# Study of variation in structural, vibrational and optical properties of Ba doped TiO<sub>2</sub>, $Ba_xTi_{(1-x)}O_{\delta}$ .

### A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Science

> by AMITESH GIHAR



DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE **JUNE, 2020** 



## **INDIAN INSTITUTE OF TECHNOLOGY INDORE**

### **CANDIDATE'S DECLARATION**

I hereby certify that the work which is being presented in the thesis entitled **Study of variation in** structural, vibrational and optical properties of Ba doped TiO<sub>2</sub>, Ba<sub>x</sub>Ti<sub>(1-x)</sub>O<sub>8</sub>. in the partial fulfillment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted in the DISCIPLINE OF PHYSICS, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from JULY, 2019 to JUNE, 2020 under the supervision of Dr. Somaditya Sen, Associate Professor.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.



**AMITESH GIHAR** 

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This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

28<sup>th</sup> June 2020

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## ACKNOLEDGEMENTS

Before saying anything, first and foremost all my innumerable thanks to almighty God to for his blessings and guidance at every stage of my life. All my respect for God for enlightening our soul with the essence of faith and showering all his blessings upon us and for having enriched me with his knowledge and wisdom to complete this thesis in a successful manner.

At first, I would like to express my deepest gratitude to my thesis supervisor **Dr. Somaditya Sen**, Associate professor, Indian Institute of Technology, Indore, initially to accept me for my M.Sc. project under his supervision and further for his continuous guidance, helpful encouragement during my project work. I will always be thankful to him for helping to build confidence in myself, for teaching life lessons in his leisure time and how to be a seeker and consistent in the research field. It was an honour to work with him. Without his ideas, it was not possible to prepare this thesis. I am so much fortunate to have his guidance in my entire research.

Further, I am sincerely thankful to my PSPC members **Dr. Preeti A. Bhobe** and **Dr. Sanjay Kumar Singh** for their timely guidance and kind help during my research work.

I am extremely thankful to my lab members Mr. Ruhul Amin, Mr. Prashant Kumar Mishra, both of them as my elder brothers, Dr. E. G. Rini, Ms. Sania Ayaz, Ms. Koyal Suman, Mr. Jayaditya, Mr. Ananta Paul, Mr. Bungkiu Kissinquinker, Mr. Prashant Gupta and Mr. Emin Varghese to create an unforgettable and pleasurable memory during lab work which I am going to miss so much.

And finally, I express my sincere heartfelt gratitude to my parents and siblings for their loving and caring support at every stage of my life. I am extremely thankful to God for giving me such a supportive family to stand with me in the best and worst phases of my life.

AMITESH GIHAR

## **DEDICATION**

With the grace of almighty dedicating to my parents and to my siblings This humble work is a sign of my love for you.

### Abstract

A complete phase transition of pure  $TiO_2$  from anatase to rutile phase generally occurs at 700°C, which has been delayed by Ba doping and this phase transition temperature increases with an increase in Ba concentration. The study of variation in the structure of crystal lattice, such as lattice parameters, crystallite size has been done. During incorporation of Ba in pure TiO<sub>2</sub>, Ba atoms intercalate the void of TiO<sub>2</sub> octahedra and form some extra phases along with the hindrance of phase transition. It also generates some intrinsic lattice strain, which results in peak broadening of the XRD pattern. This intrinsic strain has been calculated using the Williamson and Hall equation. The crystallite size is estimated using Scherrer's equation. In general, crystallite size increases with temperature and becomes more than 100 nm for pure TiO<sub>2</sub>, but it remains within a few nanometers for all Ba doping contents. For vibrational analysis, Raman spectroscopy was performed using the HORIBA Jobin Yvon LabRAM HR Evolution with a Helium-Neon laser  $(\lambda = 632.8 \text{ nm})$  as the excitation source. By performing UV-Visible spectroscopy, it was observed that the band gap decreases with an increase in temperature for pure TiO<sub>2</sub>. But as Ba is incorporated, this gap increases and the reason can be obtained from the Brostein-Moss effect in which electrons cloud generated by dopant near conduction band and it requires more energy to excite the electron from the valence band. The UV Visible spectroscopy has been carried out by software called 'Research India' with proper apparatus and instrument.

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# ACRONYMS

X-Ray Diffraction	XRD
Anatase to rutile phase transition temperature	AR-PTT
Solid State Reaction Method	SSR
Cathode Ray tube	CRT
Infra-Red	IR
Full width at half maxima	FWHM
Williamson and Hall method	WHC
Uniform Deformation Method	UDM
Electromagnetic Wave	EMW
Oxygen Deficiency	OD

## Chapter 1 An Introduction of TiO<sub>2</sub>

#### **1.1 Introduction:**

Titanium dioxide, also known as Titanium (IV) oxide or titania, belongs to the family of transition metal oxides with a chemical name TiO<sub>2</sub>. Titanium-dioxide (TiO<sub>2</sub>) is a non-toxic n-type semiconducting material. It has a wide range of bandgap (3.18eV for anatase). Because of its thermal stability and some of diverse with topnotch properties, it is widely used in chemical and pharmaceutical industries like removal of pollutants from water by water-splitting, as a photocatalyst and photovoltaics [1-7], discoloration of dyes, to manufacture sunscreen, biosensing [8-16]. It is also suitable as applications in solar cells, pigments, drugs, papers, chemical sensors [17-19], photo-electronic devices, supercapacitors [20-22] etc.

#### **1.2 Types and structure:**

The properties of  $TiO_2$  depend upon the crystal structure, nanoparticle size and morphology; therefore, they strongly depend on the synthesis method of  $TiO_2$  [23-33].  $TiO_2$  is reducible, i.e., it occurs mainly in three forms in nature depending upon its crystal structures; anatase (A), brookite (B) and rutile (R). It forms the octahedra with Ti atom at the center and six oxygen atoms with sigma bonds at the corners. As a bulk, the anatase phase is stable at room temperature, whereas brookite is metastable. Among them, the rutile phase is thermally most stable at higher temperatures; however, the synthesis method in the solution phase generally prefers anatase structure [26, 32-36]. These phases can be categorized depending upon the edges and corners shared in their octahedra as anatase shares 4 edges and 4 corners, brookite shares 3 edges and 5 corners and rutile shares 2 edges and 6 octahedra with another octahedra.



Figure 1.1: Different phases of TiO<sub>2</sub>

Anatase (space group I4<sub>1</sub>/*amd*) and rutile (space group P42/mnm) are tetragonal, whereas brookite (space group Pbca) is orthorhombic. When the particle size reduces to a very small scale, surface energy plays an important role. It has been observed that the surface energy of the anatase phase is lower than those of the brookite and rutile phase [37-39]. TiO<sub>2</sub> nanoparticles also exist in its different forms, such as nanowires, nanorods etc., depending upon the synthesis process. To investigate the morphology of TiO<sub>2</sub>, FESEM (Field Emission Scanning Electron Microscope) and TEM (Transmission Electron Microscope) are the generally favorable techniques used.

