PART-II

GROWTH AND CHARACTERIZATION OF CHalcone DERIVATIVES
CHAPTER - IV

INTRODUCTION TO CRYSTAL GROWTH AND CHARACTERIZATION TECHNIQUES

Crystals are the unacknowledged pillars of modern technology. Without crystals, there would be no electronic industry, no photonic industry, no fiber optic communications, which depend on materials/crystals such as semiconductors, superconductors, polarizer, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, non-linear optics, piezo-electric, electro-optic, acousto-optic, photosensitive, refractory of different grades, crystalline films for microelectronics and computer industries. Crystal growth is an interdisciplinary subject covering physics, chemistry, material science, chemical engineering, metallurgy, crystallography, mineralogy, etc. The reason for growing single crystals is, many physical properties of solids are obscured or complicated by the effect of grain boundaries. The chief advantages are the anisotropy, uniformity of composition and the absence of boundaries between individual grains, which are inevitably present in polycrystalline materials. The strong influence of single crystals in the present day technology is evident from the recent advancements in the above mentioned fields. Hence, in order to achieve high performance from the device, good quality single crystals are needed. Growth of single crystals and their characterization towards device fabrication have assumed great impetus due to their importance for both academic as well as applied research.

METHODS OF CRYSTAL GROWTH

Growth of crystal ranges from a small inexpensive technique to a complex sophisticated expensive process and crystallization time ranges from minutes, hours, days and to months. Single crystals may be produced by the transport of crystal constituents in the solid, liquid or
vapour phase. On the basis of this, crystal growth may be classified into three categories as follows,

- **Solid Growth** - Solid-to-Solid phase transformation
- **Liquid Growth** - Liquid to Solid phase transformation
- **Vapour Growth** - Vapour to Solid phase transformation

Based on the phase transformation process, crystal growth techniques are classified as solid growth, vapour growth, melt growth and solution growth [1]. The conversion of a polycrystalline piece of material into single crystal by causing the grain boundaries to be swept through and pushed out of the crystal takes place in the solid-growth of crystals [2]. The above methods have been discussed in detail by several authors [3-5]. The different techniques of each category are found in reviews and books by Faktor and Garret [6, 7] on vapour growth, [7] on melt, on gel growth, [8] on solution growth and Elwell and Scheel [9] on high temperature solution growth.

An efficient process is the one, which produces crystals adequate for their use at minimum cost. Better choice of the growth method is essential because it suggests the possible impurity and other defect concentrations. Choosing the best method to grow a given material depends on material characteristics.

In the above mentioned categories liquid growth includes both melt and solution growth. A survey of the methods of growth suggests that almost 80% of the single crystals are grown from the melt compared with roughly 5% from vapour, 5% from low temperature solution, 5% from high temperature solution, and 3% from the solid and only 2% by hydrothermal methods.

In contrast to the historical work, it seems that the essential task for the crystal growers at present is to gain basic knowledge about the correlation of crystal properties and the growth
conditions defined to be special parameters. This basic understanding of the deposition of atoms on to a suitable substrate surface – crystal growth – the generation of faults in the atomic structure during growth and subsequent cooling to room temperature – crystal defect structure, are the input for the design of crystal growth systems and control of growth parameters. Though the fundamentals are relatively simple, the complexities of the interactions involved and the individualities of different materials, system and growth process have ensured that experimentally verifiable predictions from scientific principles have met with limited success – good crystal growth remains as art. As a result, crystal growth has long had the image of alchemy. This is clearly expressed by the title of one of the first text books on crystal growth ‘The Art and Science of Growing crystal’ [10]. The recent advances which include reduction of growth temperature, the reduction or elimination of reactant transport variables and the use of better controlled energy sources to promote specific reactions, coupled with increased development and application of in-situ diagnostic techniques to monitor and perhaps the ultimate control lead to simplified growth systems and the crystal growth process has transferred and the field from an art to science, technique and to technology.

GROWTH FROM SOLUTION

Materials, which have high solubility and have variation in solubility with temperature, can be grown easily by solution method. There are two methods in solution growth depending on the solvents and the solubility of the solute. They are

1. High temperature solution growth
2. Low temperature solution growth
HIGH TEMPERATURE SOLUTION GROWTH

In high-temperature solutions, the constituents of the material to be crystallized are dissolved in a suitable solvent and crystallization occurs as the solution becomes critically supersaturated. The supersaturated may be promoted by evaporation of the solvent, by cooling the solution or by a transport process in which the solute is made to flow from a hotter to a cooler region. The high temperature crystal growth can be divided into two major categories:

- Growth from single component system.
- Growth from multi component system.

This method is widely used for the growth of oxide crystals. The procedure is to heat the container having flux and the solute to a temperature so that all the solute materials dissolve. This temperature is maintained for a ‘soak’ period of several hours and then the temperature is lowered very slowly.

HYDROTHERMAL GROWTH

Hydrothermal implies conditions of high pressure as well as high temperature. Substances like calcite, quartz is considered to be insoluble in water but at high temperature and pressure, these substances are soluble. This method of crystal growth at high temperature and pressure is known as hydrothermal method. Temperatures are typically in the range of 400° C to 600° C and the pressure involved is large (hundreds or thousands of atmospheres).

Growth is usually carried out in steel autoclaves with gold or silver linings. Depending on the pressure the autoclaves are grouped into low, medium and high-pressure autoclaves. The concentration gradient required to produce growth is provided by a temperature difference between the nutrient and growth areas. The requirement of high pressure presents practical difficulties and there are only a few crystals of good quality and large dimensions are grown by this technique. Quartz is the outstanding example of industrial hydrothermal crystallization. One
serious disadvantage of this technique is the frequent incorporation of OH⁻ ions into the crystal, which makes them unsuitable for many applications.

**GEL GROWTH**

It is an alternative technique to solution growth with controlled diffusion and the growth process is free from convection. Gel is a two-component system of a semisolid rich in liquid and inert in nature. The material, which decomposes before melting, can be grown in this medium by counter diffusing two suitable reactants. Crystals with dimensions of several mm can be grown in a period of 3 to 4 weeks. The crystals grown by this technique have high degree of perfection and fewer defects since the growth takes place at room temperature.

**GROWTH FROM MELT**

All materials can be grown in single crystal form from the melt provided they melt congruently without decomposition at the melting point and do not undergo any phase transformation between the melting point and room temperature. Depending on the thermal characteristics, the following techniques are employed.

1. Bridgman technique
2. Czochralski technique
3. Kyropoulos technique
4. Zone melting technique
5. Verneuil technique
In Bridgman technique the material is melted in a vertical cylindrical container, tapered conically with a point bottom. The container is lowered slowly from the hot zone of the furnace into the cold zone. The rates of movement for such processes range from about 1 – 30 mm/hr. Crystallization begins at the tip and continues usually by growth from the first formed nucleus. This technique cannot be used for materials, which decompose before melting. This technique is best suited for materials with low melting point.

In Czochralski method, the material to be grown is melted by induction or resistance heating under a controlled atmosphere in a suitable non-reacting container. By controlling the furnace temperature, the material is melted. A seed crystal is lowered to touch the molten charge. When the temperature of the seed is maintained very low compared to the temperature of the melt, by suitable water cooling arrangement, the molten charge in contact with the seed will solidify on the seed. Then the seed is pulled with simultaneous rotation of the seed rod and the crucible in order to grow perfect single crystals.

Liquid encapsulated Czochralski abbreviated as LEC technique makes it possible to grow single crystals of materials, which consists of components that produce high vapour pressure at the melting point. This refined method of Czochralski technique is widely adopted to grow III-V compound semiconductors.

In Kyropoulos technique, the crystal is grown in a larger diameter. As in the Czochralski method, here also the seed is brought into contact with the melt and is not raised much during the growth, i.e. part of the seed is allowed to melt and a short narrow neck is grown. After this, the vertical motion of the seed is stopped and growth proceeds by decreasing the power into the melt. The major use of this method is growth of alkali halides to make optical components.
In the zone melting technique, the feed material is taken in the form of sintered rod and the seed is attached to one end. A small molten zone is maintained by surface tension between the seed and the feed. The zone is slowly moved towards the feed. Single crystal is obtained over the seed. This method is applied to materials having large surface tension. The main reasons for the impact of zone refining process to modern electronic industry are the simplicity of the process, the capability to produce a variety of organic and inorganic materials of extreme high purity, and to produce dislocation free crystal with a low defect density.

In the case of vertical normal freezing, the solid-melt interface is moved upwards from the cold bottom to the hot top so as to get better quality crystals. The method is more applicable in growing single crystals of materials with volatile constituents like GaAs.

In the Verneuil technique, a fine dry powder of size 1-20 microns of the material to be grown is shaken through the wire mesh and allowed to fall through the oxy-hydrogen flame. The powder melts and a film of liquid is formed on the top of the seed crystal. This freezes progressively as the seed crystal is slowly lowered. The art of the method is to balance the rate of charge feed and the rate of lowering of the seed to maintain a constant growth rate and diameter. By this method ruby crystals are grown up to 90 mm in diameter for use in jeweled bearings and lasers. This technique is widely used for the growth of synthetic gems and variety of high melting oxides.

**ELECTRO- CRYSTALLISATION**

Electrolysis of fused salts is normally used for the commercial production of metals such as aluminum and has great technological importance. The process of crystal growth from fused salts is analogous in many respects, except for the requirement of electron transfer in deposition of the metal. Fused salt electrolysis has been used to grow crystals of oxides in reduced valence states.

