Synthesis, Growth and Characterization of a new inorganic Nonlinear Optical Crystal: Magnesium Cadmium Borate (MCB)

Submitted in partial fulfilment of the requirements for the award of Master of Science Degree in Physics

By

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DEPARTMENT OF PHYSICS

SCHOOL OF SCIENCE AND HUMANITIES

SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

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BONAFIDE CERTIFICATE

This is to certify that this project Report is the bonafide work of **C.ABIRAMI (Reg.No.40590005)** who carried out the project entitled "**Synthesis, Growth and Characterization of a new inorganic Nonlinear Optical Crystal: Magnesium Cadmium Borate (MCB)"** under our supervision from November 2021 to May 2022.

Internal Guide **Head of the Department**

Dr.P.MALLIGA **Dr.S.RAVICHANDRAN**

Submitted for Viva voce Examination held on_____

Internal Examiner **External Examiner**

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I am pleased to acknowledge my sincere thanks to the Board of Management of SATHYABAMA for their kind encouragement in doing this project and for completing it successfully. I am grateful to them.

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Finally, without the help of my friends, who supplied intriguing discussion, I could not have been able to accomplish this project.

(C. ABIRAMI)

DECLARATION

I **C.ABIRAMI (40590005)** hereby declare that the Project Report entitled "**Synthesis, Growth and Characterization of a new inorganic Nonlinear Optical Crystal: Magnesium Cadmium Borate (MCB).**" done by us under the guidance of **Dr.P.MALLIGA, is** submitted in partial fulfillment of the requirements for the award of Master of Science degree in Physics.

DATE: **SIGNATURE OF THE CANDIDATE**

PLACE: **(C.ABIRAMI)**

ABSTRACT

In recent few years, several novel NLO crystals have been developed for efficient second-harmonic generation (SHG) and other parametric processes. In the inorganic family crystals, borate crystals have attracted much attention due to their instinctive properties. Such a new inorganic nonlinear optical single crystal of Magnesium Cadmium Borate (MCB) has been successfully grown from aqueous solution using the slow evaporation technique at room temperature. The crystals obtained using the aforementioned method were characterized using different techniques. The crystalline nature of the as-grown crystal of MCB was analyzed using powder X-ray diffraction. The optical transmission study of the MCB crystal revealed high transmittance in the entire UV–vis region, and the lower cut-off wavelength was determined to be 230 nm. The presence of functional groups has been estimated qualitatively from the Fourier transform infrared spectroscopy. The frequency doubling property of NLO crystal was verified through second harmonic generation (SHG) studies.

Keywords: Nonlinear optical material, FTIR analysis, UV optical studies, second harmonic generation.

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LIST OF ABBREVIATIONS

SHG	SECOND-HARMONIC GENERATION
FTIR	FOURIER TRANSFORM INFRARED SPECTROMETER
XRD	X-RAY DIFFRACTION
UV-VIS	ULTRA VOILET SPECTROMETER
EM	ELECTROMAGNET WAVE
NLO	NONLINEAR OPTICS
SEM	SCANNING ELECTRONIC MICROSCOPE
EDAX	ENERGY DISPERSIVE X-RAY ANALYSIS
TGA	THERMOGRAVIMETRIC ANALYSIS
MCB	MAGNESIUM CADMIUM BORATE

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CHAPTER - 1

INTRODUCTION

1.1 CRYSTAL GROWTH

Crystal growth is a major stage of a crystallization process, and consists of the addition of new atoms, ions, or polymer strings into the characteristic arrangement of the crystalline lattice. The process of crystal growth includes nucleation, growth and coarsening. For a new phase to grow, a stable embryo of the new phase must from first. This process is called nucleation. The nucleus serves as a template for the crystal to grow. The growth of the crystal involves interface reaction and mass/heat transfer. In the search for new electronic materials, crystal growth plays an essential part, while crystal growth theory provides an ideal testing ground for the interplay of atomic (microscopic) and classical (macroscopic) concepts and the most practical experimental realities.

1.2 CRYSTAL GROWTH TECHNIQUES

Crystal growth may be a difficult task and therefore the technique followed for crystal growth depends upon the characteristics of the materials below investigation, like its temperature, Volatile nature, solubility in water or different organic solvents and then on the fundamental growth ways on the market for crystal growth area unit loosely.

- Growth from melt.
- Growth from vapor.
- Growth from solution.
- Growth from solid.

The fundamental common principle altogether these ways is that a nucleus is initial shaped and it grows into one crystal by organizing and collection ions or molecules with specific interactions and bonding, so the method is slow and multiple nucleation is decreased. 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. Crystals can grow using the following techniques

- *MELT GROWTH METHODS*
    - Horizontal Boat Growth Methods
        - Horizontal Gradient Freezing (HGF) method
        - Horizontal Bridgman (HB) method
        - Horizontal Zone Melting (HZM) method
    - Vertical Boat Growth Methods
        - Vertical Bridgman (VB) method
        - Vertical Gradient Freezing (VGF) method
        - Vertical Zone Melting (VZM) method
    - Pulling Methods
        - Czochralski (CZ) method
        - Liquid Encapsulated Czochralski (LEC) method
        - Kyropolous and Liquid Encapsulated Kyropolous (LEK) methods
    - Floating Zone (FZ) Method
- *SOLUTION GROWTH METHODS*
    - Simple Solution Growth Method
    - Traveling Heater Method (THM)
    - Solute Solution Diffusion (SSD) Method

- Solvent Evaporation (SE) Method
- Temperature Difference Method under Controlled Vapor Pressure (TDM-CVP)
- Hydrothermal Synthesis Method

- *VAPOR PHASE GROWTH METHOD*
  - Direct Synthesis (DS) Method
  - Physical Vapor Transport (PVT) Method
    - Open tube method
    - Closed tube method
  - Chemical Vapor Transport (CVT) Method
  - Solid Phase Reaction (Solid State Recrystallization)

1.3 ADVANTAGE AND DISADVANTAGE OF SOLUTION CRYSTAL GROWTH

1.3.1 Advantage

- Growth from free surface
- Growth of large oriented single crystal
- Control of atmosphere

1.3.2 Disadvantage

- High vapor pressure materials
- Liquid phase encapsulation
- No reproductivity of the crystal shape

1.4 Single crystal growth

The absence of the defects associated with grain boundaries can give single crystals unique properties, particularly mechanical, optical and electrical. These properties, in addition to making them precious in some gems, are industrially used in technological applications, especially in optics and electronics.

A single crystal is a material in which the crystal lattice of the entire sample is continuous and unbroken to the edges of the sample, with no grain boundaries. The absence of the defects associated with grain boundaries can give single crystals unique properties, particularly mechanical, optical and electrical. These properties, in addition to making them precious in some gems, are industrially used in technological applications, especially in optics and electronics.

1.5 NON LINEAR OPTICS

Non-linear optics (NLO) is an innovative area of research and development which plays a key role in the field of opto-electronics and photonics.[1] Materials with large second order optical non-linearities find wide applications in the area of laser technology, laser communication and data storage technology.[2] In recent years, several studies dealing with organic, inorganic and semi-organic molecules and materials for non-linear optics are being published due to the increasing demand for processable materials in the photonics applications.[1],[6] The non-linear optical responses induced in various molecules in solution and solids are of great interest in many fields of research.

The interaction of the electromagnetic field of light (normally high intensity laser light) with a nonlinear optical (NLO) material can result in the generation of new electromagnetic fields. As light passes through a species, its electric field interacts with inherent charges in the material causing the original beam to be altered in phase, frequency, amplitude and polarization. Basically, all materials exhibit optical phenomena. This includes all forms of matter (i.e) gases, liquids, and solids. The power of the optical fields require to observe these effects varies over many orders of magnitude, depending on the detailed nature of the electronic structure of the atomic and moleculer constituents of the medium, their dynamical behavior, as well as the symmetry and details of their geometrical arrangment in the medium. The important nonlinear optical materials from the device point of view are generally in soild formats and must meet a wide variety of ancillary material requirements for optical use. In general, they will require extraordinary stability with respect to ambient conditions and in high intensity light sources.

Some materials change light passing through them, depending upon orientation, temperature, light wavelength etc. (red light, lower wavelength) releasing one photon of accumulated higher energy (blue and green light, higher wavelength). NLO materials typically have a distinct crystal structure, which is anisotropic with respect to electromagnetic radiation. The importance of nonlinear optics is to understand the nonlinear behavior in the induced polarization and to analyze and to control its impact on the propagation of light in the matter.

1.5.1 ORGANIC NLO CRYSTAL

The organic non-linear materials show the non-linear behavior of light due to presence of conjugated π-π * electrons. All these crystals have a good dynamic structure and transparent in nature. These are second order frequency generator organic non-linear materials. The materials are non-centrosymmetric in nature and applicable in optical modulators, optical devices, laser frequency modulators. UV-Spectroscopy shows transparent nature in the entire visible region and near infrared region. On the contrary, precise processing technologies for organic crystals have hardly been developed. Since organic materials are very brittle, having hygroscopic properties, low melting temperatures and particular cleavage planes owing to weak intermolecular bonding, conventional processing technologies used for inorganic materials cannot be extrapolated to obtain arbitrary shape crystals and fine optical surfaces. A disadvantage of organic nonlinear optical (NLO) materials is often their low physico-chemical stability.

