Structural, Optical and Raman Spectroscopy investigations on pure and Hf-Doped Barium Titanate

Ph.D. Thesis

By Aanchal Sati



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by Aanchal Sati



DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled Structural, Optical and Raman Spectroscopy investigations on pure and Hf-Doped Barium Titanate in the partial fulfillment of the requirements for the award of the degree of Doctor of Philosophy 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 2017 to November 2020 under the supervision of Dr. Pankaj R. Sagdeo, Associate Professor, Indian Institute of Technology Indore

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.

Signature of the student with date (Aanchal Sati)

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ABBREVIATIONS

BHT	BaTi _{1-x} Hf _x O ₃
Ultra-Violet Visible	UV-VIS
Band gap	Eg
Urbach Energy	E_u
Critical Temperature	Tc
X-ray Diffraction	XRD
Diffuse Reflectance Spectroscopy	DRS
Kubelka-Munk Function	F(R)
Charge-coupled device	CCD
Ferroelectric	FE
Room Temperature	RD
Temperature-dependent	TD
Pseudo Jahn-Teller effect	PJTE
Full-Width Half Maxima	FWHM
Adiabatic potential energy surface	APES
Positive Up Negative Down	PUND
Switched charge density	Qsw

Chapter 1

Introduction

In this chapter, a brief review of the literature on barium titanate and its application in science and technology have been illustrated. The chapter is concluded with motivation and the questions that the present thesis seeks to answer.

1.1 Introduction

Perovskite-type oxides with the chemical formula ABO₃ have attracted much attention owing to their various unique properties and potential technological applications[1-4]. These oxide perovskites have great advantages as one tailor the properties of these materials such as its crystallographic, electronic, optical properties by means of doping at A and B site independently or simultaneously [5–8]. The most recent novel applications of perovskites are based on piezoelectric, ferroelectric, and related phenomena. The study of ferroelectricity in perovskite compounds has been a vast subject for investigation, not only because of its technical importance but also for understanding the physics of phase transitions[9,10]. The ferroelectric and piezoelectricity properties have mostly been observed in lead-based perovskite compounds, such as (PbLa)(ZrTi)O₃(PLZT), $Pb(Sc_{1/2}Ta_{1/2})O_3(PST),$ and $Pb(Mg_{1/3}Nb_{2/3})O_3(PMN)[11-14]$. However, these compositions bear a possible hazard due to the toxicity and volatility of lead, which has inspired the development of lead-free ceramics. Therefore, a lot of effort has been made towards investigating environmentally friendly 'Pb-free' ceramic materials. Doping impurity in ceramics is a common way of improving its performance. In recent years, BaTiO₃ with isovalent substituted materials are found to be promising candidates for potential

applications in the areas of microwave communications and optoelectronic devices due to its high dielectric constant and low loss characteristics[5,6,15,16].

Moreover, the physical properties of BaTiO₃ are sensitive to variation in temperature, particle size, impurities, crystal structure, and defect densities[17,18]. The solid solution of BaTiO₃ with any other suitable perovskite compounds enhance various exciting properties and device feasibility. It is very easy to dope respective materials at Ba and Ti sites independently or simultaneously. Extensive studies have been carried out for studying the effect of substitution on dielectric relaxation, electrical properties, the ferroelectric phase transition of BaTiO₃[6,19– 21]. All these properties will depend on the type of dopant and the occupied site of the dopant in the BaTiO₃ lattice. The dopant incorporation into A or B site of any perovskite depends upon the ionic radii difference between the dopant and the corresponding site. Because of the large difference in the ionic radii of Ba (1.47Å) and Ti (0.68Å), the relatively small ions go to the Ti site whereas the larger ions go to the Ba site. Dopant valency also alters the various physical and chemical properties of BaTiO₃. Substituting material having the same valency as that of Ba and Ti ion does not create any vacancy in the system whereas doping material having different valency causes charge imbalance for maintaining electrical charge neutrality which requires the creation of vacancy on Ba/Ti site or in oxygen sublattice[6,20,22]. Based on the various applications different types of dopants are taken, for example, on transducer application A-site doping with Sr^{2+} is used to reduce Curie temperature below 120°C whereas Pb²⁺ is doped to vary Curie temperature above $120^{\circ}C[23,24]$. Also, to increase the stability range of the tetragonal phase Ca^{2+} is doped at A-site[15]. The reason behind decreasing the Curie temperature is to achieve a high permittivity value near room temperature. A large number of modified lead-free BaTiO₃ based ceramics have been studied, due to their environmentally friendly properties, and some of them are potentially valuable materials.

Further, it is believed that the physical properties of BaTiO₃ perovskite such as ferroelectricity, optical properties, etc. are largely originated by its crystal structure (periodic arrangements of atoms), and by changing the rotation and distortion of the TiO₆ octahedra it is observed that various properties of such oxides may be tuned with precision[25– 27]. This change in the rotation and distortion associated with the TiO_6 octahedra can change the O-Ti-O bond angles, Ti-O, and Ba-O bond lengths[28,29]. At this turn, it is necessary to know that the Ti-O, Ba-O bond lengths, and O-Ti-O bond angle can be modulated either by external pressure or by doping/replacement of ions at the Ba/Ti site[30-33]. Further, several distortions can be present in the crystal structure and these distortions may occur simultaneously in the same structure. Moreover, it is well known that the applicability of dielectric materials for charge storage applications is largely governed by the value of the dielectric loss[34,35]. Furthermore, the dielectric properties of the dielectric ceramics are influenced by their vibrational modes [34–36]. Ferroelectrics are one type of special dielectric material, having various applications in electronics. Therefore, the correlation between the vibrational modes and the ferroelectric and dielectric properties is one of the important aspects.

1.2 History and Technological advancements of BaTiO₃

BaTiO₃ (BT) was one of the very first polycrystalline ceramic materials that exhibited ferroelectricity. The story of the discovery of Barium titanate is fascinating and began with secrecy in the early 1940s, as World War II was underway[36,37]. The research was accelerated due to the issue with the supply of mica as at that time mica was used in most capacitors. The preparatory reports were based on the doping studies of titanium dioxide (TiO₂) with barium oxide (BaO), which produces ceramic materials that have very high dielectric permittivity[38,39]. To understand the dielectric anomaly in ceramic BaTiO₃, concurrent work had been conducted by several countries, including the United State[40], United Kingdom[36], USSR[41], and Japan[42]. At that time, it was believed that ferroelectricity can exist only in the naturally occurred crystals such as Rochelle salt and related hydrogen bonding

crystals[43,44]. As far back in the mid-1600s, Rochelle salt was a popular material as it was easily available and its single crystals can be readily grown[45]. But, the water solubility of Rochelle salt eventually stopped its use in later years. In 1945 and 1946, the work of Hippel's group[46] at the Massachusetts Institute of Technology and, Wul and Goldman[41] in the USSR established that the source of unusually high dielectric constant in BaTiO₃ was associated with its ferroelectric properties. This was affirmed for the first time that BaTiO₃ can constitute the ferroelectricity in such a simple ternary oxide compound.

At the end of the second world war, the physical properties and phase transitions of BaTiO₃ became the topics of profound research[46– 48]. The crystallographic investigations of BaTiO₃ played a major role in scientific advancement, the detailed description of the crystal structure of BaTiO₃ was first possibly proposed by Megaw[49], Kay and Voudsen[50] in the United Kingdom, and soon confirmed by Miyake and Ueda[51] in Japan. Furthermore, in 1945 Gray[52] has discovered the piezoelectric properties in BaTiO₃ when he observed that the domains within the grains can orient by an external electric field. This produces a ceramic material that acts similarly to a single crystal having both ferroelectric and piezoelectric properties. Later on, Forsbergh[53] observed the ferroelectric switching of domains under mechanical stress. Thus, the transformation of an inert ceramic to the electromechanically active ceramics under the effect of the electrical aligning process or poling process could be understood very deeply and had been highly noticeable by many industries for their commercial success[52,54].

