SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF NICKEL TITANATE CERAMIC

A PROJECT REPORT SUBMITTED TO THE

UNIVERSITY OF KERALA

In fulfillment of the requirements for the degree of

BACHELOR OF SCIENCE

in

PHYSICS

submitted by

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MAY 2023

DECLARATION

We, the B.Sc. Physics students of All Saints' College, hereby declare that the work presented in this project report entitled **"Synthesis and Structural Characterization of Nickel Titanate ($NiTiO_3$) Ceramic"** is an authentic record of our own for the partial fulfillment of the requirements for the award of the B.Sc. Degree in Physics under University of Kerala and has been carried out under the guidance of Dr. Anjana P.S, Assistant Professor and Head, Department of Physics, All Saints' College, Thiruvananthapuram.

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CERTIFICATE

Certified that this project report entitled **"Synthesis and Structural Characterization of Nickel Titanate ($NiTiO_3$) Ceramic"** is a bonafide report of the work done by **Ms. Gopika M (Reg No. 23020100016), Ms. Lekshmi Balaji (Reg No. 23020100017), Ms. Megha Hari S (Reg No. 23020100019) and Ms. Dhara Krishnan .B.S. (Reg No. 23020100027)**, in partial fulfillment of the requirements for the award of the degree, **Bachelor of Science in Physics,** Kerala University during the period 2020-2023.

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External Examiners

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DECLARATION

I hereby declare that the project report entitled "**A Study on the V-I Characteristics of Light Emitting Diodes**" is an independent work carried out by us in partial fulfillment of the requirements for the B.Sc Degree in Physics under the University of Kerala. I have completed this project under the supervision and guidance of Dr. Dhanya Chandran, Assistant Professor (On Contract), Department of Physics, All Saints' College, Trivandrum.

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Chapter 1

INTRODUCTION

Material science is the study of the properties of solid materials and how those properties of solid materials are determined by a material composition and structure. A combination of solid-state physics, metallurgy, and chemistry gave rise to it. Due to the wide range of material qualities, they cannot be fully understood within the framework of a single classical field. Materials can be chosen or designed for a huge variety of purposes, from structural steels to computer microchips, with a fundamental understanding of the sources of qualities. Many engineering sectors, such as electronics, aerospace, telecommunications, information processing, nuclear power, and energy conversion, rely on materials science. Metals, polymers, semiconductors, and ceramics make up the majority of the diverse materials studied and used in materials science. Explanations of the history, development, and manufacture of metallurgy, elastomer (natural and synthetic rubber), plastic, man-made fiber, industrial glass, and ceramics are given in detail. Atomic and molecular structures are discussed in chemical elements and matter. Since the dawn of time, ceramics have been with humans. Archaeologists have discovered ceramics that were produced by humans at least 25,000 years ago. Clay, a common earthy ingredient, was used to make primitive ceramics, which were subsequently burned in domes. As human ingenuity developed, people began burning these items at higher temperatures to produce ceramic products that were harder. The human races developed more effective firing procedures as a result of their need to obtain tougher materials. The human spirit and the mystique of nature have grown greatly from simple earthenware to contemporary advanced ceramics. The ceramic materials include brick, cement, glass, tiles, pottery, diamond, graphite, quartz, pottery cups and bowl. The electronic component like microchips, capacitors, resistors are also ceramic. Liquid crystal TV and Gorilla glass in smart phone are advanced ceramics. Material science is crucial to the investigation of materials, goods, structures, or other components that malfunction or are not intended to do so and cause property damage or personal injury. Such investigations are key to understanding, for example, the causes of various aviation accidents and incidents. The subject of material science is very vast and unlimited. One can sub divide the field of study into four such as Science of materials, Mechanical behavior of Metals, Engineering metallurgy and engineering materials. Application of material science is in the field of energy, ground transportation, aerospace, computers and communication, and medicine. Ceramics are the only materials that don't harm the environment; `thus, they don't degrade over time from things like corrosion, erosion, abrasion, thermal shock, etc. Ceramics are the only materials that will last into the future, despite their fragility. We can therefore refer to them as a strong-fragile aspect of human life.

1.1 Introduction to ceramics

Ceramics are materials that are inorganic, meaning they are not from living materials, and non-metallic, additionally ceramics are solids. Ceramics are typically formed from blends of clay, earthen matter, powder and water. Many household elements are ceramics, including tiles, bricks and toilets. The name “Ceramics” comes from the Greek word “Keramos” meaning “potter’s clay”. The first type of ceramics made by humans were pottery objects or figures made from clay either alone or in combination with other materials like silica, hardened and sintered in fire. Later types of ceramics were glazed and fired to create smooth, coloured surfaces reducing porosity by layering glassy, amorphous ceramic coatings on top of crystalline ceramic substrates. Today, many substances that are categorized as ceramics don’t even include clay, compounds of metals and non-metals are what modern ceramics are defined as.

Ceramics can also be found in watches (quartz tuning forks-the time keeping devices in watches), snow skies (piezoelectric-ceramics that stress when a voltage is applied to them), automobiles (spark plugs and ceramic engine parts found in race cars) and phone lines. Depending on their method of formation, ceramics can be dense or lightweight. Ceramics are corrosion resistant, hard and brittle materials. The majority of ceramics are also excellent insulators and can withstand high temperatures. Ceramics can also be served to conduct electricity. Some ceramics, like superconductors, also display magnetic properties. Many ceramics contain a mixture of ionic and covalent bonds between them. That is why they exist in crystalline, semi-crystalline and vitreous form. Ceramic materials can be found as single crystals or as poly-crystalline materials.

Examples of ceramic materials are: Silicon-carbide, Barium titanate, Boron oxide, Porcelain, Yttrium barium copper oxide etc.

1.1.1 Features of Ceramics

The general features of ceramics are:

- They have high hardness.
- They are brittle and have poor toughness.
- They have high melting point.
- They have low ductility.
- They have high compression strength.
- They show optical transparency to a variety of wavelengths.
- They are wear-resistant.
- They are oxidation resistant.
- They are chemically stable.
- They have elevated surface tension.
- They have low electrical and thermal conductivity.
- They are strong and durable.
- Light can induce photoconductivity in them.

1.1.2 Classification of Ceramics

Ceramics can be classified in many ways. But the two most important classification are based on their composition and uses.

Based on Application:

- **<u>Glasses</u>**

Glasses are a familiar group of ceramics-containers, windows, mirrors, lenses, etc. They are non-crystalline silicates containing other oxides, usually CaO, Na_2O, K_2O and Al_2O_3 which influence the glass properties and its colour. A typical property of glasses that is important in engineering applications is their response to heating. There is no definite temperature at which the liquid transforms into a solid as with crystalline materials. A specific temperature, known as glass transition temperature or fictive temperature is defined based on viscosity above which material is named as supercooled liquid or liquid, and below it is termed as glass.

- **Clay products**

Clay is one of the most widely used ceramic raw materials. It is found in great abundance and popular because of the ease with which products are made. Clay products are mainly two kinds-structural products (bricks, tiles, sewer pipes) and white wears (porcelain, China wear, pottery, etc.)

- **Refractories**

These are described by their capacity to withstand high temperatures without melting or decomposing, and their inertness in severe environments. Thermal insulation is also an important function of refractories.

- **Abrasive ceramics**

Abrasive ceramics are used to grind, wear, or cut away other materials. Thus, the prime requisite for this group of materials is the hardness or wear resistance in addition to high toughness. As they may also be exposed to high temperature, they need to exhibit some refractoriness. Diamond, silicon carbide, tungsten carbide, silica sand, and aluminium oxide/corundum are some typical examples.

- **Cement**

Cement, plaster of Paris and lime come under this group of ceramics. The characteristic property of these materials is that when they are mixed with water, they form a slurry which sets subsequently and hardens finally. Thus, it is possible to form virtually any shape. They are also used as bonding phases for example between construction bricks.

- **Advanced ceramics**

Advanced ceramic materials are newly developed and manufactured in a limited range for specific applications. Usually, their electrical, magnetic, and optical properties and a combination of properties are exploited. Typical applications: heat engines, ceramic armours, electronic packaging, etc.

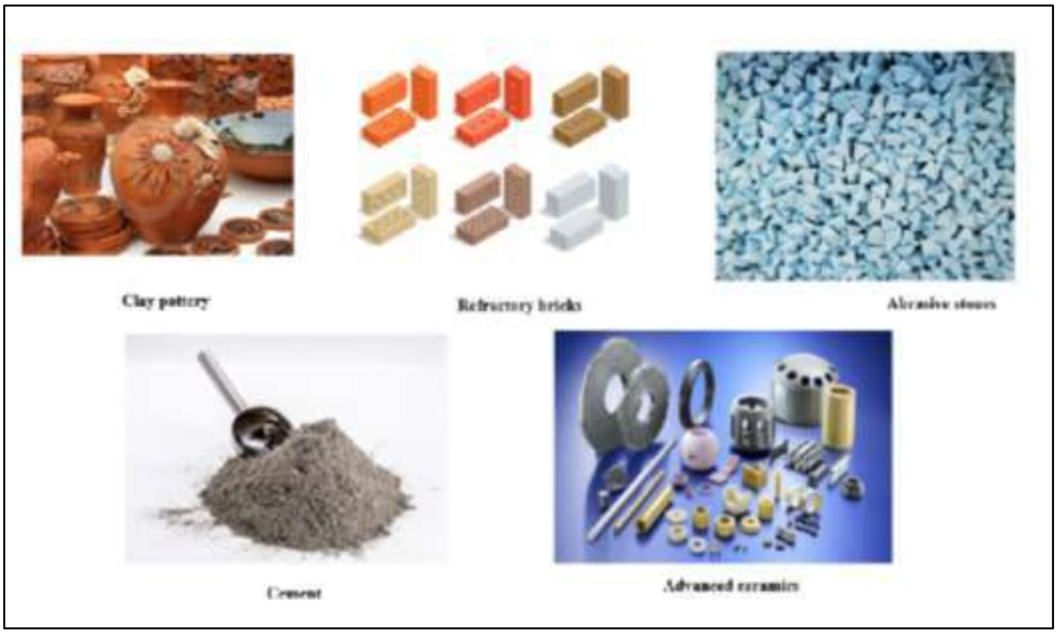
Clay pottery
Refractory bricks
Abrasive stones
Cement
Advanced ceramics

Figure 1.1: Ceramics classified on the basis of their applications.

Based on their composition:

- Oxides
- Carbides
- Nitrides
- Sulphides
- Fluorides

Some typical ceramics and respective applications are as follows:

- **Aluminium oxide/Alumina (Al_2O_3)**

It is one of the most commonly used ceramic materials. Alumina is used in many applications such as to contain molten metal, where the material is operated at very high temperatures under heavy loads, as insulators in spark plugs, and in some unique applications such as dental and medical use. Chromium-doped alumina is used for making lasers.

- **Aluminium nitride (AlN)**

Because of its typical properties such as good electrical insulation but high thermal conductivity, Aluminium nitride is used in many electronic applications such as in electrical circuits operating at a high frequency. It is also suitable for integrated circuits. Other electronic ceramics include-barium titanate($BaTiO_3$) and cordierite($2MgO-2Al_2O_3-5SiO_2$).

