ‘k₁’ is usually referred to as the standard hardness. Meyers’ index ‘n’ which represents work hardening capacity of the material can be determined by plotting ‘log P’ versus ‘log d’.

Combining Equations (2.3) and (2.4), we have

\[ H_v = 1.8544 k_1 d^{n-2} \]  \hspace{1cm} (2.5)
\[ H_v = 1.8544 k_1 (1+2/n) P ^{(1-2/n)} \]  \hspace{1cm} (2.6)
\[ H_v = b P ^{(n-2)/n} \]  \hspace{1cm} (2.7)

The above expression shows that ‘Hᵥ’ should increase with increase in ‘P’ if n > 2 and decrease with the same if n < 2. According to Onitch and Hanneman ‘n’ should lie between 1 and 1.6 for softer ones.

Elastic stiffness constant ‘C₁₁’ of a material can be calculated from the Woosters’ empirical relation as given in equation (2.8):

\[ C_{11} = H_v ^{7/4} \]  \hspace{1cm} (2.8)

If the stiffness constant C₁₁ is high, it reveals that the binding forces are quite strong.

In the present investigation, Microhardness studies have been carried out on the grown crystals using a SHIMADZU HMV-2T Vickers microhardness tester (Figure 2.11) fitted with a Vickers diamond pyramidal indenter attached to an incident light microscope.
2.10 DIELECTRIC STUDIES

One of the most important parameters widely used is the relative dielectric constant or relative permittivity. The study of dielectric constant of a material gives an insight into the nature of bonding in the material.

The dielectric constant is 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. The relative dielectric constant $\varepsilon_r$ or relative permittivity is given in equation (2.9):
\[ \varepsilon_r = \varepsilon/\varepsilon_0 \]  \hspace{1cm} (2.9) \\
\[ \varepsilon = \varepsilon_0 \frac{C}{d} \]  \hspace{1cm} (2.10) \\
\[ C = \varepsilon_r \varepsilon_0 \frac{A}{d} \]  \hspace{1cm} (2.11) \\

Where ‘A’ is the area of the sample and ‘d’ is the thickness of the sample. The relative permittivity \( \varepsilon_r \) is usually known as permittivity. It is always greater than unity. The capacitance \( C_0 \) of a parallel plate condenser having a capacitance \( C \) in air can be given by,

\[ C = \varepsilon_r C_0 \]  \hspace{1cm} (2.12) \\
\[ \varepsilon_r = C/C_0 \]  \hspace{1cm} (2.13) \\

\( \varepsilon_r \) can be found by the measurement of capacitance. The higher the dielectric constant, the lower the electrostatic binding and hence higher is the lattice energy. Major contributions to the dielectric constant are from:

- The extrinsic nature of the material
- The electronic polarizability
- The ionic polarizability
- The deformation of the ions

In the present work, the dielectric conductivity studies for the crystal were done with DIGITAL LCRZ METER, TH2816A in the range of frequencies between 50 Hz-200 KHz at room temperature.

**2.11 PHOTOCONDUCTIVITY STUDY**

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.
Photo-absorption and hence photo-conduction takes place by one of the following mechanisms:

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

**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.

**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 are 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.

In the present work, the photoconductivity study on the crystals was carried out by using **Keithley 485 Picoammeter** at room temperature. The variation of both dark current ‘I_d’ and photocurrent ‘I_p’ with applied field was analysed. 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°C to perfect dryness. A DC power supply, 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. The experimental set-up for measuring photoconductivity is as shown in Figure 2.12 and the instrumental make is shown in Figure 2.13.
Figure 2.12 Experimental set-up for measuring photoconductivity

Figure 2.13 Instrumental make of Keithley 485 Picoammeter
2.12 A.C. IMPEDANCE SPECTROSCOPY

Most of the crystals applied in the nonlinear optics possess piezoelectric properties. A method has been recently proposed for the intrinsic temperature measurement and the accurate determination of the weak linear optical absorption of the piezoelectric optical materials. In the present work the interaction of the single-mode high-power laser radiation with crystals is investigated by means of the radio frequency impedance spectroscopy. The most common approach is to calculate the crystal electrical impedance at the fixed frequency of the external voltage applied to the crystal from the measured amplitude and the phase shift of the resulting alternating current flowing through the crystal. The crystal complex electrical impedance is determined in the wide radiofrequency range from $10^{-4}$ to $10^9$ Hz. The experimental set-up for measuring a.c. impedance is shown in Figure 2.14.

In the present work, the AC impedance was measured by employing an Impedance analyzer, EG & G Princeton Applied Research, USA.

![Figure 2.14 Block-scheme of the experimental setup for the crystal complex electrical impedance measurements.](image-url)
2.13 NLO TEST – KURTZ POWDER SHG METHOD

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 powder technique remains an extremely valuable tool for initial screening of materials for second harmonic generation. Employing this technique; Kurtz surveyed a very large number of compounds.