#### **1.3 Phase Transition:**

Earlier, during the preparation of TiO<sub>2</sub>, an amorphous phase was formed till the annealing temperature about 400°C. Then on increasing the temperature, the octahedra rearrange themselves to form the anatase phase about 450°C. The anatase phase is stable at lower temperatures. But on further increasing the temperature, there is a phase transition from anatase to rutile ( $A \rightarrow R$ ) starts ~450-500°C, then a mixed phase (both anatase and rutile) ~500-700°C and completely converts into rutile at 700°C for pure TiO<sub>2</sub>.

The anatase to rutile phase transition temperature (AR PTT) can be promoted or delayed by doping pure  $TiO_2$  with suitable dopants. It has been observed that metal oxides having a melting point lower than that of  $TiO_2$  promotes the AR PTT

and vice-versa [40]. This phase transition may be because of oxygen deficiency, synthesis technique, calcination temperature with time and mostly due to ionic radii of doping elements. In this work, Ba has been doped in pure  $TiO_2$  and samples are prepared with different Ba doping concentrations. It is obvious that Ba will hinder the AR PTT.

#### **1.4 Possible reasons for AR PTT:**

Since the anatase phase, as mentioned earlier, is stable around room temperature, on increasing the temperature while the conversion of  $A \rightarrow R$ , the octahedra aggregates themselves and the c-axis contracts, which fills up the voids in anatase phase and forms the rutile phase. But for the samples doped with an element, this AR PTT depends upon a few more factors. One of these factors is the melting point of dopant (described earlier). The most promising reason is the ionic radii of dopants. It is observed that while doping pure TiO<sub>2</sub> with elements having a size greater than the oxygen, doping elements intercalated the octahedra of the TiO<sub>2</sub> matrix, which produces a huge deformation in the lattice and inhibits AR PTT while dopants inserted or substituted inside, originates the oxygen deficiency (OD) [41]. This OD provides extra space to promote AR PTT. But OD can not only be the reason for the promotion of phase transition.

#### **1.5 Motive of the project:**

The nature of phase transition also depends on the concentration of Ba. And also, the increase in the Ba concentration will eventually form  $BaTiO_3$  from pure  $TiO_2$ at Ba:Ti=1:1. Since  $TiO_2$  and  $BaTiO_3$  have a tetragonal (P42/mnm) structure, the symmetry structure in both remains the same. The physical and chemical properties will also be modified with an increase in concentration.  $BaTiO_3$  is the first discovered ferroelectric material with a very high dielectric constant. It is mainly used in RAM, actuators, transducers and many memory applications.

The motto of this project is to study the variation of physical and chemical properties with a change in Ba doping concentration. So, there are initially four samples corresponding with the Ba concentration  $(Ba_xTi_{(1-x)}O_\delta)$ ; x=0.000, 0.015,

0.031 and 0.062. Hence these variations of properties have been shown in further detail by performing characterization methods such as XRD, Raman and UV-Visible spectroscopy.

## Chapter 2 Properties and Applications

Titanium dioxide (TiO<sub>2</sub>) has been widely studied, it is found in plastics, paints, rubber, crayons, synthetic fibers, ceramics, cosmetics (as a sunscreen and many others) etc. Since it behaves as a semiconductor, there are many promising uses in photocatalysis and as photovoltaics, sensors, self-cleaners etc. New physical and chemical properties evolve when the size of the particle decreases from bulk to smaller and smaller up to nano range. And surface area of nanoparticles is very helpful in devices based on TiO<sub>2</sub>. Hence, TiO<sub>2</sub> is commercially available nanosized material used in many fields because of low-cost, non-toxicity, biocompatibility and high stability.

#### 2.1 Photocatalytic process:

The photocatalytic process is widely used to activate a substrate (photocatalyst; semiconductor) in the presence of light, which accelerates a chemical reaction but remains unconsumed itself [42-45]. During the process, photocatalysts are irradiated with UV or visible light (where the energy of radiation is higher than the bandgap of semiconductor), which excites the electrons from the valence band to the conduction band and hence generates a positive electron-hole (h<sup>+</sup>) in the valence band as shown in figure 2.1. The electron-hole charge carriers (h<sup>+</sup><sub>VB</sub> + e<sup>-</sup><sub>CB</sub>) may recombine and dissipate the energy in the form of heat or light.

Semiconductor +  $h\nu \rightarrow h^+_{VB} + e^-_{CB}$ 

 $e^{-}_{CB} + h^{+}_{VB} \longrightarrow Energy$ 

But the charge carriers which do not undergo recombination can migrate to the surface of photocatalyst and start secondary reactions with the surface absorbed materials. For example, electrons on the surface may react with oxygen to produce superoxide or hyperoxide radicals, which can further degrade organic pollutants, whereas holes in the valence band may react with water to oxidize hydroxyl ion and produce hydroxyl free radicals (•OH) which can oxidize organic pollutants or microorganisms. [46]



Figure 2.1: Photocatalytic process in a semiconductor

#### 2.2 Water photo splitting:

Among all kinds of semiconductors, TiO<sub>2</sub> is one of the most prominent photocatalysts having high photoreactivity, exceptional chemical stability, simple and assured availability and economical price [47-54]. One of the applications of TiO<sub>2</sub>, water splitting is also very helpful to collect hydrogen and oxygen gases without using any external voltage. This process is carried out by connecting an electrochemical circuit with titanium dioxide and platinum black as two electrodes. When the surface of the TiO<sub>2</sub> semiconductor is irradiated by using UV light ( $\lambda < 415$ nm), a photocurrent flows from the platinum electrode to the TiO<sub>2</sub> electrode through the external circuit. There is an oxidation reaction (oxygen evolves) at the TiO<sub>2</sub> electrode and reduction (hydrogen evolves) at the platinum electrode [55]. In this way, water can be decomposed by this process. Following reactions takes place during this process,

 $TiO_{2} + 2 h\nu \longrightarrow 2 e^{-} + 2h^{+}$   $H_{2}O + 2 h^{+} \longrightarrow \frac{1}{2}O_{2} + 2H^{+} \qquad (at TiO_{2} electrode)$   $2H^{+} + 2 e^{-} \longrightarrow H_{2} \qquad (at Pt electrode)$ Hence, the final reaction is,

 $H_2O + 2hv \longrightarrow \frac{1}{2}O_2 + H_2$ 

#### 2.3 Self-cleaning process:

There are lots of TiO<sub>2</sub> based self-cleaning products such as tiles, glass, tents etc.; which are extensively used in Japan; they can be kept clean because of photocatalytic and super hydrophilic nature of TiO<sub>2</sub>. As organic soilage (like oil) is gradually absorbed, it can be decomposed by the photocatalytic activity of TiO<sub>2</sub>, whereas organic contaminants can be washed off by rainwater because of it's high hydrophilic property. It is true that self-cleaning surfaces will become dirty someday in the future and also this process depends on the amount of rainfall, condition of sunlight, accumulation rate of soilage etc. But this self-cleaning process reduces the rate of contamination and hence it saves cost and time both.