- **Silicon carbide (SiC)**

It is known as one of the best ceramic materials for very high-temperature applications. Silicon carbide is used as coatings on other materials for protection from extreme temperatures. It is also used as an abrasive material. It is used as a reinforcement in many metallic and ceramic-based composites. It is a semiconductor and is often used in high-temperature electronics. Silicon nitride (Si_3N_4) has properties similar to those of SiC but is somewhat lower, and found applications in such automotive and gas turbine engines.

1.1.3 Properties of Ceramics

The properties of ceramic materials, like all materials, are dictated by the types of atoms present, the types of bonding between the atoms, and the way the atoms are packed together. This is known as the atomic scale structure. Most ceramics are made up of two or more elements. This is called a compound. For example, alumina(Al_2O_3) is a compound made up of aluminium atoms and oxygen atoms.

Atoms in ceramic materials are held together by a chemical bond. The two most common chemical bonds for ceramics are covalent and ionic bond. For metals, the chemical bond is called the metallic bond. The bonding of atoms together is much stronger in covalent and ionic bond than in metallic bond. That is why, metals are ductile and ceramics are brittle. Due to their wide range of properties, they are used for a multitude of applications.

Thermal properties

- **Thermal expansion coefficient**

When materials are heated, their size and volume increases, in a phenomenon known as thermal expansion. The coefficient of thermal expansion ratio indicates how much a material expands in one degree celsius temperature rise. Ceramics have low coefficient of thermal expansion, less than half that of most steels.

- **Thermal conductivity**

The property that defines the heat transmitted through a material is called thermal conductivity. Some materials have high levels of conductivity and others have low levels of conductivity. The thermal conductivity of silicon carbide is good, while zirconia has low thermal conductivity.

- **Melting point and working temperature**

Ceramics of all types are known for their ability to withstand high temperature. For example, Alumina melts at temperatures approaching 1800^0C, well above the melting point of metallic materials.

Electric properties

- **Good electrical insulation as well as conductivity**

The bulk of ceramic materials are dielectric which means that they are in general electrically non-conductive. But these are semiconductor ceramics that depend on their temperature and applied voltage level to conduct electricity.

Chemical properties

- **High resistance to corrosion and chemical attack**

In most technical ceramic materials, ionic bonds are predominant, resulting in extremely strong chemical resistance properties. Ceramics are preferred materials for use in harsh environments because they are highly resistant to corrosion and wear.

Mechanical properties

- **Hardness**

The most distinctive characteristic of advanced ceramics is their extreme hardness, where for example, Alumina has a hardness almost three times than of stainless steel.

- **Low ductility**

The two most common chemical bonds for ceramic materials are covalent and ionic bonds. the bonding of atoms together is much stronger in covalent and ionic bonding. Hence ceramics are brittle and have low ductility.

- **Strength**

Strength of metal is greater than the strength of ceramics and that is greater than the strength of polymers.

Optical properties

- Ceramics can be transparent, translucent, or opaque for one particular composition.
- The colour of many ceramics can be changed by small additions: additives, dopant s, or point defects.
- Ceramics can reflect and refract light.
- Ceramics can emit light in response to an electric field or illumination by light of another wavelength.
- Many ceramics and glasses show good transparency to infrared (IR) radiation. This property has led to the use of glasses for optical fibers for high speed communications.

1.1.4 Advantages of Ceramics

- In comparison to metals and polymers, ceramic materials are the obvious choice for use in extreme conditions: severe changes in temperature or pressure, corrosion, particularly if these conditions present themselves at the same time or over a prolonged period of time.
- They have high wear, tear, pressure and chemical attack resistance.
- Most of them have extreme hardness and hence, they can be used as abrasive powder and cutting tools.
- Ceramics can be easily moulded and made into many useful things.
- A glazed ceramic product does not stain and its colour does not fade.
- They have high chemical stability and durability superior to metal products such as copper wear, iron wear and aluminium wear. Daily use porcelain has a certain resistance

to acids, alkali salts and carbon dioxide in the atmosphere. It does not react easily with these substances and does not rust and age.

- They are efficient thermal insulators and have high melting point. It enables employing them as refractory materials.
- Due to their low mass density, they produce lightweight components.

1.1.5 Disadvantages of ceramics

- They have low degree of ductility.
- They have brittle nature which cause unexpected fractures.
- Even for identical specimen, there is a wide range of variation in strength.
- Although the innovations are beneficial, ceramics are costly.
- When ceramics are machined incorrectly, the structure will lose its strength.
- Ceramics are difficult to machine.
- Their tensile strength is low.

1.1.6 Applications of ceramics

- Silicon carbide and tungsten carbide are technical ceramics that are used in body armor in defense field (Alumina is most commonly used.), wear plates for mining, and machine components due to their high abrasion resistance.
- Uranium oxide (UO_2) is a ceramic that is used as a nuclear reactor fuel.
- Zirconia is a ceramic that is used to make ceramic knife blades, gems, fuel cells and oxygen sensors.
- Barium titanate is a ceramic that is used to make heating elements, capacitors, transducers, and data storage elements.
- Stealite is a ceramic that is used as an electrical insulator.
- Because of their lightweight, they are used in aerospace industry. We use silicon carbides in jet engine turbines, primarily on the turbine blades. The windshield and the window panes are made of ceramic glass. Ceramics are also employed as thermal protection system in engine parts.
- Ceramics are used in communication industry because of its adjustable dielectric constant, low temperature coefficient of capacitance, low coefficient of thermal expansion and great durability.

1.2 Dielectric

Many of the ceramic materials are dielectrics and hence the study of the theory of dielectrics is significant. Dielectrics in general can be described as materials that are electric insulators which ordinarily do not conduct electricity since they do not contain any free charge carriers for conduction. The energy band model of a dielectric materials are comparatively larger in dielectric materials. Electrons are very tightly bound to the atoms so that at ordinary temperature they cannot be dislodged by applied electric fields. They, however, contain positive and negative charges which are bound together and they can move a bit within the molecule. Their cumulative effect account for the characteristic behavior of dielectric materials.

When dielectric medium is placed in electric field, electric polarization occurs. The positive charge within the dielectric is displaced minutely in the opposite direction of the electric field, the negative charges are displaced minutely in the direction opposite to the electric field. This slight separation of charge (polarization) is responsible for the reduction of electric field within the dielectric.

The dielectric is mainly classified as: Polar and Non polar molecules

- **Polar Molecule**: In the absence of an external electric field the centres of mass of the positive and negative charges in a molecule of dielectric do not coincide, it is called Polar molecule.
  Eg: HCI, H_2O, NH_3, etc.

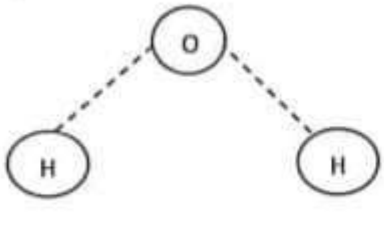

Figure1.2 (a): Polar molecule: H_2O

- **Non-Polar Molecule**: If in the absence of an external electric field the centres of mass of the positive and negative charges in a molecule of a dielectric coincide, it is called non-polar molecule.
  Eg: H_2, CO_2, CH_4, etc.

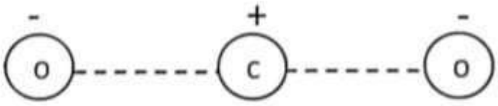

Figure 1.2 (b): Non polar molecule: CO

1.2.1 Properties of Dielectrics

The term Dielectrics is a combination of two words- 'Dia' and 'electric'. The electric conductivity of a perfect dielectric is zero. A dielectric store and dissipate the electrical energy similar to an ideal capacitor some of the main properties of a dielectric material are Electric polarization, Electric Susceptibility, Dielectric constant, Dielectric Breakdown etc.

- **Electric Polarization**:

The process of producing electric dipoles by an electric field is called polarization in dielectrics.

- **Dielectric constant**:

Dielectric constant is the ratio between the absolute permittivity of the medium and the permittivity of free space.

- **Electric Susceptibility**:

When a dielectric material is placed in an electrical field, it becomes electrically polarized. This is known as electric susceptibility.

- **Dielectric Breakdown**:

When higher electric fields are applied, the insulator starts conducting and behaves as a conductor. In such conditions, dielectric materials lose their dielectric properties. This phenomenon is known as Dielectric Breakdown. It is an irreversible process. This leads to the failure of dielectric materials.

Dielectric materials include solids such as glass, porcelain, etc. liquids such as chemically pure water, methyl chloride (CH_3Cl), etc. and gases such as Hydrogen, Nitrogen, Ammonia (NH_3), etc.

1.2.2 Sources of Polarizability

The net polarizability of a dielectric material results mainly from the following three types of contributions:

- Electronic polarizability
- Ionic polarizability
- Dipolar or orientational polarizability

The extent to which a particular polarizability contributes depends on the nature of the dielectric and the frequency of the applied electric field.

1.2.2.1 Electronic Polarizability

The electronic polarizability arises due to the displacement of the electron cloud of an atom relative to its nucleus in the presence of an applied electric field.The polarization as well as the dielectric constant of a material at optical frequencies results mainly from the electronic polarizability.

1.2.2.2 Ionic Polarizability

Ionic polarization occurs in ionic materials because the electric field displaces cations and anions in opposite directions

$$\boldsymbol{P_i = N\alpha_i E_0} \tag{1.1}$$

where, α_i is the ionic polarizability. Orientational polarization can occur in substances composed of molecules that have permanent electric dipoles.

1.2.2.3 Dipolar Polarizability

A molecule, such as H_2O, having a permanent dipole moment is called a dipolar or polar molecule and a substance comprising such molecules is called a dipolar substance. The dipolar polarizability is the property of dipolar substances. In the absence of an external electric field, the dipoles have random orientations and there is no net polarization. However, when the field is present, the dipoles orient themselves along the field and produce orientational or dipolar polarizability.

1.2.3 Frequency Dependence of Total Polarizability

The total polarizability of a dielectric is given by the expression:

$$\boldsymbol{\alpha} = \boldsymbol{\alpha}_i + \boldsymbol{\alpha}_e + \boldsymbol{\alpha}_d \tag{1.2}$$

It decreases with increase in frequency as shown in figure. This type of variation of polarizability can be explained on the basis of the relaxation times of the various contributing polarization processes. When the frequency of the applied field is quite large as compared to the inverse of the relaxation time for a particular polarization process, the contribution of that process to the polarizability is negligible. As relaxation time is maximum for the dipolar process and minimum for the electronic process, the dipolar contribution disappears first followed by ionic and electronic contributions.