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 Figure 2.15. A Q-switched, mode locked Nd: YAG laser was used to generate about 6mJ/pulse at the 1064 nm fundamental radiation. This laser can be operated in two modes. In the single shot mode the laser emits a single 8 ns pulse. 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 of about 6.2 mJ. A fundamental laser beam of 1064 nm wavelength, 8 ns pulse in depth with 10 Hz pulse rate was made to fall normally on the sample cell. The power of the incident beam was measured using a power meter. The transmitted fundamental wave was passed over a monochromator (Czerny Turney Monochromator), which separates 532 nm (SHG signal) from 1064 nm and absorbed by a CuSO4 solution. CuSO4 solution removes the 1064 nm light. BG38 filter removes the residual 1064 nm light. The green light was detected by a photomultiplier tube (Hamamatsu RC 109, a visible PMT) and displayed on a storage oscilloscope (TDS 2052 B 500 MHz phosphor digital
oscilloscope). Potassium dihydrogen phosphate, KDP and Urea crystals were powdered to identical size and were used as reference materials in the SHG measurement.

Figure 2.15 Schematic experimental set up for SHG efficiency measurement.

In the present work, the NLO property of the crystal was tested by Kurtz powder SHG test using Q-Switched Nd: YAG laser (1064 nm) with Quanta Ray Series as the source and Coherent Molelectron Powermeter as the photomultiplier to record the output radiation.

2.14 LASER DAMAGE THRESHOLD STUDY

An important related property of NLO crystals is the threshold for catastrophic laser induced damage. Laser induced damage in optical materials is a phenomenon involving interaction of high power laser radiation with matter and various physical, chemical, mechanical, optical and other aspects of materials come into play. It is evident that the harmonic conversion efficiency is proportional to the power density of the fundamental beam. Hence, a convenient way to increase the efficiency is to focus the beam into
the crystal. But, this often leads to breakdown of the materials, catastrophically damaging the crystal. It is then useful to prescribe the maximum permissible power for a particular crystal, defined as damage threshold.

It is believed that the formation of an ionized region of dense plasma is the first and the most important step in a damage event. In recent times, there have been several effects to model the laser damage processes by taking the pulse shape and duration into account. Laser damage in general manifests itself as a localized microscopic entity. Microscopic examination of the damage sites created in different materials often suggests the mechanism responsible for such a process. The damage in NLO materials like KDP and Deuterated Potassium Phosphate (DKDP) manifests itself as micro-cavity whose sizes are insensitive to the wavelength of the laser beam, suggesting a wavelength independent absorption mechanism. However, the damage mechanisms vary from material to material and hence damage studies become important for newly discovered materials. Laser damage measurement was carried out on the crystal at 1064 nm. The single shot surface damage thresholds have been determined. The laser damage threshold depends on pulse duration, focal spot geometry, sample quality, previous history of the sample, experimental technique employed etc. Recent investigations into laser damage in various optical materials by nanosecond pulses have shown that the temperature reached at the damage site could be as high as 12000 K. One can expect the damage to be of thermal origin. However, one cannot rule out other mechanisms being operative simultaneously, as the damage mechanism is quite complex and depends on the nature of the material and various experimental parameters.

The experimental set-up used for the measurement of laser damage of the samples is shown in Figure 2.16. A Q-switched Nd: YAG laser
(Continuum USA, Model: Surelite-III) of wavelength 1064 nm and pulse width 10 ns, TEM$_{00}$ single shot mode was used. The energy of the laser pulses was controlled by an attenuator (combination of λ/2 plate and glan polarizer) and delivered to the test sample located near the focus of a plano-convex lens of focal length 30 cm. The occurrence of single pulse damage was observed by monitoring the fall of transmitted intensity as detected by a fast PIN type Si photodiode and traced in a digital storage oscilloscope (Tektronix: TDS 3054B). A reference pyro-electric energy meter records the energy of the input laser pulse for which the crystal gets damaged. The laser damage threshold was calculated using the relation in equation (2.14):

$$P = \frac{E}{\tau A}$$  \hspace{1cm} (2.14)

Where ‘$P$’ is the Laser damage threshold in GW/cm$^2$, ‘$E$’ is the energy required breaking the crystal, ‘$\tau$’ is the response time in ns and ‘$A$’ represents the beam area.

**Figure 2.16 Functional Block Diagram of the Setup used for laser damage threshold measurement**
2.15 CONCLUSION

The present chapter describes a brief review on literature survey of NLO materials and the various characterization techniques to assess the suitability of the single crystals grown by slow evaporation solution growth method for nonlinear optical device applications. The structural characterization and crystal system classification were carried out using single crystal X-ray diffraction technique. The CHNS and EDAX studies were performed to determine the qualitative and quantitative analysis of the elements in the grown crystals. The linear and nonlinear optical spectroscopic studies were performed to analyze the composition, identification of functional groups and transparency window of the grown single crystals. Since the entire thrust is with respect to NLO application, the SHG property was estimated. In addition, the mechanical, thermal, dielectric, photoconductivity and laser damage threshold of the grown crystals were also investigated.