SYNTHESIS, GROWTH, AND CHARACTERISATION OF NEW INORGANIC NLO SINGLE CRYSTAL

Submitted in partial fulfillment of the requirements

for the award of

MASTER OF SCIENCE DEGREE

IN PHYSICS

By

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(DEEMED TO BE UNIVERSITY)

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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **NASREEN SAYED (Reg.No.40590015)** who carried out the project entitled “**SYNTHESIS,GROWTH, AND CHARACTERISATION OF NEWINORGANIC NLO SINGLE CRYSTAL”** under our supervision from November 2021 toMarch 2022

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DECLARATION

I **NASREEN SAYED (Reg.No. 40590015)** hereby declare that the project report entitled “**SYNTHESIS, GROWTH, AND CHARACTERISATION OF NEW INORGANIC NLO SINGLE CRYSTAL”** done by me under the guidance of**Dr.P. MALLIGA**(Internal) submitted in partial fulfillment of the requirements for the award of Master of Degree in Physics.

DATE:

PLACE: **SIGNATURE OF THE CANDIDATE**

ABSTRACT Crystal growth has been pursued on a commercially important scale since around 1950. Defense-related activities since 1940 (such as piezoelectric crystals for sonar transducers). Thesalt can be purified using crystallization. Crystal growth plays an important role in the search for new digital materials. Without crystals, the digital industry, fiber optic communications, and photonic industry wouldn't exist. All of these depend on the material/crystal. Solid-state lasers, nonlinear optics, radiation detectors, transducers, magnetic grenades, etc. Over the last few decades, there has been increasing demand and interest in crystal growth processes, especially given the growing demand for materials for technical applications. NLO (Nonlinear Optical) materials play a major role in nonlinear optics because they have a significant impact on information technology and industrial applications.

A new inorganic nonlinear optical single crystal of magnesium nitroborate was successfully grown from an aqueous solution by slow evaporation techniques at room temperature. Crystals with a characteristic shape and size of [9 × 5 × 3 mm^3] were obtained after 45 days. Crystals grown by these techniques will be further used for characterization studies. The presence of functional groups is qualitatively estimated by FTIR, which is a very useful technique for confirming the identity of pure compounds and has a high wavenumber accuracy. Single-crystal XRD provides report a = 5.042. b = 14.3; c = 9,580; Alpha = 90.1, Beta = 96, Gamma = 90.00; Volume = 646.189ccc, and the crystal system is monoclinic. UV-Vis also provides reports as if the spectrum was recorded in near IR, visible, and UV range, and. The lower cut-off frequency is within 289 nm. SHG (Second Harmonic Generation) can be a nonlinear optical process that can analyze the NLO characteristics of a crystal.

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SHG	**SECOND-HARMONIC GENERATION**
FTIR	**FOURIER TRANSFORM INFRARED SPECTROMETER**
XRD	**X-RAY DIFFRACTION**
UV-VIS	**ULTRA VOILET SPECTROMETER**
EM	**ELECTROMAGNET WAVE**
NLO	**NONLINEAR OPTICS**
KDP	**POTASSIUM DEUTERIUM PHOSPHATE**
SEM	**SCANNING ELECTRONIC MICROSCOPE**
EDAX	**Energy Dispersive X-Ray Analysis**
TGA	**Thermogravimetric analysis**
MNB	**MAGNESIUM NITRO BORATE**

CHAPTER 1

INTRODUCTION TO CRYSTAL GROWTH AND NONLINEAR OPTICS

1.1CRYSTAL-GROWTH

A solid crystalline material in which components such as atoms, molecules, and ions are arranged in a regular pattern that spans a total of three spatial dimensions. Crystal growth is an important step in the crystallization process and is composed of atoms, ions, and compounds that correspond to the characteristic arrangement of the crystal lattice. Crystalsnaturally form from magma, hot aqueous solutions, or hot gases. It is necessary to enhance the beauty of crystals by trial and error in order to cut and shapecrystals, but it was in the early 20th century that we understood the structure and classification of crystals. Crystalline materials can be divided into crystalline materials and amorphous materials according to the particle composition. The concept of crystal lattices, unit cells, point clouds (32), space groups (230), 14 lattice types, and 7 crystal systems was established at the end of the 19th century.

1.2CRYSTALGROWTHMETHODS

Crystal growth can be a difficult task and the technique followed for crystal growth can be depended upon the characteristics like its temperature, nature, soluble in which solvents like water or different organic or inorganic solvent, etc. There isa different fundamental way of growing crystal in the market for crystal growth area unit loosely. The Range ofthe growing crystalfrom small inexpensive techniques to complex expensive techniques for that the process of crystallization will depend on time ranges fromminutes, hours, days, and months. The methods of growing crystal purely depend on the characteristics and size of the material. The single crystal can synthesize by transport of crystal constituent in the solid, liquid, or vapor state. Crystal growth is often to be classified into three categories: -

- Solid growth (solid to solid phase transformation)
- liquid growth (liquid to solid phase transformation)

- vapor growth (vapor to solid phase transformation)

Based on the phase transformation crystal growth are again classified into:-

1. Growth from melt.
2. Growth from solid.
3. Growth fromliquid.
4. Growth from vapor.

After these fundamental principles come together and form a nucleus and that is the initial shape further, it grows into a crystal by arranging the constituent particles with the specific bonding's and interactions, sowhen this method is slow then multiple nucleation's will decrease. Crystal growth method and size of the adult crystal disagree wide and area unit determined by the characteristics of the fabric. associate degree economical method is that the one, that produces crystals adequate for his or her use at minimum price. the expansion methodology is important as a result of it suggests the doable impurity and different defect concentrations. selecting the simplest methodology to grow a given material depends on material characteristics.

The solution growth technique is elaborately mentioned during this chapter.For resolution preparation, it is veryessential to possess the solubility knowledge of the material at completely different temperatures. Sintered glass filters of various pore size area unitswere used for resolution filtration. The clear resolution, saturated at the required temperature is taken during a growth vessel. Forthe growth by a slow evaporation method, the vessel is sealed at the top to stop the solvent evaporation. Solvent evaporation at constant temperature will be achieved by providing a controlled vapor leak by making tiny holes at the top of the vessel. A tiny low crystal suspended within the resolution is employed to check the saturation. By variable, thetemperature, a state at whichwherever neither the incidence of growth nor dissolution is established. Then the tiny seed is replaced with an honest quality seed. All the unwanted nuclei, therefore,present at the surface harm the seed area unit so it is removed by dissolving at a temperature on top of the saturation. Growth is initiated when saturation. Solvent evaporation can even be useful in initiating the expansion. the standard of the adult crystal depends on the (a) nature of the seed, (b) cooling rate used, and (c) agitation of the solution.

1.3 ADVANTAGE AND DISADVANTAGE OF SOLUTION CRYSTAL GROWTH

1.3.1 Advantage

1)Growth will be on the free surface.

2)Growth of well-orientated single crystal.

3)Control of atmosphere.

1.3.2 Disadvantage

1) It has high vapor pressure material.

2) Liquid phase encapsulation.

3) There could be very much less reproductivity of the crystal shape

1.4 Optimization of material: -

The growth of perfect quality single crystals can be done by slow cooling and slow evaporation techniques whichrequire optimized conditions. The process is given below

1)solvent selection

2)purity of the material

3)solubility of the material

4)solution preparation

5)seed preparation

6)temperature and crystal habits

1.4.1***Solvent selection*:-**

A solution must be a is homogeneous mixture of a solute and solvent. A solvent in which solute is going to be dissolved and which is present in small quantities.For a given solute, there may be different solvents so the crystal growth from the solution must be chosen in a way that depends on these given factors. A solvent must be chosen in a way that should contain all these properties:

i) The solubility of the given solvent must be high.

ii) It should have a high-temperature coefficient of solute solubility.

iii)less viscosity.

iv) less volatility.

v) It should be non-toxic.

vi) cost-effective.

1.4.2*Purity of the Material*:-

An essential prerequisite for success in crystal growth is the availability of the highest purity material. since someimpurities may be presentin the crystal lattice so the solution must have high purity resulting in the formation of flaws and defects. Sometimes impurities may slow down the crystallization process by getting adsorbed on the growing face of the crystal which changes the crystal habit. Careful repetitive use of standard purification methods of recrystallization followed by repeated filtration with the help of Whatman filter paper will result in an increase of purity.

1.4.3*Solubility*:-

Solubility is a vital parameter, that dictates the expansion procedure. If the solubility gradient is extremely little, slow evaporation of the solvent is that the different possibility for crystal growth to keep up the super saturation within the answer. The solubility of the substance may be determined by dissolving the substance within the solvent maintained at a relentless temperature with continuo's stirring. The solubility curve may be aforethought from the number of dissolved and temperature by repetition the measurements for various temperatures. The liquid within which you compound is soluble is termed the solvent, the opposite liquid the precipitant. As your compound is a smaller amount soluble during a mixture of the 2 liquids, you'll grow crystals by slowly intermixture a (not too) focused answer of your compound precipitate.

The solubility data at different temperatures shows the supersaturation levels. The magnesium nitrate and boric acid solution was prepared in water and maintained at room temperature with continuous stirring to ensure homogeneous temperature andconcentration. On completely dissolved it reaches saturation,this process was repeated for every 5ºC in water from 30ºC to 50ºC.

The solubility curve obtained is shown in Fig.1.1

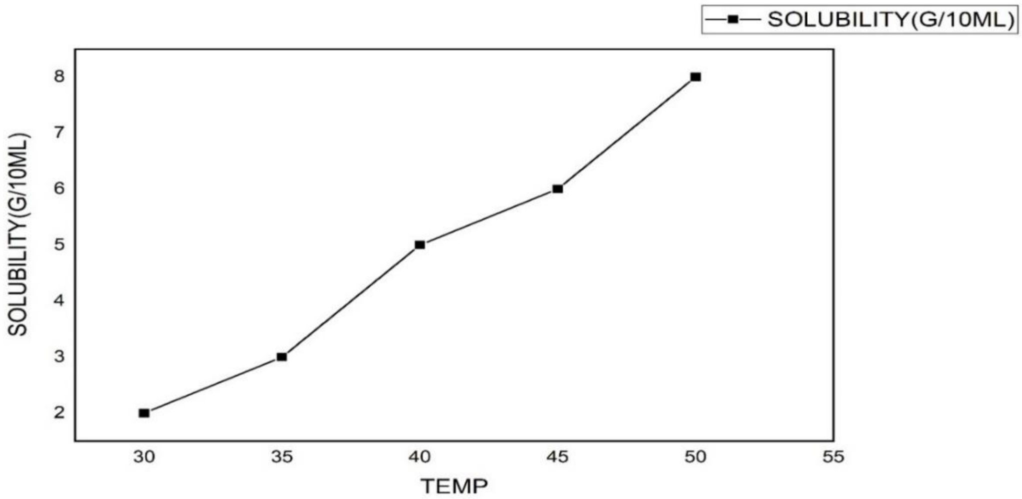


Fig 1.1 Solubility graph

1.4.4*Solution preparation*:-

Most important part Of solution preparation, is to have the solubility data of the material at different temperatures. Sintered glass filters are used with different pore size to obtain purity in the solution. After filtering a clear solution is obtained and saturated at the desired temperature is taken in a growth vessel. So for growth of the crystal by a slow evaporation method, the glass vessel is sealed with a thin cover to prevent solvent evaporation. Solvent evaporation at constant temperature is achieved by providing a controlled vapor leak.

1.4.5*Seed preparation*:-

Seed crystals are made through self-nucleation in a saturated solution during gradual evaporation (Figure 1.2). Seeds of good visual quality, devoid of inclusions and flaws, are selected for growth. Because strain-free refacing of the seed crystal results in a low dislocation concentration, a few layers of the seed crystal must be dissolved before the growth can begin. Defects in an incomplete seed grow throughout the bulk of the crystal, lowering its quality. As a result, seed crystals are carefully prepared. The bulk crystal is usually of a slightly higher grade than theseed.