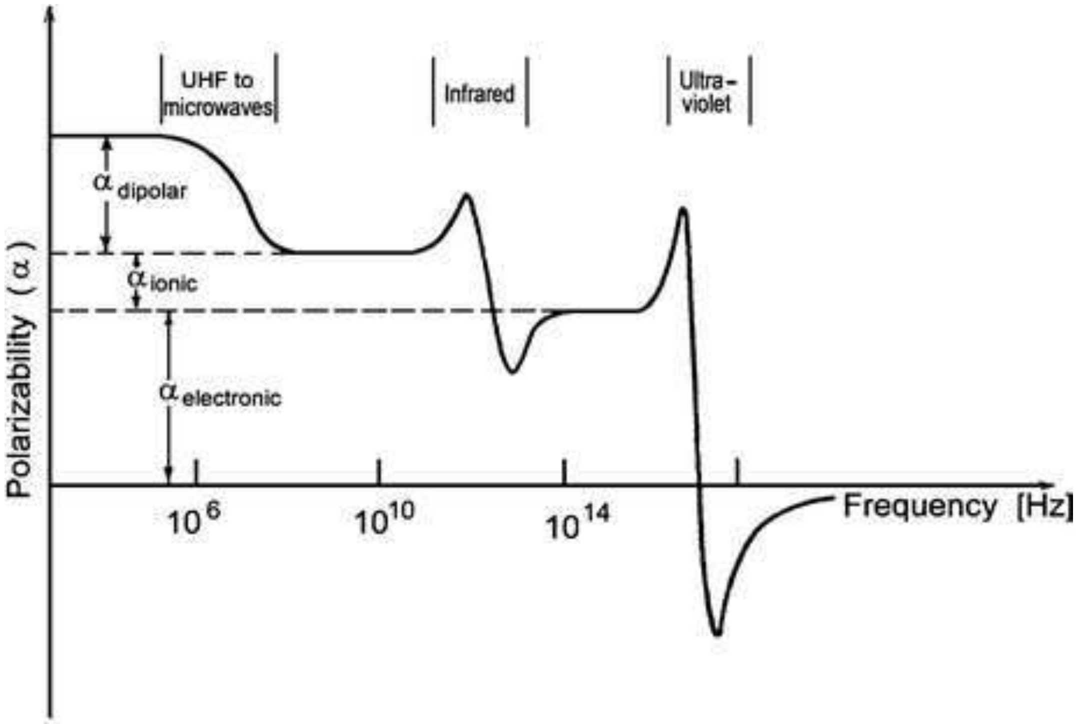

Figure 1.3: Frequency dependence of various contributions to polarizability

(Courtesy https://www.skedsoft.com/books/physics-for-engineers-2/sources-of-polarizability)

1.2.4 The Dielectric Constant and Molecular Polarizability

The dielectric constant ε is defined by the equation,

$$\boldsymbol{D} = \boldsymbol{\epsilon E} \tag{1.3a}$$

where D is the electric displacement and E the average field inside the dielectric.

In terms of the polarization P, the displacement vector D is

$$\boldsymbol{D} = \boldsymbol{\epsilon E} + \boldsymbol{P} \tag{1.3b}$$

The polarization P arises as a result of the polarization of the molecules, and is given by

$$\boldsymbol{P} = \boldsymbol{N_p} \tag{1.3c}$$

where N is the concentration of the molecules and p the electric moment of each of these molecules. The electric moment is proportional to the field, and is given by

$$\boldsymbol{P} = \boldsymbol{\alpha E} \tag{1.3d}$$

where α is the molecular polarizability. Substituting this into the above equations, we may express the relative dielectric constant in terms of the polarizability,

$$\boldsymbol{\varepsilon_r} = \mathbf{1} + \left(\frac{\boldsymbol{N_\alpha}}{\boldsymbol{\varepsilon_0}}\right) \tag{1.3e}$$

This result, which ignores the local-field correction holds well in gases. In liquids and solids, however, the local-field correction is appreciable, and must be included. We then find the local field to be

$$\boldsymbol{E_{loc}} = \boldsymbol{E} + \left(\frac{\mathbf{1}}{\mathbf{3}\boldsymbol{\varepsilon_0}}\right) \tag{1.3f}$$

which leads to the Clausius-Mosotti relation,

$$\frac{\boldsymbol{\varepsilon_r} - \mathbf{1}}{\boldsymbol{\varepsilon_r} + \mathbf{2}} = \boldsymbol{N\alpha}/\mathbf{3}\boldsymbol{\varepsilon_0} \tag{1.3g}$$

1.2.5 Applications of Dielectric Materials

Some of the applications of the dielectrics are as follows:

- The dielectric properties are important to understand the propagation of electromagnetic waves through the material media and fabricate various devices such as capacitors, microphones, etc.
- In the substation equipment where medium and high voltages flow, dielectric material is used.
- In energy storing device such as capacitors, dielectric material is a separate layer for the conducting pair of plates.
- Practically, for high voltage driven transformers, brushes and switch gears are coated with dielectric materials.
- The exposable components for example, cables are firmly coated with dielectrics so that they are protected from hazardous effects.
- The liquid type of dielectrics is a cooling medium for the transformers, rheostats, and capacitors.

Chapter 2

CRYSTALLOGRAPHY AND X-RAY DIFFRACTION

2.1 Introduction

From very early times it was known that many solid substances must have a symmetric internal structure. This was mainly from the observations of their external features such as the perfection with which faces of certain solid pieces appear in nature, constancy of angles between such faces etc. such substances came to known as crystalline substances and others lacking such systematic appearances were termed as non-crystalline (amorphous & polycrystalline). Hence quartz was recognized as crystalline while most of the metals are not. Striking departure from those conventional methods of study of crystals come about at suggestion by German physicist Max Von Laue in 1912. He stated that crystals might act as natural gratings for X-rays, providing information about the X-rays as well as about the regular arrangement of atoms in crystals. Friedrich and Knipping working together with Laue confirmed this experimentally and it marked the beginning of new branch of science, the Crystallography.

Crystallography is the science of crystals and crystalline state. It concerned with the nature of regular atomic or molecular arrangement within a crystal, the binding of atoms or molecules and the physical and chemical properties that result from certain arrangement. This has developed so much an extend that scientists are able even to synthesize new materials with pre-determined properties.

2.2 Structure of crystals

A crystal is a solid whose atoms are arranged in a highly ordered repeating pattern. The Science which deals with the study of geometrical forms and physical properties of crystalline solids are called Crystallography. The arrangement of atoms in a crystal is conveniently described by the arrangement of imaginary points in space which has a definite relationship with the atoms of the crystal. This set of imaginary points forms a frame work on which actual crystal structure is based. Such an arrangement of infinite number of imaginary points in three-dimensional space with each point having identical surroundings known as space lattice or point lattice. To obtain a crystal structure an atom or a group of atoms must be placed on each lattice point in a regular fashion. Such an atom or a group of atoms is called the basis and acts as a building unit or Structural unit for the complete crystal structure. Thus, a lattice combined with a basis generates the crystal structure. Mathematically it is expressed as;

$$\boldsymbol{Crystal\ Structure = Lattice + Basis}$$

A lattice is a mathematical concept, the crystal structure is a physical concept.

2.2.1 Unit cell

The building blocks for constructing the complete lattice are known as unit cell. The unit cell may be defined as the smallest units of the lattice which on continuous repetition, generates the complete lattice. Unit cell is divided into primitive and non-primitive unit cell. Primitive unit cell is the smallest volume cell. All the lattice points belonging to a primitive cell lie at its corners. There are the effective number of lattice points in a primitive unit cell is one. A non- primitive cell may have the lattice points at the corners as well as at other locations inside and on the surface of the cell, and therefore the effective number of lattice points in a non- primitive cell is greater than one. The crystallographic axes a, b and c drawn from one of the lattice points determine the size and shape of a unit cell. The angles α, β, ϒ represents the angle between the vectors b and c, c and a, a and b respectively. The lengths a, b, c and angles α, β, ϒ are collectively known as lattice parameters or lattice constants of a unit cell.

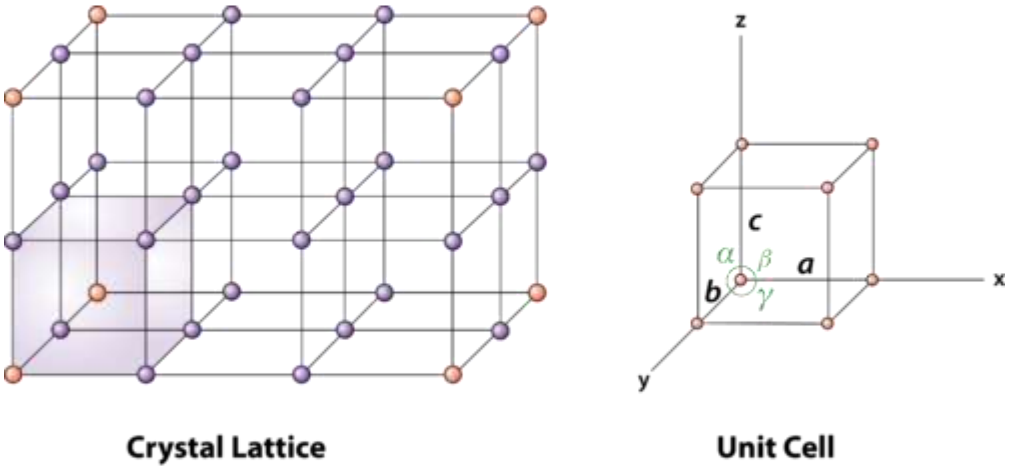

Figure 2.1: Representation of Unit Cell & Crystal Lattice

(Courtesy https://www.coursehero.com/study-guides/cheminter/unit-cells/)

2.2.2 Type of lattices

The number of point groups in two dimensions are 10 and in three dimensions are 38. These point groups form the basis for construction of different type of lattices. Such lattices are called Bravais lattices. 10-point groups in two dimensions produce 5- and 32-point groups in three dimensions produce 14 distinct Bravais lattices. These Bravais lattices further become parts of 4 and 7 distinct crystal systems respectively.

Two dimensional lattices

The four crystal systems of two-dimensional space are oblique, rectangular, square and hexagonal. The rectangular crystal system has two Bravais lattices namely rectangular primitive and rectangular centered. In all these are five Bravais lattices which are listed in table along with the corresponding point groups.