The discovery of $BaTiO_3$ become a way to stop the continuously running hypothesis, in which it was considered that the ceramic materials cannot be used in the piezoelectric property only just because, these materials are sintered at high temperature and thus loses their crystallinity by cancelling the throughout randomly oriented crystallites. In contrary to this, a detailed study suggests about the ferroelectric crystallites in these ceramics in which the external applied electric field to the material can align or reoriented the crystallites as in the case of magnetic materials with their magnetic moment alignment. Other than these properties, many other results have been evolved in the BaTiO₃ ceramics and pointed out by Jaffe[55] in his famous article on "Piezoelectric ceramics" that (1) the dielectric constant of BaTiO₃ ceramics is found considerably high, for which its ferroelectric behavior may create the permanent internal dipole moment hence, exhibiting high dielectric constant and thus the beginning of a new class of ferroelectrics in the simple octahedral ABO₃ type oxygen group (2) Ceramics as a whole is found very similar to a single crystal because of the internal dipoles of the crystallite aligned in a particular direction with the effect of external electric field direction. Jaffe also introduced the concept of a morphotropic phase boundary to the piezoelectric community.

Furthermore, the theoretical approaches have been put forward to understand the experimental results[56]. A merge study of ferroelectrics, mainly BaTiO₃, between structural, dielectric. thermal, and electromechanical properties has been elucidated in mid of 1949-1951 by Devonshire's group[57,58]. Further, this study has been carried out by Ginzburg, Landau, and Lifshitz[59-61] in 1954 in a particular form of statistical theories of the phase transition to invent a high-quality single crystal, but still, every new theory needs to perform a detailed characterization and study should be correlated to the established theoretical foundations. For example, Miller and Weinreich[62] extended the concept of the nucleation and growth of ferroelectric domains that were developed initially by Merz with Remeika's single crystal[63]. These basic studies set a platform for understanding the polarization dynamics in the current aspects. Besides this study, McQuarrie and Behnke[64] were the first research groups who synthesized the quaternary system between BaTiO₃, BaZrO₃, CaZrO, and CaTiO₃ and evaluate the structural and dielectric study on these systems. Various other investigations were growing in the same era on these quaternary systems between BaTiO₃, BaSnO₃, SrSnO₃, and CaSnO₃[65]. Since all this research was exponentially rising only to raise the temperature stability of piezoelectric property but after these investigations, it was still challenging. Meantime, the ferroelectric and piezoelectric field found a major breakthrough with the discovery of a solid solution of PbTiO₃ and

PbZrO₃[24,66]. These systems showed the variation of the crystal structure with a variation of Zr/Ti concentration and thus attracted much attention from Japanese scientists for exploring these fields [67,68]. All scientific community and industry convert their attention to this family of material for finding the piezoelectric application. However, the intersect was not converted from the BT-based materials because it shows the dielectric properties and can be used in a capacitor which makes this material more relevant and important in the family of ABO₃ perovskite. Furthermore, from 1960 to 1990, an expansion of the ferroelectric community established a new field associated to the electro-optics and thermistors using PZT and BT- based material and thereafter the ferroelectric materials continued to evolve in many applications for device engineering[40,69,70]. However, it is also point to be mentioned that, the operational temperature range for piezoelectric is limited for the technological utility and thus this group of material could not constitute the solution from lead-free material[69]. Therefore, further research is still needed to make the technology transfer of BT-based materials into the industry for manufacturing the lead-free piezoelectric/ferroelectric material.

1.3 Crystal structure and Phase-transitions of BaTiO₃

Barium titanate belongs to the family of perovskite materials with general formula ABO₃. The crystal structure of BaTiO₃ has been shown in fig.1.1 in which the Ba²⁺ is located at the corner of the cubic unit cell, while the Ti⁴⁺ is in the cell center. The O²⁻ anions are at the face centers of the unit cell and constitute TiO₆ octahedra[71,72]. At room temperature, BaTiO₃ is ferroelectric having tetragonal symmetry with the space group P4mm[26,51,73]. In this ferroelectric phase, the atoms are displaced from the centrosymmetric position of Ti ions within the TiO₆ octahedra which involves a slight extension of the c-axis and contraction of the a-axis[73,74,74]. In the cubic paraelectric phase, all the six Ti-O distances are equals whereas in the tetragonal phase the Ti, O1, and O2 atoms are displaced parallel to the c-axis forming two unequal Ti-O1 and four equal Ti-O2 distances[75,76]. The spontaneous polarization in the

tetragonal phase originates from the displacement of cations and anions from their equilibrium position in opposite directions[76,77]. The spontaneous polarization disappears in the cubic phase i.e. above the transition temperature (T_c). For practical applications, the control of T_c is of great importance in the ferroelectric materials.

BaTiO₃ is known to demonstrate the successive structural phase transition due to which it always leads to a fundamental text-book example i.e. BaTiO₃ can exist in different crystallographic structures such as cubic, tetragonal, orthorhombic, and rhombohedral depending on different temperature ranges [28,48,53,78]. The cubic phase of Barium titanate is centrosymmetric having Pm3m space group. Therefore, it is both non-piezoelectric and paraelectric. The structural phase transition from the cubic phase to the lower symmetry ferroelectric phases is related to the softening of the zone-boundary phonon modes at the Curie temperature (T_c). On cooling from the high temperature (<400K) paraelectric cubic phase, at ~393K it transforms into the ferroelectric tetragonal phase, with further cooling, it changes its structure to orthorhombic and then rhombohedral at 278K and 197K, respectively [28,48,53,78]. Along with the tetragonal phase, the orthorhombic and the rhombohedral phase also exhibit ferroelectricity [45,71]. The tetragonal unit cell results from the distortion of the unit cubic cell of the paraelectric phase due to the off-center displacement of the oxygen (O^{2-}) and titanium ions (Ti^{4+}) in the opposite directions along <100>. Since there are six equivalents <100> direction in the cubic phase, the polar axis can be any one of these directions. The orthorhombic distortion is induced by the displacement of titanium and oxygen ions along one of the <110> cubic directions. In the rhombohedral distortion, the polar axis of this phase lies along one of the original cubic <111>direction. The rhombohedral distortion can be visualized as the stretching of the original cube along one of the body diagonals resulting from the displacement of Ti⁴⁺ and O²⁻ ions. There are eight equivalent directions in the cubic phase and the spontaneous polarization may be parallel to any of these directions. These phase transitions occur with strong dielectric softening, as shown in fig.1.2 by three distinct maxima in the relative

permittivity. These structural phase transitions have also been probed by various techniques such as x-ray diffraction[77], Raman spectroscopy[79,80] and, extended x-ray absorption spectroscopy[78], and the signature of the same is also observed in the bandgap measurements[81,82].



Figure 1.1: The ideal cubic $Pm\overline{3}m$ structure of $BaTiO_3$. Ba is a large 12-fold coordinated cation and Ti is a small 6-fold coordinated cation.



Figure 1.2: Changes in lattice parameters and anomalies in relative permittivity during the sequence of phase transitions in BaTiO₃. The unit cell distortions in each of the ferroelectric phases of BaTiO₃ are illustrated on the right side of the figure[72].

1.4 Dielectrics

The term dielectric is referred as the ability of a material to store electrical energy. When a dielectric material is placed in an electric field, it acquires a surface charge due to induced polarization. The induced polarization is caused by the relative displacement of positive and negative charges in the dielectric or by rotation of permanent electric dipoles present in the material. BaTiO₃ is the well-known dielectric materials, which have practical application. Basically, polarization in the material occurs due to four possible mechanisms: electronic, ionic, orientation, and space charge[83]. The electronic polarization occurs due to the shift of the electronic charge cloud of an atom with respect to the positive nucleus under the influence of the electric field thus producing a dipole. The ionic polarization is due to the small displacement of ions from their equilibrium positions and hence inducing a net dipole moment under the application of an external field[84]. The dipolar/orientation polarization is due to the alignment of electric dipoles, which are oriented along the field direction. The space charge/interface polarization involves limited movement of charges resulting in the alignment of charge dipoles under applied field which generally happens at the grain boundaries or any other interface such as an electrode-material interface. Therefore, when a dielectric material is placed in an external electric field all levels of polarization take place. For an applied ac field, the different polarization mechanism will respond differently and hence have a different amount of phase lag. Thus, over a wide frequency range, different types of polarization cause several dispersion regions as shown in fig.1.3. The electronic polarization is the fastest and typically persists at frequencies between $\sim 10^{13}$ - 10^{15} Hz. In contrast, ionic polarization is slow and typically occurs at frequencies between $\sim 10^9 - 10^{13}$ Hz whereas dipolar polarization participating motion of molecules occurs below 10^9 Hz. Interface or space charge polarization occurs at frequencies below 50 Hz.



Figure 1.3: Schematic figures of frequency dependence of polarization.