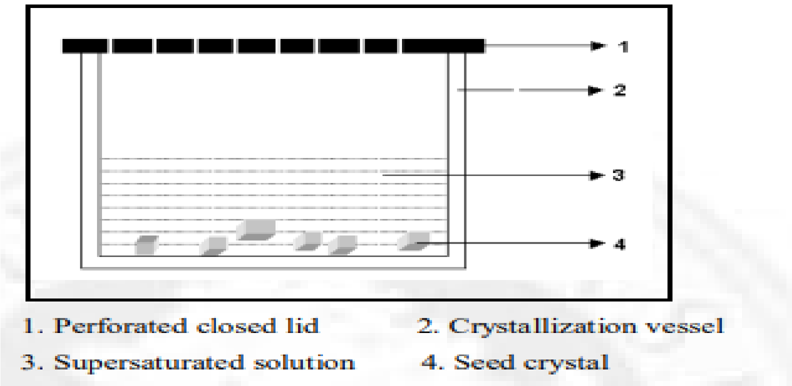


Fig 1.2 Seed Preparation

1.5VAPOUR GROWTH METHOD:-

In this method, the gaseous molecules are directly converted into crystals in the solid state. This could be achieved by (PVD)physical vapor deposition or (CVD) chemical vapor deposition. By this crystallization process we can grow bulk crystals., thin coating, and epitaxial films..

a.Chemicaltransport method.

b. Physical transport method.

1.6MELT GROWTH METHOD:-

Melt growth is the process of crystallizing, melting, and resolidifying a pure substance into crystals. This process does not introduce impurities during the crystal growth process, except for the possibility of contamination by the crucible material and the surrounding atmosphere, and the growth rateis not much faster than other possible methods.

a) Bridgman method.

b) Czochralski method.

c) Verneuil method.

d) Zone melting method.

e) Kyropoulos technique.

f) Skull melting.

1.7SOLTION GROWTH METHOD: -

In this method the crystal are grown from an aqueoussolution. This methodis widely used for bulk crystal preparations.This is the non-complex method in which crystals are grown for crystal growth at a particular temperature that is usually lower than the melting point. Based on the nature of the solvent it is classified as.

a. Low-temperature solution growth.

b. High-temperature solution growth.

c. Hydro-Thermal growth.

d. Gel Growth.

1.7.1 Low-temperature solution growth:-

by this method wide varieties of crystals are being synthesized; this method is one of the oldest methods for crystal growth. This method is usually used for growing single crystals when the starting material is unstable at a high temperature. The major advantages of this method are it is versatile, has simplicity, and the ambient temperature gets employed and this method uses simple instruments which provide good precision.Further, it is divided into three classes

a. Temperaturegradient method.

b. Slow cooling method.

c. Slow evaporation method.

1.7.1.1Temperature gradient method:-

The crystal is grown from transporting the material to the hotter region to the cooler region where the solution becomes supersaturated. The main advantage of this method is the economy of solvent and solute, the crystal has been grown ata fixed temperature.

1.7.1.2Slow cooling method:-

This method works mainly for solute and solvent systems that are less soluble and the solvent boiling point is less than 100°C. This method is usually used for the bulk crystal growth of materials with high solubility and a large positive temperature coefficient. Supersaturation can be achieved by reducing the temperature of the solution and employing low cooling rates using a temperature controller. Due to only cooling in the bottom with the use of a suitable temperature gradient, crystal growth occurs only at the bottom of the crucible.

1.7.1.3 Slow evaporation method:-

Thisis the easiest way to grow a crystal with suitable components and there is no temperature complication becausethe temperature is kept constant, andthe solvent gets evaporated then the crystals are grown. And this method works with a compound that is sensitive to ambient temperature.the quality of crystals obtained is fixed because they are grown at a constant temperature but the growth rates vary from system to system and this method is suitable for such materials, which have a very small temperaturecoefficient of solubility.

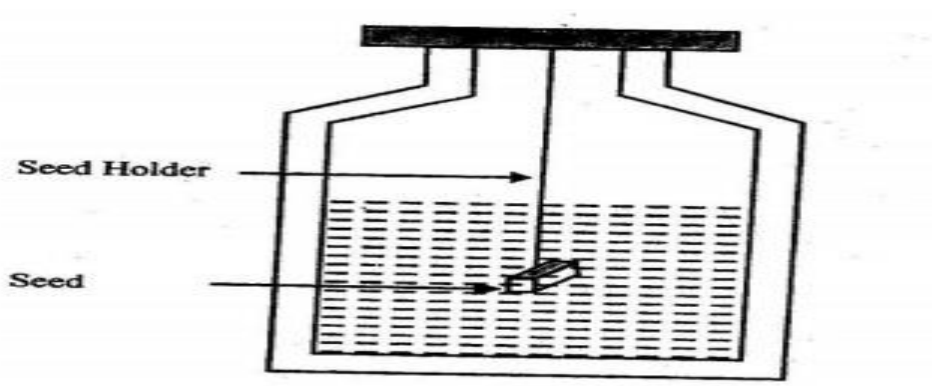


Fig1.3 Mason jar

1.8 OPTICAL MATERIALS:-

The efficiency of optical materials depends on the flow of light which could be manipulated for splitting, absorbing, reflecting, and focusing an optical beam and this all depends on the wavelength of the light used, other than the material characteristics Glass, polymers, plastic materials or crystalline materials could be used for fabricating optical material and some of the important properties of the material like refractive index, degree of transparency, thermal stability, hygroscopicity, uniformity of the material, chemical resistivity, and availability of suitable coatings for these materials (Abdul Nasir The Mercury, cadmium, and telluride is transparent in the infrared region at photon energies below the energy gap. For lithography in the ultraviolet region, fused silica is used since it has the capacity of transmitting the light to about 248nm (Brian Caldwell 1998). It can be applied in high-energy lasers, spacecraft windows, cancer detection using ultraviolet-laser-induced autofluorescence, blanks for large astronomical mirrors, and optical imaging. In printing microchips using fluorine excimer lasers, calcium fluoride crystals are used and it transmits light into the ultraviolet region to about 140nm. Apart from this, when the light of sufficient intensity is used, the nonlinear effects in materials could be detected and the different nonlinear phenomena exhibited by various materials are briefly present.

1.8.1 Nonlinear optics: -

Non-linear optics requires the interaction of intense beam of light with materials and hence it remained unknown until the discovery of lasers and second harmonic generation (SHG) was first reported in 1961 by Peter Frankenetal . even though some of the nonlinear effects have been revealed before the development of lasers (Gilbert N. Lewis et al. 1941). The theoretical aspects involved in these nonlinear processes were first described in Bloembergens's monograph "nonlinear optics". When an electromagnetic (EM) wave propagates through any material, the electric and magnetic field components of the EM wave interact with the electrons and ions present in the material thus inducing polarization of their local distribution causing an oscillation in charges of the atoms. The 9 magnitude of the induced polarization depends on the nature of the electronic structure of the material. Optical signal processing, integrated optics, and transfer storage are some of the processes in which these nonlinear optical phenomena could be employed.The energy of the new gauge boson generated by the nonlinear interaction should be adequate to the energy of the photons used. Figure 4shows the photons concerned within the second harmonic generation methodThe different nonlinear optical processes that can occur in a lossless medium are:-

1. Second-harmonic generation (SHG)
2. Thirdharmonic generation (THG)
3. Sum frequency generation (SFG)
4. Difference frequency generation (DFG)
5. Optical parametric generation (OPG)
6. Pockels' effect.
7. Optical rectification.

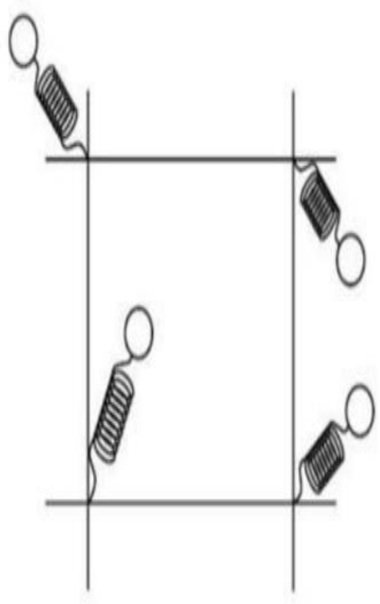


Fig1.4 Electrons in a nonlinear crystal are bound in a potential well, holding the electrons to lattice points

At the frequency of this electronic field, the electrons in a conventional optical material fluctuate about their equilibrium position. Associate in Nursing oscillation amendment can radiate at its frequency of oscillation, therefore these electrons within the crystal "produce" light at the frequency of the initial light-weight wave, according to the fundamental law of physics. With the invention of the first operational optical apparatus and the subsequent demonstration of frequency doubling phenomena, the field of nonlinear optics was born about five decades ago. These breakthroughs not only sparked a surge in interest in optical device research but also paved the way for future advancements in nonlinear optics. Photonic technologies have become increasingly relevant due to the tremendous growth and development of nonlinear optical materials during the last decade*.* a vital component of our daily lives Nonlinear optical materials are being considered as critical components for long-term photonic technologies such as optical computing, telecommunications, optical interconnects, high-density information storage, sensors, image processing, switches, and so on, as the demand for data systems grows***.***

1.8.1.1*Second harmonic generation*: -

In Second-harmonic generation (SHG), photons with the same frequency interacting with an NLO material combine to generate a photon with twice the energy and half the wavelength of the primary photons. Second-order NLO materials have a wide variety of applications in frequency doubling, parametric amplification, parametric oscillation, frequency up conversion, difference frequency generation, etc. The magnitude of the non-linear coefficient depends upon the direction of the electronic wave function and the asymmetry of the electron clouds (Robert J. Pressley 1971; Demtroder 1981). Therefore, non-centrosymmetric crystals exhibit a good SHG response. Potassium dihydrogen phosphate (KDP), lithium triborate (LBO), β-barium borate (BBO), lithium niobate (LiNbO3), potassium niobate (KNbO3),etc. These are some of the most popular non-linear optical materials used to generate the SHG signal (Nikogosyan 2005).

1.8.1.*2 Third harmonic generation*: -

Third harmonic generation (THG) is a process of nonlinear frequency conversion where the resulting optical frequency is three times that of the input laser beam. In THG, generation of light with a tripled frequency (one-third the wavelength) is observed, wherein three photons combine creating a single photon at three times the frequency (generation of 355 nm light by frequency tripling of a laser beam with 1064 nm). This can be achieved by using Nd: YAG or Nd: YVO4 laser.

Generation of blue light is possible by frequency tripling in neodymium laser with an output of 1.3 μm. Third-order NLO materials find application in optical switching, optical data processing, optical communications, optical logic gates, nonlinear spectroscopy, coherent UV-light generation, optical limiting, passive laser mode-locking, and waveguide switches and modulators (Boyd 2003). Large third-order nonlinearity is exhibited by organic molecules and conjugated polymers having structures with a large number of delocalized and polarisable electrons. Although organic materials are less applicable for coherent UV light generation, due to the lack of transparency in the UV region, they are essential for other third-order NLO applications**.**

1.8.1.3 *Sum frequency generation* (SFG):-

Nonlinearity in crystalline materials with inversion symmetry can be induced by sum-frequency generation, in which two electromagnetic waves with frequencies ω1 and ω2 interact in an NLO medium and induce nonlinear polarizability. The NLO material produces an optical wave with frequency ω3 equal to the sum of the two input wave frequencies ω1 and ω2. In the equation, the energy of the output wave is represented. ω 1 plus ω2 equals ω3. Some common applications include the generation of red light (i.e., red lasers) by combining the outputs of a 1064nm Nd: YAG laser and a 1535 nm fiber laser (doped with rare-earth ions such as Er^{3+}, Nd^{3+}, Yb^{3+}, Tm^{3+}, or Pr^{3+}). Similarly, UV light is generated by combining the output of a 1064-nm Nd: YAG laser.Laser with frequency-doubled light at 532 nm results in 355 nm UV light.

1.8.1.4 *Difference frequency generation* (DFG) :-

The process of generating difference frequencies is described by the equation ω1 - ω2 = ω3. In this case, the frequency of the generated wave is the difference between the frequencies of the inputs. It is used to create tunable mid-IR lasers with wavelengths ranging from 3 to 2μm. It has a wide range of applications, including remote sensing (Suter et al. 2012), pollutant monitoring (Phillips et al. 2010), laser-based countermeasures, and narcotics or explosives detection (Castro-Suarez et al. 2013). For DFG, crystals such as silver gallium sulphide (AGS), silver gallium selenide (AGSE), and orientation patterned gallium arsenide

(OP-GaAs) are used due to their high conversion efficiency and phase-matching bandwidth stability without temperature or angular tuning (Mathieu Giguère 2013).

1.8.1.5 *Optical parametric generation* (OPG):-

The inverse process of sum-frequency generation is optical parametric generation. It divides a single high-frequency photon (pumping wavelength λp) into two low-frequency photons (signal wavelength λs and idler wavelength λi, $\omega s + \omega i = \omega p$. Inorganic crystals with optical parametric generation properties, such as barium borate (-BaB_2O_4, BBO) and lithium borate (LiB_3O_5, LBO) (Zhang et al. 1993), are used primarily in dye lasers.