Table 2.1: Two dimensional Bravais Lattices

Sl.no	Crystal system	Bravais lattice	Conventional unit cell	Unit cell characteristics
1	Oblique	Oblique	Parallelogram	$a \neq b, \gamma \neq 90^\circ$
2	Rectangular	1. Rectangular primitive 2. Rectangular centred	Rectangle	$a \neq b, \gamma = 90^\circ$
3	Square	Square	Square	$a = b, \quad \gamma = 90^\circ$
4	Hexagonal	Hexagonal	60°Rhombus	$a = b, \quad \gamma = 120^\circ$

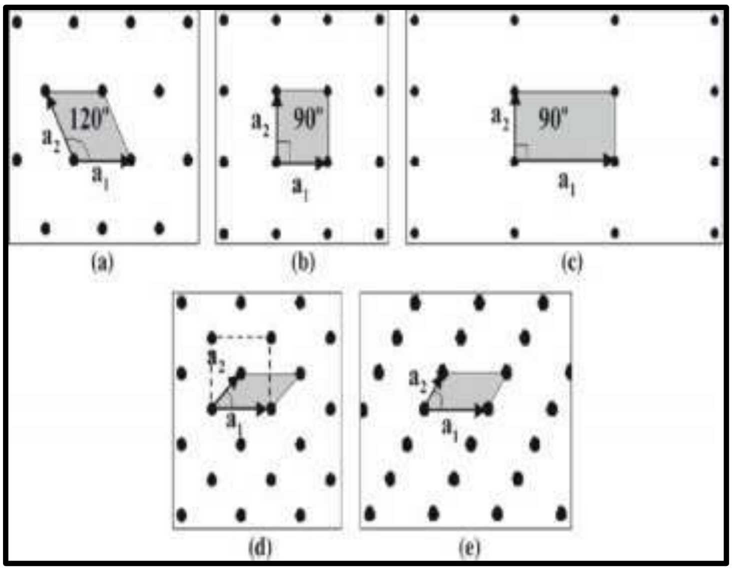

Figure 2.2: Two dimensional Bravais lattices (a)Hexagonal (b)Square (c)Rectangular primitive (d)Rectangular centred (e)oblique

(*Courtesy https://www.researchgate.net/*)

Three dimensional lattices

All the seven crystal systems of three-dimensional space are simple cubic, Tetragonal, orthorhombic, rhombohedral (trigonal), hexagonal, monoclinic and triclinic. These are shown in figure (1.3.4) in the form of their conventional unit cells. The symbols P, F, I represent simple or primitive, face-centered and body centered cells respectively. A base or end centered cell is that which has lattice points at corners and at one of the pairs of opposite faces. The seven Bravais lattices are listed in table in the decreasing order of symmetry given below;

- **Cubic**

The cubic crystal system is also known as the isometric system. The crystallographic axes used in this system are of equal length and are mutually perpendicular, occurring at right angles to one another. It contains simple, body centered, face centered unit cell. All crystals of the isometric system possess four 3-fold axes of symmetry. Examples of minerals which crystallize in the isometric system are halite, magnetite, and garnet. Other examples are Au, Cu, and NaCl.

- **Tetragonal**

Tetragonal crystal system is referred to three mutually perpendicular axes. The two horizontal axes are of equal length, while the vertical axis is of different length and may be either shorter or longer than the other two. Crystals of this system all possess a single 4-fold symmetry axis. It contains simple and body centered unit cell. Oxygen, calcium sulphate and tin oxide are the examples.

- **Orthorhombic**

Crystal systems are referred to three mutually perpendicular axes, each of which is of a different length than the others are orthorhombic. Crystals of this system uniformly possess three 2-fold rotation axes. KNO_3, $BaSO_4$ are the examples.

- **Monoclinic**

Crystals of the monoclinic system are referred to three unequal axes. Two of these axes are inclined toward each other at an oblique angle; these are usually depicted vertically. The third axis is perpendicular to the other two. The two vertical axes therefore do not intersect one another at right angles, although both are perpendicular to the horizontal axis. Monoclinic crystals demonstrate a single 2-fold rotation axis. Monoclinic crystal system includes pyroxene, amphibole, and orthoclase.

- **Triclinic**

Crystals of the triclinic system are referred to three unequal axes, all of which intersect at oblique angles. None of the axes are perpendicular to any other axis. Crystals of the triclinic system may be said to possess only a 1-fold symmetry axis, which is equivalent to possessing no symmetry at all. Examples include plagioclase, microcline, turquoise and amblygonite.

- **Trigonal**

Crystals of the trigonal system are referred to three equal axes; they are equally inclined to each other at an angle other than right angle. It contains one three-fold rotation axis. Examples are calcite, dolomite, low quartz, and tourmaline.

- **Hexagonal**

Hexagonal crystal system is referred to three crystallographic axes which intersect at 120° and a fourth which is perpendicular to the other three. This fourth axis is usually depicted vertically. Ruby, cinnabar, and graphite are some examples.

Table 2.2: Three dimensional Bravais Lattices

S.no.	**Crystal System**	**Lattice parameters**	**Bravais lattice**	**Examples**
1	Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90°$	Simple Body-centred Face-centred	Cu, Ag
2	Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	Simple Body-centred	TiO_2, β-Sn
3	Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	Simple Body-centred End-centred Face-centred	Ga, Fe_3O (cementite)
4	Rhombohedral or Trigonal	$a = b = c$ $\alpha = \beta = \gamma \neq 90°$	Simple	As, Sb, Bi
5	Hexagonal	$a = b \neq c$ $\alpha = \beta = 90°$, $\gamma = 120°$	Simple	Mg, Zn, Cd, NiAs
6	Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90° \neq \beta$	Simple End-centred	$CaSO_4.2H_2O$ (gypsum)
7	Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$	Simple	$K_2Cr_2O_7$

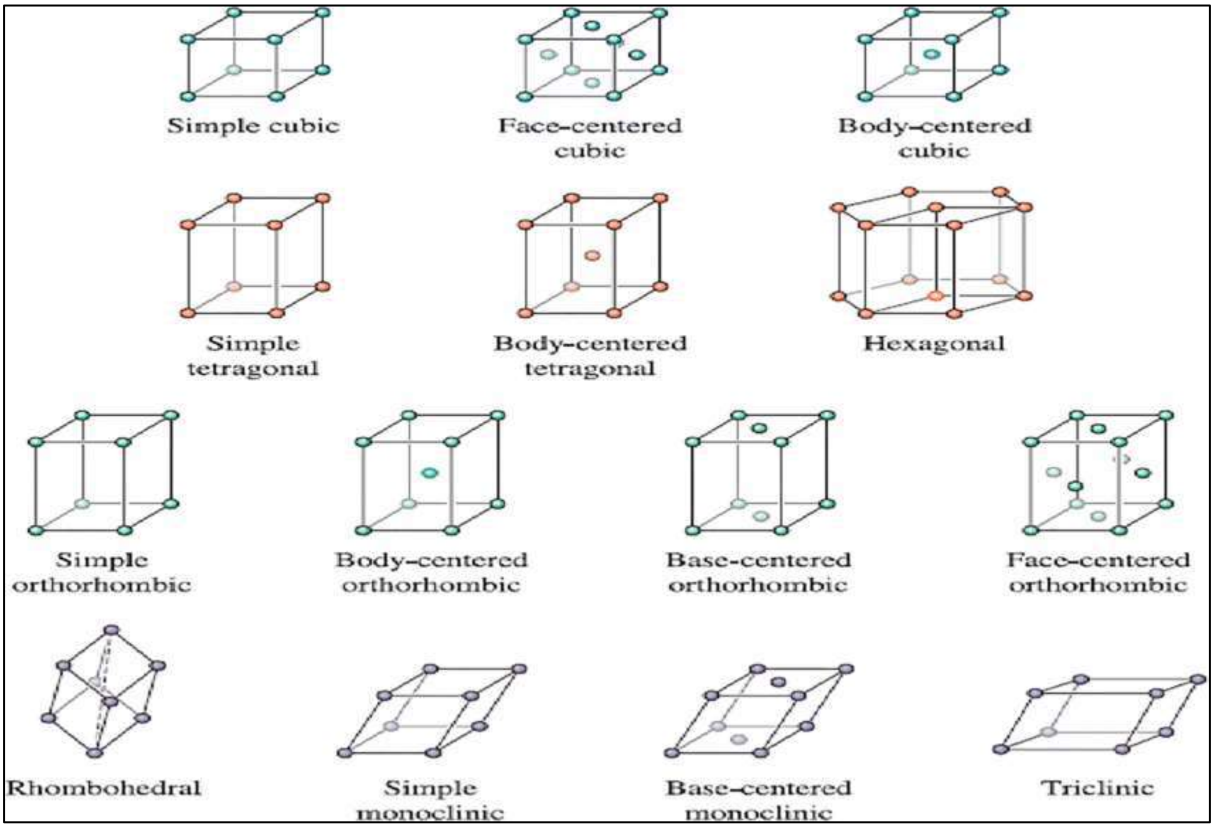

Figure 2.3: Three-dimensional Bravais Lattice
(Courtesy https://www.researchgate.net/publication/337197552)

2.2.3 Relation between lattice parameter and atomic radius in a unit cell.

- For simple cubic: $a = 2R$
- For Body-centered cubic(bcc): $a = \frac{4R}{\sqrt{3}}$
- For Face-centered cubic (fcc): $a = 2\sqrt{2}R$

Where a = lattice parameter and R= atomic radius

2.2.4 Packing Fraction

In crystallography, atomic packing factor, packing efficiency, or packing fraction is the fraction of volume in a crystal structure that is occupied by constituent particles. It is a dimensionless quantity and always less than unity.

$$\boldsymbol{Packing\ fraction = \frac{Volume\ occupied\ by\ the\ atoms\ in\ the\ unit\ cell}{Total\ volume\ of\ the\ unit\ cell}}$$

Packing fraction of

- ➔ Simple cubic = 52.36%
- ➔ BCC structure = 68.02%
- ➔ FCC structure = 74.05%

2.2.5 Relation between Lattice parameter and density of the unit cell

The relation is as follows;

$$\boldsymbol{\rho = \frac{nM}{a^3 N_A}} \qquad (2.1)$$

where,

ρ = density of the unit cell,
n = number of atoms on the unit cell,
M=molecular mass
a =lattice constant,
N_A =Avogadro number = $6.022 \times 10^{23} mol^{-1}$

2.3 X-ray crystallography

X-ray crystallography is the study of geometrical forms and physical properties of crystalline solids using X-rays. X-rays are electromagnetic waves whose wavelengths are in the neighborhood of 1A°. Except for the fact that their wavelength is so short they have the same physical properties as other electromagnetic waves such as optical waves. The wavelength of an X-ray is thus of the same order of magnitude as the lattice constants of crystals and it is this which makes X-rays useful in the analysis of crystal structures.

2.3.1 X-ray diffraction

When an atomic electron is irradiated by a beam of monochromatic x-rays it starts vibrating with a frequency equal to that of the incident beam. Since an accelerating charge emits radiations, the vibrating electrons presents inside s crystal become sources of secondary radiations having the same frequency as the incident x-rays. These secondary x-rays spread out in all possible directions. The phenomenon may also be regarded as scattering of x-rays by atomic electrons. If the wavelength of incident radiations is quite large compared with the atomic dimensions, all the radiations emitted by electrons shall be in phase with one another. The incident x-rays however have the same order of wavelength as that of the atomic dimensions; hence the radiations emitted by electrons are in general out of phase with one another. These radiations may therefore undergo constructive or destructive interference producing maxima or minima in certain directions.

2.3.2 The Bragg's treatment: Bragg's law

In 1912 W.H Bragg and W.L Bragg put forward a model which generates the conditions for diffraction in a very simple way. They pointed that a crystal maybe divided in to various sets of parallel planes. The directions of diffraction lines can then be accounted for if x-rays are considered to be reflected by such a set of parallel atomic planes followed by the constructive interference of the resulting reflected rays. Thus, the problem of diffraction of X-rays by the atoms was converted in to the problem of reflection of x-rays by the parallel atomic planes. Hence the words ‘diffraction’ and ‘reflection’ are mutually Inter changeable in Bragg's treatment. Based on these considerations Bragg derived a simple mathematical relationship which serves as a condition for the Bragg reflection to occur. This condition is known as Bragg’s law.