The behavior of dielectric material is generally characterized by the temperature, field, and frequency dependence of its "permittivity" (ϵ). The permittivity is the ability of the material to polarize under the influence of the applied field, thus reducing the total electric field inside the material. The permittivity (ϵ) can be expressed in terms of the total electric displacement field D caused by the applied field (E) as

$$\mathbf{D} = \boldsymbol{\varepsilon} \cdot \mathbf{E} \tag{1.1}$$

For vacuum, the permittivity is denoted as ε_0 , which is equal to 8.854 x 10^{-12} F/m. The linear permittivity of homogeneous material is usually given relative to that of vacuum, as a relative permittivity ε_r (also called dielectric constant)

$$\varepsilon_{\rm r} = \frac{\varepsilon}{\varepsilon_0} \tag{1.2}$$

The total electric displacement field D, in a dielectric caused by some external field E, has two components, the one for the vacuum part and the other arising from the material itself. Thus

$$D = \varepsilon_0 \cdot E + P \tag{1.3}$$

$$D = \varepsilon_0 \cdot E + \varepsilon_0 \chi_e \tag{1.4}$$

$$D = \varepsilon_0 \cdot E(1 + \chi_e) \tag{1.5}$$

Where χ_e is the electric susceptibility of the material.

In an applied ac electric field, the vacuum permittivity ε_0 remains invariant but the response of the normal materials generally depends on the frequency of the applied field. The frequency dependence of the normal material is due to the fact that the material's polarization does not respond instantaneously to the applied field, i.e. the response has a phase difference with respect to the applied field. Therefore, for this reason, permittivity is often treated as a complex function of the frequency (ω) of the applied field.

$$\varepsilon^* = \varepsilon' + j\varepsilon'' \text{ and } tan\delta = \frac{\varepsilon'}{\varepsilon''}$$
 (1.6)

where ε^* is the complex dielectric constant which consists of real part ε' which is a measure of energy stored and imaginary part ε'' is the measure of the loss or dissipative energy from the applied electric field (includes the effects of both dielectric loss and conduction loss), tan δ is the dissipation factor/loss tangent/loss angle (the ratio of the imaginary part of the dielectric constant to the real part). Usually, the representation of the dielectric properties/data is the variation of ε' , ε'' and $tan\delta$ as a function of temperature and frequency. The investigation of the dielectric constants over a wide frequency range, i.e. dielectric spectrum, is necessary to study relaxations (time-dependent dielectric behavior).

1.5 Ferroelectrics

Ferroelectrics are polar materials that possess spontaneous polarization in the absence of an electric field. The direction of the polarization vector can be reoriented by the application of a sufficiently high external electric field. Ferroelectric materials are identified by the ferroelectric hysteresis-loop in the polarization (P) vs electric field (E). This P-E hysteresis loop in ferroelectric materials is a consequence of the reduction in the electrostatic and elastic energies [85,86]. The regions where the polarization is uniformly oriented are called ferroelectric domains and the boundary between these domains is called domain wall. The domain walls are generally formed to reduce the energy of the system. The walls separating the two domains with opposite polarization directions are called 180⁰ domain walls, and the walls separating domains with perpendicular direction are called 90° domain walls[87]. Fig.1.4 shows the domain orientation for the 180° and the 90° domains. The domain's walls orientation depends on the crystal symmetry. For example, the tetragonal phase of $BaTiO_3$ consists of both 180^0 and 90^0 domain walls. For the orthorhombic symmetry 60° , 90° , 120° , and 180° domains are permitted, and for the rhombohedral symmetry, 71° , 109° , and 180° domains are allowed[88]. The application of an electric field orients the domain polarization in the direction of the applied field and transform the multi-domain state into a single domain state.



Figure 1.4: (*a*) Schematic illustrations of 180° and 90° domain walls[89]. (*b*) Both the 180° ferroelectric stripe domain (bottom-left) and conventional 90° ferroelectric stripe domain (top-right) in BaTiO₃[87].

Fig.1.5(a) shows a typical polarization versus electric field loop of a ferroelectric material. At low electric field, the polarization increases linearly. Upon application of a large electric field, all the dipoles get oriented along the field direction and reach the saturation state and the ferroelectric behaves like a linear dielectric again. After the saturation point, the reversal in the field does not return the ferroelectric polarization (P_r) exists in the material. Therefore, electric field should be applied in the opposite direction to bring the polarization back to zero. The electric field required to decrease the polarization to zero is called the coercive field (E_c). At coercive field, the polarization state is again random and there is no net polarization.

The phenomenon of ferroelectricity is observed in the polar class of non-centrosymmetric crystals[55,90]. The ferroelectrics are characterized by a maximum of the real part, ε' , of the complex permittivity at the Curie temperature T_c. Above T_c, the material becomes paraelectric[84]. The dielectric permittivity (ε') shows a sharp peak at the Curie temperature (T_c) and follows the Curie-Weiss law (for T > T_c) given as follows (Fig. 1.7(b))[71,83]

$$\varepsilon = \varepsilon_{\infty} + \frac{c}{(T - T_c)} \tag{1.7}$$

where C is Curie constant, T_c is the Curie temperature; ε_{∞} is the dielectric permittivity contribution due to electronic polarizability. The Curie temperature in the above formula is a constant while the Curie point is the actual temperature of the structural phase transition from a polar to a non-polar state or vice-versa. For a first-order phase transition, T_c is greater than T₀ while in a second-order phase transition the two temperatures are equal (i.e., $T_c=T_o$)[71]. Here, ferroelectric phase transitions are categorized into two parts[71], i) displacive type where the ferroelectric transformation is due to displacement of an ion with respect to another (e.g. BaTiO₃, PbTiO₃, and PZT, etc.) and ii) order-disorder type where ferroelectric phase transition is associated with the individual ordering of ions (e.g. KH₂PO₄ and NaNO₂, etc.). Moreover, the chemical substitution in ABO₃ perovskites produces the random lattice disorder which can lead to the formation of dipolar impurities and defects that have a profound influence on the static and dynamic properties of the ferroelectric materials[90]. When these dipolar entities possess more than one equivalent orientation, they may undergo dielectric relaxation in an applied ac field.



Figure 1.5: (*a*) Polarization–electric field hysteresis loop of the ferroelectric crystal[38] (b) Temperature-dependent of dielectric permittivity showing paraelectric to ferroelectric phase transition below Curie temperature, Tc[91].
1.6 Relaxor ferroelectrics

The relaxor behaviour in the ferroelectric materials is one of the hot topics in the field of ferroelectricity and its origin has been the focus of interest in solid-state physics[90]. The relaxor behaviour has been observed and studied most extensively in disordered ABO₃ perovskites[92,93]. The ferroelectric relaxors materials are similar to the normal ferroelectric materials but have randomness associated with one or more of the atoms in the unit cell. Most of the well-known relaxor ferroelectrics are complex compounds with the perovskite ABO₃ structure having disorder at A/B-sites. A signature of the relaxor state is a broad frequency-dependent peak in the real part of the temperature-dependent dielectric susceptibility (ϵ ') that can spread in the temperature interval of hundreds of degrees[92]. It should also be emphasized that the imaginary part of the dielectric constant ε'' (or tan δ) can also reveal the relaxor behavior in a frequency-dependent peak[92]. Fig.1.6 shows the temperature dependence of the dielectric permittivity ε of the model relaxor ferroelectric, PMN[94]. The peak of ε enhances with decreasing the frequency and its peak position simultaneously shifts toward the lower temperature. Therefore, in contrast to the normal ferroelectric response, the dispersion in the dielectric permittivity covers a wide frequency range from MHz to GHz. Further, it is also important to note that, the occurrence of polar nanodomains is a cause of relaxor behavior. However, such types of nanodomains find in many ABO₃ relaxors at a temperature far above the peak in $\varepsilon'(T)$, and their manifestation is considerably important for understanding the relaxor properties[92,95,96].



Figure 1.6: Temperature dependence of the real part of the dielectric permittivity (upper curve) and of the tan δ (lower curve) of PMN. The numbers (1)–(6) show the results from a frequency of 0.4 kHz to a frequency 4.5 MHz [94].