1.5.2 INORGANIC NLO CRYSTAL

New inorganic nonlinear-optical (NLO) materials are necessary for solid-state lasers to generate coherent radiation in the ultraviolet (UV) and deep-UV regions. Inorganic materials are defined as chemical compounds that contain no carbon (C). However, elementary carbon (C) (as graphite or diamond) and compounds of carbon and, for example, nitrogen, oxygen, or silicon are also classified as inorganic. Examples of such inorganic compounds include carbon monoxide (CO), silicon carbide (SiC), and carbonic acid (H_2CO_3), and salts thereof. All other types of carbon-containing compounds are called organic materials. Inorganic materials, exhibiting second order nonlinear optical properties

have attracted in the recent past due to their ability to process into crystals, wide optical transparency domain, large nonlinear figure of merit for frequency conversion, fast optical response time and wide phase matchable angle. Molecular hyperpolarizability of inorganic nonlinear optical crystal are used in optical switching (modulation), frequency conversion (SHG, wave mixing) and electro-optic applications especially in EO modulation. Historically, inorganic NLO materials have been chronicled more extensively inorganic oxide crystal, LiNbO3, KNbO3, KDP and KTP, etc., have been studied for device application like piezoelectric, ferroelectric and Electro-optics.

1.5.3 SEMI ORGANIC NLO MATERIAL

In semi organic materials, the organic ligand is ionically bonded with inorganic host that resulted in new materials having high optical nonlinearities. Complexes of amino acids with inorganic salts are promising materials for optical applications such as optical communication, optical computing, optical information processing, optical disk data storage, laser fusion reaction, laser remote sensing. The high nonlinearity, high resistance to laser-induced damage, low angular sensitivity and good mechanical hardness of semi-organic crystals combine in the strong NLO properties and chemical flexibility of organic materials with the physical sturdiness and excellent transmittance of inorganic materials

CHAPTER– 2

REVIEW OF LITRERATURE

According to G.D.Chryssikos et al .The Raman spectra of glass systems containing cadmium borate and cadmium borogermanate have been measured and analysed. Adding more cadmium oxide to glasses with a constant germanium-to-boron ratio modified both boron and germanium network-forming centres, encouraging the development of non-bridging oxygen-containing groups in particular. In glass series with constant cadmium oxide concentration and rising germanium to boron ratio, a competitive modification of boron over germanium centres has been observed.

According to M. Packiya raj et al.The slow evaporation approach is used to create a novel inorganic nonlinear optical single crystal of sodium cadmium tetra chloride (SCTC) from 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 across the UV–Vis range. Vicker'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 using Kurtz's powder approach, indicates that it has 1.75 times the nonlinear optical (NLO) efficiency of KDP. The crystal exhibits conventional dielectric behaviour when the dielectric constant and dielectric loss are shown as a function of log frequency at various temperatures. The etching research 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 findings show that SCTC crystal might be a promising material for nonlinear optical device applications.

According to Divya M et al. The slow evaporation process is used to generate single crystals of Nickel Boro Phthalate (NBP). Single crystal x-ray diffraction is used to examine the crystal lattice characteristics, and the crystal structure is

discovered to be triclinic. The existence of functional groups has been subjectively evaluated using Fourier transform infrared spectroscopy, and elemental analysis has been performed using an Energy dispersive x-ray spectrum research. The UV-visible spectral investigations reveal a wide window of transparency throughout the visible and infrared spectrum, with a fundamental frequency of 285 nm. The dielectric constant, polarizability, susceptibility, optical and electrical conductivity, and other optical characteristics are graphically represented. The Z scan approach is used to analyse third-order nonlinear characteristics utilising a continuous wave 532 nm diode-pumped Nd:YAG laser. The crystal's self-defocusing tendency and negative nonlinearity are indicated by the closed aperture mode. The saturation absorption within the crystal is shown in open aperture mode. The nonlinear optical parameters n2, nonlinear absorption coefficient, and nonlinear susceptibility (3) are also calculated.

According to G.Pasupathi et al. By using a slow evaporation approach, single crystals of potassium diboro-oxalate (PDO), a new semi organic material, were produced from aqueous solution. Single crystal X-ray diffraction analysis was used to estimate the lattice parameters for the generated crystals, and powder X-ray diffraction analysis was used to establish the crystallinity of the formed crystal. Using Fourier transform infrared (FTIR) analysis, the existence of functional groups was qualitatively evaluated. The UV cut-off wavelength for the formed crystal is 240 nm, according to the optical absorption spectra, and the band gap was estimated. TG/DTA analysis was used to investigate the generated crystal's thermal stability. The Kurtz powder approach was used to do the second harmonic generation and phase-matchable tests. SEM pictures were used to examine the crystal perfection.

According to R.Arivuselvi et al. By using a solution growth slow evaporation process, a non-linear optical material called Barium Calcium Borate (BCB) was effectively developed from an aqueous solution. Single crystal X-ray diffraction analysis was used to identify the structure, composition, and lattice parameter of the formed crystal. The discovered infrared bands were allocated, and the peaks indicate that the crystal contains inorganic molecules with a minor quantity of water molecules. The optical band gap (4.85 eV) of this borate family crystal is

greater than that of other crystals in the family. The second harmonic efficiency of NLO was three times that of KDP. Dielectric behaviour of the grown crystal reveals that for the grown crystal has higher dielectric constant (ε>4500) in low frequencies at different temperatures and its activation energy (4.6 eV @100 Hz, and 4.9 eV @1 kHz) is increasing with respect to frequencies.

According to K.C.Bright et al. Slow evaporation was used to create single crystals of l-alanine cadmium chloride (LACC), an organometallic nonlinear optical material. Various characterisation methods were used on the generated crystals, including single crystal and powder XRD, FTIR, UV–vis, and TGA-DTA. The mechanical characteristics of the crystals indicate that this material falls under the hard material group. The Kurtz and Perry powder approach proved second harmonic generation. Dielectric constant, dielectric loss, ac and dc conductivity, and their related activation energies have all been investigated electrically. This material's low dielectric constant and dielectric loss make it a promising contender for microelectronic applications.

According to Sagadevan Suresh .Slow evaporation was used to create single crystals of zinc thiourea chloride, a nonlinear optical material. Single crystal X-ray diffraction experiments were used to identify the crystal structure and lattice properties of the generated crystal. The material formed in an orthorhombic crystal structure, according to single crystal XRD. Optical experiments were conducted, and it was discovered that the specimen's transmission tendency in relation to light wavelength is practically more suited for opto-electronic applications. 4.30 eV is discovered to be the optical band gap. The UV–vis–NIR spectrum was used to calculate optical constants such as the band gap, refractive index, reflectance, extinction coefficient, real (r) and imaginary I components of the dielectric constant, and electric susceptibility. The dielectric constant and dielectric loss of zinc thiourea chloride were studied at various temperatures and frequencies ranging from 50 Hz to 5 MHz. Electronic parameters of the formed crystal, such as valence electron plasma energy, Penn gap, Fermi energy, and electronic polarizability, have also been calculated.

According to P. A. Angeli Mary et al. A novel semi organic nonlinear optical material, Bis Thiourea Zinc Chloride (BTZC), has been created. The solubility tests were conducted out at temperatures ranging from 30 to 55 degrees Celsius. At room temperature, single crystals of BTZC were produced by slowly evaporating a saturated aqueous solution. The single crystal X-ray diffraction method was used to determine the lattice properties of the produced crystals. In the region of 200-2000 nm, the UV-Vis-NIR transmittance spectra was observed. The FT-IR spectrum was recorded in the 400-4000 cm-1 range, and the spectral bands were compared to those of other thiourea complexes.

According to S.M.Ravi Kumar et al .The slow evaporation approach has been used to grow single crystals of bis(thiourea) cadmium formate (BTCF). Powder XRD is used to characterise the produced crystals. Scanning electron microscopy was used to examine the surface morphology of BTCF (SEM). The sample's cut-off wavelength is about 290 nm, with a large optical transmission window (290–2000 nm) as confirmed by the UV-vis-IR spectrum. BTCF's laser damage threshold is determined to be greater than KDP's. Thermal analysis using TGA and DTA methods confirms that the material decomposes about 190 °C. The conductivity of BTCF rises with temperature, according to the dc conductivity research.

According to Sagadevan Suresh . Slow evaporation was used to form an optically clear and bulk single crystal of potassium boro-oxalate (KBO). The crystal system was discovered and lattice parameters were obtained using single crystal X-ray diffraction research. UV–vis spectroscopy was used to determine the optical characteristics of the KBO crystal. UV–vis spectroscopy was used to determine optical constants such the refractive index, extinction coefficient, electric susceptibility, and optical conductivity. The Brewster angle technique was used to calculate the refractive index of the formed crystal. The FTIR spectrum was used to confirm the existence of several functional groups. As a function of different frequencies and temperatures, the dielectric constant and dielectric loss were measured. The research of AC electrical conductivity found that conduction was affected by both frequency and temperature.