Figure 2.2 Self cleaning property of TiO<sub>2</sub>

#### 2.4 Purification of air:

 $TiO_2$  has a variety of applications in daily life in which purification of indoor air is one of them. An air cleaner works on photocatalysis and consists of  $TiO_2$  based filters, UV lamp and a fan for air circulation. These filters are arranged in a porous honeycomb structure. These  $TiO_2$  based photocatalyst decomposes the adsorbed pollutants despite accumulating them and hence provides better air quality. In addition, these filters also kill bacteria present in indoor air, which is the best application in hospitals, institutes, schools etc. The air cleaners are available in different sizes, from being used as air purifiers in cars, to an entire factory. These filters may be poisoned after long term use, but it can easily regenerate by being simply washed with water.



Figure 2.3: A photograph of TiO<sub>2</sub> based porous ceramic filters for air cleaner.

#### 2.5 As a pigment:

 $TiO_2$  has a very high refractive index as well as can scatter and reflect the light in the visible spectrum [56]. On using this in paints, papers or plastics, it gives them brilliance and opacity.

# Chapter 3 Synthesis Process

#### **3.1 Description of all types of synthesis methods:**

To prepare the samples there are several methods used in the laboratory. Some of them are explained below.

#### 3.1.1 Solid state reaction (SSR) method:

This method for the preparation of samples is widely used to synthesize polycrystalline solids. The reaction is generally carried out at higher temperatures  $\sim$ 1000-1500°C for a proper reaction rate. The SSR reactions depend on the surface area of reactants, their structure, activity etc.

After measuring the sample precisely, they are ground by using *Agate Mortar* and *Pestle* about 40-50 minutes. For uniformity of reactants, sometimes alcohol or acetone are used. Because of the volatile nature of alcohol/acetone, they evaporate completely in 10-15 minutes during the grinding process. Further, for the SSR reaction, the sample is contained in crucibles (having a much higher melting point) and is placed in a programmable furnace for the required time [57].

For example, the reaction for the preparation of  $TiO_2$  on using precursors  $TiOSO_4.2H_2O$  and  $Na_2C_2O_4$ ;

 $TiOSO_{4.}2H_{2}O + Na_{2}C_{2}O_{4} \xrightarrow{grind} TiOC_{2}O_{4} + N_{2}SO_{4} + H_{2}O$  $TiOC_{2}O_{4} \xrightarrow{calcine} TiO_{2} + CO + CO_{2}$ 

#### 3.1.2 Hydrothermal method:

To synthesize a single crystal whose formation depends on the solubility of minerals in hot water under high pressure, the hydrothermal method is used. Further, the crystal formation takes place by using an apparatus called *Autoclave*, containing minerals with water.

An autoclave is made up of a thick steel wall container having a high melting point. After that, a temperature gradient is maintained across the crystal growth chamber. The nutrient solute gets dissolved at the hotter end, whereas the desired crystals are deposited at the cooler end. Hence, good quality crystals are obtained by this method. This method is widely used to synthesis quartz, gems etc.



Figure 3.1: Autoclave instrument: used in hydrothermal method

#### 3.1.3 Sol-gel method:

This method is widely used to synthesize oxides of Ti and Si. In this method, precursors (with a purity of about 99.99%) are taken in a definite proportion to get the desired concentrations, which gets dissolved in dilute HNO<sub>3</sub>.

Precursors are the compounds containing the elements required for sample preparation. Thereafter, after mixing them, gelling and burning agents are added to form a gel. And on continuously heating at 80°C they form a blackish powder

and further, for removal of carbon and nitrogen, they are annealed at a higher temperature (~450°C). Hence, samples are formed with the desired concentration.



#### 3.2 Sample prepared by Sol-gel method:

Figure 3.2: A schematic process of sol-gel method.

For sample preparation using this method, TALH (Dihydroxy-bis titanium  $C_6H_{18}N_2O_8Ti$ ; Alpha Aser, purity 99.99%) and Ba(NO<sub>3</sub>)<sub>2</sub> (Alpha Aser, purity 99.99%) were used as precursors for Ti and Ba elements respectively. Then, a precisely measured amount of Ba(NO<sub>3</sub>)<sub>2</sub> was added in DI water, which was dissolved in dilute HNO<sub>3</sub>. Thereafter, a measured amount of TALH was added to this solution and was kept on a hot plate with constant stirring using magnetic beads for about an hour, keeping the temperature knob in the off position. Further, gelling agent (citric acid) and burning agent (ethylene glycol) were added to the solution to make a yellowish gel; it was heated at 80 °C for a few hours. On constant heating for about 4 hours, the solution becomes a gel and because of the burning agent, samples prepared gets burned and forms black ashes. Here, firstly four samples were prepared with different concentrations labeled as TBO (x=0.00,

pure TiO<sub>2</sub>), TB1 (x=0.015), TB2 (x=0.031) and TB3 (x=0.062). And for the removal of carbon and nitrogen from the powdered samples, they were kept in an automatic furnace at 280°C for 4 hours. A yellowish powder (for pure TiO<sub>2</sub>) and white powders (for different Ba doping concentrations) were obtained. These samples were further calcined at the interval of 50°C to study their properties as it is the motive of this project.

## Chapter 4 Experimental Techniques Used

Several experimental techniques have been performed on the samples of different concentrations to investigate the variation in properties like XRD (for structure), Raman (for vibrational) and UV-Visible spectroscopy (for bandgap).

#### 4.1 X-ray diffraction

#### **4.1.1 Introduction:**

An XRD is an experimental technique, which is used worldwide in science to determine the atomic or molecular structure of crystals by the diffraction of X-rays in specific directions. These X-rays are generated by Cathode Ray Tubes (CRTs), filtered to make it monochromatic and then collimated to concentrate and is then directed towards the samples [58]. XRD peaks are formed by the constructive interference of monochromatic X-rays at specific angles from each set of lattice planes of the sample. By measuring the angles and observed intensity from diffraction data, one can determine the lattice parameters, bond lengths, bond angles, lattice deformation etc. X- Rays are used to produce the diffraction pattern are generally has a wavelength between 0.1–100 Å.