Moreover, Viehland's group[95] proposed that the frequency dependence and non-Debye relaxation in such material that was deviating from the Curie-Weiss law are due to the formation of local nano-polar regions. On cooling the material by the freezing temperature T_f , a remanent polarization is found to occur in the material when micropolar regions merge into the domains and further cooling yields the normal ferroelectric behavior which shows the expression of hysteresis. Therefore, in order to understand the relaxors in-depth, there must be at least some differences in properties compared to normal ferroelectric materials, such distinction is as follows and are shown in fig.1.7[90]:

- 1. The normal ferroelectric materials show a well-defined PE hysteresis loop and large remanent polarization as shown in fig.1.7(a). Whereas, a relaxor ferroelectric exhibits a so-called slim loop and small remanent polarization, as shown on the right-hand side.
- 2. The remanent and the saturation polarization of a ferroelectric decrease with increasing temperature and completely disappear at the ferroelectric transition temperature (T_c). The disappearing of polarization at Tc is continuous for a second-order phase transition and discontinues for a first-order phase transition as shown in fig.1.7(b).
- 3. The static dielectric susceptibility, or dielectric constant (ϵ ') of a ferroelectric exhibits a sharp, narrow peak at T_c (fig.1.7c). By contrast, a relaxor exhibits a very broad ϵ '(T) peak and strong frequency dispersion in the peak temperature (T_m) and in the magnitude of ϵ ' below T_m.
- 4. The temperature dependence dielectric permittivity ε' of ferroelectric materials is defined by a Curie Weiss law above Tc as shown by the linear response of 1/ ε' versus T in fig.1.7(c). Oppositely, relaxor exhibits strong deviation from this law, but follow the relation

$$\frac{1}{\varepsilon'} = A + B(T - T_m)^2$$

This relation was derived theoretically and validated experimentally from the Gaussian distribution of $T_{c.loc}$ of the polar-regions.



Figure 1.7: Comparison of normal and relaxor ferroelectrics[90].

To understand the physics of relaxor ferroelectrics various models have been developed. Smolensky, Kirillov, and Isupov[97] proposed a composition fluctuation model in which the broad maximum of dielectric permittivity is interpreted in terms of a diffused phase transition comprising of a series of local phase transitions. But this model fails for many complex perovskites having B-site random cations which do not show any diffuse phase transition. Further, L. E. Cross[92] developed a super paraelectric model in which he postulated that in relaxor ferroelectric small-sized noninteracting polar clusters exist which permit dynamical (thermal) disordering over a specific range of sizes analogous to spin clusters in the superparamagnetic state. In analogy with magnetic spin glasses, Viehland et al.[95] introduced a dipolar glass model and suggested that individual polar clusters interact with each other by means of dipolar interactions. In 1992, Westphal, Kleemann, and Glinchuk[98,99] proposed a random- field model in which they assume that the relaxor state is composed of polar nanodomains discretely separated by domain walls, i.e., a ferroelectric nanodomain state.

1.7 BaTiO₃: Its importance and modifications

BaTiO₃ is the most studied ferroelectric material that has been used to suffice the need for high dielectric constant material for the energy storage application. BaTiO₃ has been extensively used in the electronics industry due to its high dielectric constant and low loss characteristics. Due to excellent dielectric properties, BaTiO₃ has also been used as resonators, dynamic random-access memory, sensors, actuators, etc. Owing to the simple structure of BaTiO₃, it can accommodate different types of dopants, ensuring easy tailoring of its properties for various technological aspects. The microstructure, dielectric, and ferroelectric behavior of BaTiO₃ can be modified, by a wide variety of possible substitutions at Ba²⁺ sites (A site) or Ti⁴⁺ sites (B site) independently or simultaneously[7,25,100,101]. In recent years, BaTiO₃ and isovalent substitutions seem to be promising candidates for potential applications in the areas of microwave communications and optoelectronic devices[102,103]. A large number of modified lead-free BaTiO₃ based ceramics have been studied, due to their environmentally friendly properties, and some of them are potentially valuable materials. Some of these ceramics display composition-dependent relaxor behavior[14,73]. This relaxor behaviour varies with the substitution of different types of ions and the level of substitution[20,104,105]. In the literature, various experimental evidence is present which suggests that the presence of the disorder the of is necessary for occurrence the relaxor

behaviour[73,106,107]. The chemical substitution in ABO₃ perovskites produces the random lattice disorder which can lead to the formation of defects and dipolar impurities that influence the dynamic and static properties of these materials. The presence of nanopolar domains plays a key role in the occurrence of relaxor behavior. The presence of nanopolar regions can also be probed by using Raman spectroscopy as it is very sensitive to probe the local symmetry[108,109].

Numerous studies have been performed to reveal the relationship between the electrical properties and doping concentration for BaTiO₃[16,110–112]. Of these, BaTi_{1-x}Zr_xO₃ has received renewed attention because Zr is chemically more stable than Ti[113,114]. It involves the isovalent substitution of titanium by zirconium, the dielectric and piezoelectric properties are found to change drastically as a function of Zr substitution level. With increasing Zr content, the Curie temperature decreases and the peaks transform from sharp to diffuse type and for higher substitution level it exhibits relaxor behavior [16,114–116]. The T_c value corresponding to the paraelectric to ferroelectric transition gets shifted to a lower temperature and the rhombohedral to orthorhombic and orthorhombic to tetragonal phase transition temperature shifts to higher temperatures on substitution of Zr^{4+} at the Ti^{4+} site. The B-site cations Zr⁴⁺, Hf⁴⁺, and Sn⁴⁺ have similar effects as modifiers. In these systems, the coexistence of phases can exist near phase boundaries. These phase boundaries usually called the morphotropic phase boundaries can greatly enhance permittivity and piezoelectricity. Based on the dielectric anomaly temperatures, the phase diagram of the solid solution between barium titanate and zirconium titanate is shown in fig.1.8. As clear from the figure that the line of paraelectric-ferroelectric transitions decreases but the lines of the inter-ferroelectric transitions increases with an increase in Zr concentration such that stability fields of the four phases (cubictetragonal-orthorhombic-rhombohedral) converge on approaching the line of Curie points. Thus, the phase diagram of BaTiO₃-xBaZrO₃ is of the pinching type. The temperature range of this coexistence is likely to be increased due to random elastic strain induced in the lattice by substitution of Zr at the Ti site. In lead zirconate titanate by the TEM

results, it has been observed that the existence of morphotropic phase boundaries is due to the formation of nanodomains. Moreover, the theoretical calculations based on fundamental thermodynamic principles also support this phenomenon.



Figure 1.8: *Phase diagram of barium titanate-barium zirconate*[117,118].

Further, the isovalent substitution of Hf at Ti site in BaTiO₃ has also come up as a new possible substitute for the lead-free relaxor ceramics. In literature Anwar et al.[73,105] investigated the phase transition behaviour of BaTi_{1-x}Hf_xO₃ that can be changed from a normal phase transition to displacive and further to the relaxor phase transition. Das et al.[119] found a double hysteresis loop in BaTi_{1-x}Hf_xO₃ ($0 \le x \le 0.15$) which indicates the appearance of antiferroelectricity. Since the applicability of dielectric materials for charge storage application is largely governed by the value of the dielectric loss. Hence, it is extremely important to understand the possible contributors to the dielectric loss in greater detail. Some reports on perovskite oxides suggest that the value of the dielectric loss is critically controlled by the magnitude of bandgap (Eg), electronic disorder, and electron-phonon coupling[81,120–124].

1.8 Raman spectroscopic investigations on BaTiO₃ and similar oxides

The Raman spectroscopy is a well-known versatile technique to probe the local structure which may control the dielectric behavior mainly the ferroelectric-relaxor cross-over in ceramic materials. Furthermore, it is also widely used for the detection of the structural distortion in the perovskite materials and to calculate the strength of electron-phonon interaction. For an ideal cubic symmetry, first-order Raman scattering is forbidden by the symmetry/Raman selection rule. In pure BaTiO₃, numerous independent investigations have proven that the two broad asymmetric modes at 275 and 514 cm⁻¹ in the Raman spectrum persist well into the cubic paraelectric phase even though symmetry precludes the observation of first-order spectra. The appearance of first-order Raman modes in the paraelectric phase of BaTiO₃ can be understood based on the disordered structure model proposed by Comes et al. Further, Ouni et al. have shown the coexistence of first and second-order Raman lines in pure BaTiO₃ and concluded that all the Raman modes in BaTiO₃ are of first-order but second-order processes lying close to these positions contribute to a broadening of these peaks. In addition, the structural disorder in the A or B sub-lattice can also relax the Raman selection rule. In various literature, it has been observed that the Raman spectroscopy is also useful to determine the site occupancy of the dopants in BaTiO₃. In the temperature-dependent Raman spectra of pure BaTiO₃, as shown in fig.1.9, there is no evidence of any mode in the region around 800cm⁻¹. However, in the solid solution of BaTiO₃ with two or more B-site species, as shown in fig.1.10(a), the presence of dissimilar ions in the center of the octahedra creates asymmetry and thus the breathing A1g mode becomes Raman active. Although, as shown in fig.1.10(b) that the direct substitution of the dopant onto the A-site of BaTiO₃ does not allow the A1g breathing mode to become Raman active and this mode is only