CHAPTER – 3

AIM AND SCOPE OF THE PRESENT INVESTIGATION

3.1 THE PRESENT INVESTIGATION DEALS WITH,

- Synthesizing the chosen materials for the growth of single crystals
- Determining the solubility of the materials
- Growth of single crystal
- Identifying the crystal structure by single crystal X-ray diffraction analysis
- Identifying the mode of vibration of different molecular groups using Fourier Transform Infra-Red analysis.
- Characterization done for the grown crystals by UV-Vis-NIR, NLO.

Future attempt of my work is to concentrate on the further study like, electric study like dielectric analysis, mechanical study like Vickers hardness test and structure study like EDAX analysis of sample magnesium nitrate and phthalic acid combination crystal and enhance them for their application in the field of medical use laser technology.

3.2 CHARACTERISATION STUDIES

3.2.1 Powder XRD Analysis

Diffraction occurs when light is scattered by a periodic array with long-range order, producing constructive interference at specific angles. The atoms in a crystal are periodically arranged thus diffract light. The wavelength of X-ray are similar to the distance between atoms, Powder X-ray Diffraction (PXRD) techniques uses this principle to elucidate the crystalline nature of materials. The scattering of X-rays from atoms produce a diffraction pattern that contains information about the atomic arrangement in crystal. Amorphous materials like glass do not have periodic array with long-range order so; they do not produce any significant peak in diffraction pattern. In powder X-ray diffraction, the diffraction

pattern is obtained from a powder of the material, rather than an individual crystal. Powder diffraction is often easier and more convenient than single crystal diffraction as it does not require individual crystals. A diffraction pattern plots intensity against the angle of the detector, 2θ. The result obtained is called diffract gram (Figure 3.1). In a diffraction pattern, the peak position depends upon the wavelength. Absolute intensity (number of X-rays observed in a given peak) may vary by instrumental and experimental parameters. Diffractometers can be operated both in transmission and in reflection configurations.

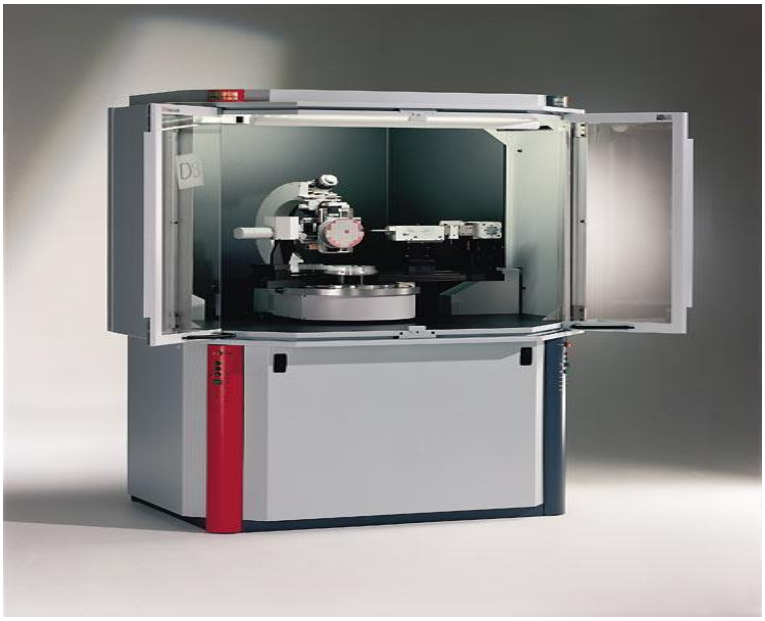

FIG 3.1 POWDER XRD EXPERIMENTAL SETUP

3.2.2 Fourier transform infrared spectral analysis (FTIR)

This infrared spectroscopy method is used to identify organic, polymeric, and in some cases, inorganic materials. The FTIR test relies on infrared light to scan samples and observe bond properties. The principles of IR show that molecules vibrate and bonds stretch and bend when they absorb infrared radiation. It works by passing a beam of IR light through a sample, and for an IR detectable transition, the molecules of the sample must undergo dipole moment change during vibration. When the frequency of the IR is the same as the

vibrational frequency of the bonds, absorption occurs and a spectrum can be recorded.

With IR, different functional groups absorb heat at different frequencies. It is dependent upon their structure and a vibrational spectrum can be used to determine the functional groups present in a sample. (FTIR) is a technique which is used to obtain infrared spectrum of absorption, emission, and photoconductivity of solid, liquid, and gas. It is used to detect different functional groups. Once a sample is placed during a beam of infrared light, the sample can absorb radiation at frequencies reminiscent of molecular wave frequencies, however can transmit all alternative frequencies. The frequencies of radiation absorbed are measured by associate infrared spectroscope, and also the ensuing plot of absorbed energy vs. frequency is named spectrum of the fabric. Identification of a substance is feasible as a result of totally completely different materials have different vibrations and yield different infrared spectra. Moreover, from the frequencies of the absorption it's doable to see whether or not varied chemical teams are gift or absent during a chemical structure. Additionally to the characteristic nature of the absorption, the magnitude of the absorption because of a given species is said to the concentration of that species.

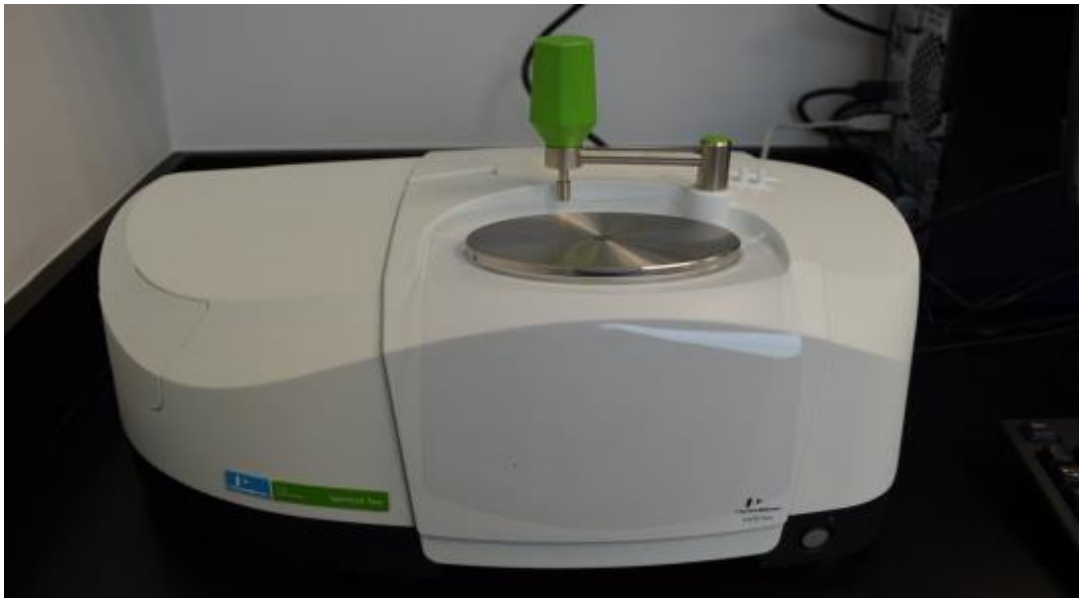

FIG 3. 2 Experimental setup of Perkin Elmer FT-IR Spectrometer

3.2.3 UV-Visible spectral analysis

With UV-Vis spectroscopy, the UV-Vis light is passed through a sample and the transmittance of light by a sample is measured. From the transmittance (T), the absorbance can be calculated as A=-log (T). An absorbance spectrum is obtained that shows the absorbance of a compound at different wavelengths. The amount of absorbance at any wavelength is due to the chemical structure of the molecule. UV-Visible/NIR spectroscopy can be divided into ultraviolet, visible, and near-infrared regions of the spectrum. The ultraviolet region is defined as 180 to 400 nm, visible between 400 and 800 nm, and the near-infrared is from 800 to 3200 nm. Near-infrared light is generally poorly absorbed because its photon energy is insufficient to induce electronic transitions and its frequency is greater than the natural vibration frequency of most chemical bonds. However, since the frequency in the NIR is close to the overtone frequency of many natural vibrations, weak substance-specific absorption bands can be detected. Generally, the foremost favoured transition is from the high occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). for many of the molecules, all-time low energy occupied molecular orbitals square measure s orbital, that correspond to letter of the alphabet bonds. The p orbitals square measure at somewhat higher energy levels, the orbitals (nonbonding orbitals). With the separate paired 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. a number of the vital transitions with increasing energies are: nonbonding to pie, nonbonding to letter of the alphabet, pie to pie, letter of the alphabet to pie and letter of the alphabet to letter of the alphabet. A beam of sunshine from a noticeable and or ultraviolet source of illumination (coloured red) is separated into its part wavelengths by a prism or optical device. every monochromatic (single wavelength) beam successively is split into 2 equal intensity beams by a half-mirrored device. One beam, the sample beam passes through tiny low clear solvent. The intensity of those light-weight beams is then measured by electronic detectors and compared. The intensity of the reference beam, that ought to have suffered very little or no light-weight absorption, is outlined as I0. The intensity of the sample is outlined as I. Over short amount of your time, the prism

spectroscope mechanically scans all the part wavelengths within the manner represented. The ultraviolet region is generally from two hundred to four hundred nm, and visual portion is from four hundred to 800nm.The transitions measured during this region square measure typically associated with overtone and combination bands of mid-infrared wave modes. altogether the compounds (other than alkanes), the electrons bear varied transitions. a number of the vital transitions with increasing energies are: nonbonding to pie, nonbonding to letter of the alphabet, pie to pie, letter of the alphabet to pie and letter of the alphabet to letter of the alphabet.