#### 4.1.2 Bragg's law:

The incident X-rays interact with the sample; the sample produces constructive interference (and diffracted rays) when satisfying the following condition known as Bragg's law.

#### $2dsin\theta = n\lambda$

Where  $\theta$  is diffraction angle,  $\lambda$  is the wavelength used in X-ray, d is the interplanar distance and n should be integral. This law relates to the X-ray wavelength with the diffraction angle and the lattice spacing in the crystalline samples.



Figure 4.1: Bragg's diffraction on a crystallite plane

#### 4.1.3 Working procedure:

X-Ray diffractometer consists of three fundamental elements, X-ray tube, sample holder and detector. They have their specific function to obtain diffraction peaks. As said earlier, X-rays are generated by using CRTs by heating the filament inside it to produce electrons, these electrons then get accelerated by the application of an accelerating potential towards the target and finally bombards the target. When electrons have enough energy to remove electrons of the inner shells of material, then a characteristic X-ray spectrum gets produced. These spectra consist of the most common  $K_{\alpha}$  and  $K_{\beta}$  components. Now,  $K_{\alpha}$  contains two elements  $K_{\alpha 1}$  and  $K_{\alpha 2}$  ( $K_{\alpha 1}$  has slightly less wavelength and twice the intensity of  $K_{\alpha 2}$ ). The specific wavelengths are characteristics of target materials (e.g., Cu, Fe etc.). Further, these rays are filtered out by using foils or crystal monochromators to produce a monochromatic X-ray. Since  $K_{\alpha 1}$  and  $K_{\alpha 2}$  are much closer in wavelength such that the average of the wavelengths of these two is considered. Copper is the most common target material used in diffraction with the wavelength of Cu K<sub> $\alpha$ </sub> radiation ( $\lambda$ =1.5418Å). Further, these X-rays are collimated and direct towards the sample.

#### 4.1.4 Detector:

As the sample and detector both rotate, the intensity of reflected X-rays are recorded. As the geometry satisfies the Bragg's law, i.e.,  $2dsin\theta = n\lambda$ , then constructive interference occurs and a peak in intensity appears. The detector measures and processes the X-ray signal and then converts it into a count rate signal which further appears on the monitor screen.



Figure 4.2: A schematic diagram of X-ray diffractometer components.

The X-ray diffractometer setup is such that the sample rotates in the path of collimated rays by an angle 2 $\theta$  whereas the detector rotates by 2 $\theta$  degree mounted to collect these diffracted rays. An instrument that is used to rotate the sample is known as *goniometer*. Generally, for powder pattern,  $\theta$  varies from 5° to 70°. XRD is widely used in studies of geology, material science, engineering, pharmaceutical industries, forensic science, microelectronics industry, biology and many more.

#### 4.1.5 Miller Indices:

A Miller index is a way to describe different lattice planes of a crystal lattice uniquely. To determine the miller indices, the points should be identified, which intersects a, b and c axes. Thereafter, the intercepts should be measured in a simplified fraction. Further reciprocal of the fractions are taken, from this, we get the miller indices. They are generally denoted as (h,k,l) values.

#### 4.1.5 Structural analysis:

Earlier, powder diffraction was considered to have limited use in crystallography because of the superposition of intensities observed, which limits the structural information. Therefore, XRD had only been used to identify the phase. But as time passed, a procedure developed, called Rietveld refinement, extracting maximum information of crystal lattice by fitting the curve of entire XRD diffraction data. This method revolutionized the use of XRD for structural analysis. This method was earlier developed for neutron powder diffraction [59], and then further for X-ray powder diffraction data. This refinement technique is a curve fitting procedure by taking account of multiparameters (taking into account multiple parameters). The out file of the refined data gives information about crystal structure (lattice parameters, atomic positions, displacement factors etc.). Furthermore information such as crystallite size, intrinsic strain and crystallite; the phase fraction can be estimated, which is discussed in detail in the next chapter. FullProf Suite software is generally used for Rietveld refinement and profile matching.

#### 4.1.6 Rietveld- refinement:

In the Rietveld method, a model is fitted for a data. On being a correct model, it predicts what the 'true' values of intensities should be. The simulated values of intensity obtained from the model are labeled as  $y_{c,i}$  where c stands for 'computed'. The Rietveld method optimizes the function of the model to minimize the weighted sum of the squared differences of the observed and

computed intensities, i.e., it minimizes  $\Sigma_i w_i (y_{c,i} - y_{o,i})^2$  where  $w_i$  is labeled as weight and is equal to  $1/\sigma^2[y_{o,i}]$  [60]. There is a straightforward index called weighted profile ( $R_{wp}$ ).

Where  $R_{wp^2} = \Sigma_i w_i (y_{c,i} - y_{o,i})^2 / \Sigma_i w_i (y_{o,i})^2$ .

If there is an ideal model which gives the true value for each  $y_{o,i}$ , then there the average value of  $(y_{c,i} - y_{o,i})^2$  becomes equal to  $\sigma^2[y_{o,i}]$  and hence the expected value of  $w_i(y_{c,i} - y_{o,i})^2$  becomes one. There is also a quantity "Rexp (the best possible  $R_{wp}$ )" called as expected R-factor ( $R_{exp}$ ) can be expressed as  $R_{exp}=N/\Sigma_i w_i(y_{o,i})^2$  where N is the number of data points.

Again, a statistical term called "Chi squared ( $\chi^2$ )". Since the expected value of  $(y_{c,i} - y_{o,i})^2 / \sigma^2 [y_{o,i}]$  becomes one when the model is ideal. Therefore, the term  $\chi^2$  is defined as the average of these values.

i.e.  $\chi^2 = (1/N)\Sigma_i(y_{c,i} - y_{o,i})^2 / \sigma^2[y_{o,i}]$  [61]. This  $\chi^2$  value can also be determined by the ratio of  $R_{wp}^2$  and  $R_{exp}^2$  i.e.  $\chi^2 = R_{wp}^2/R_{exp}^2$ . This  $\chi^2$  determines the goodness of fit of the curve. Below figure 4.3 shows one of the Rietveld refinement fitted data as it is used in this project.



Figure 4.3 Rietveld refined data of pure  $TiO_2$  annealed at  $500^{\circ}C$ .

At the time of the refinement process,  $\chi^2$  gets very large when the model is poor and thereafter, its value decreases as the model comes to a better agreement with data. The least-squares method in refinement never causes  $\chi^2$  to increase but the value may increase when the parameters are correlated. The value of  $\chi^2$  should never be less than one. The most appropriate way to get a quality Rietveld fit is by viewing the observed and calculated patterns graphically and it should also be ensured that the model is chemically plausible.