sensitive to modifications of the B-site occupancy. The presence of this mode in literature has been considered as a signature of relaxor behaviour. Further, a similar mode has also been predicated purely due to structural disorder [24]. Thus, it appears that there exist mixed opinions about the Raman mode around~800 cm⁻¹, i.e., whether this mode arises due to the asymmetry in the breathing mode (A_{1g}) [30, 31] or relaxation or structural disorder [24]. Therefore, it is important to remove this ambiguity and to understand the origin of this mode in greater detail and to understand the possible correlation between the electronic and phononic disorder which has been discussed in detail in chapter-6. Moreover, Raman spectroscopy has also been widely used to investigate the strength of electron-phonon interaction in various materials qualitatively[125-127]. Fano model is found to be very successful for qualitative analysis of the electron-phonon interaction parameter and the corresponding asymmetry in the line shape also known as the Fano line shape of the Raman modes which is a signature of the electron-phonon interaction[128-131]. In the next section, the Fano model has been discussed in detail.



Figure 1.9: Temperature-dependent Raman spectra of pure BaTiO₃.



Figure 1.10(a): Temperature-dependent Raman spectra of Sr doped BaTiO₃.



Figure 1.10(b): Temperature-dependent Raman spectra of Zr doped BaTiO₃.

1.9 Raman study to calculate the strength of electronphonon coupling via Fano model

Raman spectroscopy is a powerful and sensitive tool to probe the local structure and can provide thorough information into the local distortion, disorder, and strain present in the ceramic materials[132-134]. In a crystalline material, only transitions with $k \approx 0$ are allowed by the momentum selection rule of first-order Raman scattering[135,136]. However, disorder relaxes the Raman selection rule for $k \approx 0$, which allows first-order Raman scattering by phonons of larger k values and causes the asymmetric broadening of the phonon modes in the Raman spectra[137-139]. The asymmetry in the Raman line shape can be explained by the Fano model. In general, the Fano resonance occurs when a discrete energy state interferes with a continuum band of states. The Fano effect is characterized in terms of asymmetric Raman line shape along with antiresonance peak[125,128,129,140]. Since the Fano effect is caused by interference of electronic and phononic continuum, and interference may be constructive as well as destructive, therefore resonance (due to constructive interference) and anti-resonance (due to destructive interference) both are simultaneously observed in the Fano spectrum. The schematic illustration of Fano interference is shown in fig.1.11. The Fano interaction between discrete phonon state and continuum of electronic states can be studied by Raman scattering or IR spectroscopy or by other spectroscopies[130,141-143].



Figure 1.11: The schematic illustration of Fano interference[128].

Fano model is found to be very successful for qualitative analysis of the electron-phonon interaction parameter and the corresponding asymmetry in the line shape also known as the Fano line shape of the Raman modes which is a signature of the electron-phonon interaction[82,125–128,141,144,145]. As a result of Fano interaction, this asymmetry can be expressed with the Fano function.

$$I(\omega) = I_c \frac{|q+\varepsilon|^2}{1+\epsilon^2} + I_b(\omega)$$
(1.8)

Where q is asymmetry parameter, Γ is the Raman linewidth and ε is equal to $(\omega - \omega_p)/\Gamma$, where; ω_p is the renormalized phonon frequency. The inverse of the asymmetry parameter is proportional to the electron-phonon interaction i.e. a lower value of q means stronger electron-phonon interaction[126,128]. The presence of the Fano effect will also result in increased half-width of the Raman modes. Fig.1.12 shows a plot of the Fano curve for various values of q. As clear from the figure that when $|q| \rightarrow \infty$ the line shape of Raman modes is completely determined by the transition through the discrete state only and the transition to the continuum is very weak, resulting in a Lorentzian profile. The q=0 case is described by a symmetrical dip, sometimes called an antiresonance. As an example, the Fano fitting for Silicon, Magnetite (Fe₃O₄), and Barium titanate (BaTiO₃) is depicted in fig.1.13.



Figure 1.12: Fano line shape for the various value of q[146].



Figure 1.13(a): Fano fitting for doped silicon[130].



Figure 1.13(b): Fano fitting Magnetite (Fe_2O_3) at different temperatures[147].



Figure 1.13(c): Fano fitting for Barium titanate (BaTiO₃)[148]

1.10 Optical spectroscopic investigations on BaTiO₃

The UV visible optical absorption is potentially being used to probe the important parameters of semiconducting material; such as bandgap (E_g)[82,149,150], electronic disorder i.e. Urbach energy (E_u)[150,151], and defect states[152,153]. Fig.1.14 shows the various regions of the absorption curve for aluminum-doped zinc oxide thin films[154]. In addition, the temperature-dependent optical absorption spectroscopy has also been used to provide information related to the bandgap, electron-phonon interactions, excitonic effects, amount of disorder, etc[155–157]. To understand the variation of bandgap as a function of temperature different models have been proposed[157–159]. However, to calculate the strength of the electron-phonon coupling Bose-Einstein model has been found to be very effective[157,159–161]. In the next section, the Bose-Einstein model has been discussed in detail.



Figure 1.14: Various regions of the absorption curve for aluminum-doped zinc oxide thin films[154].

In order to understand the effect of structural phase transition on E_g and E_u , many efforts have been made in the past few years[82,159,161,162]. Several studies have been reported to understand the temperature dependence of E_g and E_u on BaTiO₃[82,159,161–163]. In the temperature-dependent bandgap and Urbach energy data of BaTiO₃, as shown in fig.1.15(a&b) respectively, it is observed that E_g decreases whereas E_u increases with an increase in temperature. From the figure, it has been observed that at phase transition temperature there is a sharp anomaly in the value of both E_g and E_u . This anomaly is a signature of tetragonal to cubic structural phase transition. In literature, the decreasing behavior of band gap with an increase in temperature has been understood by considering the change in electron-phonon interaction[81] (which take cares of change in the value of lattice parameter/spontaneous

polarization), a change in the carrier concentration of electrons/holes[164] (screening effect) and a possible change in the grain/particle size[165]. Moreover, Urbach energy is a measure of the total disorder present in the system (thermal disorder, structural disorder, chemical disorder, polar disorder, defects, etc.) and it is generally observed that E_u scales up with thermal disorder. In order to explain the behaviour of E_u , many efforts have been made by various research groups [151,162,166]. In the case of polar materials (dielectric), it has been observed that the change of the shape of the absorption edge across transition temperature is a result of an enormous change in the electron-phonon interaction near the phase transition of electron-phonon interaction with temperature in BaTiO₃ and its possible contribution to understanding its various physical properties. In chapter-5, the possible contribution of electron-phonon coupling on dielectric properties has been discussed.



Figure 1.15(a): *Temperature-dependent variation of band gap of BaTiO*₃[82].



Figure 1.15(b): *Temperature-dependent variation of Urbach energy of BaTiO*₃[168].

Further, it is important here to note that the vibronic theory appears to be very successful to understand the origin of ferroelectricity in the high symmetric cubic phase [169]. According to vibronic theory i.e. pseudo-Jahn Teller effect (PJTE), the vibronic coupling (electron-phonon coupling) creates local dipolar distortions of dynamic nature, resonating between two or more equivalent orientations resulting in spontaneous symmetry breaking[75,76,170]. The origin of all the four phases in BaTiO₃ is explained by the adiabatic potential energy surface (APES) induced by the PJTE [75]. Since the trigonal well is the only minima of APES, thus depending upon the off-center displacement of the transition metal ion along one of the eight equivalent trigonal directions the resulting phase is identified. The resulting nature of phase transitions is treated as order-disorder. As the PJTE is of local origin therefore in the macroscopic picture, the paraelectric cubic phase of BaTiO₃ is centrosymmetric but as in the cubic phase, all the eight minima are equivalent as shown in fig.1.16 and hence the cubic phase is a para-electric phase, a small perturbation to the system in form of doping, strain, etc. makes the above-mentioned eight minima as non-equivalent, which may lead to finite local dipole-moments.