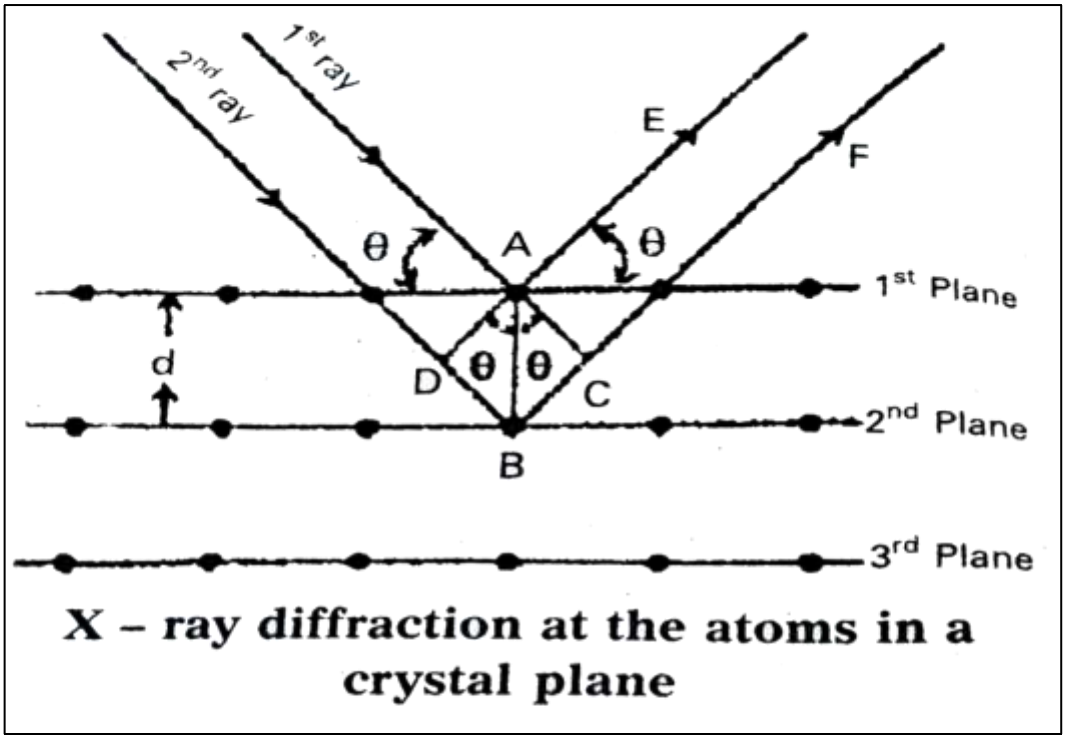

Figure 2.4: Bragg's reflection of x-rays from the atomic planes.
(Courtesy https://www.doubtnut.com/question-answer-chemistry/)

To obtain the Bragg's law consider a set of parallel atomic planes with inter- planar spacing d and having Miller indices (h k l). Let a parallel beam of x-rays of wavelength λ be incident on these parallel planes at a glancing angle ϴ Such that the rays lie in the plane of the paper. Consider a two such rays 1 and 2 which Strike the first two planes and get partially reflected at the same angle ϴ in accordance with the Bragg's treatment as shown in Figure 2.4**.** The diffraction is the consequence of constructive interference of these reflected rays. Let PL and PM be the perpendiculars drawn from the point P on the incident and reflected portions of ray 2 respectively.

The path difference between rays 1 and 2 is given by DB+BC

Since DB = BC = $d\ sin\theta$

We get,

Path difference = $2d\ sin\theta$

For constructive interference of rays 1 and 2 the path difference must be an integral multiple of wavelength λ.

$$\boldsymbol{2d\, sin\theta = n\lambda} \tag{2.2}$$

Where n is an integer. This equation is called the Bragg's law.

2.3.3 Methods of X-Ray Diffraction

The phenomenon of x-ray diffraction is employed to determine the structure of solids as well as for the study of x-ray spectroscopy. The underlying principle in both the cases is the Bragg's law as given by equation,

$$\boldsymbol{2d\, sin\theta = n\lambda}$$

Considering only the first order reflections from all the possible atomic planes, real or fictitious, the Bragg's law may be written as

$$\boldsymbol{2d\, sin\theta = \lambda} \tag{2.3}$$

The reflection take place for those values of d,θ *and* λ which satisfy the above equation. For structural analysis, x-rays of known wavelength are employed and the angles for which reflection take place are determined experimentally. The d values corresponding to these reflections are then obtained from the Bragg's equation. Using this information, one can proceed to determine the size of the unit cell and the distribution of atoms within the unit cell. In the x-ray spectroscopy, x-rays are incident on a particular cleavage surface of a single crystal so that the interplanar spacing d is known. The angle for which reflections take place are determined experimentally. The wavelength λ of the incident x-rays is then obtained from Bragg's equation.

It may be noted that the x-rays used for diffraction purposes should have wavelength which is the most appropriate for producing diffraction effects. Since Sinθ should be less than unity,

Bragg's law yields,

$$\boldsymbol{\lambda < 2d} \tag{2.4}$$

Normally, d~3 Å. Therefore,

$$\boldsymbol{\lambda < 6\text{Å}} \tag{2.5}$$

Longer wavelength x-rays are unable to resolve the details of the structure on the atomic scale whereas shorter wavelength x-rays are diffracted through angles which are too small to be measured experimentally.

In x-ray diffraction studies, the probability that the atomic planes with right orientations are exposed to x-rays is increased by adopting one of the following methods:

1. A single crystal is held stationary and a beam of white radiations is inclined on it at a fixed glancing angle θ, i.e., θ is fixed while λ varies. Different wavelengths present in the white radiations select the appropriate reflecting planes out of the numerous present in the crystal such that the Bragg's condition is satisfied. This technique is called the Laue's technique.
2. A single crystal is held in the path of monochromatic radiations and is rotated about an axis, i.e., λ is fixed while θ varies. Different sets of parallel atomic planes are exposed to incident radiations for different values of θ and reflections take place from those atomic planes for which d and θ satisfy the Bragg's law. This method is known as the rotating crystal method.
3. The sample in the powdered form is placed in the path of monochromatic x-rays, i.e., λ is fixed while both θ and d vary. Thus, a number of small crystallites with different orientations are exposed to x-rays. The reflections take place for those values of d, θ and λ which satisfy the Bragg's law. This method is called the powder method.

➢ **The Laue’s method**

An experimental arrangement used to produce Laue's patterns is shown in Figure. It consists of a flat plate camera which contains a collimator with a fine hole to obtain a very fine beam of x-rays. The sample is placed on a goniometer which can be rotated to change the orientation of the single crystal. Two flat photographic films are used, one for receiving the transmitted diffracted beam and the other for receiving the reflected diffracted beam for back reflection experiments. Such experiments are performed particularly when there is excessive absorption of x-rays in the crystal.

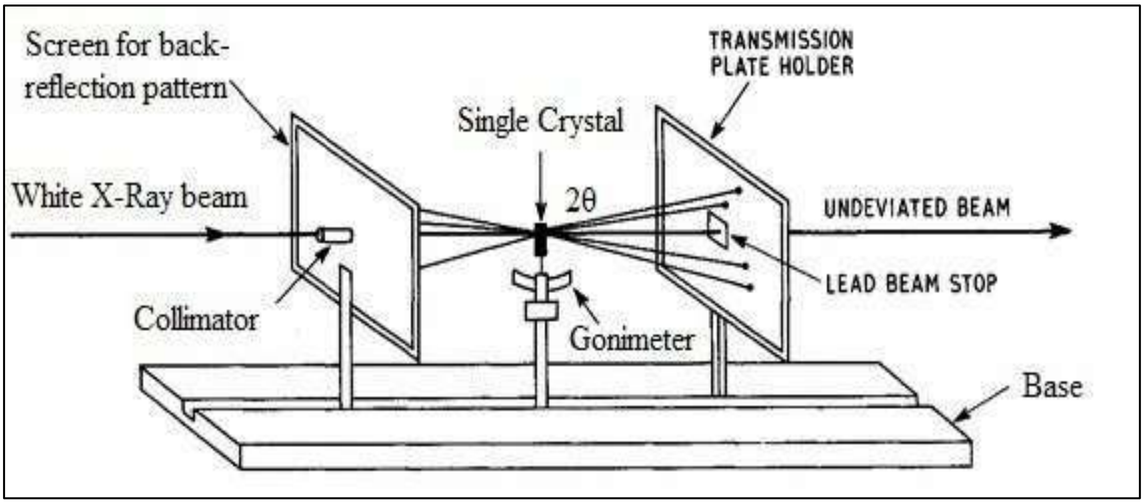

Figure 2.5: Schematic representation of Laue method of x-ray diffraction.
(*Courtesy https://www.quora.com/How-is-the-Laue-method-used-in-studying-crystals*)

Initially a single crystal specimen having dimensions of the order of 1mm x 1mm x 1mm is held stationary in the path of white x-rays having wavelengths ranging from 0.2 to 2 Å. Since the crystal contains a number of sets of parallel atomic planes with different interplanar spacings, diffraction is possible for certain values of λ and d which satisfy the Bragg's condition. Thus, diffraction spots are produced on the photographic films as shown in Figure. The crystal can be rotated with the help of goniometer to change its orientation with respect to the incident beam. By doing so, the diffraction condition may be satisfied for a new set of atomic planes and hence a different type of pattern may be obtained on the photographic film. The symmetry of the crystal is, however, reflected in each pattern. The Laue's method is mostly used to determine the crystal symmetry. For example, if a crystal having four-fold axial symmetry is oriented so that its axis is parallel to the beam, the resulting Laue's pattern also exhibits the four-fold symmetry. The symmetry of the pattern helps to determine the shape of the unit cell. It is, however, not practicable to determine the structure of the crystal by this method. It is because a number of wavelengths may be reflected from a single plane in different orders and may superpose at a single point resulting in the loss of a number of reflections. The symmetry of the Laue's pattern also helps to orient the crystals for various solid- state experiments. Another application of the Laue's method is the determination of imperfections the crystal. An imperfect or strained crystal has atomic crystal planes which are not exactly plane but are slightly curved. Thus, instead of sharp diffraction spots one gets streaks in the Laue's pattern. This type of streaking on Laue's photographs is called *asterism.*