1.8.1.6 *Linear electro-optic effect (or) Pockels effect :-*

In the presence of an external electric field, the Pockels effect causes a linear change in the refractive index of a medium. In this case, a direct current (DC) field is applied to a medium through which an optical wave propagates. The change in polarisation caused by the presence of these two interacting field components effectively changes the medium's refractive index. $NH_4H_2PO_4$ (ADP), KH_2PO_4 (KDP), $LiNbO_3$, $LiTaO_3$, and CdTe are the most common crystals used as Pockels cells (Bahaa E.A. Saleh & Malvin Carl Teich 2007).

1.8.1.7 *Optical rectification :-*

It is a second-order phenomenon based on the inverse process of the electro-optic effect (Rice et al. 1994). Radiation from a ruby laser was transmitted via potassium dihydrogen phosphate (KDP) and potassium deuterium phosphate (KDdP) crystals for the first time in 1962 (Bass et al. 1962). The generation of terahertz radiation with lasers is possible thanks to an optical rectification mechanism found in semiconductors and polymers (Tonouchi 2007).

1.9 NON-LINEAR OPTICAL MATERIAL: -

NLO materials in which a non-linear polarization is involved in the application of an intense electric field may exhibit any of the above-discussed effects depending on the material characteristics. For the successful utilization of these NLO materials in various devices for a wide range of applications, these compounds have to meet the following requirements.

1. Large non-linear figure of merit for frequency conversion
2. A broad optical transparency domain 13
3. High laser damage threshold
4. Fast optical response time
5. Wide phase matchable angle
6. Ease of fabrication
7. Mechanical strength and thermal stability
8. Non-toxicity and good environmental stability

NLO materials have been the subject of intense study over the past few decades and are also being currently investigated by many research groups across the globe. Hence advances in the development of NLO materials can be considered under the following categories.

1. Discovery of new NLO materials.
2. Growth of promising NLO crystals.
3. Improving the characteristics of NLO crystals

1.9.1. Inorganic NLO crystals :-

The inorganic crystal of the NLO can be ionic or covalent crystals formed when disagreements play a major role in the crystal growth process. Since the first SHG report was made in 1961, in this field they have seen remarkable growth in crystal development through the development of semiconductor and NLO photorefractive crystals. Some of the most common inanimate materials have high efficiency, excellent thermal stability, good electro-optic transmission and high electro-optic coefficients and with photoconductivity (Dongfeng Xue& Henryk Ratajczak 2005; Dongfeng Xue&Siyuan Zhang 1999; Sun et al. 2005). Some common examples are potassium dihydrogen phosphate (, KDP), potassium deuterium phosphate (KDdP), ammonium dihydrogen phosphate (NH4H2PO4, ADP), potassium titanyl phosphate (KTiOPO4, KTP), lithium niobate (LiNbO3), PN barium titanate (BaTiO3), lithium iodate (LiIO3), etc. Various semiconductors such as gallium arsenide (GaAs), cadmium sulphide (CdS), cadmium telluride (CdTe), zinc germanium phosphide (ZnGeP2), Cadmium arsenide (CdGeAs2), and silvergallium selenide ($AgGaSe_2$) is a suitable NLO infrared materials. Nikogosyan (2005), conducted a comprehensive study of all NLO structures of diversity. The BBO is an NLO crystal capable of second, third, and fourth harmonic Nd: YAG lasers and the leading NLO crystal of the fifth-generation harmonic. The efficiency of BBO conversion is 70% in SHG, 60% in THG, and 50% in FHG. KTP is also a well-known NLO crystal with a coefficient of SHG approximately three times that of KDP.The inorganic NLO materials even though possess bulk susceptibility and have the same physical properties, also disadvantage like absorption in the visible region, poor response time, degradative photorefractive effects, low laser damage threshold, and poor optical transparency (Fan et al. 1984). In this group, the borates constitute an important class of compounds, because of the extremely wide variability of borate crystal chemistry that leads to the creation of different structure types (Xue et al. 2000). Borate NLO materials possess high chemical stability, a high laser damage threshold, good optical quality, and a wide range of spectral transparency. Some important inorganic borate crystals like lithium triborate (LiB_3O_5, LBO), lithium tetraborate, beta barium borate (βBaB_2O_4, BBO), and potassium Penta borate tetrahydrate ($KB_5O_8.4H_2O$) have been widely used in NLO devices for UV laser generation. Furthermore, among all the borate structures reported to date, 36% are non-centrosymmetric while among the reported inorganic crystal structures only the reported inorganic crystal structures are present. 15% are non-centrosymmetric structures (Aka andamp; Brenier 2003).Borate crystals are superior in UV applications to other commonly used NLO materials such as potassium dihydrogen phosphate or lithium niobate because of their high transmittance at wavelengths down to 155 nm combined with their higher laser damage threshold (Petra Becker 1998).

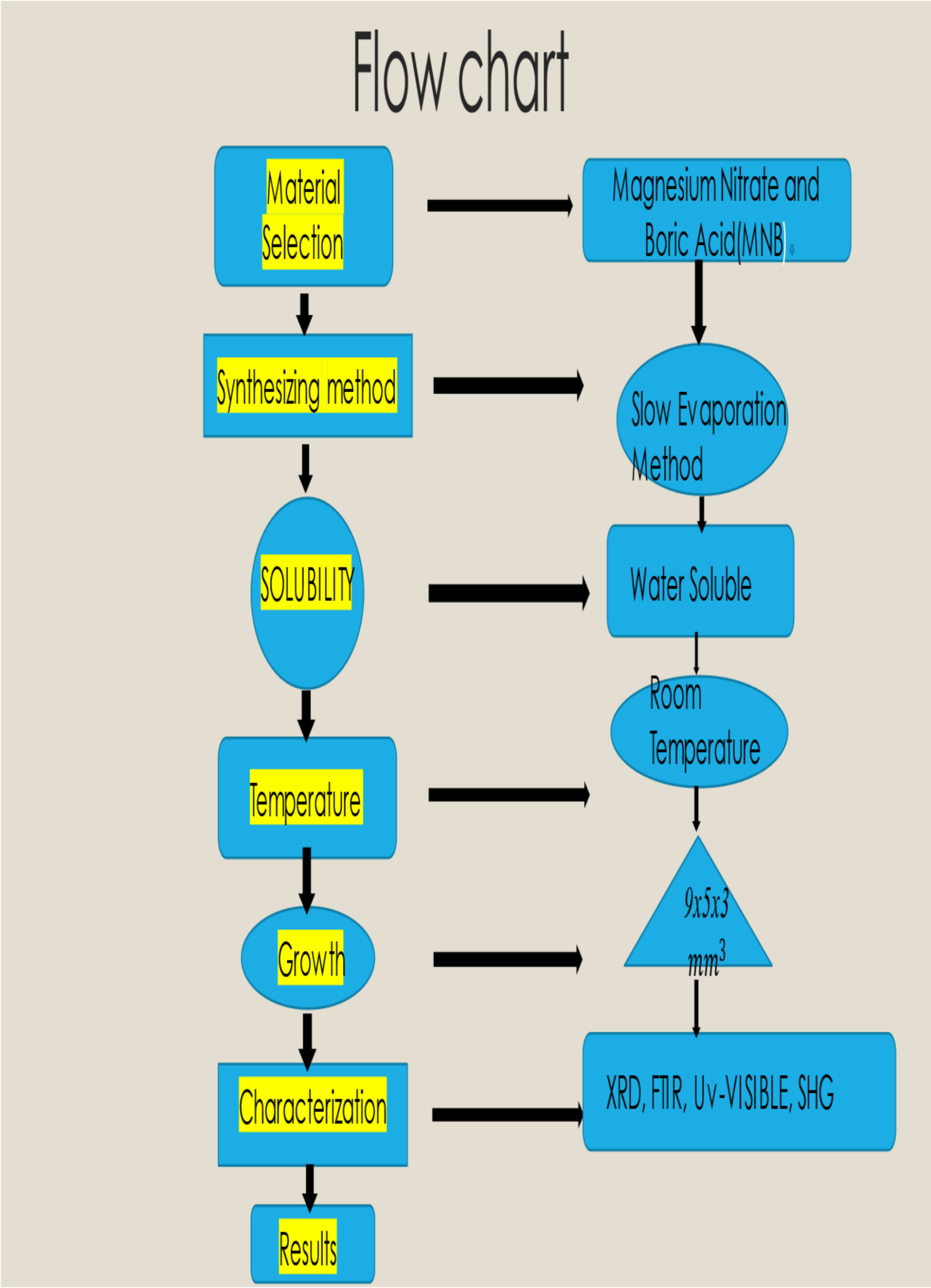
1.9.2. Organic NLO crystals: -

The organic NLO materials have been discussed in detail in several publications and excellent reviews such as Davydova et al. (1970), SantanuBasu (1984), Suresh et al. (2012). organic materials show admirable NLO properties because of their electronic structure with π conjugated systems between donors and acceptors (Patil et al. 2014; Prakash et al. 2013). T non-centrosymmetric in the distribution of these π-electronic clouds could lead to huge NLO efficiency which is 10 to 100 times larger than that of inorganic NLO materials (Bhuvanaetal.

2007).They also exhibit large optoelectric coefficients, low dielectric constants, faster optical responses, and ultrafast responses to external electric fields (Neeti Goel et al. 2013). Hence, organic materials are superior to their inorganic counterparts in terms of crystal preparation and production of better devices with large nonlinearities, i.e., they have wide applications in areas such as information storage, optical communication, optical data storage, optoelectronics, laser technology, and telecommunications (Sudhahar et al. 2013). One of the most widely investigated organic NLO crystals is 4-N, N-dimethylamino-4'-N-methyl-stilbazoliam tosylate (DAST) reported by Marder et al. 1989. Its second-order NLO coefficient is ten times as large as the inorganic standard LiNbO3. The NLO efficiency of a new organic material 4- methoxy benzaldehyde- N-methyl 4-stilbazolium tosylate (MBST) is 17 times greater than that of urea (Perumal et al. 2002). The main drawbacks of organic crystals are (Chemla&Zyss 1987) their poor physicochemical stability, low hardness, and cleavage tendency hindering their device application.

1.9.3. Semi-Organic crystal:-

Semi-organic crystals have a combination of good thermal and mechanical properties of inorganic with high optical nonlinearity of purely organic compounds.Semi-organic materials have the benefits and drawbacks of both organic and inorganic features. Semi-organic crystals have a restriction on nonlinearity in inorganic materials, and their moderate effectiveness in raising technology levels and producing organic single crystals has prompted scientists to develop novel ways. Clearly, one solution was to create hybrid inorganic-organic materials with minimal trade-offs in their respective advantages. Semi-organics are the name for this new type of material. The production of inorganic salts from chiral chemical compounds is a common example. The monohydrate of L-Histidine tetrafluoroborate (L-HBF) is an example of this class. Tartrates, Oxalates, and amino salts, for example, are more NLO active. Forming metal coordination complexes of inorganic compounds is an alternate way. It is not necessary for the organic portion to be asymmetric. Semi-organic crystals have high mechanical strength, chemical stability, high damage threshold, high transparency range but the Inorganic materials have excellent, mechanical and thermal properties and due to the presence of nonlinearity possess extended πelectron delocalization.



Flow chart
Material Selection
Magnesium Nitrate and Boric Acid(MNB)
Synthesizing method
Slow Evaporation Method
SOLUBILITY
Water Soluble
Room Temperature
Temperature
Growth
9x5x3 mm3
Characterization
XRD, FTIR, Uv-VISIBLE, SHG
Results

CHAPTER -2

2. REVIEW OF LITERATURE:-

Massive changes in new technologies are frequently attributed to the development of new materials of greater quality. Fabrication of new materials using new techniques ultra-pure silica glass that allowed for the creation of ultra-low-loss fibres The main stimulus for optical fibre connection was provided. The sudden rise in popularity of Another key milestone was the creation of fibre amplifiers using erbium-doped glasses. Enabled transmission rates of 50 gigabits per second in this area. Such a high standard. Standard electronic amplifiers are incapable of achieving high amplification rates. The high price Speed and a high degree of parallelism in optics will lead to optoelectronics throughout time. A growing number of functions will be implemented optically in systems. The progress that has been made in synthesizing novel optical materials with excellent performance, on the other hand, is critical to the advancement of photonic technology. Nonlinear optical materials are predicted to play a key role in enabling optoelectronic and photonic technologies in this regard.