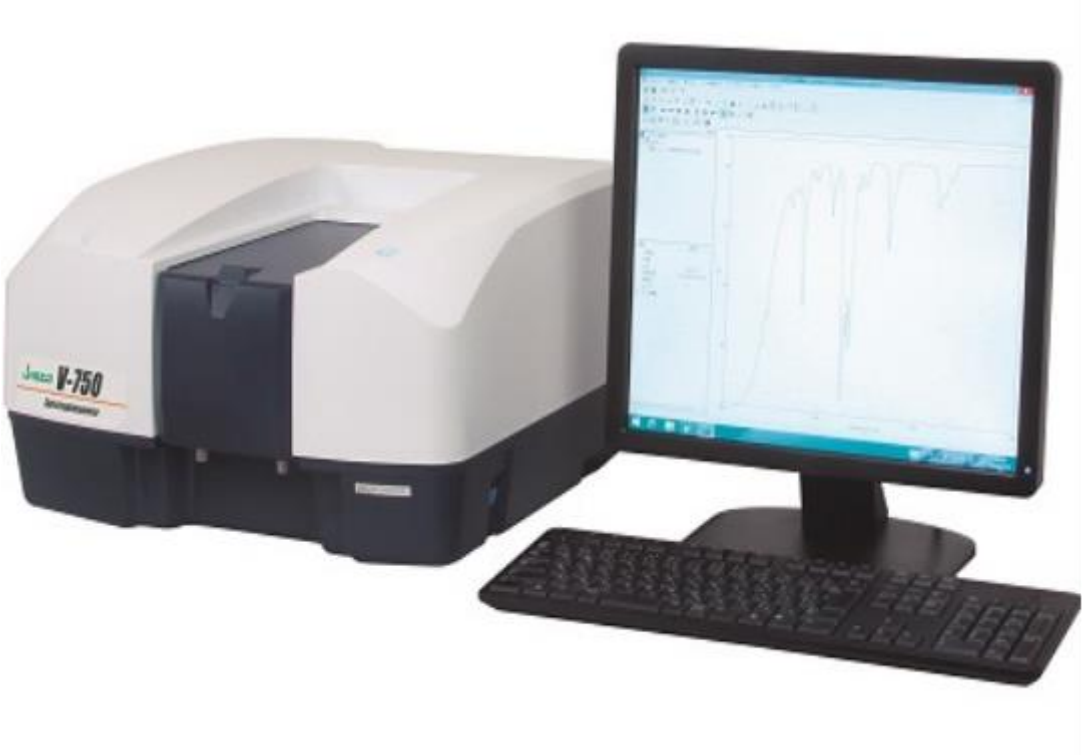

FIG 3.3 Experimental setup of UV-Vis-NIR Spectrophotometer

The experimental arrangement of Varian Cary 5E UV-Vis-NIR Spectrophotometer is shown in Figure 3.3. UV-Vis-NIR spectroscopy might be defined as the measurement of the absorption or emission of radiation associated with changes in the spatial distribution of electrons in atoms and molecules. In practice, the electrons involved are usually the outer valence or bonding electrons, which can be excited by the absorption of UV or visible or near IR radiation.

3.2.4 Experimental Setup of SHG Measurement

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.

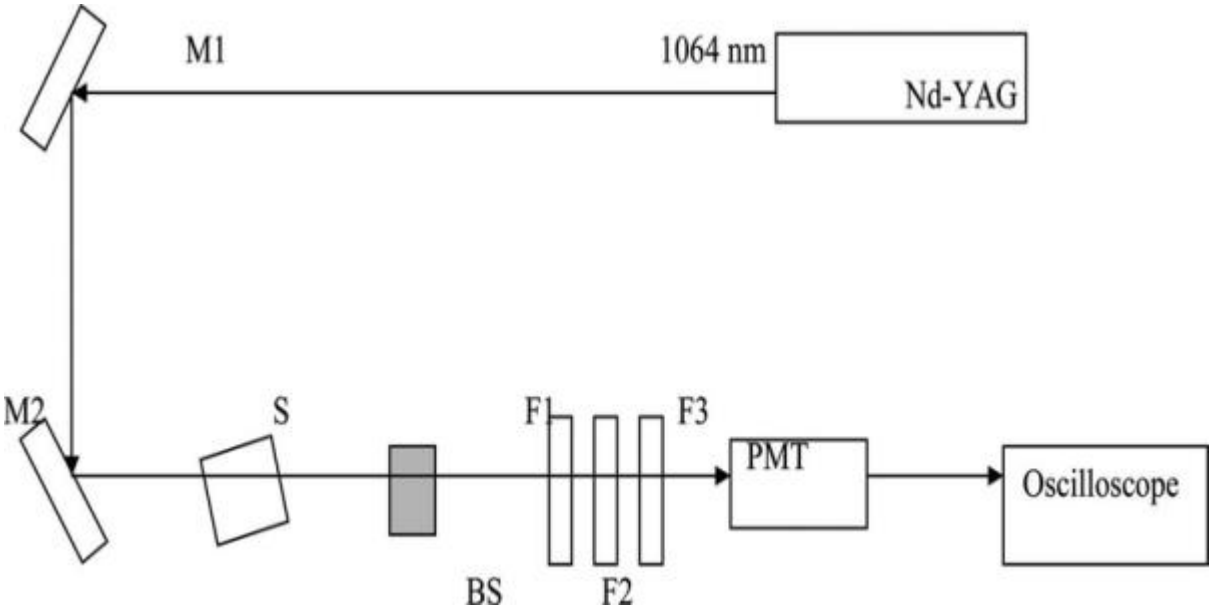

FIG 3. 4 Schematic setup of SHG

The SHG measuring setup is schematically shown in Figure 3.4. The SHG light-weight was collected solely in reflection by the focusing objective and separated from the basic and attainable two-photon fluorescent light-weight by consecutive long-pass dichroic mirror and narrowband interference filter (16.5 nm information measure targeted at 532 nm), and detected by a cooled photomultiplier tube connected to a gauge boson tally unit. To ease the sample positioning, a white-light imaging arm was enforced within the magnifier.

To avoid changes to the input polarization of the irradiation thanks to the imaging arm, a flip mirror was wont to steer the white light-weight to the

imaging lens and a consecutive camera once required. Imaging was done by formation scanning the sample at the focal plane of the magnifier objective employing a 3-axis piezo-actuated translation stage. The constituent dwell time was a 150ms, averaged double and for the 5 mm x 5 mm scanning area, 100 x 100 pixels were used. Nonlinear optical (NLO) materials play a significant role in nonlinear optics and particularly, they need an excellent impact on info technology and industrial applications. this may be basically copied to the advance of the performance of the NLO materials. The nonlinear optical property of the only crystals is tested by passing the output of Nd: YAG Quanta ray optical maser. The experimental setup used for SHG studies square measure. A Q-switched, mode barred Nd: YAG optical maser was wont to generate concerning 6mJ/pulse at the 1064 nm. This optical maser is operated in 2 modes. Within the single shot mode the optical maser emits one 8 ns pulse. In the multi shot mode the optical maser produces an eternal train of 8 ns pulses at a repetition rate of ten Hz. In the gift study, one shot mode of eight ns optical maser pulse with a spot radius of 1mm was used.

3.2.5 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a sample is heated at a constant rate.

TGA measures weight changes in a material as a function of temperature (or time) under a controlled atmosphere. Its principle uses include measurement of a material’s thermal stability, filler content in polymers, moisture and solvent content, and the percent composition of components in a compound.