#### 4.2 Optical and vibrational analysis:

Vibrational transitions can be observed in either IR or Raman spectra. These are very sensitive instruments use to analyze the structure of crystal lattice. Going to the past, when mercury discharge lamps were used as a monochromatic source and photographic film were used as detectors, the data received used to be a milestone. However, in 1942 photoelectric detectors were taken in use and further in 1966, lasers were used as a source of excitation in Raman spectroscopy.

#### 4.2.1 Raman Spectroscopy:



Figure 4.4: The process of Raman scattering

Raman spectroscopy is a non-destructive technique used to investigate a crystal and extract information like crystal structure, phase, crystallinity and molecular interactions. The crystal lattice is made up of a periodic array of atoms. When electromagnetic radiation is scattered by molecules of sample, photons polarize the molecular electron cloud and leaves it at a higher energy state. This state (a virtual state) is not stable and in a very short period of time, photons are reemitted as scattered light [62]. In this scattering event, the majority of the photons scatter back with the energy unchanged, i.e., the frequency of the scattered photons is equal to that of the incident photons. This type of scattering is known as Rayleigh scattering. Only very few photons (about 1 in  $10^7$ ) are scattered back with a change in their energy or frequency. This is known as Raman scattering

When the molecule gains energy in the scattering process or photon loses its energy, the wavelength of the corresponding photon increases, which is known as Stokes Raman scattering (after G.G. Stokes). Conversely, when the molecule loses or photon gains energy, the wavelength of photon decreases and this is called Anti-Stokes Raman scattering.

Molecular vibrations can also be probed by using Infra-Red (IR) spectroscopy, which is complementary to Raman spectroscopy. In IR spectroscopy, the only vibration which may change the polarization vectors, are active, whereas, in Raman spectroscopy, the vibrations must affect the polarizability tensor. Thus, in centrosymmetric systems, a vibration cannot be both IR and Raman active, which gives rise to the complementary of two [63].

#### 4.2.1 Phonon-confinement:

In the current interest of physics, nanostructured materials are highly preferable because of their vast applications like in catalysis, in optoelectronic devices and in metallurgy. These properties of nanomaterials can be explained properly with the understanding of the relation of their grain/particle size. Vibrational or optical properties are not affected much until the size corresponding to their bulk values of the grains is less than 20 nm. The grain size and properties of these nanomaterials may depend on the different synthesis processes.

Phonons are the quanta of vibrational energy in the crystal lattice. In simple monoatomic solid, having 1 atom per primitive cell (copper) has only three acoustic phonon branches corresponding to three degrees of freedom of their atomic motion. In addition, a monoatomic solid having 2 atoms per primitive cell (diamond, diatomic compound like GaAs) has three acoustic with three optic

phonon branches. In general, for crystals having N atoms in their unit cell can have 3 acoustic phonon branches with 3N-3 optic phonon branches. Phonons can propagate in the crystal lattice as a wave and disperse according to their frequencies ( $\omega$ ) or equivalently their wave-vectors in the Brillouin Zone. This dispersion is governed by the dispersion relation of phonons (the relation between phonon frequency ( $\omega$ ) and their wave vectors (q)). Phonon wave propagation gets interrupted as they reach the grain boundary. These grain boundaries reflect these waves and confine them within the boundaries. This phenomenon is called phonon confinement. The significance of phonon confinement can be observed in vibrational spectra only when the grain size is less than 20 lattice parameter.

There are three types of confinement based on the dimensionality of materials. All bulk materials with 3-dimensional geometry correspond to zero-dimensional confinement means no restriction in the propagation of phonons. The first dimensional/degree of confinement is found in a single or multilayered thin film as the phonons and charge carriers are restricted along the z-direction. Further, single or multiple-quantum-well structures; semiconductor superlattice are known examples for 2-dimensional confinement as the charge carriers are phonons that are restricted in a plane only. The occurrence of 2D confinement is also found in nanowires and carbon nanotubes. The highest degree of confinement is found in quantum dots [64] because of the restriction of the propagation of phonons in all directions.

Phonons are confined in the nanocrystals and all phonons over the entire Brillouin zone contribute to the first-order Raman spectra. The weight of off-centered phonon increases as the decrease in crystallite size and phonon dispersion gives rise to the asymmetric shift and the broadening of Raman modes.[65]

### 4.3 Optoelectronic study:

#### **4.3.1** Absorption spectroscopy:

There are different chemical species and things with a characteristic color such as the green in cucumber, red in tomato, green in chlorophyll, yellow in quinone, colorlessness in aspirin and many more. All these colors of different things depend on the absorption of light in the visible region of the electromagnetic spectrum (EMW, 400-800 nm). When white light is irradiated on a surface of an object, it may absorb one or more components of that white light (here components refer to VIBGYOR). And those colors which are not absorbed get reflected back. For example, red light is reflected from the tomato's shell, the green light is reflected from the cucumber's surface. And hence we are able to see different objects with different colors in our daily life.

Light is an electromagnetic wave (EMW, a form of energy) which travels at a very high speed. It is a combination of its different components with different wavelengths or frequencies. In combination, these components form a spectrum called the electromagnetic spectrum.



Figure 4.5: Electromagnetic spectrum of light.

The spectrum of light gives the distribution of energy of different radiations such as the visible region, which exists from 390 nm to 780 nm. Greater the frequency (or shorter wavelength) corresponds to the higher energy of EMW.

#### 4.3.2 Lambert-Beer law:

UV Visible spectroscopy gives information about the absorption of radiation in the UV and visible regions of the electromagnetic spectrum. The molar absorptivity  $\varepsilon$  can be defined by Lambert-Beer law. According to this law, when light crosses a thin width of an absorbing sample, the intensity of light reduces and can be expressed in terms of transmittance (T).

$$T = \frac{I}{I_0}$$

The absorbance of light for a sample is related to transmittance by following relations;

$$A = \log_{10}(I/I_0)$$

Further, the more light will be absorbed in a higher concentrated sample and the attenuation is also proportional to the width of the sample. On summarizing the above factors, absorbance can be given as,

$$A = \varepsilon. c. l$$



Figure 4.6: Absorption of light, Lambert-Beer law

Where l is the width, c is concentration and  $\varepsilon$  is molar absorption coefficient (extinction coefficient) of the sample. The extinction coefficient is a sample-specific constant. This relation is known as Lambert-Beer law.

## Chapter 5 Results and Discussions

All the experimental techniques were discussed in the previous chapter, these had been applied to samples of different Ba doping concentration to investigate the variation in properties because of the phase transition as in XRD (for structure), Raman (for vibrational) and UV-Visible spectroscopy (for bandgap). Further, as these characterizations were done, it is obvious to discuss the result and consequences obtained. Therefore, those results have been elucidated thoroughly in this chapter.