Inorganic nonlinear optical materials are now widely used in a wide range of photonic applications. Many NLO inorganic single crystals have been identified as possible optical and electro-optical device candidates. With the development of a significant number of devices utilizing solid-state laser sources, nonlinear optical materials have taken on new significance.

1)Investigation on growth and characterization of a new inorganic NLO material: Zinc sulphate (ZnSO4:7H2O) doped with Magnesium Sulphate (MgSO4:7H2O)G. Pasupathi , P. PhilominathanDepartment of Physics, A.V.V.M Sri Pushpam College (Autonomous), Poondi, Thanjavur – 613 503, Tamil Nadu, India

At room temperature, a single crystal of Zinc sulfate doped with Magnesium sulfate, a nonlinear material, was formed from an aqua solution using a slow evaporation approach. To confirm the formation of new crystals, good quality single crystals were produced using a slow evaporation process (four weeks) and the crystals were subjected to single-crystal X-ray diffraction and FT-IR studies.

The TGA and DTA results show that the material is thermally stable. The UV–Visspectrum indicates the material's high optical transparency, and the Kurtz powder method confirmed the presence of the second harmonic generation. When compared to inorganic crystals, organic NLO crystals can have extremely large nonlinear susceptibilities, but their utility is limited by low optical transparencies, poor mechanical properties, low laser damage thresholds, and the inability to create and grow big crystals. Inorganic NLO materials, on the other hand, are known to have good mechanical and thermal properties [1,2]. As a source of Mg^{2+} ions, epsomite ($MgSO_4:7H_2O$) has a wide range of applications in medical (acute therapy of cardiac arrhythmia) and agriculture (fertilizer)[3]. When doped with specific activators, this material is effective for nonlinear optical (NLO) applications. We describe the formation and characterization of a novel inorganic material, Zinc sulfate ($ZnSO_4:7H_2O$) doped with Magnesium sulfate, in this study. The optical second harmonic generation efficiency of the formed crystal is high. To the best of our ability, this crystal was having NLO property.

2)Growth and Spectral properties of NLO Single Crystals: L-Tyrosine and L-Tyrosine Succinate Hydrobromide,V.Sheelarani 1 and J. Shanthi *, Department of Physics, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore 641 043, Tamilnadu, India.

NLO Single Crystal Growth and Spectral Properties: L-Tyrosine and L-Tyrosine Succinate Hydrobromide Slow evaporation using rotoevaportor were used to generate single crystals of L-Tyrosine and L-Tyrosine Succinate Hydrobromide (LTSHB), a novel nonlinear optical compound. The powder X-ray diffraction pattern of the produced crystals reveals a high degree of crystallinity. The transparency of the crystals in the visible range is indicated by the UV-Vis spectrum. FTIR research has revealed the presence of a functional group. The grown LTSHB crystal's second harmonic generation efficiency is determined to be 1.2 times that of a typical KDP crystal.

*3)*A new Non-Linear Optical Material and Mechanical Studies for pure and Sarcosine Doped L-Tartaric acid of Single Crystal by slow Evaporation Method ,Ravichandran,Department of Physics, National College (Autonomous), Trichy-620001, India.S. Aron Rabi,Department of Physics, Loyola College of Arts & Science, Mettala, Namakkal-636202 India.

A new non-linear optical material made of sarcosine doped L-tartaric acid crystals produced at room temperature using the slow evaporation method. FTIR spectral analysis detected the vibrational frequencies of functional groups doped L-tartaric acid in the produced crystal. The optical transmission research demonstrates that the doped crystal has better transparency across the visible area, which is beneficial for NLO applications. Powder X-Ray diffraction and Single X-Ray diffraction studies were used to determine the crystalline size and cell parameters. Spectral analysis was used to evaluate the presence of dopant in a sample generated by L- tartaric acid crystals with the addition of sarcosine. The mechanical strength of the formed crystal is revealed by Vickers Microhardness investigations. Nd: YAG pulsed SHG effectiveness of pure sarcosine doped L-tartaric acid crystal verified Using the Kurtz-Perry techniques.

4) Synthesis, Growth and Optical, Mechanical, Electrical and Surface Properties of an Inorganic New Nonlinear Optical Crystal: Sodium Cadmium Tetra Chloride (SCTC), M. Packiyaraj's , S M Ravi Kumaretal

The slow evaporation technique is used to create a novel inorganic nonlinear optical single crystal of sodium cadmium tetrachloride (SCTC) from an aqueous solution at ambient temperature. Powder X-ray diffraction is used to examine the crystalline quality of the formed crystal. Single crystal X-ray diffraction confirms the lattice parameters and crystal system. A study of optical transmission on SCTC crystal reveals good transmittance throughout the UV–Vis range. Vickers’s micro hardness test is used to determine the mechanical strength of the generated crystal. The crystal's second harmonic generation (SHG) efficiency, as determined by Kurtz's powder approach, indicates that it has 1.75 times the nonlinear optical (NLO) efficiency of KDP. The crystal exhibits conventional dielectric behavior when the dielectric constant and dielectric loss are plotted as a function of log frequency at various temperatures. The etching study is used to investigate the SCTC crystal formation process. SEM/EDAX spectrum is used to examine the surface characteristics of a formed crystal. The z-scan technique is used to explore the third-order nonlinear optical property of the produced crystal, and the results show that SCTC crystal could be a promising material for nonlinear optical device applications.

5) The Growth and the Optical, Mechanical, Dielectric and Photoconductivity Properties of a New Nonlinear Optical Crystal—L-Phenylalanine-4-nitrophenol NLO Single Crystal,Sagadevan Suresh, Crystal Growth Centre, Anna University, Chennai, India.

Slow evaporation was used to grow nonlinear optical single crystals of L-phenylalanine-4-nitrophenol. The grown crystal was subjected to single-crystal X-ray diffraction analysis to confirm its monoclinic crystal structure and space group P21. The optical transmission study reveals the crystal's transparency throughout the visible region, with the cut-off wavelength determined to be 320 nm. 3.87 eV is found to be the optical bandgap. The transmittance of the L-phenylalanine-4-nitrophenol crystal was used to calculate the refractive index (n), extinction coefficient (K), and real (r) and imaginary I dielectric constant components. Vickers' microhardness tester was used to investigate the mechanical behavior of the grown crystals. At various temperatures, the dielectric constant and dielectric loss of L-phenylalanine-4-nitrophenol are measured in the frequency range of 50 Hz to 5 MHz.The photoconductivity study confirms the sample's negative photoconductive nature.

6) Synthesis, Crystal Growth, Structural, Optical, Thermal and Mechanical Properties of Semiorganic Nonlinear Optical Material: L-Cystine Dihydrochloride,January 2010,Journal of Minerals and Materials Characterization and Engineering , Th Uma Devi, N Lawrence ,R. Rameshbabu.

A single crystal of L-cystine dihydrochloride, a semi-organic nonlinear optical material, was grown from an aqueous solution. A low temperature (173 K) crystal structure measurement revealed that the crystal belongs to the noncentrosymmetric space group C2. High-resolution X-ray diffraction (HRXRD) rocking curve measurements were used to assess the structural perfection of the grown crystal. Fourier transform infrared (FTIR) spectroscopic studies were also carried out to identify the various vibrational modes of the compound's fundamental groups. The UV–vis transmission spectrum was measured between 200 and 1000 nm. The Kurtz powder technique was used to determine the efficiency of second-harmonic conversion, which is 0.35 times that of KDP. TGA and DTA were used to investigate the thermal properties of L-Cysteine Dihydrochloride.

7)Synthesis, Structural, Optical, Mechanical and Electrical Properties of Semi-Organic Nonlinear Optical Material: Lithium Para-Nitrophenolate Trihydrate October 2015 , Journal of Chemical and Pharmaceutical Sciences,SelvakumarSingaravel, A. Leo Rajesh.
Slow evaporation was used to grow a semi-organic nonlinear optical single crystal of barium bis-Para nitrophenolate para nitrophenol tetrahydrate. Single-crystal X-ray diffraction was used to perform structural analysis, which confirmed that the crystal is an orthorhombic crystal system with space group Fdd2. The crystal structure revealed that the title compound's eight coordinate barium atom lies on a crystallographic two axis in an environment of two pairs of symmetry-related nitro chelating ligand anions, a pair of nitro-O coordinating neutral p-nitrophenolate ligand, and four water molecules, forming a single supermolecule structure. The FTIR and Micro-Raman spectra were used to identify functional groups. According to the optical study, the crystal has high transmittance in the visible region, which is useful for optoelectronics applications. The efficiency of the crystal's second harmonic generation (SHG) was measured using the Kurtz-Perry powder technique and was found to be 16.2 times that of KDP.

8) Synthesis, crystallography, DFT, MTT assay, and molecular docking studies of an exocyclic double-bonded crystalline chalcone DavidSamuvel Michael [a]M.KrishnaPriya[b]J.Sidharthan[c]M.Kumar[d]RajaduraiVijaySolomon[a]D.Reuben Jonathan

Slow evaporation was used to grow smaller size p-MHB single crystals from various solvent solutions and seeded controlled cooling of the solution was used to grow a large dimensional p-MHB single crystal with dimensions of 45 42 62 mm3. [Vanillin nicotinamide was grown using the slow evaporation method with ethanol as the solvent (VN). A new mixed compound, sodium rubidium phosphate tellurate, was created by slow evaporation at room temperature, as confirmed by

X-ray single-crystal diffraction. Key findings and conclusions Slurry, liquid-assisted grinding, slow evaporation, and, more recently, microwave-assisted and supercritical solvent can all be used to create polyphenol-based cocrystals. The optical quality magnesium doped -glycine single crystal was grown using slow evaporation. The Claisen-Schmidt condensation reaction was used to create a bicyclic chalcone 2-(4-methoxybenzylidene)-3,4-dihydro-2H-naphthalene-1-one (MDN) with an exocyclic double bond, which was then crystallized using the slow evaporation solution method. Four multicomponent crystals of favipiravir (FPV) were prepared using slow evaporation or liquid-assisted grinding to improve its poor permeability and tablet ability, including three cocrystals (FPV-theophylline).

9) Efficient growth techniques and properties of Benzophenone Single Crystals for NLO Applications: A Review, Selvakumar. P, Arun Kumar. R, GRD Centre for Materials Research, PSG College of Technology, Coimbatore, India, Arivanandhan. M, Hayakawa. Y, Kawai. H, Shizuoka University, Hamamatsu, Japan.

Because benzophenone is one of the most promising organic NLO materials for high energy laser photonic applications, this review will concentrate on the growth, efficiency, and applications to improve the structural and physical properties of organic NLO benzophenone crystals, they are melted.To improve the structural and physical properties of organic NLO benzophenone crystals, they are melted. The slow evaporation method, the Microtube-Czochralski method, and the Vertical Bridgman method have all been discussed as methods for growing bulk and high-quality benzophenone crystals. As discussed further below, it is acknowledged that the size and efficiency of the growing benzophenone single-crystal vary depending on the techniques used. A pure benzophenone crystal's SHG efficiency was also compared to that of a standard KDP crystal. The benzophenone crystal's optical transparency has also been investigated.

10) Synthesis, Crystal Growth and Characterization of Organic NLO Material: M-Nitroacetanilide, Ramesh Rajendran' January 2011Advances in Materials Physics and Chemistry,

At a constant temperature of 40°C, single crystals of m-Nitroacetanilide (mNAa) were successfully grown from a methanol solution using the slow evaporation method. Estimates for mNAa solubility studies were made. The cell dimensions were determined using single-crystal X-ray diffraction (XRD) study. The functional groups were confirmed using Fourier transform infrared (FTIR) analysis. Proton placement was determined using Nuclear Magnetic Resonance Spectroscopy (NMR) spectral analysis. UV-visible and fluorescence spectral analyses were performed on the grown crystals. The as-grown crystal's thermal properties were determined using thermogravimetric and differential thermal analysis.

Chapter - 3

3.1 OBJECTIVES OF THE RESEARCH

• To find new non-linear inorganic crystals and work on their synthesis.

• To evaluate the newly synthesized compounds in order to identify novel structural features and determine their properties in order to select potential crystals for various NLO applications.

3.2 SCOPE OF THE RESEARCH WORK

For laser and material processing, discovering and designing high-efficiency nonlinear optical (NLO) crystals for the visible and ultraviolet (UV) areas is important. Nonlinear optical materials, both inorganic and organic, have advantages and disadvantages. It is simple to create inorganic nonlinear optical crystals. The traditional solution growth procedure can be used to grow them into huge crystals. organic crystals, on the other hand, are less efficient than their inorganic counterparts. Inorganic crystals have high mechanical strength in general. Organic materials are difficult to generate and have lower mechanical strength than inorganic materials. Despite having 34 flaws, inorganic materials exhibit a strong nonlinear activity. Semi-organic crystals were produced to combine the benefits of organic and inorganic materials.