Applications

Principle uses of TGA include measurement of a material’s thermal stability and its composition. Typical applications include:

- Filler content of polymer resins
- Residual solvent content

- Carbon black content
- Decomposition temperature
- Moisture content of organic and inorganic materials
- Plasticizer content of polymers
- Oxidative stability
- Performance of stabilizers
- Low molecular weight monomers in polymers
- Principle of Operation

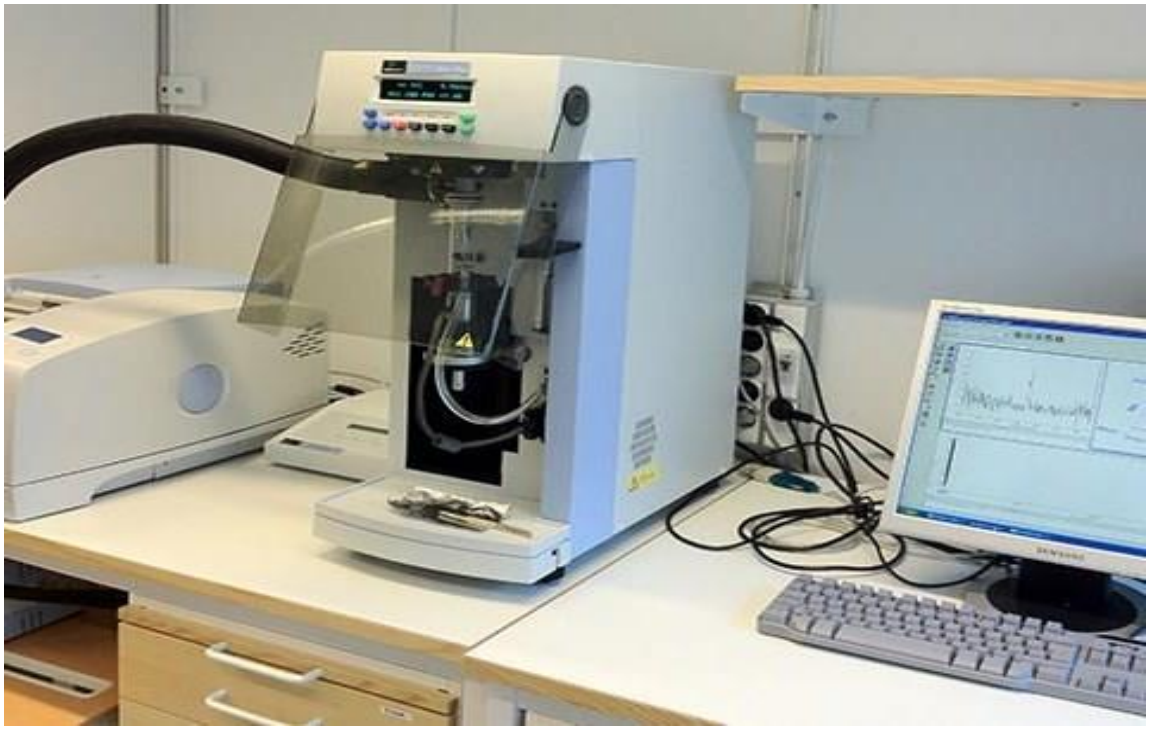

FIG 3.5 Thermogravimetric analysis setup

A TGA analysis is performed by gradually raising the temperature of a sample in a furnace as its weight is measured on an analytical balance that remains outside of the furnace. In TGA, mass loss is observed if a thermal event involves loss of a volatile component. Chemical reactions, such as combustion, involve mass losses, whereas physical changes, such as melting, do not. The weight of the sample is plotted against temperature or time to illustrate thermal transitions in the

material – such as loss of solvent and plasticizers in polymers, water of hydration in inorganic materials, and, finally, decomposition of the material.

3.4.6 Scanning Electron Microscope (SEM)

Scanning Electron Microscope (SEM) is a type of electron microscope that scans surfaces of microorganisms that uses a beam of electrons moving at low energy to focus and scan specimens. The development of electron microscopes was due to the inefficiency of the wavelength of light microscopes. electron microscopes have very short wavelengths in comparison to the light microscope which enables better resolution power.

FIG 3.6 Scanning Electron Microscope

Unlike the Transmission Electron Microscope which uses transmitted electrons, the scanning electron Microscope uses emitted electrons. The Scanning electron microscope works on the principle of applying kinetic energy to produce signals on the interaction of the electrons. These electrons are secondary electrons, backscattered electrons, and diffracted backscattered electrons which are used to view crystallized elements and photons. Secondary and backscattered electrons are used to produce an image. The secondary electrons are emitted from the specimen play the primary role of detecting the morphology and topography of the

specimen while the backscattered electrons show contrast in the composition of the elements of the specimen.

The signals generated during SEM analysis produce a two-dimensional image and reveal information about the sample, including external morphology (texture), chemical composition, when used with the EDS feature, and orientation of materials making up the sample. The EDS component of the system is applied in conjunction with SEM analysis to determine elements in or on the surface of the sample for qualitative information. It also measures elemental composition for semi-quantitative results and identifies foreign substances that are not organic in nature and coatings on metal.

CHAPTER – 4

MATERIAL SELETION AND EXPERIMENTAL METHODS

4.1 MATERIAL SELECTION

As compared to organic crystals, the inorganic crystals have good physio-chemical stabilities, short UV cut-off wavelength and large second order non-linearities. Due to these reasons, the inorganic crystals are gaining popularity in the field of nonlinear optics. Most recent work has demonstrated that organic crystals can have very large non-linear susceptibilities as compared with inorganic crystals, but their use is impeded by low optical transparencies, poor mechanical properties, low laser damage thresholds and inability to produce and process large crystals. The inorganic materials are widely used in these applications because of their high melting point, high mechanical strength and high degree of chemical inertness. In the inorganic family crystals, borate crystals have attracted much attention due to their instinctive properties. The first borate based NLO crystals KB5O8.4H2O (KB5) – (1975). Intense work began after the advent of LBO and BBO crystals. (Examples lithium borate LiB3O5 (LBO), β-Ba2B2O4 (BBO), CsLiB5O10(CLBO), SrBe2B2O7(SBBO), etc,). Have excellent transmission properties in combination with NLO behaviour. Therefore, these new materials used for NLO applications and expanding the frequency range provided by the conventional laser sources. In the present work, a novel inorganic NLO material, Magnesium Cadmium Borate (MCB) is grown, and its optical properties are investigated.

4.2 EXPERIMENTAL PROCEDURE

4.2.1 Synthesis

The Magnesium Cadmium Borate (MCB) single Crystal was synthesized by magnesium nitrate, Cadmium nitrate and boric acid in amount of 8.2305 g/mol, 10.1758 g/mol and 3.425 g/mol in double distilled water. The purity of the synthesized salt was further increased by repeated recrystallization. The crystal synthesize shown in the figure 4.1

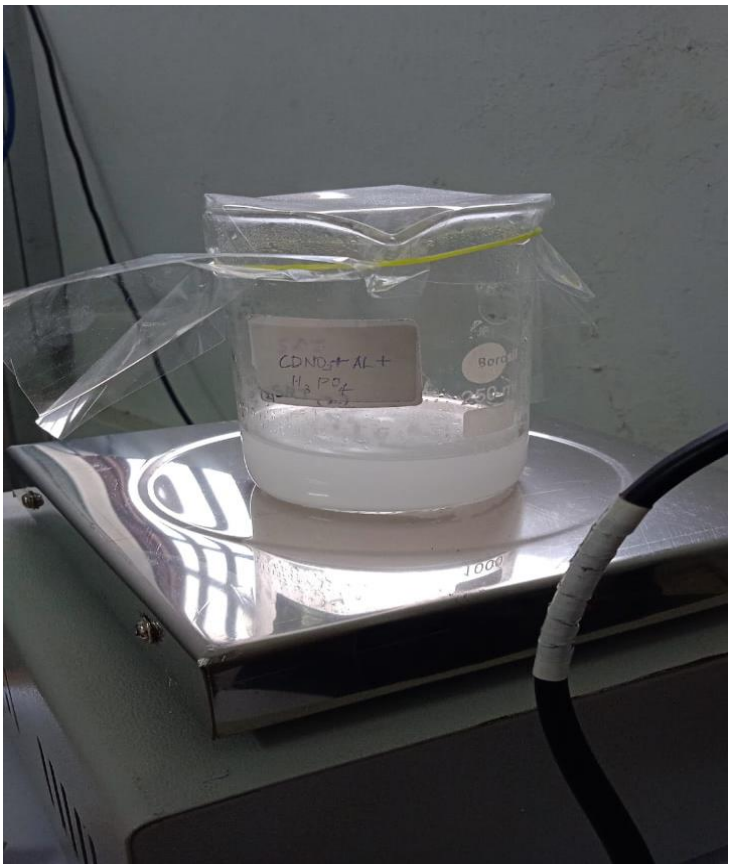

FIG 4. 1 CRYSTAL SYNTHESIZE

4.2.2 Crystal growth

Magnesium Cadmium Borate (MCB) was synthesised by slow evaporation technique. The starting materials used for synthesis were of analytical reagent grade of Magnesium nitrate, Cadmium nitrate and boric acid at 1:1:1 ratio. The calculated amount of Magnesium nitrate, Cadmium nitrate and boric acid salts were added with double distilled water according to the solubility and, finally the whole solution was mixed with continuous stirring for 1 hours using magnetic stirrer to obtain homogenous mixture. The completely dissolved solution was filtered using whatman filter paper to remove the suspended impurities and allowed to crystallize by slow evaporation method at room temperature for two months of the time period. 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 Cadmium Borate Crystal with dimensions 8x8x4 mm3 was obtained. The photograph of grown crystal is shown in the Fig.4.2