- **Rotating crystal method**

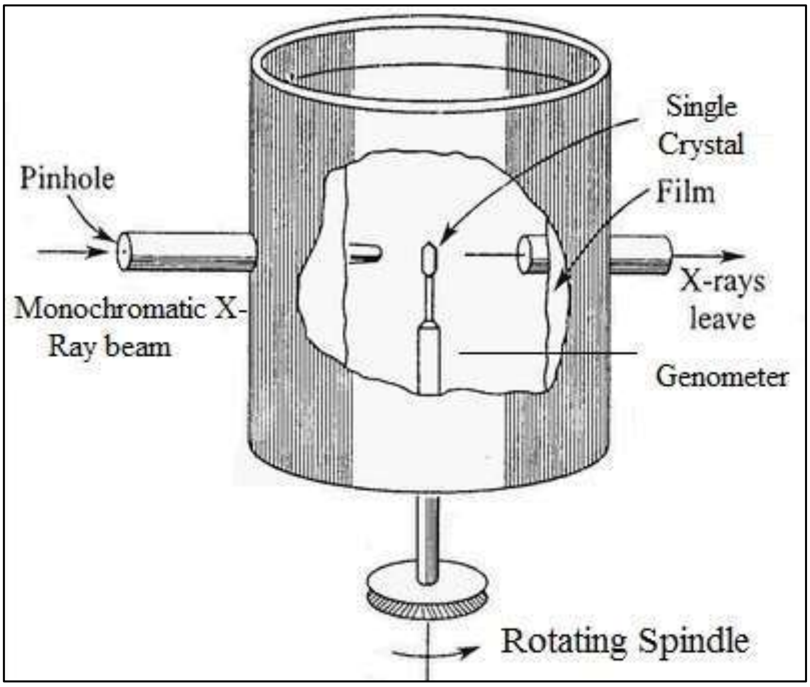

Figure 2.6: Schematic representation of Rotating crystal method of x-ray diffraction. *(Courtesy https://www.tutorsglobe.com/homework-help/physics/experimental-crystal-structure-determination-75516.aspx)*

In this method, a monochromatic beam of x-rays is incident on a single crystal mounted on a rotating spindle such that one of its crystallographic axes coincides with the axis of rotation which is kept perpendicular to the direction of the incident beam. The single crystal having dimensions of the order of 1 mm is positioned at the center of a cylindrical holder concentric with the rotating spindle as shown in Figure. A photographic film is attached at the inner circular surface of the cylinder. The diffraction takes place from those planes which satisfy the Bragg's law for a particular angle of rotation. The planes parallel to the axis of rotation diffract the incident rays in a horizontal plane. However, reflections cannot be observed for those planes which always contain the incident beam. The planes inclined to the rotation axis produce reflections above or below the horizontal plane depending upon the angle of inclination. The horizontal lines produced by diffraction spots on the photographic film are called layer lines. If the crystal is positioned such that its c-axis coincides with the axis of rotation, all the planes with Miller indices of the type (h k 0) will produce the central layer line. Likewise, the planes having Miller indices of the type (h k 1) and (h k $\bar{1}$) will produce the layer lines above and below the central line respectively, and so on. These layer lines are shown in Figure. The vertical spacing between the layer lines depends on the distance between the lattice points along the c-axis. Hence the distance **c** can be measured from the photographic film. Similarly, one can determine the translation vectors **a** and **b** on mounting the crystal along **a** and **b** axes respectively. Thus, the dimensions of the unit cell can be easily determined.

➢ Powder method

This is the most widely used diffraction method to determine the structure of crystalline solids. The sample used is in the form of a fine powder containing a large number of tiny crystallites with random orientations. It is prepared by crushing the commonly available polycrystalline material, thus eliminating the tedious process of growing the single crystals.

The experimental arrangement used to produce diffraction is shown in figure. It consists of a cylindrical camera, called the Debye-Scherrer camera, whose length is small as compared to the diameter. The finely powdered sample is filled in a thin capillary tube or is simply pasted on a wire by means of a binder and mounted at the center of the camera. The capillary tube or wire and the binder should be of a non-diffracting material. A collimated beam of monochromatic x-rays is produced by passing the x-rays through a filter and a collimator. The x-rays enter the camera through the collimator and strike the powdered sample. Since the specimen contains a large number of small crystallites (-10^{12} in 1 mm^3 of powder sample) with random orientations, almost all the possible θ and d values are available. The diffraction takes place for those values of d and θ which satisfy the Bragg's condition, i.e., $2d \sin\theta = n\lambda$, λ, being a constant in this case. Also, since for particular value of the angle of incidence θ, numerous orientations of a particular set of planes are possible, the diffracted rays corresponding to fixed values of θ and d lie on the surface of a cone with its apex at the sample and the semi vertical angle equal to 2θ. Different cones are observed for different sets of d and θ for a particular value of n, and also for different combinations of θ and n for a particular value of d. The transmitted x-rays move out of the camera through an exit hole located diametrically opposite to the entrance hole. A photographic film is attached to the inner side of the curved surface of the camera. Each cone of the reflected beam leaves two impressions on the film which are in the form of arcs on either side of the exit hole with their centers coinciding with the hole. Similarly, cones produced by back-reflected x-rays produce arcs on either side of the entrance hole. If the sample consists of coarse grains rather than fine particles, a spotty diffraction pattern may be obtained. This is because a sufficient number of crystallites with all possible orientations may not be available in a coarse-grained sample. In such a case, the sample has to be rotated to obtain almost continuous diffraction arcs. The film is exposed for a long time (a few hours) in order to obtain reflected lines of sufficiently high intensity. It is then removed from the camera and developed. The arcs produced by reflected rays appear dark on the developed film. The angle θ corresponding to a particular pair of arcs is related to the distance S between the arcs as

$$\mathbf{4\theta\ (radians) = S/R} \tag{2.6}$$

where R is the radius of the camera. If θ is measured in degrees, the above equation is modified as

$$\mathbf{4\theta\ (degrees) = (57.296S)/R} \tag{2.7}$$

The calculations can be made simpler by taking the radius of the camera in multiples of 57.296. For example, taking R= 57.296 mm, we get

$$\mathbf{\theta\ (degrees) = S\ (mm)/4} \tag{2.8}$$

Thus one-fourth of the distance between the corresponding arcs of a particular pair in mm is a measure of the angles θ in degrees. Knowing all the possible $\theta's$ and considering only the first order reflections from all the possible planes, Bragg's equation is used to calculate the interplanar spacing for various sets of parallel planes which contribute to these reflections. Thus, we have

$$\mathbf{d=\lambda / (2\ Sin\theta)} \tag{2.9}$$

These d values are used to determine the space lattice of the crystal structure.

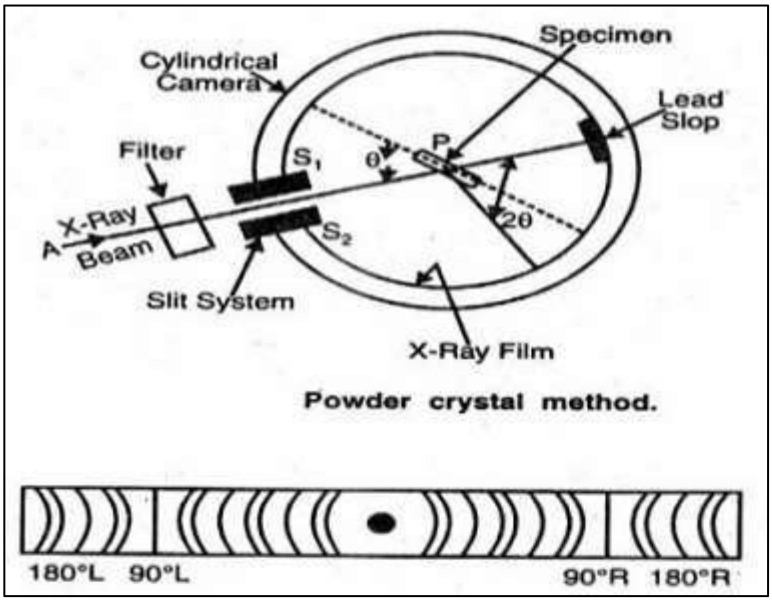

Figure 2.7: Schematic representation of Powder method of x-ray diffraction.

(*Courtesy* [*https://www.tutorsglobe.com/homework-help/physics/experimental-crystal-structure-determination-75516.aspx*](https://www.tutorsglobe.com/homework-help/physics/experimental-crystal-structure-determination-75516.aspx))

In modern x-ray diffractometers, the photographic film is replaced by a radiation detector, such as ionization chamber or scintillation detector, which records the positions and relative intensities of the various reflected lines as a function of the angle 2θ.The detector is mounted on a goniometer and is capable of rotation above the sample at different speeds. The whole system is computerized. The availability of a lot of software makes the system versatile.

➢ **Bragg's x-ray spectrometer**

Bragg's spectrometer used to determine the wavelength of x-rays is shown in Figure 2.8. Bragg's spectrometer is similar in construction to an ordinary optical spectrometer.

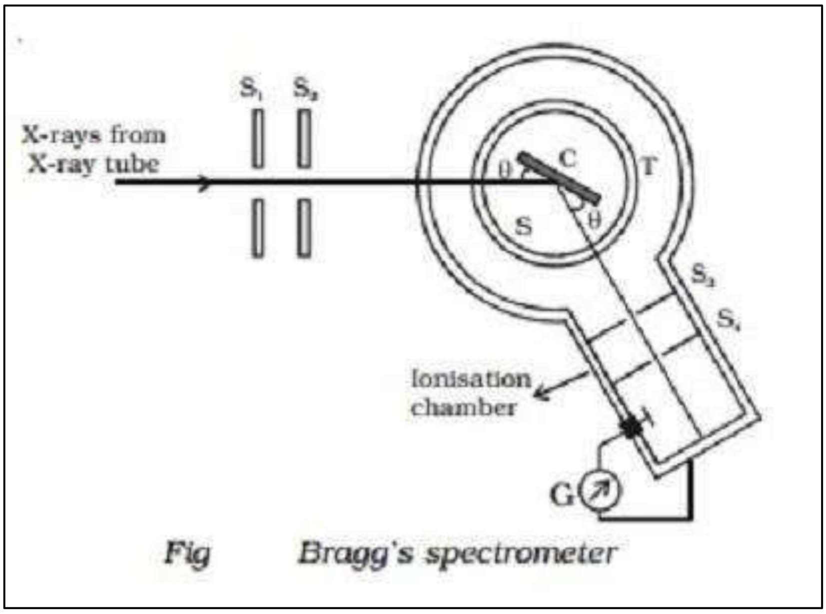

Figure 2.8: Schematic representation of Bragg's Spectrometer

(*Courtesy https://www.sbistudy.com/bragg-method*)

X-rays from an x-ray tube are made to pass through two fine slits S_1 and S_2 which collimate into a fine pencil. This fine x-ray beam is then made to fall upon the crystal 'C' (usually sodium chloride crystal) mounted on the spectrometer table. This table is capable of rotation about a vertical axis and its rotation can be read on a circular graduated scale S. The reflecting beam after passing through the slits S_3 and S_4 enters the ionization chamber. The x-rays entering the ionization chamber ionize the gas which causes a current to flow between the electrodes and the current can be measured by galvanometer G. The ionization current is a measure of the intensity of x-rays reflected by the crystal.

The ionization current is measured for different values of glancing angle θ. A graph is drawn between the glancing angle θ and ionization current.