1. Using the solution growth approach, create new inorganic non-linear optical crystals.

2. Use single-crystal X-ray diffraction to describe the new NLO crystals.

3. To support the characterization of the chemical, as well as to determine the lower cut-off wavelength and functional group contained in the NLO crystals, perform FTIR, UV-visible.

4. Conduct optical investigations to verify the non-linear optical properties of the produced crystals using second-order harmonic generation non-linear optical susceptibility.

5. To carry out FTIR, UV-visible, to support the characterization of the compound as well as to determine the lower cut-off wavelength and functional group present in the NLO crystals.

The future attempt of my work is to concentrate on the further study of thermal studies like photoconductivity, thermogravimetric analysis, TGA/DSC, electric study like dielectric analysis, mechanical studies like Vickers hardness test, and structure studies like SEM / EDAX analysis of sample magnesium nitrate and phthalic acid combination crystal and enhance them for their application in the field of optoelectronic and electronic fabrication processes.

CHAPTER 4

INSTRUMENTS FOR CHARACTERIZATION

4.1SINGLE CRYSTALXRD:-

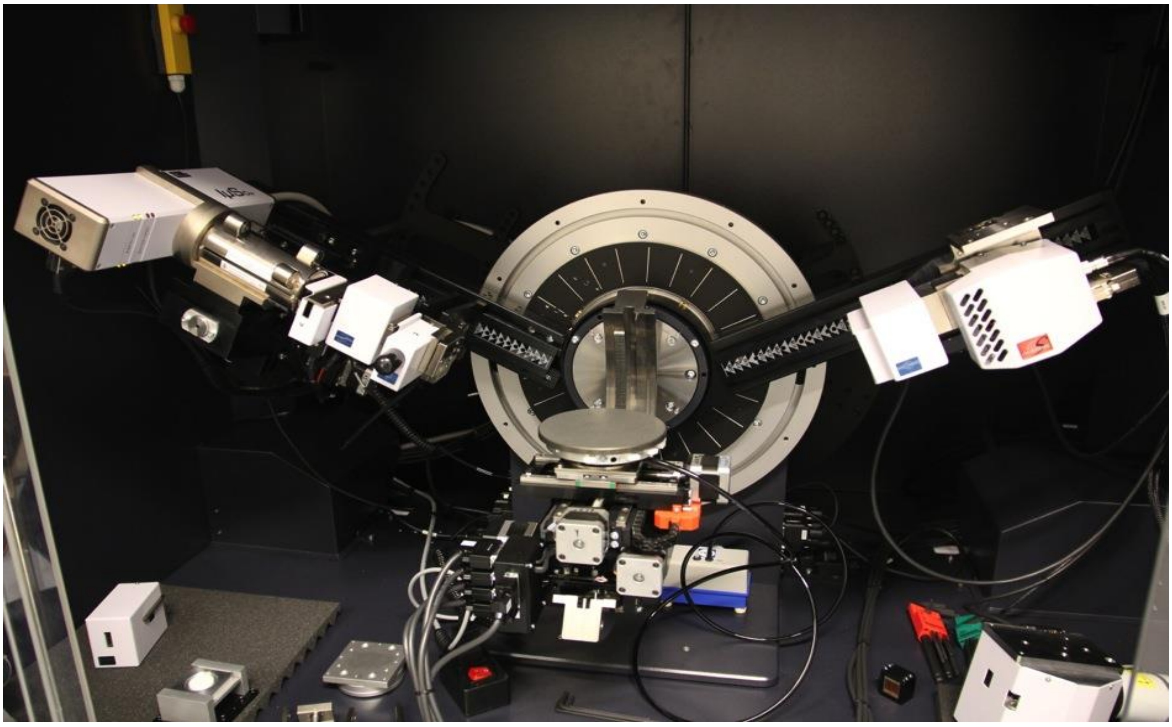


Fig 4.1 setup of BRUKER Kappa Apex 2 CCD diffractometer

Fig 4.2 Instrumental setup of BRUKER Kappa Apex 2 CCD diffractometer

X-rays of a single crystal Diffraction is a non-destructive technique for extracting detailed information about the crystal's lattice parameters, crystal system, and crystalline nature, including such unit cell dimensions, bond lengths, and bond angles. And it's directly related to single-crystal refinement, which includes interpreting the data obtained by X-ray analysis and graphing the results to acquire the crystal structure. In 1912, the scientist Max von Laue discovered that crystalline solids act as three-dimensional optical phenomenon gratings for X-ray wavelengths, similar to plane spacing in a very spacial lattice. The investigation of precise crystal structures and atomic spacing of constituent particles is now usually done using X-ray diffraction. X-ray diffractometers are designed to produce high-quality diffraction data while still being versatile and its wide applications.

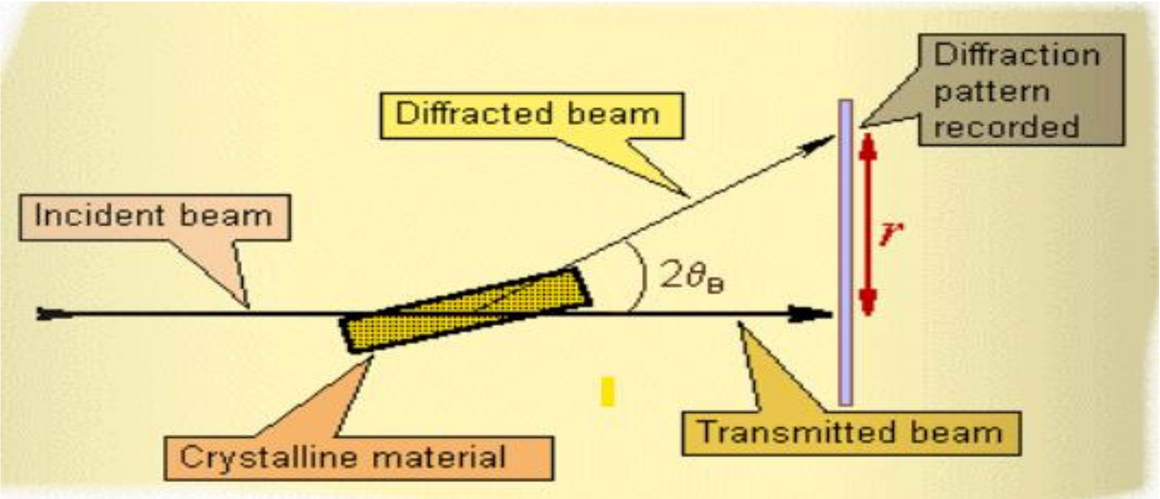


Fig 4.3 Schematic diagram of XRD

Constructive interference between monochromatic X-rays and a crystalline sample is the basis of X-ray diffraction. A beam tube generates these X-ray area units, which also are filtered to provide monochromatic radiation, collimated to focus, and directed at the sample. Once Bragg's law (n=2d sin) is fulfilled, the incident rays interact with the sample and produce constructive interference (and a diffracted ray). This is shown in Fig.5.2. In a crystalline structure material, this rule connects the wavelength of an electromagnetic wave to the optical phenomenon angle as well as the lattice spacing. The area units of diffracted X-rays are then detected, processed, and tallied. All possible optical phenomenon directions of the lattice must be altered by altering the pure mathematics of the incident rays, the orientation of the focused crystal, and also the detector. all doable optical phenomenon directions of the lattice ought to be earned.

The creation of x-rays in a thermionic vacuum tube was aided by all-optical phenomenon methods. The diffracted beams are collected, and the X-rays are directed at the sample. The angle between incoming and diffracted photons is a critical element of all-optical characteristics. Instrumentation for powder and single-crystal optical phenomena differs on the far side. The following is the general process for collecting intensity data with a single crystal XRD:

• Choose an appropriate crystal.

• the diffraction maxima's position.

• diffraction spot and cell parameters refinement and indexing.

• data collecting on the intensity.

4.1.1ADVANTAGES AND LIMITATIONS OF SINGLE-CRYSTALX-RAY DIFFRACTION

4.1.1.1Advantage:-

•It is the fastest and most powerful technology.

•XRD instruments are easily available.

•Detailed crystal structure, including unit dimensions, bond-lengths, bond-angles, and site-ordering information.

•Non-destructive.

• It is the best way to identify an unknown sample, powder material, bulk crystal which are homogeneous.

•The result analysis is quick, it take10 to 30 minutes to develop, which contributes to the usefulness of XRF in research and development.

4.1.1.2Limitations :-

• XRD also has size limitations.

• Optically clear sample.

• Twinned samples are often handled with difficulty.

• Data collection generally requires 24- 72 hours.

4.2EXPERIMENTAL SETUP OF FTIR SPECTROMETER:-

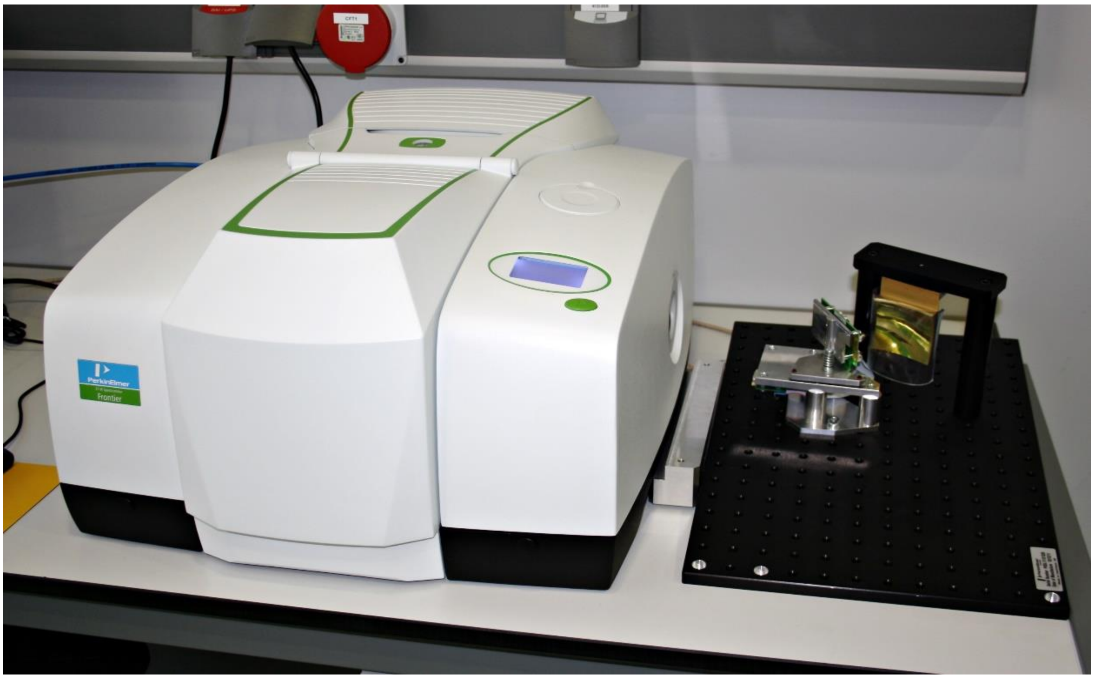


Fig. 4.4 Experimental Setup of Fourier Transform Infrared Spectroscopy.