#### 5.1 XRD:

#### **5.1.1 Phase Transition:**

XRD is a fundamental tool to investigate the structure of any material. In this project, four samples were prepared as TB0 (pure TiO<sub>2</sub>, x=0.000), TB1 (x=0.015), TB2 (x=0.031) and TB3 (x=0.062), using the sol-gel method. Further, these four samples were annealed from 450°C to 850°C, with an interval of 50°C and their XRD patterns are plotted. The X-Ray diffraction of different samples annealed at different temperatures was performed by using the Bruker D2 phaser diffractometer having X-Ray wavelength 1.5408Å CuK<sub> $\alpha$ </sub> radiation. The XRD patterns for samples annealed at 450°C are in good agreement with the anatase phase (space group  $I4_1/amd$ ). At 450°C, none of the samples show any other peak corresponding to the rutile phase. But as the annealing temperature increases, TiO<sub>6</sub> octahedra rearranges itself to minimize the void available among these octahedra and thus forms a new phase (rutile with P42/mnm) gradually. This phase transition temperature depends on the dopants with many reasons like the melting point of dopant, ionic radii of the dopant as discussed in an earlier chapter. The temperature at which the rutile phase starts to emerge is termed as T1 temperature and the temperature at which it is completely converted to a stable rutile phase is termed as a critical temperature T2.



Figure 5.1: Variation in XRD pattern for all TB samples annealed at different temperatures.

Here, a mixed-phase (anatase and rutile) came along with an extra phase had been observed in each of the samples between the temperature T1 and T2. This extra phase was investigated using Expert High Score software and founded to be BaTi<sub>5</sub>O<sub>11</sub> (having space group *P121/n1*). This new phase was further confirmed by a mix phase profile matching of TB3 (x =0.062) sample anneald at 850°C as shown in figure 5.2. It can be observed from the XRD pattern that this extra phase increases with increase in Ba doping concentration. For TB0 sample, T1 is observed at 550°C and T2 at 750°C. Since on introducing Ba dopant, A $\rightarrow$ R PTT is delayed, for both TB1 and TB2 samples T1 is at ~750°C and for TB3 it is at ~700°C.



Figure 5.2 Determining the extra phase (BaTi<sub>5</sub>O<sub>11</sub>) came by profile matching of TB3 sample (x = 0.062) annealed at 850°C.

Four more samples were synthesized having Ba doping concentrations (x= 0.12, 0.25, 0.31 and 0.37) and kept on an automatic furnace for sintering from 450 °C to 1100 °C to study the variation in properties with a change in Ba concentration. It is observed that as the concentration increases from x=0.12, the different derivative of Ba, Ti and O forms and tends towards the formation of BaTiO<sub>3</sub>. One of the derivatives had been discussed earlier in TB samples from TB0 to TB3, which was BaTi<sub>5</sub>O<sub>11</sub>. Thereafter, three more samples were synthesized with Ba doping concentration (x=0.43, 0.46 and 0.5). These three samples were also kept on an automatic programmable furnace and sintered at 1350°C. It can be observed that on increasing the temperature in a particular sample these derivative

gradually decreases and with increasing Ba concentration also these derivative content decreases and finally forms  $BaTiO_3$  for x=0.5.



Figure 5.3: Variation of XRD patterns of Ba concentration from x=0.37 to x=0.5 (BaTiO<sub>3</sub>)

#### **5.1.2 Phase fraction:**

The estimation of rutile phase percentage in  $A \rightarrow R$  is done by using Spurr and Mayer's equation [66] and is given as,

$$FR = \frac{1}{1 + 1.26 * \frac{I_{a(101)}}{I_{r(110)}}}$$

where  $I_{a(101)}$  and  $I_{r(110)}$  are the most intense peak of anatase and rutile phases respectively. The variation in phase transition temperature AR PTT can be observed from the graph. The TB0 sample (x=0) starts from its amorphous phase and forms anatase ~450-500°C and rutile phase emerges from 550°C and gets completely converted into rutile ~750°C. Whereas this anatase to rutile phase transition is hindered for different Ba doping concentrations, such samples as discussed earlier. The most promising reason for hindrance is the ionic radii. Since the ionic radii of Ba<sup>+2</sup> (1.35Å) is much larger than that of Ti<sup>+4</sup> (0.745Å), it is difficult for Ba<sup>+2</sup> to substitute Ti atom as Ti<sup>+4</sup> from TiO<sub>6</sub> octahedra and intercalate the void of the adjacent  $TiO_6$  octahedra. Hence, on increasing the temperature, Ba atom restricts the rearrangement of these octahedra and  $A \rightarrow R$  phase transition gets hindered.



Figure 5.4: Magnified view of  $A \rightarrow R$  transition and rutile phase fraction for different Ba doping concentrations.

#### 5.1.3 Crystallite size:

It had been discussed earlier that as the temperature increases,  $A \rightarrow R$  phase transition occurs on account of which c-axis decreases and the void volume decreases. As a result, the rutile phase becomes more compact and stable than anatase. It is said that during phase transition, crystallite size increases with the rise in temperature. But this was confirmed when the crystallite size was estimated by using Scherrer's equation [67] given as,

$$D = \frac{k\lambda}{\beta\cos\theta}$$

where D is the crystallite size, k is Scherrer's constant (~0.9),  $\lambda$  is the wavelength used for XRD (~1.5408Å),  $\beta$  is the full width of half maxima (FWHM) of the most intensed peak and  $\theta$  is the diffraction angle (radian). The temperature dependence of the crystallite size for all TB samples prepared reveals the continuous growth of nanocrystals. It was observed that for the TB0 sample, crystallite size increases with temperature and becomes more than 100nm. This equation does not give an accurate value of crystallite size for more than 100nm. Therefore, for TB0 samples at temperatures of more than 600°C, this data is not much accurate. However, it was also observed that for samples TB1, TB2 and TB3, the crystallite size increases and remains up to 35 nm even at a higher temperature. The thermodynamic stability of the phase of TiO<sub>2</sub> also depends on the size of the crystal.



Figure 5.5: Variation of crystallite sizes of Ba doping concentration TB samples annealed at different temperatures.

It has been reported that for crystals having a size less than or equal to 14 nm, the anatase phase is highly stable whereas if crystallite size becomes larger than 35 nm, rutile phase becomes more stable which is shown in the plotted graph and as a result, it can be seen that the  $A\rightarrow R$  phase transition is hindered with an increase in the Ba doping concentration.

#### **5.1.4 Lattice parameters:**

Using the XRD pattern of different doping samples, lattice parameters (a,b and c) have been calculated by Rietveld refinement. This refinement was performed using FullProf Suite software (freeware). In the series of samples, the variation of

the lattice parameter for TB500°C with different doping concentrations are shown here. As already discussed, the ionic radius of  $Ba^{+2}$  (1.35Å) is much larger than that of Ti<sup>+4</sup>(0.745Å); therefore, Ba intercalates the void of TiO<sub>2</sub> octahedra instead of substituting Ti. That's why the final refinement was done by not considering Ba atom in the atomic position.