$$MgN_2O_6 + CdN_2O_6 + 4H_3BO_3 \longrightarrow MgCdB_4O_{10} + 4NO_2 + 6H_2$$

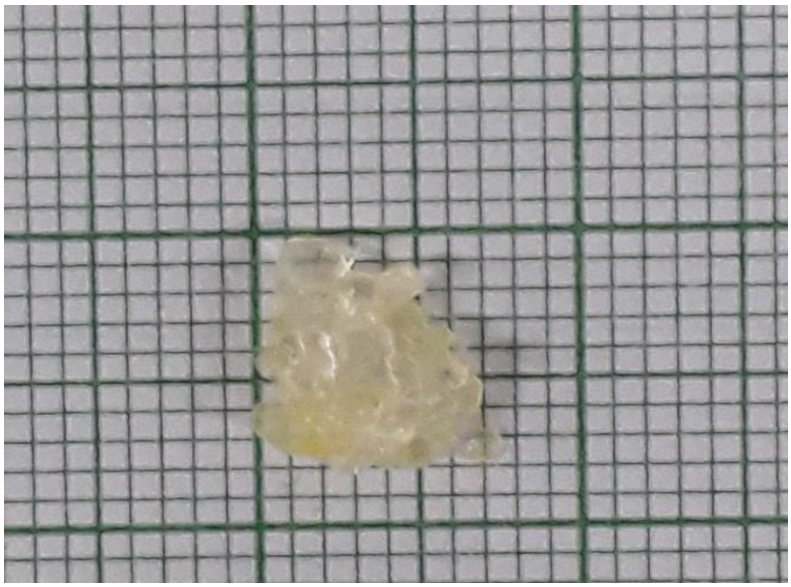

FIG 4.2 Grown crystal

CHAPTER - 5

RESULTS AND DISCUSSION

5.1 Powder X-ray diffraction analysis

Powder XRD for grown Magnesium Cadmium Borate (MCB) crystals was conducted, and the XRD pattern is shown in Figure 5.1. The powder sample was scanned over the range of 10–80º at a scan rate of 0.2º/s using CuKα radiation with a wavelength of 1.545Aº. The obtained powder X-ray diffraction data were analyzed and compared with JCPDS data. The strong orientation is reflected by the peak at 27.97º, 28.25º, 28.39º, 29.13º confined the presence of magnesium nitrate and Cadmium nitrate. Peaks at 58.16º and 58.34º show the presence of boric acid. The limited number of sharp peaks without any broadening in the XRD pattern confirms that the as-grown MCB possesses good crystallinity.

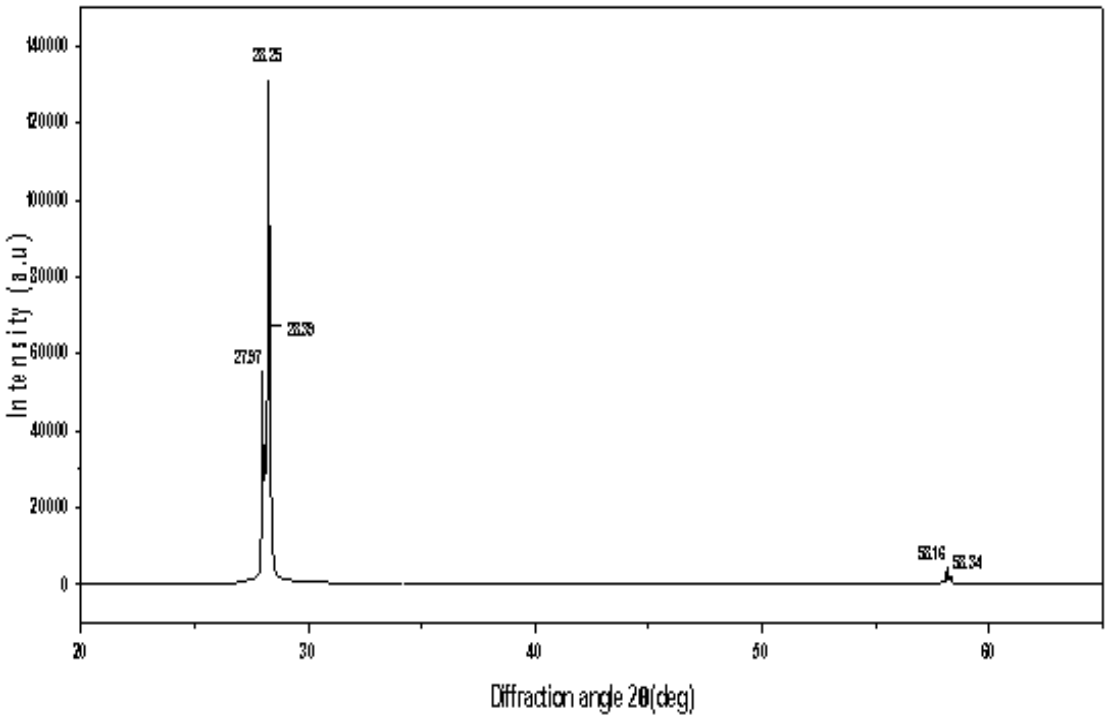

FIG 5. 1 ***Powder X-ray diffraction pattern for MCB crystal***

5.2 Fourier transform infrared spectral analysis (FTIR)

Infrared spectrum studies were carried out to expound the presence of functional groups. In the FT-IR spectrum of grown crystal of MCB, the peaks are observed according to the wave number ranging from 4000 - 400 cm^{-1}. The sample is made as a pellet by using KBr. The FTIR spectrum of Magnesium Cadmium Borate crystal (MCB) is shown in Figure 5.2. The spectrum shows the presence of all the functional groups in MCB crystal. The N-H stretch and O-H stretching are observed at 3225.39 cm^{-1} and 2514.71 cm^{-1}. The Nitrogen atoms presence show N-O anti symmetric stretching that are observed at 1543.31 cm^{-1} as strong absorption. The medium B-O Asymmetric stretching is observed at 1454.60 cm^{-1} and 1387.57 cm^{-1}. The O=C=O stretching shows the strong absorption at 2383.16 cm^{-1} and 2339.18 cm^{-1}. The C-O stretching with strong absorption observed at 1193.29 cm^{-1}. C=C bending was observed at 887.92cm^{-1} and 810.34cm^{-1}. Peaks at 643.9 cm^{-1} shows B-O symmetric stretching. The N-H stretch, O-H stretch, N-O stretch and B-O stretch confirms the presence of nitrate and acid groups in grown crystal. Table 1. shows the assigned functional groups.

Table 1. FTIR assignment for MCB compound

FTIR EXPERIMENTAL VALUES	Assignments
3225	N-H STRETCH
2514	O-H STRETCH
1543	N-O STRETCH
2383	O=C=O STRETCHING
1454	B-O ASYMMETRIC STRETCH
643	B-O SYMMETRIC STRETCH
887,810	C=C BENDING

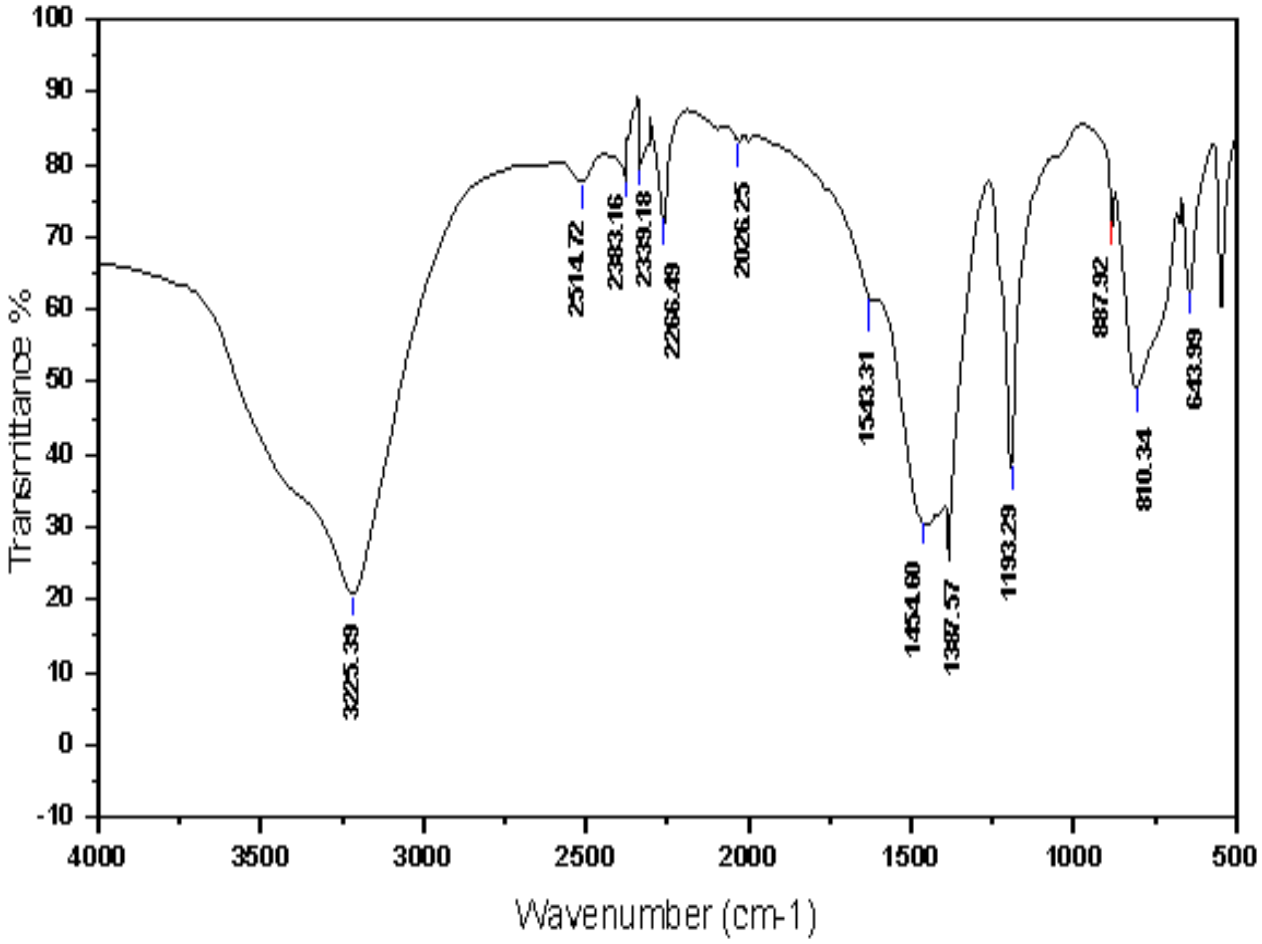

Figure 5.2 FTIR spectrum of MCB

5.3 UV-Visible spectral analysis

Since single crystal is mainly used in optical applications, the optical transmissions range and the frequency of cut off wavelength (200-400nm) are essential for the SHG output in the range for using lasers applications. The optical absorption plays an important role in identifying the potential of the NLO material.