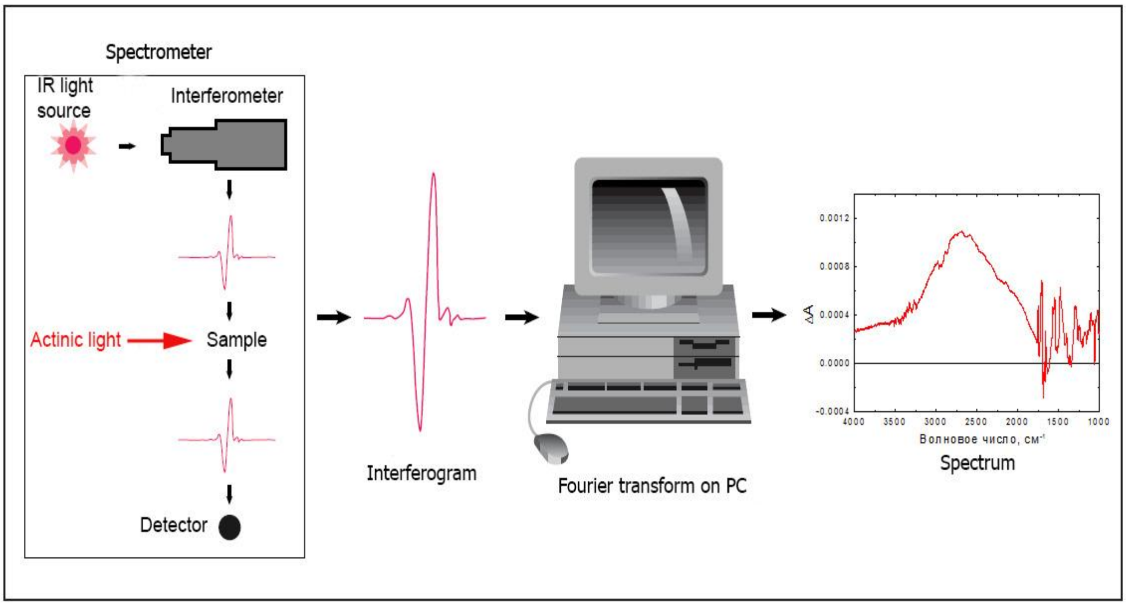


Fig. 4.5 Schematic Diagram of Fourier Transform Infrared Spectrometer

The Infrared qualitative analysis is employed to study elaborately the chemical composition which are presentinthe sample.IR-radiations move through the sample to the supply spectrumMolecules which is associated with overall electric doublet and once they are exposed to IR-radiation it fluctuates the (EM) radiation. These fluctuations are nothing but the footprints of chemical compositions of the sample. Hence, to review the chemical composition of the sample the fluctuations of EM-radiations are recorded by the photometer. Fourier transform rework is utilized to urge the signal. Attenuated total reflection (ATR) may be a sampling technique employed in conjunction with infrared qualitative analysis that permits samples to be examined directly within the solid or liquid state. singular wetness defends style protects Spectrum from environmental effects permitting it to be employed in tougher environments, and with extended intervals between chemical agent amendment to lower maintenance value. Atmospherically Vapor Compensation (AVC) options a sophisticated digital filtering rule selected to deduct greenhouse emission and H_2O absorptions mechanically in real-time. the employment of Sigma-Delta converters within the digitization of the FT-IR interferogram improves dynamic vary, reduces spectral artifacts, and it increase ordinate one-dimensionality. Includes basic transmission practicality with nonmandatory totally integrated, strong universal sampling ensures untroubled measurements. The spectrum originated if from the wave motion of the molecule. The wave frequencies are a type of fingerprint for the compounds that are used for characterization of organic, inorganic, and semi-organic compounds. The band intensities are proportional to the concentration of the compound and therefore qualitative estimations also are doable. The IR qualitative analysis is additionally administrated by the exploitation Fourier transform technique. The interference pattern obtained from a two-beam measuring device because the path distinction between the two beams is altered, once Fourier remodels, offers rise to the spectrum. Infrared qualitative analysis is a very important technique in chemical science. it's a simple thanks to determining the presence of a composition of molecule. Also, one will use the distinctive assortment of absorption bands to verify the identity of a pure compound or to find the presence of specific impurities. Analysis by infrared qualitative analysis relies on the actual fact that molecules have specific frequencies of internal vibrations. These frequencies occur within the infrared region of the magnetic force spectrum: 4000cm^{-1}~ 400 cm^{-1}.

once a sample is placed between the passing beam of infrared light, the sample absorbs all the radiation at variable frequencies of molecular wave frequencies, however, can transmit all alternative frequencies. The frequencies of radiation absorbed are measured by the infrared spectroscope, and also the ensuing plot of absorbed energy vs. frequency is named the spectrum of the sample. Identification of a substance is feasible as a result of totally completely different materials having different vibrations and yielding different infrared spectra. moreover, from the frequencies of the absorption, isno varied chemical teams are gifted or absent during a chemical structure. additionally, to the characteristic nature of the absorption, the magnitude of the absorption of a given sampleis said to be the concentration of that present sample.

4.2.1 ADVANTAGES AND LIMITATIONS OF FOURIER TRANSFORM INFRARED SPECTROSCOPY: -

4.2.1.1Advantages:-

• Fourier Transform Infrared Spectroscopy, or FTIR, seems to be a very rapid screening technique for extracting a high-quality spectrum.

• In comparison to the dispersive instrument, this spectroscopy offers a better signal-to-noise ratio.

• This spectrum can be obtained quickly with FTIR, which saves time.

• FTIR can also be used to analyse gases, solids, even liquid.

• There is no need for external calibration while utilizing FTIR, and the results are accurate.

• The FTIR method is non-destructive.

• Fourier transform infrared spectroscopy can easily distinguish between organic and inorganic substances.

• Because the mirror coupled to the interferometer is the only moving part in the FTIR, the mechanical breakdown is less than that of other instruments.

• Multiple gaseous elements can be analyzed at the same time.

• Even small quantities of contaminants can be detected using FTIR.

•Even small quantities of pollutants can be detected using FTIR.

• The FTIR instrument is correctly calibrated due to a laser beam.

• It usually takes 1 to 2 seconds to perform a scan.

• Produce High-resolution images.

4.2.1.2Limitations :-

•Due to its small size, the sampling chamber of an FTIR can have several restrictions.

• The Infrared beam can be obstructed by mounted items. Only small things, like rings, can usually be checked.

• Because certain materials totally absorb infrared radiation, obtaining a reliable result may be impossible.

4.3EXPERIMENTALSETUP OF ULTRAVIOLET-VISIBLE SPECTROSCOPY: -

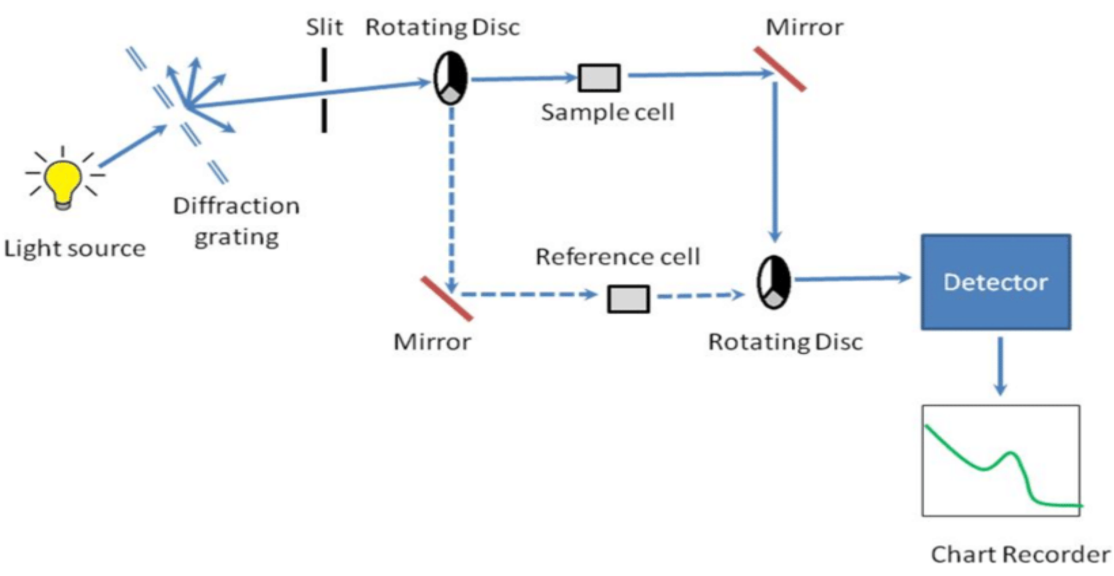


Fig. 4.6 Schematic Diagram of Uv-Visible spectrometer

In analytical chemistry, UV spectroscopy is a useful instrument. Electron spectrum analysis is the opposite of UV spectrum analysis. This is because to the fact that it entails the transition of electrons from low to high energy or excited states. At wavelengths ranging from 200 nm to 800 nm, measurements in the ultraviolet/visible range (UV-VIS) are made. When a molecule absorbs ultraviolet or visible light, a transition occurs between the molecule's electron energy levels. It is used for optical and electronic characterization to characterize materials such as films, powders, monolithic solids, and liquids. In general, moving from a highly occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) is the preferred transition (LUMO). For many compounds, low-energy molecular orbitals always square orbitals, and p-orbitals and S orbitals, which correspond to letter of the alphabet bonds. The p orbitals and S orbital measure at somewhat higher energy levels, the orbitals (nonbonding orbitals). With the separate pair of electrons lie at higher energy levels. The unoccupied or anti-bonding orbitals (pie* and sigma*) square measure the best energy occupied orbitals. altogether the compounds (other than alkanes), the electrons bear varied transitions. Nonbonding to pie, nonbonding to the letter of the alphabet, pie to pie, letter of the alphabet to pie, and letter of the alphabet to letter of the alphabet are some of the other key transitions with increasing energies. A prism or optical device splits a beam of sunlight from a visible and or ultraviolet source of illumination (colored red) into its component wavelengths. A half-mirrored device splits every monochromatic (single wavelength) beam into two equal intensity beams. The sample beam is one of the two beams that pass through the little low-clear solvent. The intensity of the light beams is then measured and compared using electronic detectors. The reference beam's intensity, which should have suffered little or no light-weight loss, absorption, is symbolized by the symbol I0. The sample's intensity is denoted by the letter I. The prism spectroscope mechanically scans all of the component wavelengths in the way indicated in a short amount of time. The ultraviolet zone is normally between 200 and 400 nm, with a visible component between 400 and 800 nm. Overtone and combination bands of mid-infrared wave modes are commonly related to transitions detected in this area. The electron within compounds (apart from alkanes) have a variety of transitions. Nonbonding to pie, nonbonding to the letter of the alphabet, pie to pie, letters of an alphabet to pie, & letter of the alphabet to letter of the alphabet are just a few of vital transitions with growing energies.

Fig4.7 Experimental setup of UV-Vis-NIR Spectrophotometer

4.3.1ADVANTAGES AND LIMITATION OF ULTRAVIOLET-VISIBLE SPECTROSCOPY:-

4.3.1.1 Advantages:-

• The UV-VIS spectrophotometer's accuracy is the main benefit.

• The UV-VIS spectrometer is simple to operate.

• Ensure a stable operation

• An instrument that is cost-effective

• Cover the entire ultraviolet and visible spectra.

•It can be used for qualitative or quantitative techniques.

• A UV-VIS spectrophotometer can be used to obtain the derivative graph.

• It can be used to investigate medication deterioration.

4.3.1.2 Limitations:-

• Only those molecules with chromophores are examined.

• pH, temperature, pollutants, and impurities can all alter the absorption results.

• It is only feasible to examine liquid samples.

• It takes time to get ready for operation.

•The sample reading can be influenced by how the cuvette is handled.

4.4 EXPERIMENTAL SETUP OF KURTZ AND PERRY SHG ANALYSIS :-

Second-harmonic generation (also called frequency doubling or abbreviated SHG) is a nonlinear optical process, in which two photons with the same frequency interacting with a nonlinear material are effectively "combined" to get new photons with twice the energy, and thus twice the frequency and half the wavelength of the initial photons. Second-harmonic generation, as an even-order nonlinear optical effect, is merely allowed in media without inversion symmetry.