**GROWTH FROM VAPOUR**
The growth of single crystal material from the vapour phase is probably the most versatile of all crystal growth processes. Crystals of high purity can be grown from vapour phase by sublimation, condensation and sputtering of elemental materials. To obtain single crystals of high melting point materials, this method is used. Molecular beam techniques have also been applied recently to crystal growth problems. The most frequently used method for the growth of bulk crystals utilizes chemical transport reaction in which a reversible reaction is used to transport the source material as a volatile species to the crystallization region. Finding a suitable transporting agent is a formidable, problem in this technique. It is rarely possible to grow large crystals because of multi-nucleation.

The commercial importance of vapour growth is the production of thin layers by chemical vapour deposition (CVD), where usually irreversible reactions e.g. decomposition of silicon halides or of organic compounds are used to deposit materials epitaxially on a substrate. Doping can be achieved by introducing volatile compounds of dopant elements into the reaction region. The thickness of the doped layer can be controlled.

LOW TEMPERATURE SOLUTION GROWTH

Growth of crystals from aqueous solution is one of the ancient methods of crystal growth. The method of crystal growth from low temperature aqueous solutions is extremely popular in the production of many technologically important crystals. It is the most widely used method for the growth of single crystals, when the starting materials are unstable at high temperatures [1] and also which undergo phase transformations below melting point. The growth of crystals by low temperature solution growth involves weeks, months and sometimes years. Though the technology of growth of crystals from solution has been well perfected, it involves meticulous
work, much patience and even a little amount of luck. A power failure or a contaminated batch of raw material can destroy months of work.

Materials having moderate to high solubility in temperature range, ambient to 100 °C at atmospheric pressure can be grown by low-temperature solution method [11]. The mechanism of crystallization from solutions is governed, in addition to other factors, by the interaction of ions or molecules of the solute and the solvent which is based on the solubility of substance on the thermodynamical parameters of the process; temperature, pressure and solvent concentration [5]. The advantages of crystal growth from low temperature solution nearer the ambient temperature results in the simple and straightforward equipment design which gives a good degree of control of accuracy of ±0.01°C. Due to the precise temperature control, supersaturation can be very accurately controlled. Also efficient stirring of solutions reduces fluctuations to a minimum. The low temperature solution growth technique is well suited to those materials which suffer from decomposition in the melt or in the solid at high temperatures and which undergo structural transformations while cooling from the melting point and as a matter of fact numerous organic and inorganic materials which fall in this category can be crystallized using this technique. The low temperature solution growth technique also allows variety of different morphologies and polymorphic forms of the same substance can be grown by variations of growth conditions or of solvent. The proximity to ambient temperature reduces the possibility of major thermal shock to the crystal both during growth and removal from the apparatus.

The main disadvantages of the low temperature solution growth are the slow growth rate in many cases and the ease of solvent inclusion into the growing crystal. Under the controlled conditions of growth the solvent inclusion can be minimized and the high quality of the grown crystal can compensate the disadvantage of much longer growth periods. After many
modifications and refinements, the process of solution growth now yields good quality crystals for a variety of applications. Growth of crystals from solution at room temperature has many advantages over other growth methods though the rate of crystallization is slow. Since growth is carried out at room temperature, the structural imperfections in solution grown crystals are relatively low [7].

Among the various methods of growing single crystals, solution growth at low temperatures occupies a prominent place owing to its versatility and simplicity. After undergoing so many modifications and refinements, the process of solution growth now yields good quality crystals for a variety of applications.

In the low temperature solution growth, crystals can be grown from solution if the solution is supersaturated i.e., it contains more solute than it can be in equilibrium with the solid. Three principal methods are used to produce the required supersaturation:

i. Slow cooling of the solution

ii. Slow evaporation of the solvent

iii. The temperature gradient method.

Low temperature solution growth is a well-established technique due to its versatility and simplicity. It is possible to grow large crystals of high perfections as the growth occurs close to equilibrium conditions [12]. It also permits the preparation of different morphologies of the same materials by varying the growth conditions.
i. SLOW COOLING TECHNIQUE

It is the best way to grow single crystals by solution technique. The Main limitation is the need to use a range of temperature. The possible range of temperature is usually small so that much of the solute remains in the solution at the end of the run. To compensate this effect, large volumes of solution are required. The use of a range of temperatures may not be desirable because the properties of the grown material may vary with temperature. Even though the method has technical difficulty of requiring a programmable temperature control, it is widely used with great success. The temperature at which such crystallization can begin is usually within the range 45 - 75 °C and the lower limit of cooling is the room temperature.

ii. SLOW EVAPORATION METHOD

This method is similar to the slow cooling method in view of the apparatus requirements. The temperature is fixed constant and provision is made for evaporation. With non-toxic solvents like water, it is permissible to allow evaporation into the atmosphere. Typical growth conditions involve temperature stabilization to about ± 0.005°C and rates of evaporation of a few ml /hr. The evaporation techniques of crystal growth have the advantage that the crystals grow at a fixed temperature. But inadequacies of the temperature control system still have a major effect on the growth rate. This method is the only one, which can be used with materials, which have very small temperature coefficient of stability.

iii. TEMPERATURE GRADIENT METHOD

This method involves the transport of the materials from a hot region containing the source material to be grown to a cooler region where the solution is supersaturated and the crystal grows. The main advantages of this method are that
(a) Crystal grows at a fixed temperature

(b) This method is insensitive to changes in temperature provided both the source and the growing crystal undergo the same change.

(c) Economy of solvent and solute.

On the other hand, changes in the small temperature differences between the source and the crystal zones have a large effect on the growth rate. Excellent quality crystals of ferroelectric and piezo-electric materials such as Ammonium dihydrogen phosphate (ADP), Potassium dihydrogen phosphate (KDP) and Triglycine sulphate (TGS) are commercially grown for use in devices by the low temperature solution growth method.
INSTRUMENTATION TECHNIQUES

4.1 INTRODUCTION

Nowadays, scientists and engineers have an impressive array of powerful and elegant tools for acquiring quantitative and qualitative information about the composition and structure of matter. There are variety of crystals grown having numerous applications in science and technology. It is always important to characterize these crystals with various angles of interests by different instruments [13]. This chapter describes a brief review of different experimental characterization techniques, which are used by the present author to characterize the grown crystals.

4.2 INSTRUMENTATION TECHNIQUES OF CHARACTERIZATION

4.2.1 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY- NMR

Nuclear Magnetic Resonance spectroscopy is a powerful and theoretically complex analytical tool. It is important to remember that, with NMR, we are performing experiments on the nuclei of atoms, not the electrons. The chemical environment of specific nuclei is deduced from information obtained about the nuclei.

NUCLEAR SPIN AND THE SPLITTING OF ENERGY LEVELS IN A MAGNETIC FIELD

Subatomic particles (electrons, protons and neutrons) can be imagined as spinning on their axes. In many atoms (such as $^{12}$C) these spins are paired against each other, such that the nucleus of the atom has no overall spin. However, in some atoms (such as $^1$H and $^{13}$C) the nucleus does possess an overall spin. The rules for determining the net spin of a nucleus are as follows;
1. If the number of neutrons and the number of protons are both even, then the nucleus has NO spin.

2. If the number of neutrons plus the number of protons is odd, then the nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2)

3. If the number of neutrons and the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3)

The overall spin, $I$, is important. Quantum mechanics tells us that a nucleus of spin $I$ will have $2I + 1$ possible orientations. A nucleus with spin 1/2 will have 2 possible orientations. In the absence of an external magnetic field, these orientations are of equal energy. If a magnetic field is applied, then the energy levels split (Figure 4.1). Each level is given a magnetic quantum number, $m$.

![Figure 4.1: Energy Level for a Nucleus with Spin Quantum Number 1/2](image)

When the nucleus is in a magnetic field, the initial populations of the energy levels are determined by thermodynamics, as described by the Boltzmann distribution. This is very important, and it means that the lower energy level will contain slightly more nuclei than the higher level. It is possible to excite these nuclei into the higher level with electromagnetic
radiation. The frequency of radiation needed is determined by the difference in energy between the energy levels.

**CHEMICAL SHIFT**

The magnetic field at the nucleus is not equal to the applied magnetic field; electrons around the nucleus shield it from the applied field. The difference between the applied magnetic field and the field at the nucleus is termed the nuclear shielding.

The chemical shift is

\[ \delta = \frac{\text{distance downfield from TMS (Hz)}}{\text{operation frequency of the spectrometer (MHz)}} \text{ parts per million (ppm)} \]

The s-electrons in a molecule have spherical symmetry and circulate in the applied field, producing a magnetic field which opposes the applied field. This means that the applied field strength must be increased for the nucleus to absorb at its transition frequency. This upfield shift is also termed diamagnetic shift. Electrons in p-orbitals have no spherical symmetry and they produce comparatively large magnetic fields at the nucleus, which give a low field shift. This "deshielding" is termed paramagnetic shift.

In proton (\(^1\)H) NMR, p-orbitals play no part, which is why only a small range of chemical shift (10 ppm) is observed. We can easily see the effect of s-electrons on the chemical shift by looking at substituted methane, \(\text{CH}_3\text{X}\). As X becomes increasingly electronegative, so the electron density around the protons decreases, and they resonate at lower field strengths. Chemical shift is defined as nuclear shielding / applied magnetic field and is measured relative to a reference compound. For \(^1\)H NMR, the reference is usually tetramethylsilane, \(\text{Si}\).
(CH₃)₄NBr. Bruker AVANCE III 500 MHz (AV 500) NMR Spectrometer (Figure 4.2) and DMSO-d6 as solvent.

**FIGURE 4.2: BRUKER AVANCE III 500 MHZ (AV 500) NMR SPECTROMETER**

### 4.2.2. FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT-IR)

The term ‘spectroscopy’ is generally used for the analytical techniques based on the interaction of electromagnetic radiation with matter and variation of particular physical quantity with frequency of radiation. In spectroscopy, the measurements of absorbance / transmittance of electromagnetic radiation, due to interaction with sample by molecules that are carried out in a gas or vapour state or dissolved molecules/ions or solid depending upon requirement. Spectroscopy is used for both qualitative and quantitative investigations.