The optical absorption spectra of Magnesium Cadmium Borate crystal was recorded in the region between 200nm-800nm, at a scanning speed of 200nm/min using JASCO UV-Vis NIR spectrometer. The recorded spectra shown in Figure 5.3. The absorbance found to be good in the entire visible and IR region. The spectrum shows two peaks, one at 266nm corresponds to π-π^* transition and another intense peak at 230nm corresponds to n-π^* transition. The cut-off

wavelength of MCB crystal has good absorbance at 230nm. So MCB single crystal found to be suitable for optoelectronic applications.

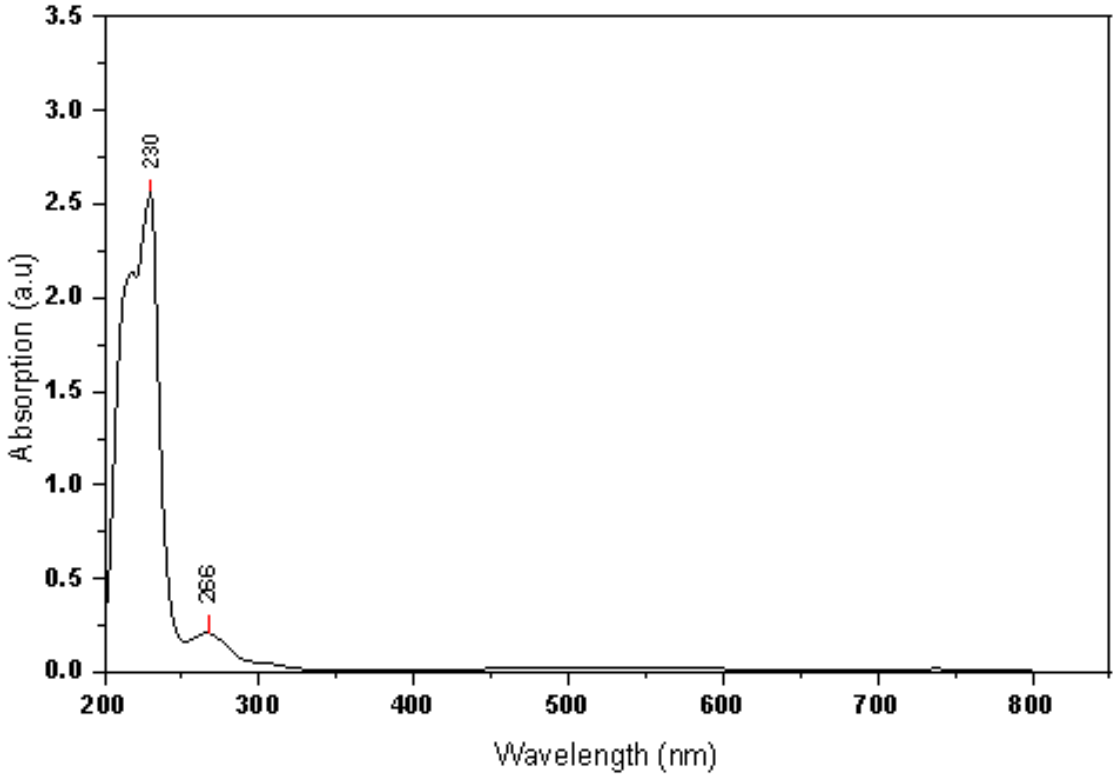

Figure 5.3. Absorption spectrum of MCB crystal

5.4 Optical Band gap Energy

For optical device fabrication, the crystal should have high transparency in a considerable range of wavelength. The UV cut-off wavelength of the grown MCB crystal was found to be 230nm and it is useful to make them potential material for optical device fabrication. The optical absorption coefficient (α) was calculated using Beer's law. The band gap energy (E_g) was calculated from linear part of the Tauc's plot drawn between $(\alpha h\nu)^2$ and photon energy ($h\nu$). The band gap energy of the grown crystal MCB was plotted in the Figure 5.4. The band gap of the MCB crystal is found to 5.25eV.

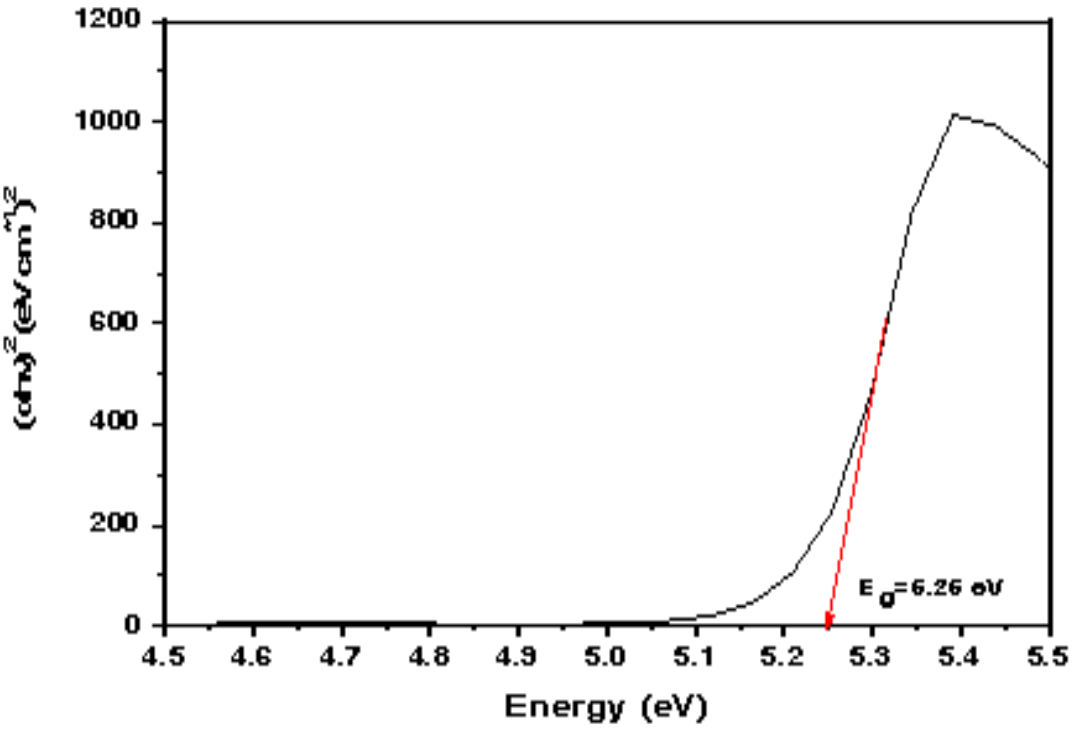

FIG 5.4 Band gap energy of the MCB crystal

5.5 Kurtz and perry SHG test

Non-centrosymmetric crystals needs to possess NLO efficiency which has been tested using Kurtz powder technique. When the output frequency is doubled in the grown powdered sample after passing a beam 1064nm from Q-switched Nd: YAG laser the NLO efficiency is tested. The MCB crystal emit bright green light (λ=532 nm) proving that it possess NLO efficiency. The SHG efficiency of MCB crystal has 1.36 times greater than KDP crystal. This result recommends that the Magnesium Cadmium Borate crystal can be efficient for nonlinearity optical device application.