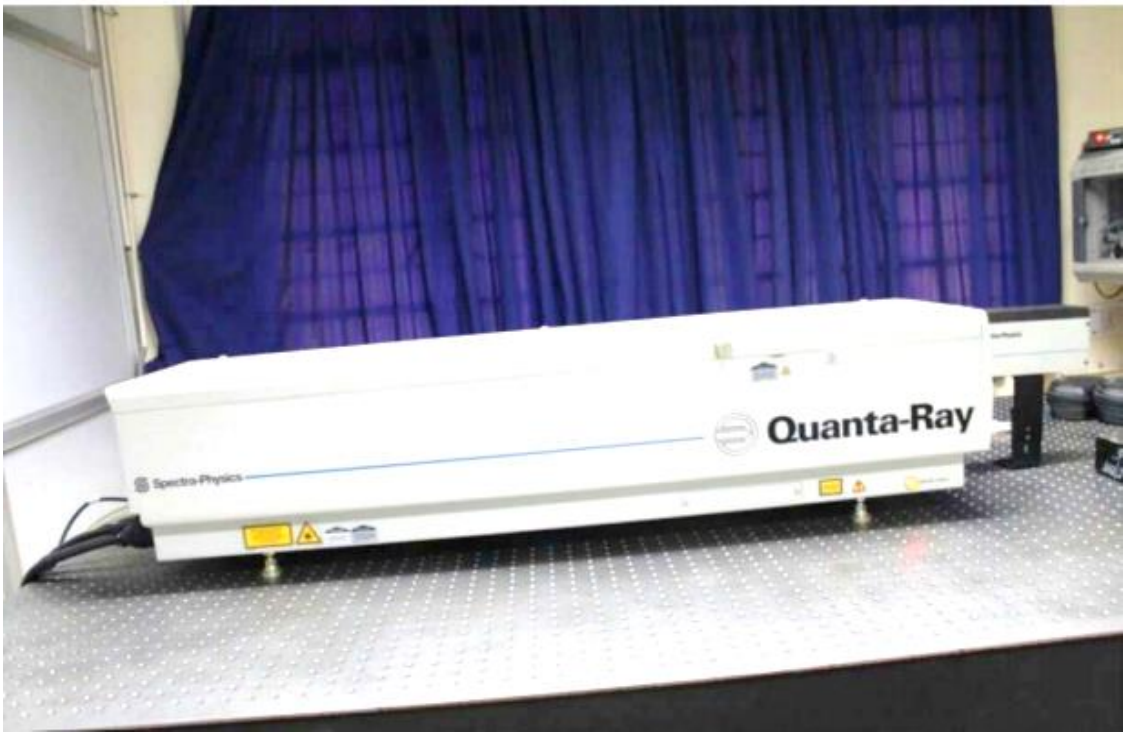


Fig 4.8 Second Harmonic Generation (SHG) Instrumentation

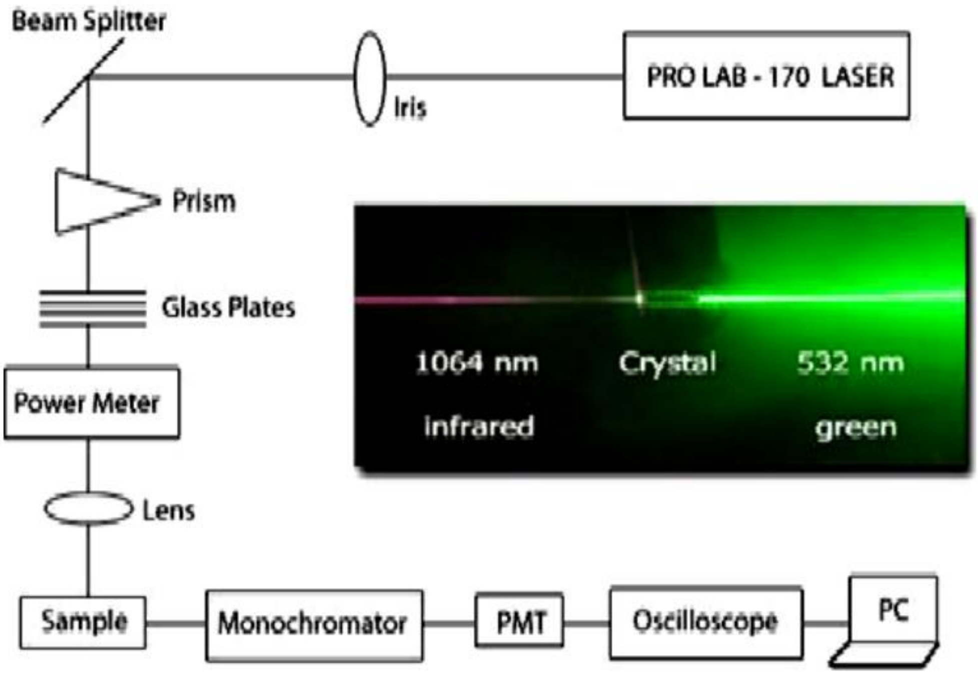


Fig 4.9 Schematic diagram of second harmonic generation

Figure 4.9 depicts the SHG measurements setup schematically. A consecutive long-pass dichroic mirror and narrowband interference filter (1064 nm information measure targeted at 532 nm) separated the SHG light-weight from the basic and attainable two-photon fluorescent light-weight, which was detected by a cooled photomultiplier tube connected to a gauge boson tally unit. A white-light imaging arm was placed within the magnifier to assist with sample positioning. To avoid changes in the input polarisation of the irradiation due to the imaging arm, a flip mirror was used to direct white light-weight to the imaging lens and, if necessary, a subsequent camera. A 3-axis piezo-actuated translation stage was used to scan the sample at the focal plane of the magnifier objective. The constituent dwell time was 150ms, averaged double, and 100 x 100 pixels were employed for the 5 mm × 5 mm scanning area.

Second-harmonic generation, the first nonlinear optical phenomenon reported after the invention of Q-switched lasers, is now used to create tunable laser beams and to research materials. Nonlinear optical (NLO) materials are essential in nonlinear optics, and they have a big impact on information technology and industrial applications. This could be basically copied to the advancement of the NLO materials' performance. The output of an Nd: YAG Quanta ray optical maser is used to evaluate the nonlinear optical properties of the only crystals. SHG experiments are carried out in a square-measuring experimental setup. At 1064 nm, a Q-switched, mode barred Nd: YAG optical maser was found to generate approximately 6mJ/pulse. This optical maser has two modes of operation. The optical maser emits one 8 ns pulse in single-shot mode. The optical maser produces an endless train of 8 ns pulses at a steady rate in the multi-shot mo

METHODOLOGY

4.5SYNTHESIS:-

The magnesium nitro borate (MNB) single crystal was synthesized by Merck branded magnesium nitrate and boric acid in the amounts of 8.231g/mol and 3.4320 g/mol in double-distilled water. The purity of the synthesized salt was further increased by repeated recrystallization.

4.6. GROWTH: -

The starting material used for synthesis was of analytical reagent grade of Magnesium nitrate and boric acid at a 2:1 ratio. The calculated amount of Magnesium nitrate and boric acid salts was added with double distilled water according to the solubility and, finally, the whole solution was mixed with continuous stirring for 6 hours using a magnetic stirrer to obtain a homogenous mixture. The completely dissolved solution was filtered using Whatman filter paper to remove the suspended impurities and allowed to crystallize by the slow evaporation method at room temperature for about 40 days. Once seed crystals are obtained recrystallization is done by filtering the solution and one seed crystal is dropped in that solution and again kept for evaporation. Finally, a well-defined Magnesium Nitro Borate (MNB) Crystal with dimensions[9x5x3 m] was obtained. The photograph of grown crystal is shown in Fig 4.9.1

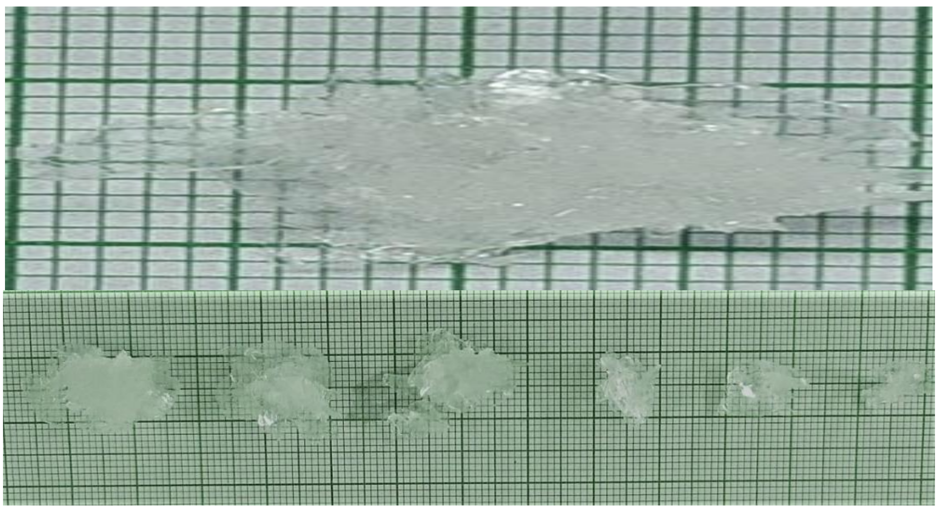


Fig 4.9.1 As a grown crystal of MNB

Fig 4.9.2 Growth of Magnesium Nitro Borate (MNB)

4.7CHARACTERIZATION: -

The single-crystal X-ray diffraction analysis was performed using a BRUKER KAPPA APEX II at room temperature and its lattice parameters and crystal system were determined. The Fourier transform infrared (FTIR)spectroscopy, is an excellent technique in the material analysis was carried out to identify the functional groups present in the crystal. FTIR spectrum was recorded on Bruker FT-IR spectrophotometer model spectrum RX1 resolution 4cm-1 with the help of KBr pellets within the wavenumber range 500cm^{-1} to 4000cm^{-1}. The optical absorption spectra of MCB crystal were recorded by UV-visible spectrometer in the region of 200-800nm using a JASCO model spectrometer at a scanning speed of 200nm/min and are presented graphically.The SHG coefficient has generated the non-linear property of the crystal.

Chapter-5

RESULTS AND DISCUSSION

5.1SINGLE-CRYSTAL XRD:-

The single-crystal X-ray diffraction analysis of Magnesium Nitro borate was carried out by BRUKER KAPPA APEX II at room temperature and its lattice parameters and crystal system were determined. The magnesium nitro borate single-crystalcrystallizes under a monoclinic crystal system with a centrosymmetric space group C2/c. The cell parameter of magnesium nitro borate (MNB) single crystal is given below in Table 5.1

Lattice parameter	**Values of crystal composition**
a (A°)	5.042
b(A°)	13.4
c(A°)	9.580
ALPHA	90.1
BETA	96.2
GAMMA	90.00
VOLUME V	646.189 ccc
CRYSTAL SYSTEM	monoclinic
SPACE GROUP	C2/c

Table 5.1 Single Crystal XRD Analysis

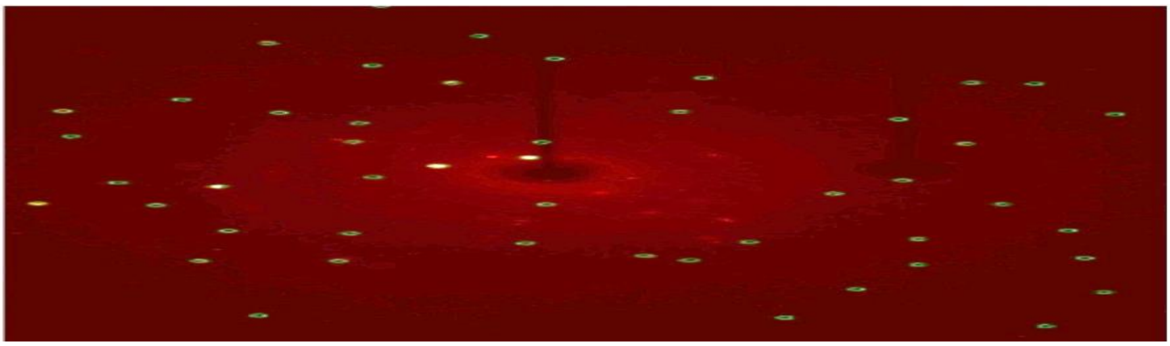


Fig 5.1 XRD pattern of the grown crystal MNB

5.2 FOURIER TRANSFORM INFRARED SPECTRAL ANALYSIS: -

The FTIR spectrum of magnesium nitro borate (MNB) single crystal has been recorded on Bruker FT-IR Spectrometer model SPECTRUM RX1 resolution 4cm^{-1}within the range of 500cm^{-1} to 4000cm^{-1}. In the FT-IR spectra of magnesium nitrate and boric acid crystal, the observed absorption peaks are sharp, medium, and weak. In the area of single bond stretches and double bond stretches we observed the strong peaks and mostly the weak peaks are observed in the fingerprint region.FTIR gives a spectral analysis like in the FT-IR spectra of magnesium phthalic (MNP) single Crystal the observed absorption peaks correspond to the **C-H** bending at 3000-3500 cm-1, AROMATICS is present **-C=C-** stretching at 2000-1500 cm-1 ALKENES group is present, **C-O** bending 1500-1000 cm-1 ALCOHOL, ESTER, ETHERS are present, and **O-H** stretching at 1000-500 cm-1 CARBOXYLIC group is present. The functional group and the graphical spectrum Table 5.2 and Figure 5.2 is given below.