In the given plot, the Reitveld-refined data and the variation in lattice parameters with concentration are shown for the TB500°C sample. It is observed that 'a=b' value increases and corresponding 'c' value decreases with the increase in Ba doping concentration. This results in a steady decrease in the c/a value of the unit cell with Ba-incorporation. The lattice volume for the unit cell of TB500°C sample, firstly increases then decreases with an increase in Ba concentration.



Figure 5.6: Rietveld refinement of TB500°C sample (at left) and variation in lattice parameters for the same samples with concentration (at right).

#### 5.1.5 Crystal lattice Strain:

The Scherrer's equation gives only the information about crystallite size but doesn't tell other things like lattice strain, which arises in nanocrystals because of the point defect or lattice deformation (due to dopants) etc. Many methods can be used to estimate the lattice strain like Williamson and Hall method, Warren Averbach method. The main reason for XRD peaks broadening is due to intrinsic lattice strain, which can be calculated using these methods. But Williamson and Hall (W-H) method is a very easy and simplified method [68]. These microstrains have been calculated by UDM (Uniform Deformation Method) by using the W-H method.

#### **UDM (Uniform Deformation Method):**

Uniform Deformation Method (UDM) considers the strain throughout the crystallographic direction, which arises due to intrinsic deformation. This intrinsic strain affects the broadening in the XRD peaks and this lattice strain induced peak broadening can be expressed as,

 $\beta_{(strain)} = 4\varepsilon . tan\theta$ 

Therefore, the total peak broadening because of size and strain in crystal lattice having hkl values can be given as,

$$\beta_{(hkl)} = \beta_{(size)} + \beta_{(strain)}$$

Where  $\beta_{(hkl)}$  is the total FWHM of the most intense peak at different diffracting planes. Now,

$$\beta_{(hkl)} = \frac{k\lambda}{D\cos\theta} + 4\varepsilon . \tan\theta$$

Here,  $\beta_{(size)} = \frac{k\lambda}{D\cos\theta}$  can be obtained from Scherrer's equation. Further, on rearranging we get,

$$\beta_{(hkl)}.cos\theta = \frac{k\lambda}{D} + 4\varepsilon.sin\theta$$

Therefore we get a linear equation of a straight line, know as the UDM equation and it is plotted with  $\beta_{(hkl)}.cos\theta$  along y-axis and  $4.sin\theta$  along the x-axis. The slope of this line gives information about the *intrinsic strain* and the intercept gives the *particle size*.

Study of variation in structural, vibrational and optical properties of Ba doped  $TiO_2 Ba_xTi_{(1-x)}O_{\delta}$ .



Figure 5.7: A fitted data of lattice strain using Williamson and Hall equation and the lattice strain calculated for TB500°C sample with concentration.

The lattice strain has been estimated for the TB500°C (anatase phase) sample. It can be seen from this graph that the strain increases with an increase in Ba concentration. However, this strain decreases with an increase in temperature.

#### 5.2 Raman Analysis:

Raman spectroscopy is a sensitive tool to get the vibrational and structural information of lattice. In this project, the Raman spectroscopy have been performed by a micro Raman system HORIBA Jobin Yvon LabRAM HR using Helium-Neon laser ( $\lambda$ =632.8 nm) as an excitation source.

Here, Raman spectrocopy of the four samples (x=0.00, 0.015, 0.031 and 0.062) annealed from 450°C to 950°C with 50°C interval each are discussed. From group theory analysis, total optical phonon modes for anatase TiO<sub>2</sub> can be given as  $\Gamma_{opt} = A_{1g}(R) + 2B_{1g}(R) + 3E_g(R) + A_{2u}(IR) + B_{2u}(IR) + 2E_u(IR)$  and for rutile these modes are  $\Gamma_{opt} = 1A_{1g}(R) + 1A_{2g}(IR) + 1A_{2u}(IR) + 1B_{1g}(R) + 1B_{2g}(R) + 2B_{1u}(IR) + 1E_g(R) + 3E_u(IR)$  [69]. In anatase phase, there are three Raman active (E<sub>g</sub>, A<sub>1g</sub> and B<sub>1g</sub>) modes while in rutile phase, four Raman active (E<sub>g</sub>, A<sub>1g</sub>, B<sub>1g</sub>, B<sub>2g</sub>) modes are found along with one multiphonon mode (M).



Figure 5.8: Variation in Raman spectra for all TB samples annealed at different temperatures.

Experimentally, these modes for anatase phase are found at 144cm<sup>-1</sup>, 197cm<sup>-1</sup>, 399cm<sup>-1</sup>, 513cm<sup>-1</sup>, 519cm<sup>-1</sup> and 639cm<sup>-1</sup> for single crystal observed by Oshaka group [70], whereas for rutile TiO<sub>2</sub> these are found at 143cm<sup>-1</sup> (B<sub>1g</sub>), 447cm<sup>-1</sup> (E<sub>g</sub>), 612cm<sup>-1</sup> (A<sub>1g</sub>), 826cm<sup>-1</sup> (B<sub>2g</sub>) and 240cm<sup>-1</sup>(M) for pure TiO<sub>2</sub>. In this study, it was observed that for pure TiO<sub>2</sub> (TB500°C, anatase), the most intense peak was observed at 143.7cm<sup>-1</sup>(E<sub>g</sub>), the least intense peak at 195.8 cm<sup>-1</sup>(E<sub>g</sub>) with three other weak peaks at 396.81cm<sup>-1</sup>(B<sub>1g</sub>), 515.29cm<sup>-1</sup>(A<sub>1g</sub>+B<sub>1g</sub>), and 639cm<sup>-1</sup>(E<sub>g</sub>). It can be seen from the graph that with an increase in Ba concentration, the A $\rightarrow$ R phase gets hindered in all TB samples. Among all the annealed samples,

TB500°C has been studied as an anatase phase with different doping concentrations. It was observed that, with an increase in Ba content, there was a shift in the peak of first  $E_g$  mode from 143.7cm<sup>-1</sup> to 147.5cm<sup>-1</sup> as well as peak broadening occurs. The broadening in peak increases from 9.5cm<sup>-1</sup> to 18.1cm<sup>-1</sup>.



Figure 5.9: Blueshift observed in the first Eg mode of TB500°C sample.