5.6 Thermogravimetric analysis

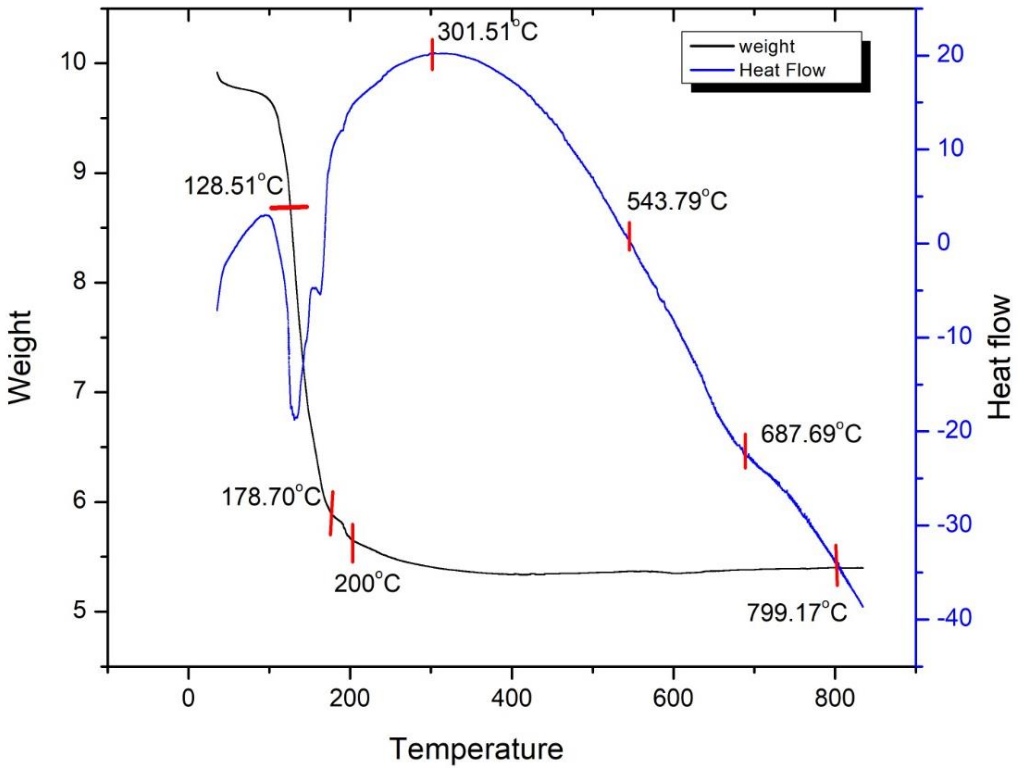

FIG 5. 5 The TGA and DTA curves of Magnesium Cadmium Borate

The TGA and DTA curves of Magnesium Cadmium Borate (MCB) are shown in Figs 5.5. The TGA measures weight change of a sample over a temperature range. DTA measures heat differences between a reference sample and a sample of interest are temperature range. To find out the melting point and any kind of phase transition of Magnesium Cadmium Borate (MCB), the DTA and TGA analysis are performed with the help of an instrument SDTQ 600 V8.3. The sample was heated at a rate of 50℃/min in protected nitrogen gas flow. It is observed that the material undergoes an irreversible endothermic transition at about 128.51℃ where the decomposition starts between 128.51℃ and 180.12℃. It indicates that the crystal is stable up to 180.12℃. Magnesium Cadmium Borate (MCB) is fully decomposed at upto 800℃.. The good degrees of crystalline of the grown crystals are shown by the sharpness of endothermic peak. It can be also seen on the TGA curve that the weight loss stars a 128.51℃ and ends a 800℃. The DTA curve shows an endothermic peak around at 301.51℃. Which indicates

the weight loss due to the liberation of volatile substance. From TGA curve a sharp slope up to 180.12℃ which corresponds to the removal of almost all the compound as gaseous product. The TGA and DTA analysis does not show any kind of phase transition Magnesium Cadmium Borate (MCB).

5.7 Crystal surface analysis by SEM

The surface morphology of Magnesium Cadmium Borate crystals were analysed by scanning electron microscope (SEM) which is used to extract the information about size and shape of the particles present in the crystal. The surface morphology of the Magnesium Cadmium Borate crystal is shown in Fig. and the following observations have been made from SEM images.

(i) At a magnifications of 20kv and at a scale of 20 µm, the crystals have smoothed surfaces. The significant differences can be observed from the following magnification and scales.

(ii) At a magnifications of 20kv and at a scale of 50 µm

(iii) At a magnifications of 20kv and at a scale of 20 µm

(iv) At a magnifications of 20kv and at a scale of 5 µm

(v) At a magnifications of 20kv and at a scale of 200 µm.

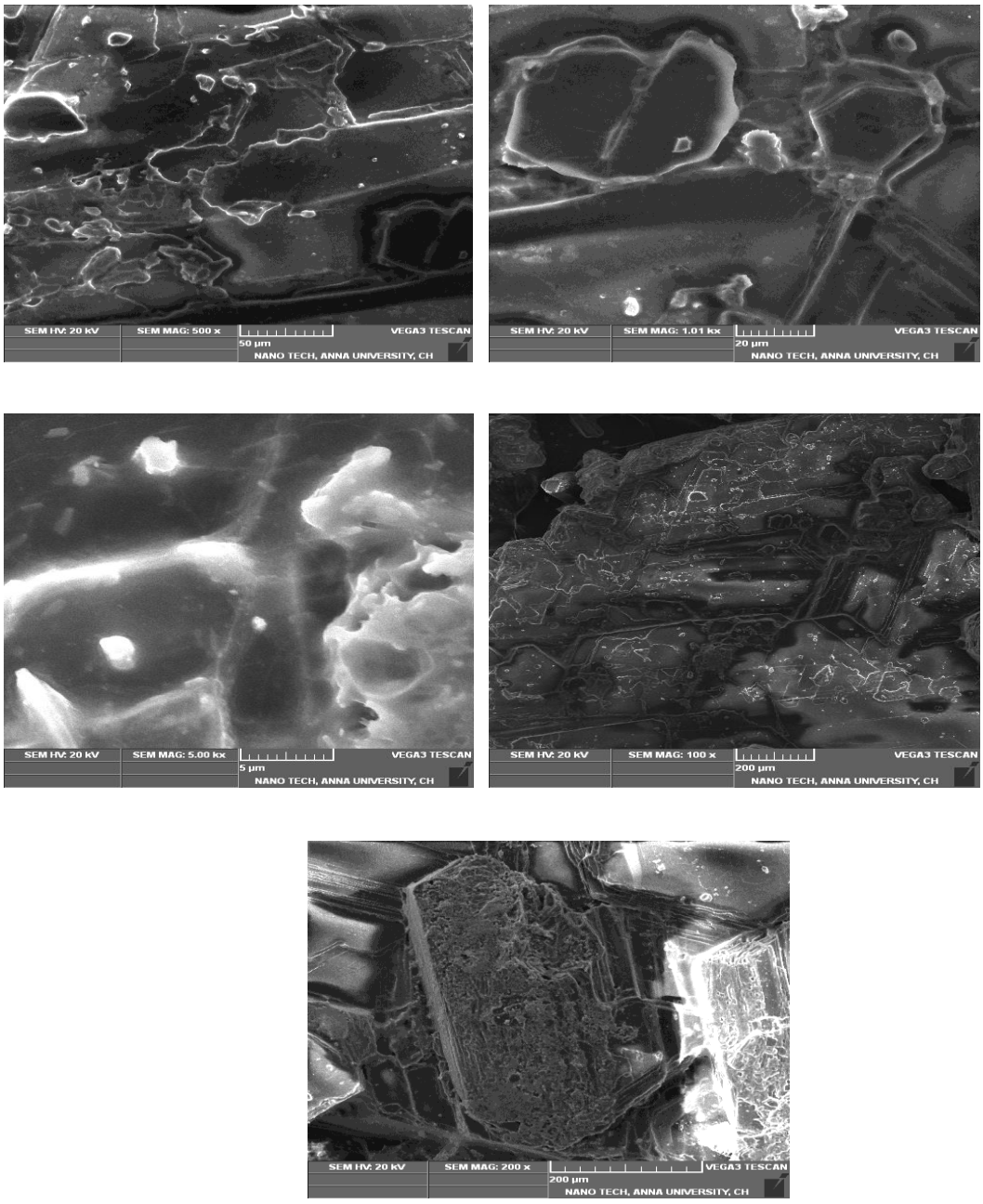

FIG 5.6 The surface morphology of Magnesium Cadmium Borate crystals

CHAPTER-6

CONCLUSION

The design, discovery and growth of novel materials, especially in single crystal form, represent national core competency that is essential for scientific progress and long-term economic growth. New materials lay at the core of many new and existing technologies, such as semiconductor electronics, solid state lasers, radiation detectors, compact disk storage, both cellular and optical communications, solar cells, fuel cells and catalysts. Single crystals are often required to achieve a materials' full functionality as well as to completely elucidate its properties. The effective NLO single crystals with efficient optical frequency conversion are the key elements for the development of laser systems, telecommunication, optical information processing, high optical disk data storage, wide range tunable sources of coherent illumination in ultra-violet, visible and infrared spectral ranges. Hence, there is a great demand to synthesize new NLO materials and grow their single crystals

A new inorganic Magnesium Cadmium Borate (MCB) compound was synthesized using Magnesium nitrate, Cadmium nitrate and Boric acid taken in equal ratio and the crystals were grown by slow evaporation technique at room temperature of 30ºC.

Powder X-ray diffraction analysis confirmed the crystalline nature 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 revealed the good transparency of the grown crystal in wide wavelength range with the lower cut-off wavelength 230nm which suits the crystal for various electro optic applications. The SHG measurement shows that the grown Magnesium Cadmium Borate crystal has higher efficiency than KDP crystal. In view of the good optical properties, better SHG efficiency of MCB crystal would be a suitable material for nonlinear optical device applications.

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