Figure 1.16: *BO*⁶ octahedra of *ABO*³ perovskite crystal structure, with atom *B* at the center (red) and six oxygen atoms (blue) at the apexes of the octahedron. The off-center positions of the atom *B* in the eight wells of the *APES* induced by the *PJTE* are denoted by the letters *a*, *b*, *c*, ... [75].

1.11 Optical study to calculate the strength of electronphonon coupling via Bose-Einstein model

The temperature dependence of the optical band gap has been used successfully to predict the strength of electron-phonon interaction. In this regard, the Bose-Einstein model for the temperature-dependent band gap was found to be very successful[157,159–161]. The electron-phonon interaction occurs due to the emission and absorption of phonons by electrons and the distribution of phonons in each phonon mode is temperature-dependent and follows the Bose-Einstein statistics. According to the Bose-Einstein distribution, with an increase in temperature the average number of phonons increases, and thus the electron-phonon interaction also increases[171]. The effects due to electron-phonon interaction can generally be described by lattice vibrations that can be represented by one or more Bose-Einstein oscillators[172]. Thus, the Bose-Einstein model for describing the variation of optical band gap with temperature contains the Bose-Einstein statistical factor[160]

$$E_g(T) = E_g(0) - a_B * \left[1 + \frac{2}{\{exp(E_{ph}/K_B T) - 1\}} \right]$$
(1.9)

Where, $E_g(T)$ represents the band gap as a function of temperature, $E_g(0)$ is the energy gap at 0 K, E_{ph} represents the average energy of phonon which strongly coupled with electron and a_B represent the strength of electron-phonon interaction. Using the Bose-Einstein model (equation-1.1), it is possible to estimate the value of electron-phonon coupling parameter and also the energy of the phonon which is strongly bound with the electronic continuum. An example, of such a fitting for semiconducting materials like Indium nitride (InN), Aluminium nitride (AlN), and lead titanate (PbTiO₃) is depicted in fig.1.17.



Figure 1.17(a&b): *Temperature dependence of band gap energy and* Bose-Einstein fitting of the experimental band gap of Indium nitride (*InN*)[173], (*b*) *Aluminium nitride* (*AlN*) [173].



Figure 1.17(c): *Temperature dependence of the band gap energy and Bose-Einstein fitting of the experimental band gap of Lead titanate* (*PbTiO*₃)[174].

1.12 Effect of strain on BaTiO₃ and similar oxides

In ABO₃ perovskite oxides, it is well-known that the strain plays a very crucial role[132,175–177]. The strain on the material can be caused by various external parameters. For example, mismatch in the size of ions or shrinkage and expansion due to temperature changes can cause strain on the material [176,178,179]. In Ca doped LaMnO₃, Sagdeo et al. [180] reported that the structural phase coexistence observed in these types of materials is due to the presence of interfacial strain present near the grain boundary. Thus, it appears that the interfacial strain plays a very major role in the perovskite-based oxides which undergo the structural phase transition as a function of temperature, pressure, or doping. BaTiO₃ is the most important ferroelectric material and is known for its various phase transitions[78,175]. When BaTiO₃ is cooled down from a hightemperature cubic state, it undergoes a symmetry lowering phase transition that generates spontaneous strain inside the ferroelectric polycrystals[181]. The presence of strain in BaTiO₃ stretches the electric polarization and shows the importance of strain engineering to improve

the performance of capacitors and other energy storage devices. Recently, in BaTiO₃ and PbTiO₃ it has been observed experimentally that the strain engineering enhances the electric polarization up to 400μ C/cm² which improves the corrosivity[175,182]. In literature, it has been observed that the strain strongly affects the ferroelectricity in perovskite-oxides[175,176,183]. Anil et al.[179] have shown that the strain also affects the optical properties of perovskite-oxides.

Earlier, various research groups have reported ferroelectricity in the centrosymmetric cubic structure at the global length scale[183,184]. Duran et al.[184] reported a well-defined polarization-electric field hysteresis loop, characteristic of a ferroelectric state, at room temperature in the cubic phase of Pr doped $SrTiO_3$ samples. The replacement of Sr^{2+} by Pr³⁺ ions produces strained lattice and disturbs the local charge compensation, as a result, the repulsion between Ti^{4+} and Pr^{3+} increases. Thus, the Ti-Pr interatomic distance increases, and as a consequence, the PE data display ferroelectric behaviour due to the non-centrosymmetry induced by the strained lattice. Similarly, in Hf doped BaTiO₃ samples, the mismatch in the size of Hf and Ti increases the distance between the off-centered Ti dipoles and thus weakened the correlation between these dipoles and distorts the oxygen octahedra. The distortion in the oxygen octahedra gives rise to local electric and strain fields. These local strain fields are random in nature and hence the long-range ferroelectric order gets disrupted and nano-polar regions are formed [19,73,105]. The role of local polar regions in the origin of polarization in the cubic phase of Hf doped BaTiO₃ samples has been discussed in detail in chapter-7. Experimentally, the strain present in the material has been probed using various techniques such as transmission electron microscopy[19], x-ray diffraction[185], neutron diffraction[186], Raman spectroscopy[132], etc.

1.13 Theme of the present study:

As discussed in the introduction part, the BaTiO₃ ceramic has been investigated by various researchers to investigate the physics of structural phase transition and to improve its dielectric properties. During a detailed literature survey, we have noticed that there are very scattered studies on the optical properties of BaTiO₃[12,22]. A noticeable study is found to be missing from the literature about the correlation between the dielectric and optical properties, such as dependence of dielectric constant and dielectric loss, with optical band gap and electronic disorder (Urbach energy). A major portion of the literature reveals the correlation of temperature dependence of dielectric constant but dielectric loss is rarely discussed for BaTiO₃. Therefore, this study emphasizes, taking care of the linewidth parameter which brings the electron-phonon coupling to explain the temperature-dependent dielectric loss in BaTiO₃. Further in the literature, Shahid et. al [19] have shown that there exist tetragonal to cubic transition in BaTi_{1-x}Hf_xO₃ at x=0.12 with Hf doping whereas Das et. al[21] have shown the ferroelectric loop for samples with x=0.15. In order to answer this question, an attempt has been adopted here to establish a possible correlation of structural disorder with induced polarization using Raman spectroscopy.

★ The well-known classical ferroelectric material BaTi_{1-x}Hf_xO₃ with different Hf doping concentration (x=0.06, 0.09, 0.12, 0.15, 0.21, 0.27 & 0.30), has been studied in its pure and doped form. The prepared samples have been studied using dielectric and optical measurements to explore the effect of Hf doping at Ti site. A new methodology has been proposed for understanding the origin of dielectric loss in terms of band-gap and Urbach energy with a proposed tunneling probability model. Since, for any dielectric material, it is expected that the electronic disorder near the band edge will contribute to the dielectric loss. Therefore, the value of electronic disorder is probed by using diffuse reflectance spectroscopy in the form of Urbach energy. Simultaneously, the vibrational properties of BaTi_{1-x}Hf_xO₃ samples have been investigated using Raman spectroscopy. In the Raman spectra, a significant new Raman mode corresponding to

~780cm⁻¹ appears with the Hf doping percentile and indicates an increment in the phononic disorder. A systematic increase in the intensity of disorder phonon mode and that of the electronic disorder suggests that structural disorder not only affects phonons but the electronic state of the system as well.

♦ A new way for understanding the temperature dependence dielectric loss of ferroelectric materials BaTiO₃ is investigated by using the temperature-dependent optical and Raman spectroscopy. The results reveal that the electron-phonon interaction parameter increases with temperature and shows a sudden increase by almost two-fold at tetragonal to cubic transition temperature. Therefore, this study also helps to establish a strong correlation between the dielectric loss and electronphonon coupling. On contrary, Hf doped BaTiO₃ samples display the polarization in the cubic phase as demonstrated by using Raman and PE measurements which indicates the presence of short-range correlated displacements of the Ti ions. Moreover, the vibronic (electron-phonon) coupling parameter increases with increasing Hf content which also signifies the existence of local dipolar regions in the perovskite structure. The impact of this explanation is suited for the presence of polarisation in the cubic phase.

The Main key aspect of the thesis work is being pointed in bullet form:

• Tunnelling probability model has been proposed to investigate the correlation between dielectric loss and band gap.

• Structural disorder affects both the Phononic and electronic state of the system.