Due to the advent of Fourier Transform technology, the scenario is completely changed. Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed.
Samples for FT-IR can be prepared in a number of ways. Sample crystal can be milled with potassium bromide (KBr) to form a very fine powder. This powder is then compressed into a thin pellet which can be analyzed. KBr is also transparent in the IR. Alternatively, solid samples can be dissolved in a solvent such as methylene chloride, and the solution placed onto a single salt plate. The solvent is then evaporated off, leaving a thin film of the original material on the plate. This is called a cast film, and is frequently used for polymer identification. For liquid samples, the easiest is to place one drop of sample between two plates of sodium chloride (salt), since salt is transparent to infrared light. The drop forms a thin film between the plates. Multiplex types of instruments employ the mathematical tool of Fourier Transform [14].

The infrared spectrum originates from the vibrational motion of the molecule. The vibrational frequencies are a kind of fingerprint of the compounds. This property is used for characterization of organic, inorganic and biological compounds. The band intensities are proportional to the concentration of the compound and hence qualitative estimations are possible. The IR spectroscopy is also carried out by using Fourier transform technique. The interference pattern obtained from a two beam interferometer as the path difference between the two beams is altered, when Fourier transformed, gives rise to the spectrum. The transformation of the interferogram into spectrum is carried out mathematically with a dedicated on-line computer.

The Perkin Elmer Spectrum1 FT-IR (Figure 4.3) instrument consists of globar and mercury vapor lamp as sources, an interferometer chamber comprising of KBr and Mylar beam splitters followed by a sample chamber and detector. Entire region of 450-4000 cm\(^{-1}\) is covered by this instrument. The spectrometer works under purged conditions. Solid samples are dispersed in KBr or polyethylene pellets depending on the region of interest. This instrument has a typical
resolution of 1.0 cm\(^{-1}\). Signal averaging, signal enhancement, base line correction and other spectral manipulations are possible.

**FIGURE 4.3: PERKIN ELMER SYSTEM ONE FTIR/ATR**

Infrared spectrum is useful in identifying the functional groups like -OH, -CN, -CO, -CH, -NH\(_2\), etc. Also quantitative estimation is possible in certain cases for chemicals, pharmaceuticals, petroleum products, etc. Resins from industries, water and rubber samples, and blood and food materials can also be analyzed. Reaction mechanisms and concentration studies are done.

4.2.3 UV - Vis NIR

The valence electrons in organic molecules and polyatomic ions, such as CO\(_3^{2-}\), occupy quantized sigma bonding, \(\sigma\), pi bonding, \(\pi\), and non-bonding, \(n\), molecular orbitals (MOs). Unoccupied sigma anti-bonding, \(\sigma^*\), and pi anti-bonding, \(\pi^*\), molecular orbitals are slightly higher in energy. Because the difference in energy between the highest-energy occupied (HOMOs) and the lowest-energy unoccupied (LUMOs) corresponds to ultraviolet and visible radiation, absorption of a photon is possible. Four types of transitions between quantized energy
levels account for most molecular UV/Vis spectra. Table 4.1 lists the approximate wavelength ranges for these transitions, as well as a partial list of bonds, functional groups, or molecules responsible for these transitions. Of these transitions, the most important are \( n \rightarrow \pi^* \) and \( \pi \rightarrow \pi^* \) because they involve important functional groups that are characteristic of many analytes and because the wavelengths are easily accessible. The bonds and functional groups that give rise to the absorption of ultraviolet and visible radiation are called chromophores.

Table 4.1: Electronic Transitions Involving \( n, \sigma, \) and \( \pi \) Molecular Orbital

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavelength Range (nm)</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma \rightarrow \sigma^* )</td>
<td>&lt;200</td>
<td>C–C &amp; C–H</td>
</tr>
<tr>
<td>( n \rightarrow \sigma^* )</td>
<td>160-260</td>
<td>H(_2)O, CH(_3)OH&amp; CH(_3)Cl</td>
</tr>
<tr>
<td>( \pi \rightarrow \pi^* )</td>
<td>200-500</td>
<td>C=C, C=O, C=N&amp; C≡C</td>
</tr>
<tr>
<td>( n \rightarrow \pi^* )</td>
<td>250-600</td>
<td>C=O, C=N, N=N &amp; N=O</td>
</tr>
</tbody>
</table>
FIGURE 4.4: T90+ UV-VIS SPECTROPHOTOMETER

UV-Visible spectroscopy (Figure 4.4) is mostly used to identify the conjugated system which has stronger absorption. The wavelength of absorption peak can be correlated with the types of bonds in a given molecules and are valuable in determining the functional groups within a molecule. The nature of the solvent, pH of the solution, temperature, high electrolyte concentration and presence of interfering substances can influence the absorption spectra of compounds, as can variations in slit width (effective band width) in the spectrophotometer.

4.2.4 PHOTOLUMINESCENCE SPECTROSCOPY (PL)

All solids, including semi conductors have “energy gap” for conducting electron. The principle of photoluminescence is explained in (Figure 4.5). In order to understand the concept of a gap in energy, first consider that some of the electrons in a solid are not firmly attached to the atoms, as they are for single atoms, but can hope from one atom to another. These loosely attached electrons are bound in the solid by differing amounts and thus have much different energy. Electrons having energies above a certain value are referred to as conduction electrons, while electrons having energies below a certain value are referred to as valence electron. Furthermore, there is an energy gap between the conduction and valance electron states. Under normal conditions electrons are forbidden to have energies between the valance and conduction bands. If a light particle (photon) has energy greater then the band gap energy, then it can be absorbed and thereby raise an electron from the valance band up to the conduction band across the forbidden energy gap. In this process of photo excitation, the electron generally has excess energy which it loses before coming to rest at the lowest energy in the conduction band. At this point the electron eventually falls back down to the valance band. As it falls down, the energy
loss is converted back into a luminescent photon which is emitted from the material. Thus the energy of the emitted photon is a direct measure of the band gap energy, e.g. the process of photon excitation followed by photon emission is called photo luminescence.

Photoluminescence is divided into two categories: fluorescence and phosphorescence. A pair of electrons occupying the same electronic ground state has opposite spins and are said to be in a singlet spin state. When an analyte absorbs an ultraviolet or visible photon, one of its valence electrons moves from the ground state to an excited state with a conservation of the electron’s spin. Emission of a photon from the singlet excited state to the singlet ground state or between any two energy levels with the same spin is called fluorescence. The probability of fluorescence is very high and the average lifetime of an electron in the excited state is only $10^{-5}$ or $10^{-8}$ s. Fluorescence, therefore, decays rapidly once the source of excitation is removed. In some cases an electron in a singlet excited state is transformed to a triplet excited state in which its spin is no longer paired with the ground state. Emission between a triplet excited state and a
singlet ground state—or between any two energy levels that differ in their respective spin states—is called phosphorescence. Because the average lifetime for phosphorescence ranges from 10 – 4 s, phosphorescence may continue for some time after removing the excitation source. The use of molecular fluorescence for qualitative analysis and semi quantitative analysis can be traced to the early to mid 1800s, with more accurate quantitative methods appearing in the 1920s. Instrumentation for fluorescence spectroscopy using a filter or a monochromator for wavelength selection appeared in, respectively, the 1930s and 1950s. Although the discovery of phosphorescence preceded that of fluorescence by almost 200 years, qualitative and quantitative applications of molecular phosphorescence did not receive much attention until after the development of fluorescence instrumentation.

The Perkin Elmer LS 45 Luminescence Spectrometer (Figure 4.6) has been developed in conjunction with a host of software and accessories to address a wide range of applications that require challenges in fluorescence, phosphorescence, chemiluminescence or bio-luminescence. This instrument uses a high energy pulsed Xenon source for excitation to minimize photo bleaching of samples and provide a long live excitation source. The Spectrophotometer can be calibrated by using a standard fluorescent material. The Luminescence spectrometer offers versatility, reliability and ease of use. This is an instrument with all of the heritage, sensitivity and reliability. This monochromator based instrument uses a high energy pulsed Xenon source for excitation. The software combines the user friendly appeal of a Windows based software package with application specific knowledge. The result is a powerful system that can be used routinely for quality fluorescence analysis.
Because of its greater sensitivity, fluorescence spectroscopy has many applications, it is increasingly employed for the identification of compounds and conformational studies, it is a powerful technique for studying the dynamical properties of biological molecules in solution. Fluorescence life time measurements can be used to obtain structural information on the fluorescing species and on kinetics of energy transfer.

4.2.5 THERMAL STUDIES

According to widely accepted definition of thermal analysis (Thermo analytical), it is a group of techniques in which physical properties of a substance and/or its reaction products are measured as a function of temperature whilst the substance is subjected to a controlled temperature program [13]. According to International Confederation for Thermal Analysis and Calorimetric (ICTAC), thermal analysis is defined as a group of techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed [15]. Nearly over a dozen thermal methods can be identified, which differ in the properties measured and temperature programs [16-18]. These methods find widespread use for both quality control and research applications of various substances, such as, polymers, pharmaceuticals, crystals, clays, minerals, metals and alloys.

CLASSIFICATION OF THERMAL ANALYSIS TECHNIQUES

Thermal analysis techniques involve the measurement of various properties of materials subjected to dynamically changing environments under predetermined condition of heating rate, temperature range and gaseous atmosphere or vacuum. Classification of thermal analysis
techniques is as shown in (Table 4.2). Among all the thermal methods, the most widely used techniques are TGA, DTA and DSC, which are employed in inorganic and organic chemistry, metallurgy, mineralogy and other areas.