The broadening in first  $E_g$  mode (FWHM) and peak shift had been calculated by fitting the Raman modes using Fityk software and is shown for all TB samples. Raman active modes arise due to the motion of oxygen ions with respect to Ti<sup>+4</sup> ion either parallel to c-axis ( $E_g$ ) or perpendicular to the c-axis ( $A_{1g}$ ,  $B_{1g}$  and  $B_{2g}$ ). The Eg vibrational mode arises due to asymmetric bending of O-Ti-O bond in (110) plane due to the antiparallel movement of the oxygen atom,  $A_{1g}$  occurs due to the symmetric stretching of O-Ti-O bonds in (110) plane due to the oscillations of the O-atom in the adjacent O-Ti-O bonds opposite to each other [71]. Whereas,  $B_{1g}$  mode occurs because of asymmetric bending of O-Ti-O bonds in (001), (110) and (-110) planes.



Figure 5.10: Variation in FWHM and Raman shift in TB500°C sample for its first  $E_g$  mode.

#### 5.2.1 Reason for Raman shift:

The shift in the first Eg mode may occur due to numerous reasons. Surface tension, non-stoichiometry and phonon-confinement can be the origin of these mode shifts. It has been reported that internal stress and surface tension do not affect mode shifting rather than that of non-stoichiometry. But among these reasons, the confinement of phonons can play a major role because the crystallite size of all TB500°C samples remain within a few nanometer scale. And it has been observed that the lattice parameters and volume decrease with an increase in Ba concentration, which decreases the interatomic distances. This decrease in distance promotes the force constant [72,73], which becomes the reason for phonon confinement. A detailed description of phonon-confinement has been discussed in the previous chapter.

#### **5.3 UV Visible Spectroscopy:**

The UV-Visible spectroscopy is a quantitative analytical technique mostly used for the absorption of chemicals near ultra-violet (180-390 nm) or visible (390-780 nm) for quantitative analysis. Here, UV-Visible spectroscopy was carried out for all TB samples (TB0, TB1, TB2 and TB3) annealed from 450°C to 850°C to calculate the bandgap. There are two types of bandgap, direct and indirect bandgap. For pure TiO<sub>2</sub>, its anatase phase has an indirect bandgap, whereas the rutile phase has both direct and indirect bandgap, which has very similar values [74]. The data recorded by this spectroscopy was the variation in reflectance with the wavelength of radiation from UV to visible region. The optical band gap was estimated by using Tauc's plot is given as,

$$\alpha h \nu = A (h \nu - E)^n$$

Where  $\alpha$  is the absorption coefficient, h is the plank's constant, v is the frequency of radiation, A is a constant and E is the bandgap. Further, since Kubelka-Munk's function F(R) can be given as,  $F(R) = \frac{(1-R)^2}{2R}$  which is directly proportional to the absorption coefficient ( $\alpha$ ), hence a modified Tauc's relation is given by,

$$F(R)hv = A(hv - E)^n$$

Here n = 2 and 0.5 corresponds to the indirect and direct bandgap respectively and R stands for reflectance. The incorporation of Ba not only changes the morphology but also affect the electronic property.

It can be seen from the graph that the bandgap for pure  $TiO_2$  decreases from its anatase (~3.2 eV) to rutile (~3.0 eV) with an increase in temperature. While, this bandgap increases with an increase in Ba concentration but remains almost constant for TB1, TB2 and TB3 samples. For the increase in the bandgap, quantum-confinement and the Burstein-Moss effect are the main reasons. In quantum confinement, the bandgap increases with a decrease in crystallite size. Since the crystallite size for pure  $TiO_2$  was increasing rapidly but the increase for other doping samples are not enough rapid and remaining within a few nanometer scales, which clearly deflects in the behavior of the bandgap variation.



Figure 5.11: Band gap variation for al TB samples with temperature

In the case of Ba doped  $TiO_2$ , there is an increase in electron cloud because of the dopant near conduction band, which provides Fermi level to shift towards the conduction band. As a result, the photon energy required to excite the electron from the valence band to the conduction band becomes higher, which results in an increase in the bandgap and is known as the Burstein-Moss effect[75].

Further, there is a term called Urbach energy, which measures the disorder in a crystal lattice. It can be calculated by using the expression  $\alpha = \alpha_0 e^{h\nu/E_u}$ , where  $\alpha$  is the absorption coefficient,  $\alpha_0$  is constant, hv is the photon energy and  $E_u$  is the Urbach energy. The disorder in a crystal lattice creates some defect states near the valence band and the conduction band. The energy corresponds to the defect states are reflected in the Tauc plot as a tail known as Urbach tail. The slop of a linear plot of ln F(R) and hv gives the value of Urbach energy (Eu) (because F(R) is proportional to  $\alpha$ ). Generally, Urbach energy decreases with an increase in the bandgap. As discussed in the previous section about all characteristics for the TB500°C sample, the variation of bandgap and Urbach energy has been shown below in figure (5.12). Since this sample agrees with the anatase phase, therefore it has an indirect bandgap, and hence for bandgap calculation, a graph between  $[F(R)hv]^{1/2}$  and hv has been plotted. The interception of the extrapolation of the linear part of the plot with the energy axis gives the value of bandgap.



Figure 5.12: Band Gap and Urbach energy calculated for all TB500°C sample.

#### **Conclusion:**

A study of phase transition of Ba doped TiO<sub>2</sub> (Ba<sub>x</sub>Ti<sub>(1-x)</sub>O<sub>2- $\delta$ </sub>;  $0 \le x \le$  0.062) with temperature and doping concentration has been done from 450°C to 850°C with 50°C intervals. A phase transition graph is plotted for all TB samples and it was observed that the A $\rightarrow$ R phase transition is shited toward higher temperatures with the doping of Ba in pure TiO<sub>2</sub>.

And also, this hindrance increases or transition temperature vaires depending upon the doping concentration. On analyzing the structure, the lattice parameters and volume of the crystal lattice are calculated and discussed for a particular annealing temperature 500°C sample and it was observed that the lattice parameter contracts and volume decrease with increasing Ba concentration. Crystallite size is calculated for the same sample using Scherrer's equation and it was observed that the crystallite size in pure TiO<sub>2</sub> increases with a rise in temperature and becomes more than 100 nm, but it remains within few nanoscales for all other TB samples. Using Williamson and Hall's equation, the intrinsic strain arises due to deformation generated by Ba dopant, which was estimated and it was found that the intrinsic strain increases for the first three samples and suddenly decreases for the last sample TB3 (x=0.062). From the Raman spectra of Ba doped samples, a clear blue shift is observed for the first Eg mode. A systematic increase in peak shifting and FWHM with increasing Ba concentration is generally because of phonon confinement and lattice contraction. On performing UV-visible spectroscopy, the bandgap decreases with an increase in temperature for pure  $TiO_2$  and further on doping Ba, the bandgap increases. This increase in bandgap can be understood from the Burstein-Moss effect. Urbach energy has been estimated and plotted for TB500°C sample. It was observed that the Urbach energy first increases with Ba incorporation and later decreases with an further increase in Ba concentration.

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