• Electron-Phonon coupling directly relates to the dielectric loss.

• Local dipolar region may establish the polarization even in the cubic system.

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1.14 Organization of the Thesis

The present chapter covers a brief introduction to this work. The remaining chapters of the thesis are summarized as follows:

Chapter 2: Experimental Techniques and Theoretical Background;

In this chapter detail about the synthesis and characterization techniques relevant to this work have been provided. The solid-state reaction method has been discussed in detail and used for preparing the BaTi_{1-x}Hf_xO₃ samples. The basic description of characterization techniques such as x-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS), dielectric spectroscopy, Raman spectroscopy, and ferroelectric measurements have been discussed. To explain the basic working principle of used-setups the schematic representation has been used.

Chapter 3: Synthesis and Characterization of Pure and Hf doped

<u>BaTiO3</u>: In this chapter, details about the synthesis of pure and Hf doped BaTiO₃ and its structural, optical, dielectric, ferroelectric, and Raman spectroscopy measurements have been provided. These characterization techniques reveal that all the results of pure and Hf doped BaTiO₃ samples can be correlated.

Chapter 4: Direct correlation between the band gap and dielectric loss in Hf doped BaTiO₃; In this chapter, the effect of Hf doping at Ti site in BaTiO₃ on the optical band gap (Eg), Urbach energy (Eu), dielectric constant (ϵ) and dielectric loss i.e. loss tangent (tan δ) have been investigated. Through the present study, a new methodology has been proposed for understanding the origin of dielectric loss. Moreover, a possible correlation between the Eg and tan δ in terms of tunneling probability has been provided in this chapter.

<u>Chapter 5: Correlation between the temperature-dependent</u> <u>dielectric loss and electron-phonon interaction in BaTiO3</u>; This chapter includes a breakthrough with presenting the strong correlation between the temperature dependence of dielectric loss, the value of bandgap, and electron-phonon interaction. It has been observed that electron-phonon interaction increases with temperature and shows a sudden increase by almost two-fold at tetragonal to cubic transition temperature. The temperature-dependent behaviour of dielectric loss in the present case appears to be governed through strong electron-phonon interaction.

Chapter 6: Effect of structural disorder on the electronic and phononic properties of Hf doped BaTiO₃; This chapter is devoted to understand the effect of structural disorder in the electronic and phononic state of Hf doped BaTiO₃ samples. The Raman and optical spectroscopy measurement on these samples indicate an increase in the structural disorder with Hf doping which indicates that structural disorder affects electronic as well as the phononic states.

<u>Chapter 7: Possible signature of structural disorder induced</u> <u>polarization in the cubic phase of Hf doped BaTiO_3</u>: In this chapter, the origin of ferroelectricity in the cubic phase of BaTi_{1-x}Hf_xO₃ has been investigated. The existence of polarization in the cubic phase of Hf doped BaTiO₃ is demonstrated by using Raman and PE measurements.

<u>Chapter 8: Conclusions and Future Perspectives;</u> This chapter summarizes the results of the present research work with concluding remarks. The possible future scope of the present study has also been discussed.

Chapter 2

Experimental Procedure

This chapter provides information about the synthesis and the characterization techniques used during the present research work. The various characterization techniques are elaborated and explained with the necessary details.

2.1 Material synthesis

2.1.1 Solid- State Reaction Method

The solid-state reaction (SSR) route is one of the most commonly used and conventional method for the synthesis of oxides-based samples[187]. In this method, the cation or anions involved in the reaction must be interchange or transported by some mechanism, from one structure to the other in order to form the resultant compound. It is difficult for the ions to move to the adjacent sites as it is believed that they are typically trapped in their appropriate lattice sites. Thus, a very high temperature is needed, often in the range of 900 to 1500 °C[188], so that ions acquire sufficient energy to diffuse through the crystal lattice. To activate the diffusion process, two-third of the melting temperature of one component is sufficient and hence enables the SSR[188]. It is not always possible that there is a reaction between two reacting species, even if thermodynamic consideration favors the product formation. Thus, there are three important factors that influence the rate of reaction between the reacting species:

- 1. Surface areas of the reacting solids,
- 2. Rate of nucleation,
- 3. Rate of diffusion of ions.

Surface area of solids: The surface area of the reacting solids depends on the particle sizes. It is possible to reduce the particle size by grinding, ball milling, freeze-drying, etc. The grain growth of both reactant and the product may occur during heating, which can reduce the surface area of the mixture. Grinding the solids maintains a high surface area and brings fresh surfaces into contact.

Rate of nucleation: Nuclei growth is another important parameter to control the overall process of SSR. In the nucleation process, the chemical reaction begins at certain discrete points in the reactant called nucleus forming sites. The nuclei are embedded in the bulk of, or distributed over the surface of the reactant. As the reaction proceeds, the size of the nuclei increases, and thus the area of the interface formed between the nuclei and reactant increases. The growing size of nuclei leads to the overlapping of the nuclei and hence reduces the area of the interface and the reaction rate starts to decrease.

Diffusions of ions: The interface formed between the nuclei and the reactant acts as a barrier and result in a longer diffusion path and slower reaction rates. Diffusion path lengths are highly influenced by the degree of homogeneity achieved during mixing, particle size of the reactants, and the contact between grains. The presence of crystal defects also enhances the diffusion process. For the diffusion process to occur, a very high temperature is required so that the ions acquire sufficient energy to diffuse through the crystal lattice and enables the solid-state reaction.

Thus, the step involved to proceed the SSR are as follows:

- > Weighing the raw materials in proper stoichiometric proportions.
- Grinding the raw materials together in the mortar and pestle to prepare a homogeneous mixture to make a larger area of contact between the reactants.
- Heating the solid powder mixture in high purity alumina boats and crucibles at a fixed rate and for the fixed time and then cooling down to room temperature.

The sintering of the samples was done using high temperature furnace having microprocessor-based PID temperature control. The reaction is often significantly facilitated by grinding and heating the sample repeatedly. The final temperature and duration of sintering are determined based on the nature and properties of the samples under preparation. We have used the solid-state reaction method to synthesize pure and doped $BaTiO_3$ and is discussed in chapter-3.

2.1.2 Preparation of Circular Pellets

The synthesized powder samples have been used to prepare highly dense circular pellets using a high-pressure hydraulic press, particularly for the PE and dielectric measurements. By means of a hydraulic press and a 10mm circular die set, the pure phase powder is pressed in the form of a circular pellet. The number of crystallites in contact may increase by pelletizing the samples. The prepared pellets are then sintered at a high temperature. The post-sintering of pellets is done to enhance grain growth, improve the crystal quality, and maximize the possible density of the samples. In the present research work, the pure phase of pure and doped BaTiO₃ powders have been pelletized at a pressure of ~ 20 ton to form 1-1.5 mm thick circular discs having a diameter of 10mm. These pellets were finally sintered at 1250°C for 24 hours in the presence of air. The final solid pellets are used for the rest of the measurements.

2.2 Characterization Techniques

2.2.1 X-Ray Diffraction

X-rays are high-energy electromagnetic radiation which can be produced by the deceleration of fast-moving electron at a target material. X-rays were produced by Wilhelm Conrod Roentgen in 1985. In 1913, W.H. Bragg and his son W.L. Bragg developed a relationship to understand why the x-ray beam appears to be reflected by the cleavage faces of the crystals at a certain angle of incidence. Since the wavelength of x-rays is comparable to the inter-atomic distances. Hence, they used xrays diffraction (XRD) as a tool to examine the structural properties of the materials. They were also awarded the Nobel prize in physics in 1915 for determining the crystal structures beginning with ZnS, NaCl, and diamond.

XRD is a powerful non-destructive characterization technique and provides useful information on structures, preferred crystal orientation, phases, and other structural parameters, such as strain, particle size, crystal defects, and crystallinity. XRD peaks are produced by the constructive interference of the monochromatic beam of x-rays from each set of lattice planes in a sample. The incident beam of x-rays is projected into the sample and interacts with the electrons of the atoms as shown in fig.2.1. The incident radiation falls on the sample at a particular angle of incidence and gets diffracted through a different set of atomic planes present in the crystal. The interaction of incident radiation with the sample interference produce constructive when Bragg's condition is satisfied[84,189]:

$$2d\sin\theta = n\lambda,\tag{2.1}$$

Where n is an integer, θ is the angle between the incident beam and the normal to the reflecting crystal planes, d is the interplanar spacing and λ is the wavelength of the x-rays. The set of crystal planes of lattices are indexed using Miller indices *hkl* and the interplanar distances d could also be written as d*hkl*. This law relates the wavelength of electromagnetic radiation to the lattice spacing and the diffraction angle in a crystalline sample. The powder sample is composed of many small and finely ground crystals, known as crystallites, and are randomly oriented. Due to the random orientation of powder material, the sample is scanned through a range of 2 θ angles so that all possible diffraction direction of the lattice can be obtained. As every compound has a set of unique d-spacings, so by converting the diffraction peaks to d-spacing the resultant compound can be obtained.