### Table 4.2: Classification of Thermal Analysis Techniques

<table>
<thead>
<tr>
<th>Classical Techniques</th>
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<tbody>
<tr>
<td><strong>TG / TGA</strong></td>
</tr>
<tr>
<td><strong>DTG</strong></td>
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<td></td>
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<tr>
<td><strong>EGD</strong></td>
</tr>
<tr>
<td><strong>TG – FT-IR</strong></td>
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<tr>
<td><strong>TG – MS</strong></td>
</tr>
<tr>
<td><strong>DTA</strong></td>
</tr>
<tr>
<td><strong>DDTA</strong></td>
</tr>
<tr>
<td><strong>DSC</strong></td>
</tr>
</tbody>
</table>

Thermal analysis (DTA) and thermo gravimetric analysis (TGA) are widely used in studies involving physicochemical changes accompanied by variation in the heat content and the weight of the material.

**THERMO GRAVIMETRIC ANALYSIS (TGA)**

Thermo gravimetric analysis 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 thermo gravimetric analysis is called thermogram (TG) and its
first derivative is called a derivative thermogram (DTG). Modern commercial TG instrument consists of following main parts:

- 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 on 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 behavior of a given substance, i.e., temperature of decomposition, stability range of an intermediate compound and the temperature at which the reaction get completed. As noted earlier that the TGA involves change in weight with respect to temperature. The acquired data obtained as a plot of mass or loss of mass in percentage as a function of temperature is considered as a thermal spectrum, or a thermogram, or a thermal decomposition curve. These thermograms characterize a system in terms of temperature dependence of its thermodynamic properties and physical-chemical kinetics.
Since the TGA involves measurement of a change in weight of a system as the temperature is increased at pre-determined rate, changes in weight are a result of the rupture and/or formation of various physical and chemical bonds at elevated temperatures that lead to the evaluation of volatile products or the formation of heavier reaction products. From such curves, parameters concerning the thermodynamics and kinetics of the various chemical reactions can be evaluated, reaction mechanism, the intermediate and final reaction products can be identified. Usually, the temperature range is from ambient to 1200°C with inert or reactive atmospheres. The derivative in TG is often used to pinpoint completion of weight-loss steps or to increase resolution of overlapping weight-loss occurrences. The shape of thermo gravimetric curve of a particular compound is influenced by the heating rate of the sample and the atmosphere surrounding it [16, 19&20].

**Applications of TGA**

- Study thermal degradation / decomposition / dehydration.
- Chemical reaction resulting in changes of mass such as absorption, adsorption, desorption.
- To check the sample purity.

**DIFFERENTIAL THERMAL ANALYSIS (DTA)**

DTA is a technique in which the temperature difference between a substance and a reference material is measured as a function of temperature whilst the substance and reference material are subjected to a controlled temperature program [15]. DTA provides information on the chemical reactions, phase transformations, and structural changes that occur in a sample during a heat-up or a cool-down cycle. The DTA measures the differences in energies released or absorbed, and the changes in heat capacity of materials as a function of temperature. The graph
of DTA signal, i.e. differential thermocouple output in micro volts on the Y-axis plotted versus the sample temperature in °C on the X-axis gives the results of DTA. Modern thermo-balance are often equipped so as to record the DTA signal and the actual thermo-gravimetric measurement, simultaneously. In addition to showing the energetic nature of weight loss events, the DTA signal can also show thermal effects that are not accompanied by a change in mass, e.g. melting, crystallization or a glass transition. Transition temperatures are measured precisely using the DTA. The DTA identifies the temperature regions and the magnitude of critical events during a drying or firing process such as binder burnout, carbon oxidation, sulfur oxidation, structural clay collapse, Alpha to Beta quartz transition, carbonate decompositions, recrystallizations, melting and cristobalite transitions, melting, solidification or solidus temperature, glass transition temperature (Tg), curie point, energy of reaction, heat capacity, and others. The transition enthalpy is estimated from the DTA curve using the heat capacity of the heat sensitive plate as a function of temperature.

Application of DTA

- Primarily used for detection of transition temperature.
- To check the sample purity.

4.2.6 MECHANICAL STRENGTH-MICROHARDNESS STUDIES

Micro-hardness tests are the simplest, cheapest and non-destructive one to assess the mechanical properties of materials, which are reviewed in detail by Mott [21].

Hardness is a characteristic of a material, not a fundamental physical property. It is defined as the resistance to indentation, and it is determined by measuring the permanent depth of the indentation. More simply put, when using a fixed force (load) and a given indenter, the
smaller the indentation, the harder the material. Indentation hardness value is obtained by measuring the depth or the area of the indentation using one of over 12 different test methods.

The Vickers hardness test method, also referred to as a microhardness test method, is mostly used for small parts, thin sections, or case depth work. The Vickers method (Figure 4.7) is based on an optical measurement system. The micro hardness test procedure, ASTM E-384, specifies a range of light loads using a diamond indenter to make an indentation which is measured and converted to a hardness value. It is very useful for testing on a wide type of materials as long as test samples are carefully prepared. A square base pyramid shaped diamond is used for testing in the Vickers scale. Typically loads are very light, ranging from a few grams to one or several kilograms, although "Macro" Vickers loads can range up to 30 kg or more. The micro hardness methods are used to test on metals, ceramics, and composites - almost any type of material.

Since the test indentation is very small in a Vickers test, it is useful for a variety of applications: testing very thin materials like foils or measuring the surface of a part, small parts or small areas, measuring individual microstructures, or measuring the depth of case hardening by sectioning a part and making a series of indentations to describe a profile of the change in hardness. The Vickers method is more commonly used.

Sample preparation is usually necessary with a micro hardness test in order to provide a small enough specimen that can fit into the tester. Additionally, the sample preparation will need to make the specimen’s surface smooth to permit a regular indentation shape and good measurement, and to ensure the sample can be held perpendicular to the indenter. Usually the prepared samples are mounted in a plastic medium to facilitate the preparation and testing. The
indentations should be as large as possible to maximize the measurement resolution. (Error is magnified as indentation sizes decrease) The test procedure is subject to problems of operator influence on the test results.

FIGURE 4.7: VICKERS HARDNESS TESTER

4.2.7 SECOND HARMONIC GENERATION (SHG)

The explanation of nonlinear effects lies in the way in which a beam of light propagates through a solid. The nuclei and associated electrons of the atoms in the solid form an electric dipole. The electromagnetic radiation interacts with these dipoles causing them to oscillate which, by the classical laws of electromagnetism, results in the dipoles themselves acting as sources of electromagnetic radiation. If the amplitude of vibration is small, the intensity of the incident radiation increases the relationship between irradiance and amplitude of vibration becomes nonlinear resulting in the generation of harmonic in the frequency of radiation emitted by the oscillating dipoles. Thus frequency doubling or second harmonic generation (SHG) and indeed higher order frequency effect occurs as the incident intensity is increased. In a nonlinear
medium the induced polarization is a nonlinear function of the applied field. A medium exhibiting SHG is a crystal composed of molecules with asymmetric charge distributions arranged in the crystal in such a way that a polar orientation is maintained throughout the crystal. The NLO property of the crystals was understood using Q-switched Nd: YAG laser as a source. KDP sample was used as the reference material.

**FIGURE 4.8: Nd: YAG LASER WITH LID OPEN SHOWING FREQUENCY-DOUBLED 532 NM GREEN LIGHT**

**Nd: YAG laser**

- Nd: YAG (Figure 4.8) (neodymium-doped yttrium aluminum garnet) is a crystal that is used as a laser medium for solid-state lasers.

- The triply ionised neodymium [Nd (III)] dopant (ie a substance added in minute amounts to another pure substance to alter its conductivity), typically replaces a small fraction of the yttrium ions in the host crystal structure, since the two ions are of similar size.

- The neodymium ion provides the laser activity in the crystal.

- Nd: YAG laser has a wave length of 1064 nm and has the capability to reach deeper layers of skin tissue than other types of lasers.
In Q-switched mode, Nd: YAG produces 2 wavelengths, one in the infrared range (1064 nm) and a second beam of 532 nm wavelengths which is useful for superficial skin lesions. Q-switching refers to the technique of making the laser produce a high intensity beam in very short pulses.
CHAPTER -V

CRYSTAL GROWTH AND CHARACTERIZATION OF HMHP-I, HMHP-II, MPEPB AND MBMC

5.1. INTRODUCTION

The crystal engineering has its roots in the field of the design and synthesis of crystalline materials of the solid-state organic chemistry [22-23]. The organic materials have received great deal of attention owing to their wide range of applications in various fields like photonic devices, superconductors, semiconductors, electrical and magnetic fields as well [24–27]. The organic materials have excellent properties compared to the conventional inorganic solids which show ultrafast response times, lower dielectric constants, better process ability characteristics and enhanced NLO responses [28]. But the practical applications of the organic nonlinear optical materials are limited because of their poor physicochemical stability and low mechanical strength [29]. For overcoming the above difficulties of the organic NLO crystals, in recent years the organic materials were mixed with inorganic materials to improve their chemical stability, physico-chemical properties, mechanical strength and nonlinear optical coefficients, which are the important parameters for an NLO crystal [30,31]. The interesting nonlinear optical effects extended to optical amplifiers, optical parametric oscillators, Q-switched intra cavity second harmonic devices, high optical damage threshold and other electro-optical applications lead to the extensive research in organic functional group materials which becomes an expanding area. The organic ionic crystals exhibit the highest figure of merit for second harmonic generation, two photon absorption (TPA) processes and UV tunable laser applications among the known organic and inorganic NLO materials, [32-34]. However, the absorption wavelength range of such organic materials, if they have a high SHG efficiency, extends to visible region and
their crystals show yellow or orange colour, which makes them useless to wavelength conversion of semiconductor lasers [35]. The search for novel nonlinear optical (NLO) materials with large quadratic nonlinearities is mainly oriented towards applications in optical communications or optical signal processing. Organic compounds are often formed by weak van der Waals and hydrogen bonds and hence possess high degree of delocalization. Thus they are expected to be optically more nonlinear than inorganic compounds. Organic crystals hold promise because of large variety of such materials and the potential to synthesize molecules according to some design principles. Among many organic compounds reported for their second harmonic generation, chalcone derivatives are noticeable materials for their excellent blue light transmittance and good crystallizability [36-38].