WAVELENGTH (nm)	BOND	FUNCTIONAL GROUP	APPEARANCE
3500nm-3000nm	C-H	AROMATICS	STRONG
2500nm-2000nm	–CC–	ALKYNES	WEAK
2000nm-1500nm	**-C=C-**	ALKENES	MEDIUM
1500nm-1000nm	C-O	ALCOHOL,ESTER, ETHERS	STRONG
1000nm-500nm	O-H	CARBOXYLIC ACID	MEDIUM
1000nm-500nm	C-CL	ALKYL HALIDIDES	WEAK

Table 5.2The Functional Group Analysis

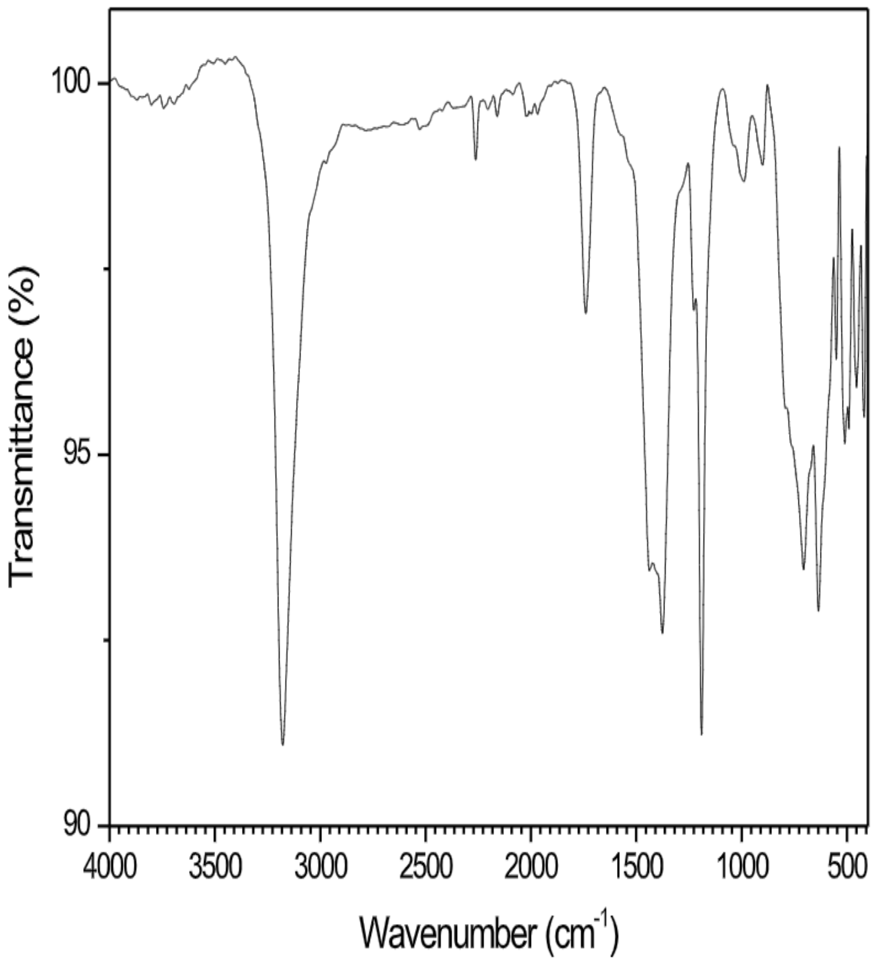


Fig 5.2 FTIR spectrum

5.3 UV-VISIBLE SPECTRAL ANALYSIS: -

Since single crystals are mainly used in optical applications, the light transmission range andcutoff wavelength (20nm0-400nm) frequency of the SHG output in the range of laser applications are essential. Absorbance plays an important role in identifying the potential of NLO materials. The light absorption spectra of the Magnesium nitro borate crystals were recorded in the 200 nm to 800 nm range at a scan rate of 200 mm / min using a JASCO UVVis NIR spectrometer. The recorded spectrum is shown in Figure 5.3. The lower limit is within 289 nm. Low absorption and cutoff wavelengths in the visible and NIR regions confirm the suitability of crystal growth in NLO applications. MNB single crystals have been found to be suitable for optoelectronic applications.

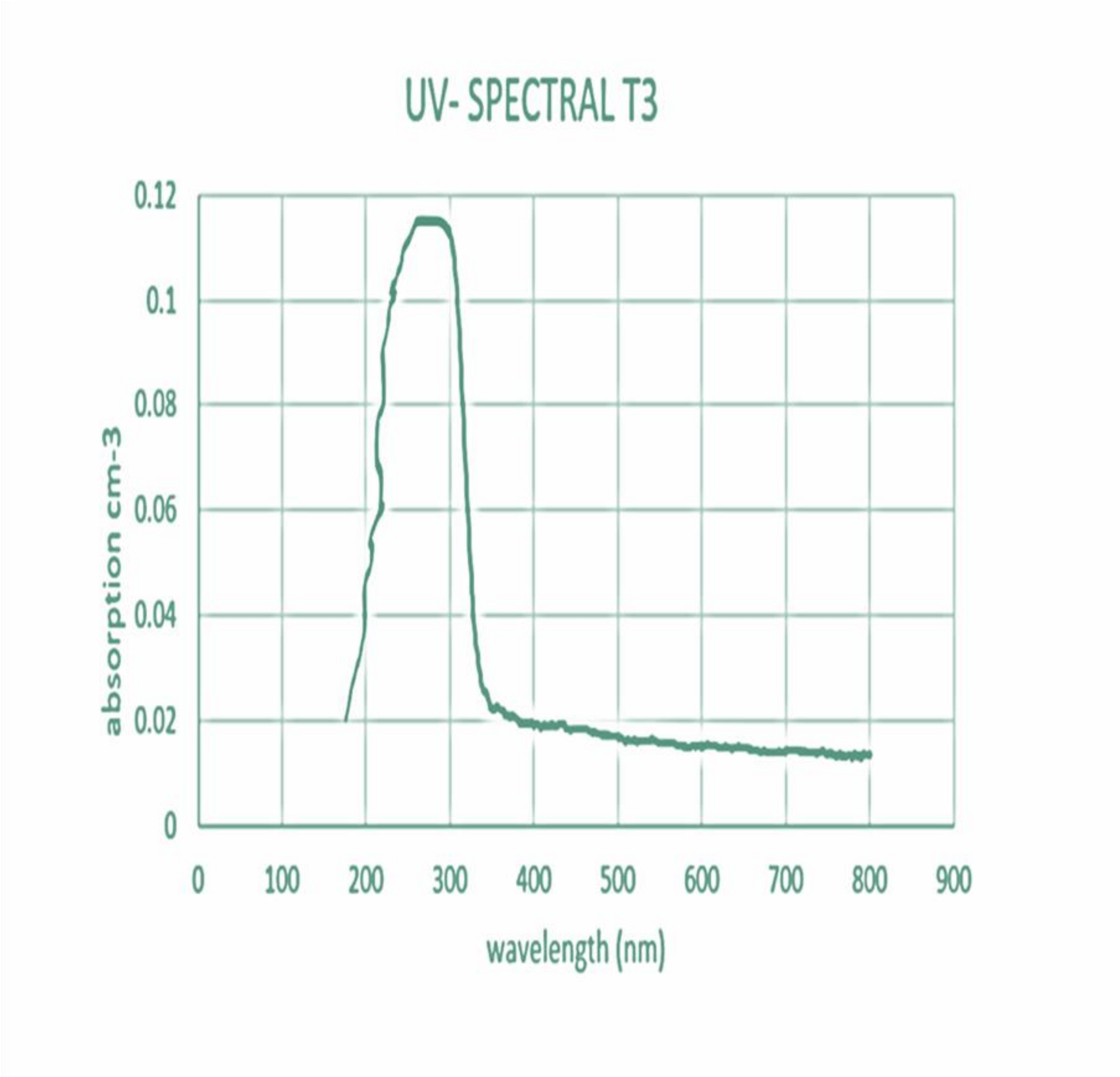


Fig 5.3 UV spectrum

5.4 KURTZANDPERRY SHG STUDY: -

The non-linear characteristics of the sample were determined by a modified version of Kurtz and Perry powder technology using an Nd: YAG laser with a pulse repetition rate of 10 Hz operating at 1064 nm. The sample was crushed into a fine powder andtightly packed in a microcapillary tube. It was installed in the path of a laser beam with a pulse energy of 3.1 mJobtained by dividing the original laser beam. The output lightpassed through a monochromator that transmitted only 542 nm second harmoniclight (green). The intensity of green lightwas recorded by a photomultiplier tube and converted into an electrical signal. This signal was displayed and recorded on the oscilloscope screen. Second-harmonic generation (SHG) conversion efficiency was calculated by the ratio of the sample signal amplitude to the potassium dihydrogen phosphate (KDP) signal amplitude recorded for the same input powder. SHG efficiency was 0.91 timesthe known KDP. The green emissionfrom the title sample indicates that the sample exhibits second harmonic generation efficiency. This result suggests that magnesium nitroborate crystals may be efficient for applications in nonlinear optical de

Chapter-6

SUMMARYAND CONCLUSION

THE FIRST CHAPTER provides a thorough introduction to crystals. This chapter describes the various methods of crystal growth, with a focus on the slow evaporation technique.provides information on material selection and the significance of the material The magnesium nitro Borate (MNB) single crystal has several advantages over other types of inorganic NLO materials due to its superior nonlinear optical response combined with moderate mechanical and thermal stability. gives detail about material selection and the importance of the material. This chapter describes the synthesis method of the chosen material as well as the composition of those materials. Also includes information on the solubility range, solubility in graph form with temperature, and solubility per gram.

THE SECOND CHAPTER This chapter presents the review of the literature on nonlinear optical crystals made of inorganic materials. deals with the literature survey of crystal growth by a slow evaporation method.

THE THIRD CHAPTER This chapter presents the thesis' objectives and scope, on nonlinear optical crystals made of inorganic materials. discusses the Aim, objective, and scope for prospects.

THE FOURTH CHAPTER also provides an overview of the various principles and instrumentation techniques used to characterize the grown crystals. The principles, theory, and instrumentation, as well as the benefits and drawbacks of various characterization techniques such as single XRD, FT-IR, UV-Vis-NIR spectra, and SHG.gives a detailed account of the studies conducted on the characterization of single crystals of the charge transfer complexes of magnesium nitrate and boric acid grown at room temperature using the slow evaporation solution growth technique.

THE CHAPTER FIVE deals withresults and discussion, Single-crystal XRD gives reporta=5.042;b=14.3;c=9.580;alpha=90.1,beta=96.2.18;gamma=90.00;volume=6 46.189ccc and crystal system is monoclinic. And UV-Vis gives a report like the spectrum was recorded at near IR, Visible and UV regions. The lower cut off wavelengths lies within 289nm. And FTIR gives a spectral analysis like in the FT-

IR spectra of magnesium phthalic (MNP) single Crystal the observed absorption peaks correspond to the **C-H**bending at 3000-3500 cm-1, AROMATICS is present **-C=C-** stretching at 2000-1500cm-1 ALKENES group is present, **C-O**bending 1500-1000 cm-1 ALCOHOL, ESTER, ETHERS are present, and **O-H** stretching at 1000-500 cm-1 CARBOXYLIC group is present.

THE SIX CHAPTER deals with the whole summary and conclusion of my work.

Conclusion

The design, discovery, and development of novel materials, particularly in single crystal form, represent a national core competency required for scientific progress and long-term economic growth. Many new and existing technologies rely on new materials, including semiconductor electronics, solid-state lasers, radiation detectors, compact disc storage, cellular and optical communications, solar cells, fuel cells, and catalysts. Single crystals are frequently required to achieve a material's full functionality and to fully elucidate its properties. Effective NLO single crystals with efficient optical frequency conversion are critical components in the development of laser systems, telecommunication, optical information processing, high optical disc data storage, and a wide range of tunable sources of coherent illumination in the ultraviolet, visible, and infrared spectral ranges.

A new inorganic Magnesium Nitro Borate (MNB) compound was synthesized using Magnesium nitrate and Boric acid is taken in equal ratios and the crystals were grown by slow evaporation technique at room temperature of 32ºC.

Single crystal X-ray diffraction analysis confirmed the lattice parameter and crystal structure of the grown crystal.The FTIR spectrum recorded for the grown sample confirms the presence of acid and nitro functional groups in the grown crystal. The optical study UV-visible spectroscopy revealed the good transparency of the grown crystal in a wide wavelength range with the lower cut-off wavelength of 289nm which suits the crystal for various electro-optic applications.The SHG measurement shows thatthe grown Magnesium Nitro Borate crystal has higher efficiency than the KDP crystal.

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