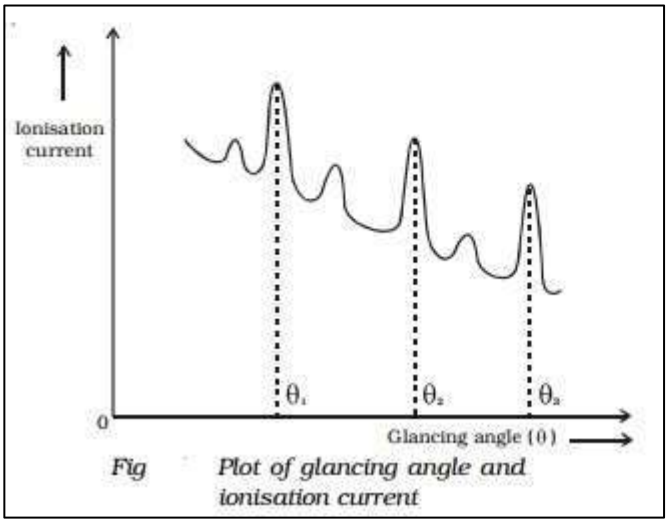

Figure 2.9: Plot of glancing angle v/s ionization current.
(*Courtesy https://www.sbistudy.com/bragg-method*)

For certain values of glancing angle, the ionization current increases abruptly. The first peak corresponds to first order, the second peak to the second order and so on. From the graph, the glancing angles for different orders of reflection can be measured. Knowing the angle θ and the spacing d for the crystal, wavelength of x-rays can be determined.

2.3.4 Advantages of x-ray diffraction

- It is the least expensive, most convenient and most widely used method to determine crystal structure.
- It is the best method for phase analysis.
- X-rays are not absorbed very much by air, so the sample need not be in an evacuated chamber.
- XRD is a non-destructive technique.
- It is a rapid and powerful technique for identifying unknown minerals and materials.
- It only requires preparation of a minimal sample for analysis. Interpreting the resulting data is relatively straightforward. The x-ray diffractometer continuously records data during the process, and presents peak positions and x-ray counts in a table.
- XRD measuring instruments are widely available.
- XRD can be used to determine the orientation of the individual grains of a crystal and to identify crystal structures in unknown substances.

- This technique will determine the internal stress, the size and shape of small crystalline areas, and measure the average spacings between the layers of rows of atoms in samples. It can determine their minerology.
- The Bragg's equation calculates the d-spacing of each peak. Once you have all the d-spacings for the sample, you can compare these readings to d-spacings of known materials to identify the samples.
- All structural information is in reciprocal space where we collect and measure (h k l) intensities, then solve and refine a crystal structure.

2.3.5 Disadvantages of x-ray diffraction

- X-rays are hazardous to use.
- X-ray diffraction has size limitations. It is much more accurate for measuring large crystalline structures rather than small ones (smaller ones that are present only in trace amounts will often go undetected by XRD readings)
- X-rays do not interact very strongly with lighter elements.
- To best identify an unknown powder material, the sample should be homogenous.
- Typically, XRD analysis requires access to standard reference data.
- Preparation of samples requires grinding them down to a powder.
- If the crystal sample is non-isometric, then the indexing of patterns can be complex when determining unit cells.
- The intensity of XRD is 10^8 times less than that of electron diffraction.

2.3.6 Applications of XRD

The analytical applications of x-ray diffraction are numerous. The method is non-destructive and gives information on the molecular structure of the sample. Perhaps its most important use has been to measure the size of crystal planes. The patterns obtained are characteristic of the particular compounds from which the crystal was formed.

- X-ray powder diffraction is most widely used for the identification of unknown crystalline materials. Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology.

- It can be used to differentiate between crystalline and amorphous materials.
- It is used for the determination of structure of crystalline materials.
- It is used for the determination of electron distribution within atoms, and throughout the unit cell.
- It can be used for the determination of orientation of single crystals.
- It is used for the determination of texture of poly-grained materials.
- It is used for the measurement of strain and small grain size, etc.
- It can be used for the identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically.
- It can also be used for the determination of sample purity.

With specialization techniques, XRD can be used to:

- Determine crystal structures using Rietveld refinement.
- Determine of modal amounts of minerals (quantitative analysis)
- Characterize thin film samples by:
    - Determining lattice mismatch between film and substrate and to inferring stress and strain.
    - Determining dislocation density and quality of the film by rocking curve measurements.
    - Measuring super lattices in multilayered epitaxial structures.
    - Determining the thickness, roughness and density of the film using glancing incidence x-ray reflectivity measurements.
- Make textural measurements, such as the orientation of grains, in a polycrystalline sample.

Miscellaneous applications include:

- Lattice parameter determination
- Purity/quality control of materials
- Determination of crystallinity of polycrystalline materials
- Particle size determination
- Soil classification based on crystallinity.
- Used to access the weathering and degradation of natural and synthetic minerals designed experiments, the factors responsible for the degradation can be revealed.

- Corrosion products can be studied by this method. When metal samples are exposed to the atmosphere, they are susceptible to corrosion.
- Tooth enamel and dentine can be examined by XRD.
- Analysis of industrial dust.
- Structure of DNA and RNA.

2.4 Dielectric properties of $NiTiO_3$

Dielectric resonators (DR) are dielectric bodies of high permittivity and high quality-factor (Q-factor) that can be used as energy storage devices. Ceramic DRs in the form of cylindrical or rectangular pucks is important in size reduction application compared to its metallic counterpart. Three important characteristics of an ideal DR are relative permittivity (ε_r), dielectric loss ($tan\delta$) & resonant frequency (τ_f). High relative permittivity (ε_r) is appreciable for resonator applications and low relative permittivity (ε_r) for millimeter wave applications. Low dielectric loss ($tan\delta$) and low temperature variation of resonant frequency (τ_f) values favor resonator applications. Hence the study of dielectric properties plays an important role in ceramic industry.

The dielectric properties of $NiTiO_3$ can be measured using an LCT meter. $NiTiO_3$ has a dielectric constant of 19.3 and a dielectric loss of 0.0002 at 1 MHz. $NiTiO_3$ has a dielectric constant of 17.8 and a Quality factor of 13000 GHz at 5 GHz.

Chapter 3

METHODOLOGY AND CHARACTERIZATION OF NICKEL TITANATE CERAMIC

3.1. Introduction

Ceramic processing is used to produce commercial products that are very diverse in size, shape, detail, complexity, and material composition, structure, and cost. The purpose of ceramics processing to an applied science is the natural result of an increasing ability to refine, develop, and characterize ceramic materials.

Ceramics are typically produced by the application of heat upon processed clays and other natural raw materials to form a rigid product. Ceramic products that use naturally occurring rocks and minerals as a starting material must undergo special processing in order to control purity, particle size, particle size distribution, and heterogeneity. These attributes play a big role in the final properties of the finished ceramic. Chemically prepared powders also are used as starting materials for some ceramic products. These synthetic materials can be controlled to produce powders with precise chemical compositions and particle size.

The next step is to form the ceramic particles into a desired shape. This is accomplished by the addition of water and/or additives such as binders, followed by a shape forming process. Some of the most common forming methods for ceramics include extrusion, slip casting, pressing, tape casting and injection molding. After the particles are formed, these "green" ceramics undergo a heat-treatment (called firing or sintering) to produce a rigid, finished product. Some ceramic products such as electrical insulators, dinnerware and tile may then undergo a glazing process. Some ceramics for advanced applications may undergo a machining and/or polishing step in order meet specific engineering design criteria.

There are numerous methods for creating ceramic powders. Mechanical methods and chemical approaches make up the two categories. Ball Milling and Conventional solid-state Reaction Techniques constitute the Mechanical approach. Chemical methods include synthesis techniques like sol-gel method, co-precipitation method, hydrothermal synthesis, combustion routes etc.

In this project, $NiTiO_3$ ceramic has been prepared using conventional solid-state method.

3.1.1. Solid State Synthesis of Ceramic

Solid state reaction is a common synthesis method to obtain poly crystalline material from solid reagents. Usually, a very high temperature is used to induce the reaction. Chemical and morphological characteristics of the reactants, such as their reactivity, surface area, and free energy change with the solid-state reaction, as well as other reaction parameters including temperature, pressure, and the reaction environment, all influence solid-state reactions. The ease of use and high-volume production are two benefits of the solid-state reaction process.

This method requires very high temperatures, which are generally attained by resistance heating and therefore may affect the fineness of the product material thus produced. The procedure involves grinding of powder oxides, carbonates, oxalate also other compounds containing the relevant metals in appropriate proportions, followed by heating of the mixture at the desired temperature, after palletizing the material. By this method several metal sulphides oxides, phosphide materials can be prepared. Platinum, silica and alumina containers are used for the synthesis of oxide materials.

This method has some disadvantages. There is no phase purity of the product. Sometimes the reactants and products form another phase. So, it becomes difficult to obtain compositionally homogeneous products by the ceramic techniques.

3.1.2 Preparation Methods of Ceramics

(a) Selection of Raw Materials

Raw material is essential in ceramics in various aspects. For producing high quality ceramics at minimal cost, use of proper raw material is crucial. The characteristics of raw materials can be affected by various factors. For the proper selection of raw materials, it is very important to know about the product specification as well as their production method. The chemical composition in a powder should be fixed and constant. The quality of the ceramic product can be affected by the imperfections in raw materials and especially when it comes to the structural applications. The rate and temperature of sintering is directly affected by the particle size. Small particles tend to form strong aggregates if it is handled improperly. Fracture origins are very detrimental in the production of ceramics and aggregates tend to form these. Raw materials with normally the same chemical composition may be significantly affected by phase. The activity of the powder is affected by temperature phase. It is higher in low temperature phase and lower in high temperature phase.

(b) Powder Preparation

The first step is to prepare the ceramic sample by weighing the exact amount of the constituent materials. Eliminating the aggregates and reducing particle size by mixing is the next step. The constituents of ceramic body need to be mixed so that the neighboring particles can inter-diffuse, which is essential for compound formation during calcination. The lack of homogeneity in ceramics can greatly affect the physical properties of the ceramics. The constituent particles are well mixed with distilled water in an agate mortar for better homogeneity. Then the mixture is dried by slow evaporation by keeping it in air for some time.

(c) Calcination

Calcination is a process in which a substance is heated under controlled temperature and environment. This is an endothermic decomposition reaction in which an oxy-salt such as carbonates or hydroxides decomposes into a solid product, releasing the gaseous products. The particle size, its distribution, extent of agglomerates and morphology are usually established during this decomposition reaction. The precursors interact by inter-diffusion of their ions in calcination process. During calcination, moisture and volatile impurities are removed and thermo-chemical reaction between constituent oxides takes place to form the desired compounds. Double calcination step is often adopted to achieve homogeneous single-phase compound.

(d) Grinding

Grinding process usually accomplished by suitable means like ball milling, agate mortar and pestle, etc. It helps to combine the constituent materials and homogenize the compositional variation arise during calcination. The ceramics can have larger inter-granular voids and low density through coarse grinding. If the grinding is too fine, the colloidal properties may interfere with subsequent forming operations.