The search for new materials with nonlinear optical (NLO) properties has been the subject of intense research due to their application in a wide range of technologies such as optical computing and optical communication [39-41]. In the past years much attention has been paid to organic NLO materials due to their promising applications in optoelectronics technology [42,43], their large non-linear response, extremely fast switching time and convenient optimization routes through molecular engineering compared to the currently studied inorganic materials [44,45]. To have strong second-order NLO properties, the compound must possess a large first-order molecular hyperpolarizability (β), and also must crystallize in a non-centro symmetric system to have a nonzero χ(2). Besides the strong NLO response, the NLO materials must also fulfill some other technological requirements for practical applications such as wide transparency extending down to UV region, fast response, thermal stability, chemical stability, mechanical stability and high laser damage threshold. It has been generally understood that for a material to have useful and highly efficient NLO properties,
the constituting molecules need first to exhibit large molecular hyperpolarizabilities, which are generally characterized by a highly extended \(\pi\)-conjugated chain with strong electron donor–acceptor pairs at the ends (D–\(\pi\)–A) [46]. Since a large molecular hyperpolarizability (\(\beta\)) is the basis of a strong second harmonic generation (SHG) response; organic molecules with long conjugation systems that usually exhibit large (\(\beta\)) values are certainly candidate molecules for NLO materials. Numerous studies dealing with chalcones have been carried out in the past few years [47-49]. For this reason, they have been the objective of several experimental and theoretical studies, aimed mainly at the determination of their crystal structures [50-52].

Chalcones are \(\alpha, \beta\) unsaturated ketones with a \(\pi\)-conjugated system provide a large charge transfer axis. The theory of charge transfer in molecules reveals the relationship between structure and NLO properties of organic compounds [53,54]. A series of chalcone materials have been reported for their very high second harmonic efficiency and third order nonlinear optical effects. Very recently chalcones have been studied for their third order nonlinear optical properties. Third order nonlinear refractive index (\(n_2\)), its sign, nonlinear absorption coefficient (\(\beta\)) and third order nonlinear susceptibility (\(\chi^3\)) of a thin nonlinear medium can be obtained from a linear relationship between the observed transmittance changes and the induced phase distortion by using Z-scan technique [55]. A strong delocalization of \(\pi\)-electrons in the prop-2-en-1-one system of chalcone determines a very high molecular polarizability and hence the remarkable third order nonlinearities [56]. Science as non-linear optical (NLO) [57], optical limiting [58], electrochemical sensing [59] and Langmuir film [42]. Various chalcone derivatives are notable materials for their second harmonic generation (SHG) [60]. In addition, different synthetic methods have been reported so far, such as,
refluxing in an organic solvent [61], the solvent-free solid-phase reaction [62], ultrasonication [63] photosensitization [64] and microwave radiation [65]. A nonlinear optical (NLO) property has been the subject of intense research due to their application in a wide range of technologies such as optical computing and optical communication [66-68]. In the past years, much attention has been paid to organic NLO materials due to their promising application in optoelectronics technology [69,70], large nonlinear response, extremely fast switching time and convenient optimization routes through molecular engineering compared to the currently studied inorganic materials [71,72]. The precise molecular recognition between chalcones and their guest provides a good opportunity for studying key aspects of supramolecular chemistry, which are also significant in a variety of disciplines including chemistry, biology, physics, medicine and related science and technology [73]. The recent growing interest in the electrochemistry (reduction and oxidation process) of macrocyclic complexes derived from recognition of biological importance of the less common oxidation states of metals [74,75].

Nonlinear optical applications find a variety of applications such as frequency conversion, light modulation, optical switching, optical memory storage and optical second harmonic generation (SHG) [76,77]. However, there is no discussion reported on the microhardness studies for this crystal to the best of our knowledge. The importance of hardness for crystals has been discussed by various researchers [78-82] for various applications, since mechanical strength is one of the important properties of any device materials represented by its hardness. As crystal a small-sized sample, it is convenient to take measurements at low loads. This low load hardness is called microhardness. Measurement of hardness provides useful
5.2. PURIFICATION

Before proceeding for crystallization it is essential to increase the purity of the material to a respectable level. Recrystallization will produce material which is pure for crystal growth. The synthesized compounds HMHP-I, HMHP-II, MPEPB and MBMC were initially dissolved to saturation in ethanol (AR grade) taken in separate containers and boiled with a little amount of activated charcoal to remove the trace impurities that give pale colour to the crystal. The solutions were filtered to remove charcoal. Then the solutions were kept in separate containers covered with filter paper. Clear crystals were obtained by evaporation of the solvent. The clear crystals were again dissolved to saturation in ethanol. The solution was filtered to avoid any insoluble impurities. The filtered solution was kept in a container covered with filter paper. The solution was allowed to evaporate to get pure crystals. This process of recrystallization was repeated two times for each variety of the crystals to get pure crystals for crystal growth, as obtained crystals show sharp melting than the unpurified compounds. The improvement in the melting point compared to crude chalcone derivative indicates that the crystals are having better purity than their crude product.

5.3. CRYSTAL GROWTH PROCEDURE FOR HMHP-I, HMHP-II, MPEPB AND MBMC SINGLE CRYSTALS

Single crystals of HMHP-I, HMHP-II, MPEPB and MBMC were grown by slow evaporation solution growth technique [85]. The solution of recrystallized HMHP-I was prepared at 30°C using absolute alcohol as a solvent. The beaker containing the solution was covered and the solution was housed in a constant temperature bath (0.1°C) and continuously stirred using Teflon coated immiscible magnetic stirrer. Utmost care was taken towards maintenance of
temperature because even minor fluctuations in temperature would lead to inclusions and defects in the growing crystals. The temperature was lowered at a rate of 0.5°C/day. After a fortnight, orange colored (HMHP-I & HMHP-II) and pale yellow colored (MPEPB & MBMC) transparent and large size crystals were obtained. The laboratory grown crystals is shown in Figure 5.1.

![Grown Crystals](image)

**FIGURE 5.1: GROWN CRYSTALS**

### 5.4. PROTON NMR SPECTRAL STUDIES ON HMHP-I, HMHP-II, MPEPB AND MBMC SINGLE CRYSTALS

$^1$H NMR spectra of the grown crystals were recorded using a Bruker Advance III 500 MHz NMR spectrometer and DMSO-d6 as internal standard.
In the spectrum of HMHP-I, singlet at δ 3.88ppm is due to the 3H of methyl group. The presence of doublets at δ6.84ppm and δ6.90ppm are corresponds to two chalcone protons. The H atoms of -3-(4-Hydroxy-3-methoxyphenyl) are appeared as three doublets at δ7.24ppm, δ7.26ppm and δ7.49ppm. The resonance at δ8.07ppm indicates the protons of 1-(4-hydroxyphenyl) moiety and the signals at δ9.63ppm and δ10.35ppm are belongs to the H atoms of OH group. These chemical shift values (Figure 5.2), are in good agreement with the reported values [86].

In the compound HMHP-II, the spectrum contains a singlet at δ 3.86ppm and is due to the 3H of methyl group. The doublet peaks at δ6.83ppm and δ6.90ppm are corresponds to two chalcone protons. The signals ranging from δ 7.62 to 7.73ppm are due to the protons of aromatic carbons and that at δ9.63ppm and δ10.01ppm are belongs to the H atoms of OH group (Figure 5.2). The observed chemical shifts are well agreed with the reported values [86].

The resonance at δ 3.84ppm of MPEPB spectrum is due to the 3H of methyl group, whereas the doublets at δ7.03ppm and δ7.05ppm correspond to two 1Hα, 1Hβ present in the carbonyl carbon. The fine spectral signals ranging from δ 7.51 to 8.28ppm are due to the protons of aromatic carbons (Figure 5.2). The chemical shift values of MPEPB derivative are comparable with the reported values [86,87]

The NMR spectrum of MBMC shows two closely spaced singlets at δ 3.45ppm and δ 3.53ppm which corresponding to two methyl group. The signals at δ 3.79, 3.84ppm are corresponding to the –CH2 protons of the cyclohexene system. The singlet at δ 5.10ppm is due to the proton attached to cyclohexene ring ortho position. The presence of three doublets ranging from δ7.22ppm to δ7.46ppm and δ 7.66 to 7.94ppm are corresponds to the protons present in the
methoxyphenyl and benzyloxyphenyl, respectively (Figure 5.2). The observed chemical shift values of MBMC are in good agreement with the reported values [86-88]

The absence of extra peaks in the spectra indicates that the grown crystals are with high degree of purity.

5.5. FT-IR SPECTRAL STUDIES ON HMHP-I, HMHP-II, MPEPB AND MBMC SINGLE CRYSTALS

FT-IR spectra of the grown crystals were recorded using FT-IR Spectrometer in the range of 4000-450cm\(^{-1}\) following KBr pellet technique to identify and confirm the various functional groups and are shown in (Figure 5.3).

**HMHP-I**

The two strong peaks observed at 3405cm\(^{-1}\) and 3137cm\(^{-1}\) are due to the free O-H stretching. The prominent signals at 2960cm\(^{-1}\) and 2815cm\(^{-1}\) are due to the aromatic C-H stretching [86]. The Peaks centered around 2673cm\(^{-1}\) and 2593cm\(^{-1}\) are attributed to –CH\(_3\) stretching. The appearance of strong peak at 1639cm\(^{-1}\) indicates the ketone functional group (C=O) [89]. The presence of peaks at 1591 cm\(^{-1}\), 1534cm\(^{-1}\) and 1512cm\(^{-1}\) are corresponds to C = C stretching [89]. C-H bending vibration is observed by the peak at 1430cm\(^{-1}\)[90]. The strong signal at 1223 cm\(^{-1}\) and 1041 cm\(^{-1}\) are belongs to the asymmetric and symmetric C-O-C stretching[91]. Existence of sharp peaks at 838cm\(^{-1}\) and 559cm\(^{-1}\) might be due to the Ar C–H deformation and C-C deformation [86].

**HMHP-II**

The two strong peaks observed at 3391cm\(^{-1}\) and 3230cm\(^{-1}\) are due to the free O-H stretching. The Peaks centered on 2943cm\(^{-1}\) are attributed to –CH\(_3\) stretching. The appearance of strong peak at 1644cm\(^{-1}\) indicates the ketone functional group (C=O) [89]. The presence of peaks at 1569 cm\(^{-1}\) are corresponds to C = C stretching [89]. C-H bending vibration is observed by
the peak at 1435 cm$^{-1}$[90]. The strong signal at 1259 cm$^{-1}$ is belongs to the C-O-C stretching [91]. Existence of sharp peaks at 834 cm$^{-1}$, 824 cm$^{-1}$ and 789 cm$^{-1}$ might be due to the Ar C–H deformation and C-C deformation [86].

**MPEPB**

The FT-IR spectrum of compound of MPEPB (Figure 5.3) shows sharp signals at 3452 cm$^{-1}$ which is assigned to strong –CH stretching. The Ar C-H weak stretching were observed at 3069, 2996, 2938 and 2841 cm$^{-1}$. The sharp peaks centered on 2598 cm$^{-1}$ is attributed to –CH$_3$ stretching [91]. The peak at 1736 cm$^{-1}$ and 1663 cm$^{-1}$ are corresponding to C=O stretching vibration of carbonyl group [86, 87]. The strong peak at 1598 cm$^{-1}$ is due to the C=C stretching [87]. The peaks centered on 1509 cm$^{-1}$ is attributed to –CH$_3$ medium bending vibration. The -OCH$_3$ rocking vibration was observed at 1266 cm$^{-1}$[86]. The signals at 1251, 1162 and 1062 cm$^{-1}$ are belongs to the C-O-C stretching [91]. The out of plane aromatic C-H bonds are observed at 816, 703 cm$^{-1}$ [92]. Existence of sharp peak at 553 cm$^{-1}$ might be due to the Ar C-C deformation [86].

**MBMC**

The FT-IR spectrum of compound of MPMC (Figure 5.3) shows sharp signals at 3456 cm$^{-1}$ which is assigned to strong –CH stretching. The Ar C-H weak stretching was observed at 3035, 2971, 2932 and 2900 cm$^{-1}$. The sharp peaks centered around 2541 cm$^{-1}$ is attributed to –CH$_3$ stretching [91]. The peak at 1654 cm$^{-1}$ is corresponding to C=O stretching vibration of carbonyl group [86,87]. The strong peak at 1596 cm$^{-1}$ is due to the C=C stretching [87]. The peaks centered around 1509 cm$^{-1}$ is attributed to –CH$_3$ medium bending vibration. The -OCH$_3$ rocking vibration was observed at 1249 cm$^{-1}$[86]. The signals at 1176, 1118 and 1028 cm$^{-1}$ are belongs to the C-O-C stretching [91]. The out of plane aromatic C-H bonds are observed at 831, 737 cm$^{-1}$[92]. Existence of sharp peak at 588 cm$^{-1}$ might be due to the Ar C-C deformation [86].
FT-IR Spectral analysis of the grown compounds clearly indicates the functional groups and confirms the chemical structure of the synthesized compounds.

5.6. UV-VIS-NIR SPECTRUM STUDIES

The optical transmittance plays a vital role in enhancing the NLO property of the crystal.

To understand the absorption behavior of the grown compounds, the UV-Vis-NIR spectra were obtained using aT90+ UV/Vis spectrometer. The UV-Vis-NIR spectrum gives information about the structure of the molecules because the absorption of UV and Visible light involves promotion of the electron in the π orbital to the high energy π* orbital [93]. The percentage of transmission enables the suitability of materials for optoelectronic applications.

**HMHP-I**

Optical absorption spectrum for the grown crystal has been recorded in the range between 200-800nm and shown in (Figure. 5.4). The absorption appears to start at 279nm and the highest peak of absorption is obtained at 362nm. The peaks at 279 and 362nm might be due to π to π* transition attributed to the presence of C=C and C=O functional groups in the compound. Complete transmittance observed in the entire visible region which extend even into IR region [86]. The band gap is calculated using the formula $E_g = \frac{12.4237}{\lambda} \text{eV}$, and is found to be 3.432eV [94]. The absence of absorption in the region between 420 and 800 nm in the UV-Vis-NIR spectrum shows that the grown crystal is a good material for optoelectronic and nonlinear optical applications.

**HMHP-II**

The absorption spectrum of the grown crystal HMHP-II has been recorded in the range between 200-900nm and shown in (Figure. 5.4).

The absorption peak at 389 nm due to π to π* transition indicates the presence of the functional groups C=C and C=O in the compound. Complete transmittance observed in the entire
visible which extend even into IR region [86]. The band gap is estimated using the formula $E_g = \frac{12.4237}{\lambda_c} \text{eV}$ and is found to be 3.194 eV [94]. There are no absorption peaks available in the region between 400 and 900 nm shows that the grown crystal can be a best candidate for optoelectronic and nonlinear optical applications.

**MPEPB**

The absorption spectrum of MPEPB was recorded in the wavelength range 200-800nm and is shown in (Figurer. 5.4). The $\pi$ to $\pi^*$ transition due to the presence of C=C and C=O functional groups in the compound was observed at 368nm. The band gap calculation was carried out using the formula $E_g = \frac{12.4237}{\lambda_c} \text{eV}$ and was estimated as 3.377eV [94]. The crystal shows a good transmittance in the entire visible which extend even into IR region [86] and hence find applications in optoelectronic devices [95].

**MPMC**

The recorded absorption spectrum of MPMC is shown in (Figurer. 5.4). The absorption peak due to C=C and C=O was found to be at 316nm and this is due to $\pi$ to $\pi^*$ transition. The band gap is calculated using the formula $E_g = \frac{12.4237}{\lambda_c} \text{eV}$. The calculated band gap value of MPMC crystal was 3.932eV [94]. Absence of complete transmittance in the visible region indicates that the crystal may not be good for NLO applications and this might be due to centro symmetric nature of the crystal.

**5.7. PHOTOLUMINESCENCE STUDIES**

Aromatic compounds with multiple conjugated double bonds are observed to exhibit strong resonance stability and fluorescence. The structure of the grown crystal contains aromatic moiety for which the Photoluminescence spectrum (PL) was recorded in the wavelength range of 200-700 nm using JY Fluorolog-3-11 Spectrofluorimeter. The recorded PL spectrum is depicted
in the (Figure. 5.5). The spectrum shows a broad emission peak at 491nm excited with 362nm for the compound HMHP-I, 438 and 482 nm excited with 389 nm for the compound HMHP-II, 407 and 457 nm excited with 368nm for the compound MPEPB and 384, 411 and 432 nm excited with 316nm for the compound MPMC, has been observed that there are strong emissions from green to red is observed with peaks at 418, 491, 565 and 667nm for this excitation. The luminescence effect of the grown crystals may be due to the presence of carbonyl group in the compounds. The emission of light which ceases after the cause of excitation in cut off is known as fluorescence and this is generally observed in those organic molecules which have rigid framework and not many loosely coupled substituent through which vibration energy can flow out [96]. The luminescence property of the chalcone derivatives can be used effectively in the field of design of optoelectronic devices and laser applications [97].

5.8. THERMAL ANALYSIS

The thermogravimetric analysis (TGA) provides a quantitative measurement of any weight changes associated with thermally induced transitions. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) response curves for the powder sample of HMHP-I are recorded using NETZSCH STA 409PC/PG thermal analyzer between the temperatures 32 and 600˚C at a heating rate of 10 ºC/min in nitrogen atmosphere and is shown in (Figure. 5.6).

HMHP-I

From the DTA thermogram (Figure. 5.6a), it is observed that there is a sharp endothermic peak at 228˚C, which corresponds to the melting point of the compound. Further, it indicates that there is small phase transition before melting. This is followed by a broad endotherm starting at 451˚C, which corresponds to the second decomposition temperature of HMHP-I. The first stage
decomposition commences at 228°C with the elimination of a molecule each of CO$_2$ and H$_2$O which is due to dehydration and decarboxylation of the ligand, respectively [98]. The sharpness of the peaks indicates a good degree of crystallinity of the sample. On further heating the compound incurs yet another major weight loss (35.79%) observed between (278.6-599.6°C) with evolution of H$_2$ molecules. The total weight loss of the sample is 58.55% at 599.6°C with the residual mass of 41.45%. The residual mass may be due to the presence of residual carbon mass [98]. Thermograms of the grown crystal clearly indicate that the crystal can be subjected to NLO applications up to 270°C [99].