3.2. Synthesis of Nickel Titanate Ceramic

The $NiTiO_3$ ceramics was prepared using conventional solid state reaction methods. High purity chemicals NiO (Aldrich, 99 %) and TiO2 (Aldrich, 99.9 %) were used as starting powders. Weighing the exact amount of the constituent materials of the sample is the first step in the preparation of the ceramic sample. The stochiometric equation used for the synthesis of $NiTiO_3$ phosphor can be written as;

$$\boldsymbol{NiO + TiO_2 \xrightarrow{yields} NiTiO_3}$$

Calculations

Molecular weight of NiO = 74.693 g/mol
Molecular weight of TiO_2 = 79.866 g/mol
Molecular weight of $NiTiO_3$ = 154.557 g/mol
In order to prepare 10 g of $NiTiO_3$,
Required amount of NiO = 4.833 g
Required amount of TiO_2 = 5.167 g

By using an electronic balance 4.833 g of NiO and 5.167 g of TiO_2 were weighed out. They were mixed together in an agate mortar using distilled water as medium. Mixed it well for 2 hours, for eliminating aggregates, reducing particle size and to attain better homogeneity. The wet mixture was dried in a hot air oven. The dried powder was collected and transferred to alumina crucible and calcined for 5 h at 1025^0 C in a high temperature furnace. The sample was naturally cooled to room temperature to obtain the final product. The calcined powder was then ground for XRD analysis.

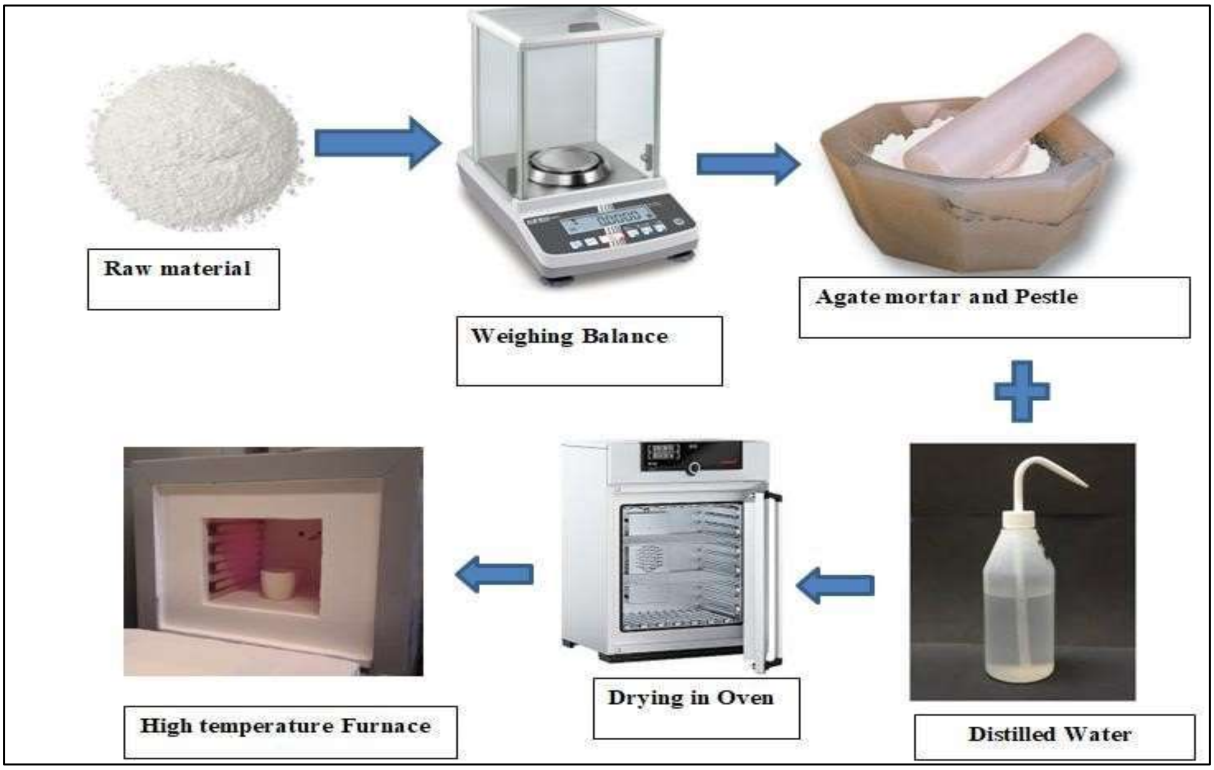

Figure 3.1: Schematic representation of ceramic synthesis.

3.3. Characterization of Ceramic Using X-Ray Diffraction Method

X-ray diffraction is an extremely important technique used for the characterization of both crystalline and non-crystalline materials. The crystalline structure and phase purity of the synthesized ceramic specimen has been checked. The X-ray diffraction (XRD) patterns of the sintered samples were recorded after grinding them into fine powder using a Philips X-ray diffractometer with Cu Kα radiation (λ=1.54 A^0) radiation with Ni filter shown in Figure 3.2. The pattern was collected over the 2Ө ranging from 10-80 degrees with a step size of 0.010 and a scanning rate of 4.00/min. X-Ray diffraction technique was used to identify and characterize the compound based on their diffraction pattern. We study diffraction of X-rays only in connection with the direct exploration of the interior of the crystal. Such a study is possible because the intensities of diffracted beams and their directions are related to the atomic arrangements in crystal. Thus, measurements of their intensities and directions would provide the desired information about the crystals. The powdered sample, CuKα radiation as incident beam, a goniometer, and a detector together give the diffraction patterns. The powdered sample stuck on a rotary slide provide all possible orientations, the angles of incidence is controlled by goniometer and the diffracted beam is received by the detector. The intensities of diffracted beam at different angle of incidence determine the peak's height. The obtained d and 2Θ values are then compared with standard Powder Diffraction File (JCPDS File). From this data, we can identify the structure and phase purity of the synthesized ceramic.

Fig. 3.2: X-ray Diffractometer

(Courtesy https://www.bruker.com/en/products-and-solutions/diffractometers-.html)

Chapter 4

RESULTS AND DISCUSSION

4.1. X-ray diffraction (XRD)

XRD patterns of $NiTiO_3$ ceramic is shown in Figure 4.1. All the diffraction peaks of the synthesized ceramic are in good agreement with standard ICDD card no. 00-033-0960. The structure of the ceramic is Rhombohedral with space group $R\bar{3}$(148) and having six formula units per unit cell. No peaks from any impurity phase were detected which confirms the formation of single-phase ceramic. The lattice parameters are a: 5.030Å and c: 13.790Å. The prominent peaks in the XRD patterns correspond to (012), (104), (110), (113), (024), (116) (018), (214), (300), (10 10) and (220) planes of the synthesized ceramic. The standard and measured 2θ values, and d values along with (h k l) values are tabulated in Table 1.

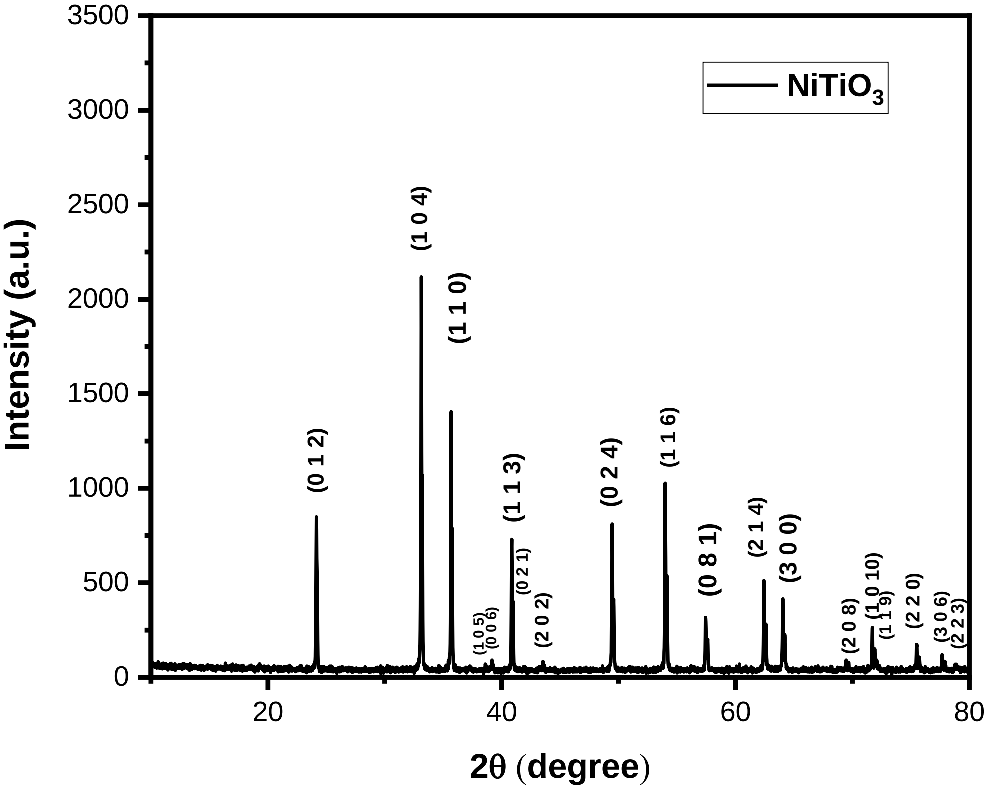

Figure 4.1: XRD patterns of $NiTiO_3$ ceramic

Table 4.1: Comparison of 2θ values and d values of synthesized $NiTiO_3$ and standard data from ICDD card 00-033-0960.

2θ(degree)		**Interplanar distance (d) values**		**hkl**
Observed	**Standard**	**Observed (A⁰)**	**Standard (A⁰)**	
24.201	24.131	3.715	3.685	(0 1 2)
33.141	33.089	2.780	2.705	(1 0 4)
35.663	35.655	2.605	2.516	(1 1 0)
38.713	38.576	2.412	2.332	(0 1 5)
39.194	39.151	2.334	2.299	(0 0 6)
40.941	40.855	2.278	2.207	(1 1 3)
41.986	41.967	2.198	2.151	(0 2 1)
43.550	43.537	2.112	2.077	(2 0 2)
49.571	49.447	1.900	1.841	(0 2 4)
54.141	54.016	1.756	1.696	(1 1 6)
57.553	57.458	1.665	1.602	(0 1 8)
62.531	62.449	1.532	1.485	(2 1 4)
64.172	64.068	1.522	1.452	(3 0 0)
69.490	69.475	1.414	1.351	(2 0 8)
71.724	71.739	1.397	1.314	(1 1 10)
72.131	72.119	1.356	1.308	(1 1 9)

75.550	75.548	1.302	1.257	(2 2 0)
77.719	77.735	1.265	1.227	(3 0 6)
78.872	78.851	1.241	1.212	(2 2 3)

Chapter 5

CONCLUSIONS

5.1 Conclusions

Nickel Titanate ceramic has been synthesized using solid state reaction method. The phase composition of the ceramic prepared was identified using X-ray diffraction method. No peaks from any impurity phase are detected which confirms the formation of single-phase ceramic. The lattice parameters are a: 5.030Å and c: 13.790Å. Synthesized ceramics have hexagonal symmetry with $R\overline{3}$ (148) space group.

5.2 Scope for Future Work

The prepared ceramic material can be subjected to study the dielectric properties at 1 MHz as well as in the gigahertz range. The study of variation in dielectric properties with doping of ceramic can also be encouraged. For low temperature cofired ceramic applications, the preparation temperature of nickel titanate ceramics can be lowered by the addition of suitable glass.

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