**HMHP-II**

From the DTA thermogram (Figure. 5.6b), it is observed that there is a sharp endothermic peak at 198.6°C, which corresponds to the melting point of the compound. Further, it indicates that there is no phase transition before melting. This is followed by a broad endothermic change starting at 361.4°C, which corresponds to the decomposition temperature of HMHP-II. The first staged composition commences at 199°C with the elimination of a molecule each of CO$_2$ and H$_2$O which is due to dehydration and decarboxylation of the ligand, respectively [98]. The sharpness of the peaks indicates a good degree of crystallinity of the sample. On further heating the compound undergoes yet another major weight loss (33.78%) observed between (350-499.7°C) with evolution of H$_2$ molecules. The total weight loss of the sample is 47.84% at 499.7°C with the residual mass of 52.15%. The remaining residual mass may be due to the presence of residual carbon mass [98]. Thermograms of the grown crystal clearly indicate that the crystal can be subjected to NLO applications only up to 200°C [99].

**MPEPB**

From the DTA thermocurve (Figure. 5.6c), it is observed that there is a sharp endothermic peak at 153.3°C, which corresponds to the melting point of the compound. Further,
it indicates that there is no phase transition before melting. This is followed by a broad endotherm starting at 412.2°C, which corresponds to the decomposition temperature of MPEPB. The first stage decomposition occurs between 160-340°C with the elimination of a molecule each of CO$_2$ and H$_2$O which is due to dehydration and decarboxylation of the ligand, respectively [98]. The sharpness of the peaks indicates a good degree of crystallinity of the sample. On further heating the compound subjected to yet another major weight loss (77.49%) observed between (370-499.7°C) with evolution of H$_2$ molecules. The total weight loss of the sample is 83.12% at 499.7°C with the residual mass of 16.88%. The remaining residual mass may be due to the presence of residual carbon mass [98]. Thermograms of the grown crystal clearly indicate that the crystal can be subjected to NLO applications up to 160°C [99].

**MPMC**

From the DTA thermogram (Figure. 5.6d), it is observed that there is an endothermic peak at 169.6°C, which corresponds to the melting point of the compound. The lack of sharpness of the curve at melting point demonstrates the higher order impurity of the sample. Further, it indicates that there is no phase transition before melting. This is followed by a broad endotherm starting at 378.1°C,

which corresponds to the decomposition temperature of MBMC. The first stage decomposition commences at 170-340°C with the elimination of a molecule each of CO$_2$ and H$_2$O which is due to dehydration and decarboxylation of the ligand, respectively [98]. On further heating the compound incurs yet another major weight loss (53.49%) observed between (340-400°C) with evolution of H$_2$ molecules. The total weight loss of the sample is 66.01% at 499.7°C with the residual mass of 40.09%. The remaining residual mass may be due to the presence of residual carbon mass [98].
5.9 MICROHARDNESS STUDIES

Hardness of a crystal plays a key role in the device fabrication. It is a measure of a material's resistance to localized plastic deformation [100]. Hardness is one of the important mechanical properties to determine the nature and the strength of a material. Before indentations, the crystal have been lapped carefully and washed to avoid surface defects, which may influence the hardness values. The indentations were made on the prominent plane of the grown crystal for the loads varying from 25 to 100x10$^{-3}$ Kg with a time of 10s. The distance between two indentation points was maintained to be more than three times the diagonal length, in order to avoid any mutual interference of indentations. It is observed that the hardness value is increased as the load increased up to 100x10$^{-3}$ Kg applied load for the prominent plane of the crystal because these loads are insufficient to soften the bonding in the molecules. Cracks may be formed above 100x10$^{-3}$ Kg load due to release of internal stress generated locally by indentation. Due to release of internal stress generated locally by indentation a crack was formed above 50x10$^{-3}$ Kg load in the case of MBMC. This point is known as breaking point of the crystal. The Vicker’s hardness number of the grown crystal has been calculated using a relationship $H_v = [1.8544 \frac{P}{d^2}]$ Kg/mm$^2$ where, $H_v$ is the Vicker’s microhardness number, $P$ is the applied load in Kg and $d$ is the average diagonal length of the impression in mm. A plot drawn between hardness number and applied load is shown in (Figure.5.7) and the observed values are listed in Table 1-4. The hardness number for the grown crystals is 48.24, 59.27, 34.37 and 199.19 Kg/mm$^2$, respectively, for the compounds HMHP-I, HMHP-II, MPEPB AND MBMC. A graph was plotted between log$P$ and log$d$ and from the slope of the graph the Meyer’s index (n) was calculated. The value of n was found to be 4.2, 2.22, 3.00 and 1.66 for the compounds HMHP-I, HMHP-II, MPEPB and MBMC, indicates that the crystals belong to soft materials [101].
6. SECOND HARMONIC GENERATION (SHG) EFFICIENCY

Nonlinear optical crystals are very important for laser frequency conversion [102]. Potassium dihydrogen phosphate (KDP) is suitable for higher harmonic generation of huge laser systems for fusion experiments because it can be grown to larger sizes and also KDP has a high laser damage threshold. KDP is a useful nonlinear optical crystal to get efficient green light by the frequency doubling of Nd: YAG laser. It has high optical nonlinearity, large temperature and angular allowance and it is non hygroscopic and mechanically hard.

The second harmonic generation efficiency measurement test on the samples was performed by the Kurtz powder SHG method [103]. This technique remains an extremely valuable tool for initial screening of materials for second harmonic generation. The second harmonic generation efficiency of the sample was measured using Q- switched Nd: YAG with input wavelength of 1064nm and input power of 0.68J. A green signal of 532nm emitted from the sample was detected using a photomultiplier tube (Hamamatsu-R 2059) and the signal amplitude is the measure of the SHG efficiency of the sample. The emission of green light confirms the second harmonic generation of the crystals. KDP with size identical to that of the sample was used as reference and the measured SHG efficiency was found to be 0.26, 0.96 and 0.23, respectively times as that of KDP for HMHP-I, HMHP-II and MPEPB. The SHG efficiency was not observed in the crystal MPMC because of centro symmetric nature of the compound. Recently, it has been reported that the enhancement in crystalline perfection could lead to improvement in SHG efficiency [104].
FIGURE 5.2: NMR SPECTRA

HMHP-I

HMHP-II

FIGURE 5.2: NMR SPECTRA
FIGURE 5.2: NMR SPECTRA

MPEPB

MPMC

FIGURE 5.2: NMR SPECTRA
FIGURE 5.3: FT-IR SPECTRUM
FIGURE 5.3: FT-IR SPECTRUM
FIGURE 5.4: UV-VIS-NIR SPECTRUM
FIGURE 5.4: UV-VIS-NIR SPECTRUM

FIGURE 5.5: PL SPECTRUM OF GROWN CRYSTALS
**FIGURE 5.5: PL SPECTRUM OF GROWN CRYSTAL**
FIGURE 5.6A: TG/DTA CURVE OF HMHP-I

FIGURE 5.6B: TG/DTA CURVE OF HMHP-II
FIGURE 5.6C: TG/DTA CURVE OF MPEPB

FIGURE 5.6D: TG/DTA CURVE OF MBMC
FIGURE 5.7A: HARDNESS GRAPH OF HMHP-I

FIGURE 5.7B: HARDNESS GRAPH OF HMHP-II
FIGURE 5.7C: HARDNESS GRAPH OF MPEPB

FIGURE 5.7D: HARDNESS GRAPH OF MBMC
Table 1: The observed values for HMHP-I

<table>
<thead>
<tr>
<th>S. No</th>
<th>Load (P) ( \times 10^3 ) Kg</th>
<th>Diagonal Length ( \times 10^{-3} ) m</th>
<th>Hardness value of ( H_v ) Kg/ ( \text{mm}^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>d1</td>
<td>d2</td>
</tr>
<tr>
<td>1</td>
<td>25</td>
<td>36.85</td>
<td>38.88</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>43.12</td>
<td>45.62</td>
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<tr>
<td>3</td>
<td>100</td>
<td>51.99</td>
<td>54.43</td>
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Table 2: The observed values for HMHP-II

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<tr>
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<th>Load (P) ( \times 10^3 ) Kg</th>
<th>Diagonal Length ( \times 10^{-3} ) m</th>
<th>Hardness value of ( H_v ) Kg/ ( \text{mm}^2 )</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>d1</td>
<td>d2</td>
</tr>
<tr>
<td>1</td>
<td>25</td>
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</tr>
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<td>2</td>
<td>50</td>
<td>37.66</td>
<td>40.89</td>
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<tr>
<td>3</td>
<td>100</td>
<td>50.52</td>
<td>55.14</td>
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### Table1: The observed values for MPEPB

<table>
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<tr>
<th>S. No</th>
<th>Load (P) X 10^{-3} Kg</th>
<th>Diagonal Length X10^{-3} m</th>
<th>Hardness value of H_V Kg/ mm^2</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>d1</td>
<td>d2</td>
</tr>
<tr>
<td>1</td>
<td>25</td>
<td>41.77</td>
<td>40.81</td>
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<tr>
<td>2</td>
<td>50</td>
<td>51.68</td>
<td>53.49</td>
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<td>3</td>
<td>100</td>
<td>65.45</td>
<td>66.60</td>
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### Table1: The observed values for MBMC

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<th>S. No</th>
<th>Load (P) X 10^{-3} Kg</th>
<th>Diagonal Length X10^{-3} m</th>
<th>Hardness value of H_V Kg/ mm^2</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>D</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>21.36</td>
<td>40.63</td>
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<td>2</td>
<td>25</td>
<td>18.97</td>
<td>128.86</td>
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<td>3</td>
<td>50</td>
<td>16.73</td>
<td>331.26</td>
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<td>4</td>
<td>100</td>
<td>28.03</td>
<td>295.99</td>
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## TECHNIQUES USED FOR CHARACTERIZATION

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
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<tbody>
<tr>
<td>XRD</td>
<td>Structure determination</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Functional group identification</td>
</tr>
<tr>
<td>$^1$H NMR</td>
<td>Identification of different type of hydrogen</td>
</tr>
<tr>
<td>UV</td>
<td>Optical absorption</td>
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<tr>
<td>Vickner’s hardness tester</td>
<td>Mechanical strength</td>
</tr>
<tr>
<td>TGA/DTA</td>
<td>Thermal Stability</td>
</tr>
<tr>
<td>Q- switched Nd: Yag</td>
<td>SHG</td>
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<tr>
<td>Agar well diffusion method</td>
<td>Anti-bacterial &amp; Anti-fungal</td>
</tr>
<tr>
<td>DPPH Assay method</td>
<td>Anti-Oxidant</td>
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<td>MTT Assay method</td>
<td>Anti-cancer</td>
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## COMPARATIVE ANALYSIS OF THE FEATURES OF THE GROWN COMPOUNDS

<table>
<thead>
<tr>
<th>Entities</th>
<th>HMHP-I</th>
<th>HMHP-II</th>
<th>MPEPB</th>
<th>MPMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>IUPAC Name</td>
<td>(2E)-3-(4-hydroxy-3-methoxyphenyl)-1-(4-hydroxyphenyl) prop-2-en-1-one</td>
<td>(2E)-1-(4-hydroxy-3-methoxyphenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one</td>
<td>4-[(2E)-3-(4-methoxyphenyl) prop-2-enoyl]phenyl benzoate</td>
<td>3-(4-methoxyphenyl)-5-(4-benzyloxyphenyl)-6-methyl-2-cyclohexen-1-one</td>
</tr>
<tr>
<td>Structural Formula</td>
<td><img src="image1.png" alt="Structural Formula HMHP-I" /></td>
<td><img src="image2.png" alt="Structural Formula HMHP-II" /></td>
<td><img src="image3.png" alt="Structural Formula MPEPB" /></td>
<td><img src="image4.png" alt="Structural Formula MPMC" /></td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C₁₆H₁₄O₄</td>
<td>C₁₆H₁₄O₄</td>
<td>C₂₃H₁₈O₄</td>
<td>C₂₇H₂₆O₃</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space Group</td>
<td>Pbca</td>
<td>Pna₂₁</td>
<td>P₂₁/C</td>
<td>P₂₁/C</td>
</tr>
<tr>
<td>Formula Weight(amu)</td>
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<td>270.27</td>
<td>358.37</td>
<td>398.48</td>
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<tr>
<td>Crystal colour</td>
<td>Orange</td>
<td>Orange</td>
<td>Pale yellow</td>
<td>Pale yellow</td>
</tr>
<tr>
<td>Melting point</td>
<td>229 ºC</td>
<td>199 ºC</td>
<td>153 ºC</td>
<td>170ºC</td>
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### FT-IR

<table>
<thead>
<tr>
<th>FUNCTIONAL GROUPS</th>
<th>HMHP-I (cm⁻¹)</th>
<th>HMHP-II(cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>free O-H stretching</td>
<td>3405</td>
<td>3391</td>
</tr>
<tr>
<td>free O-H stretching</td>
<td>3137</td>
<td>3230</td>
</tr>
<tr>
<td>–CH₃ stretching</td>
<td>2673</td>
<td>2943</td>
</tr>
<tr>
<td>C=O group</td>
<td>1639</td>
<td>1644</td>
</tr>
<tr>
<td>C = C stretching</td>
<td>1534</td>
<td>1569</td>
</tr>
<tr>
<td>C-H bending vibration</td>
<td>1430</td>
<td>1435</td>
</tr>
<tr>
<td>Structural Feature</td>
<td>Frequency 1</td>
<td>Frequency 2</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-------------</td>
<td>-------------</td>
</tr>
<tr>
<td>C-O-C stretching</td>
<td>1223</td>
<td>1259</td>
</tr>
<tr>
<td>Ar C–H deformation</td>
<td>838</td>
<td>834, 824</td>
</tr>
<tr>
<td>C-C deformation</td>
<td>559</td>
<td>789</td>
</tr>
</tbody>
</table>

**FUNCTIONAL GROUPS**

<table>
<thead>
<tr>
<th>Structural Feature</th>
<th>MPEPB (cm$^{-1}$)</th>
<th>MPMC (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong C-H stretching</td>
<td>3452</td>
<td>3456</td>
</tr>
<tr>
<td>Ar C-H weak stretching</td>
<td>3069, 2996, 2938 and 2841</td>
<td>3035, 2971, 2932 and 2900</td>
</tr>
<tr>
<td>–CH$_3$ stretching</td>
<td>2598</td>
<td>2541</td>
</tr>
<tr>
<td>C=O group</td>
<td>1736 and 1663</td>
<td>1654</td>
</tr>
<tr>
<td>C = C stretching</td>
<td>1598</td>
<td>1596</td>
</tr>
<tr>
<td>CH$_3$ medium bending</td>
<td>1509</td>
<td>1509</td>
</tr>
<tr>
<td>O-CH$_3$ Rocking vibration</td>
<td>1266</td>
<td>1249</td>
</tr>
<tr>
<td>C-O-C stretching</td>
<td>1251, 1162 and 1062</td>
<td>1176, 1118 and 1028</td>
</tr>
<tr>
<td>Ar C–H deformation</td>
<td>816, 703</td>
<td>831, 737</td>
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<tr>
<td>C-C deformation</td>
<td>553</td>
<td>588</td>
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</table>

**NMR**

<table>
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<tr>
<th>Compound</th>
<th>CH$_3$</th>
<th>CH$_2$</th>
<th>1H$\alpha$</th>
<th>1H$\beta$</th>
<th>Ar CH</th>
<th>OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMHP-I</td>
<td>3.88</td>
<td>Nil</td>
<td>6.84</td>
<td>6.90</td>
<td>7.24-8.07</td>
<td>9.63 10.35</td>
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<tr>
<td>HMHP-II</td>
<td>3.86</td>
<td>Nil</td>
<td>6.83</td>
<td>6.90</td>
<td>7.62-7.73</td>
<td>9.63, 10.01</td>
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<tr>
<td>MPEPB</td>
<td>3.84</td>
<td>Nil</td>
<td>7.03</td>
<td>7.05</td>
<td>7.51-8.28</td>
<td>Nil</td>
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<tr>
<td>MPMC</td>
<td>3.45</td>
<td>3.79</td>
<td>3.84</td>
<td>6.99</td>
<td>7.04</td>
<td>7.22-7.94</td>
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UV-VIS NIR

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<th>Parameters</th>
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<th>MPMC</th>
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<tbody>
<tr>
<td>Absorption(nm)</td>
<td>279</td>
<td>300</td>
<td>300</td>
<td>290</td>
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<td>Cut-off wavelength(nm)</td>
<td>362</td>
<td>389</td>
<td>368</td>
<td>316</td>
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<tr>
<td>Transmittance(nm)</td>
<td>420-800</td>
<td>400-900</td>
<td>400-900</td>
<td>---</td>
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<tr>
<td>Band gap</td>
<td>3.432</td>
<td>3.194</td>
<td>3.377</td>
<td>3.932</td>
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TG/DTA

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<tr>
<th>COMPOUNDS</th>
<th>Melting Temperature(ºC)</th>
<th>Decomposition Temperature(ºC)</th>
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<tbody>
<tr>
<td>HMHP-I</td>
<td>228.8</td>
<td>451.9</td>
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<tr>
<td>HMHP-II</td>
<td>196.6</td>
<td>361.4</td>
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<td>MPEPB</td>
<td>153.3</td>
<td>412.2</td>
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<tr>
<td>MPMC</td>
<td>169.6</td>
<td>378.1</td>
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</table>

CONCLUSION

A series of three new nonlinear optical (NLO) chalcone derivatives HMHP-I, HMHP-II, MPEPB and one non-NLO (MPMC) crystal, have been synthesized and their single crystals were grown by slow evaporation solution growth technique at ambient temperature.

The single crystal XRD analysis of the grown crystals are carried out using a Bruker Kappa APEXII CCD diffractometer with MoKα (λ=0.71073Å) radiation to determine the structure. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares procedures using SHELXL-08. The puckering parameters were obtained using PARST and SHELXL-97. The molecular graphic plots were drawn using the programs ORTEP-3 for Windows and PLATON. The compounds HMHP-I, HMHP-II, MPEPB and
MPMC crystallized in Orthorhombic/ Orthorhombic/ Monoclinic / Monoclinic space group Pbca, Pna2₁, P₂\(_1\)/c and P₂\(_1\)/c, respectively.

The grown crystals were screened for their anti-bacterial, anti-fungal, anti-oxidant and cytotoxic activities and found to exhibit potent activities under different environments.

Single crystals of HMHP-I, HMHP-II, MPEPB and MPMC have been grown by the temperature lowering method (0.5°C/day). The crystal system, space group and the structure of the compound were confirmed by XRD analysis. The presence of various functional groups of the compounds has been identified from FT-IR. The chemical shift associated with the different hydrogen atoms were analyzed by proton NMR spectral analysis. It is observed from the UV-Vis-NIR spectrum that the samples have good transmittance capability in the entire visible region. The peaks at 418,491, 565 and 667nm in the Photoluminescence (PL) spectrum show that there are strong emissions from green to red in the visible region. From the TGA/DTA thermograms of sample it was derived that HMHP-I & HMHP-II crystals are thermally stable up to 200°C and MPEPB & MPMC crystals are thermally stable up to 150°C. Vicker’s micro hardness test of the as synthesized compound shows that they are mechanically strong and belongs to soft materials. The SHG efficiency measurement of the crystal using Q-switched Nd: YAG laser indicates their NLO property. The enhanced optical, mechanical, thermal and NLO properties of the grown crystal (HMHP-I, HMHP-II & MPEPB) can be effectively exploited in the fields of laser technology, design of optoelectronic devices, NLO applications and for the modulation and frequency doubling purposes.