Figure 2.1: The schematic of Bragg's law of x-ray diffraction,

The powder x-ray diffractometer consists of three basics elements: an x-ray tube, a sample holder, and an x-ray detector as shown in fig.2.2. The geometry of the x-ray diffractometer is such that the x-rays generated at the cathode ray tube are focused on the sample at some angle θ , while the detector moves in a circle around the sample and reads the intensity of the x-ray at 2 θ away from the source path. The x-ray intensity is usually recorded as counts or counts per second. Typically, all powder diffractometer uses the Bragg- Brentano geometry in which the x-ray tube is fixed and the sample rotates at θ^0 /min and the detectors rotate at $2\theta^0$ /min. The instrument used to maintain the angle and rotate the sample is termed as goniometer.



Figure 2.2: Schematic of instrumentation used during x-ray diffraction measurement.

Bragg's law provides information only about the space group while the details about the atoms and their Wycoff positions are determined by the relative intensities of diffraction peaks. The diffraction peak intensity is determined by the arrangement of atoms in the entire crystal and is given by

$$I_{hkl}\alpha |F_{hkl}|^2 \tag{2.2}$$

$$F_{hkl} = \sum_{i} f_i \, e^{2\pi i (hx_i + ky_i + lz_i)} \tag{2.3}$$

Where, F_{hkl} is the structural factor, (hkl) are the Miller indices, f_i is the atomic form factor and (x_i, y_i, z_i) is the fractional atomic position of the ith atom in the unit cell. In addition to the structural factor, the intensity of diffraction also depends on other factors such as temperature, geometrical and polarization factors, etc.

In the present work, the x-ray diffraction is carried out to check the phase purity of the samples using Rigaku powder diffractometer, with Cu K_{α} ($\lambda = 1.54$ Å) radiation was employed and operated at an applied voltage of 45 kV and current of 40 mA in Bragg-Brentano geometry[190,191]. The sample stage was rotated to avoid the preferred orientation of the set of crystal planes. For the calculation of structural parameters such as

lattice parameter, bond lengths, Wycoff position of atoms, etc., Rietveld refinement of room temperature x-ray diffraction pattern is carried out using Fullprof program[192]. The detail of the experimental parameters has been discussed in Chapter-3.

2.2.2 Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique used to study the vibrational, and other low-frequency modes by inelastic scattering of light. Raman scattering is named after Indian physicist Chandrasekhara Venkata Raman who discovered it in 1928. He won the Nobel prize in 1930 for his discovery, whom he accomplished using a mercury lamp as a monochromatic source of photons and a photographic plate to record spectra. This effect becomes especially useful to spectroscopists after the invention of lasers, which can provide an intense source of monochromatic light. Raman spectroscopy is an effective tool to get more insight into the local distortion, strain, and disorder present in the ceramic materials. This is a very useful technique for studying the dynamics of a structure because the local symmetry of mixed perovskite differs from that of global symmetry.

In Raman spectroscopy, a monochromatic light source is focused on a sample, and the radiation scattered by the molecules is explored. Most of the light scattered from a molecule is elastically scattered and this process is known as Rayleigh scattering. However, a small fraction of light (approximately 1 in 1 million photons) gets scattered in all directions at frequencies different from the incident frequency and this inelastic scattering process is known as the Raman effect. Thus, the spectrum of the scattered light consists of a strong (exciting) line of the same frequency as of the incident light, together with weaker lines on either side of the strong line. The exciting line having the same frequency as that of incident light is known as Rayleigh line and the lines having a frequency less than the exciting line is called Stokes line and lines having a frequency greater than exciting lines is called anti-Stokes lines[193]. The schematic representation of Raman scattering is shown in fig.2.3.



Figure 2.3: Schematic representation of Raman Scattering.

The fundamental requirement to generate a Raman line or mode is that the incident photon must change the bond-polarizability. The interaction between the electron cloud of the sample and monochromatic light induces the electric dipole moment within the molecule based on its polarizability. For polycrystalline samples, the group theory delivers a set of selection rules based on symmetry operations in order to identify the Raman-active modes. Also, a phonon can be Raman active only in the crystal with no center of inversion. A typical Raman spectrometer consists of an exciting source (laser), illumination and collection system, monochromator, and detector as shown in fig.2.4. Details of all these components are discussed below:

2.2.2.1 The light source

Lasers are extensively used as the exciting source to induce the Raman scattering. The laser is known to be the ideal source for Raman scattering because of its high, monochromaticity, and power. Gas lasers, like argon and He-Ne lasers, have strong emission lines at 514nm and 632nm respectively. Currently, many diode lasers are also being used in Raman spectrometer in which 976, 830, and 785 nm wavelength are very popular having emission power typically several hundred milliwatts. During Raman measurement, the selection of laser depends upon the nature of the material and its molecular vibrational energy.

2.2.2.2 Sample Illumination System

In Raman spectroscopy, the sample handling is very simple because glass can be used for lenses, windows, and other components. A very small sample can also be investigated. Mainly two observations geometries are popular. For solid samples, the back-scattering geometry is often used in which the scattered and incident light beams are identical i.e. the light is scattered at 180° angle. Whereas for liquid samples the observation at 90° angles to the incident light beam is often used in the back-scattering geometry, only one surface of the sample needs to access which makes the practical experiment easier and the scattered intensity is also highest in this geometry.

2.2.2.3 Monochromator and interferometer

In Raman spectrometer, the sample is illuminated with a suitable laser beam, and the radiation from the illuminated spot is collected with a lens and sent through a monochromator. One of the great challenges in the Raman spectrometer is to remove the Rayleigh signal. Thus, the most critical component in a Raman spectrometer is the filter that damps the Rayleigh scattered light. For this, either a notch, edge pass, or bandpass filters are used depending upon the laser wavelength. The Rayleigh line is filtered out by using a suitable filter, while the rest of the scattered light is dispersed onto a detector. The most commonly used detector in the modern Raman spectrometers is a CCD (Charge Coupled Device) detector. It is a highly sensitive photon detector and is used in Raman spectroscopy because of its high sensitivity towards light. By using the CCD detector, the entire spectrum can be detected in a single acquisition. Raman spectroscopy is a powerful spectroscopic technique that is used in various scientific fields such as physics[194], chemistry[195], biochemistry[196], archaeology, and arts[197]. This technique has the potential of identifying the structure and function of tissues, cells, or

materials. In chemistry, Raman spectroscopy is used to identify molecules and study intermolecular bonds and chemical bonding[195]. In solid-state physics, it is used to characterize the materials and crystallographic orientation of samples[194]. It is an effective tool to investigate the local structures of mixed perovskite materials, where the local symmetry is different from the global symmetry[198]. It is also an extremely powerful tool to probe the signature of structural disorder present in the material[199] and is a very sensitive tool to probe the signature of the strain and the same is visible as a slight shift in the frequency of Raman phonon modes[168]. Moreover, Raman spectroscopy is known to provide information about the electron-phonon interaction[127]. In the presence of strong electron-phonon interaction, the phonon spectra lead towards the asymmetry line shape[125].

The asymmetry in the Raman line-shape can be explained by the Fano type interaction model. It was Ugo Fano, who suggested that the asymmetry in the spectral lines is based on the principle of superposition of quantum mechanics[146]. Fano interpretation of the asymmetric line-shapes is based on the interaction of a discrete state with a continuum sharing the same energy level which results in an interference phenomenon. Using this model, the asymmetry in the Raman line-shape can be explained as a result of electron-phonon interaction. The strong electron-phonon interaction is responsible for the asymmetric Raman line-shape. The detail of the experimental parameters has been discussed in Chapter-5.

In the present work, the Raman spectroscopy is recorded using Horiba (LABRAM HR) spectrometer equipped with a 633 nm excitation laser source and a CCD detector. The temperature-dependent Raman measurements were performed using a Linkam THMS600 temperature stage.

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Figure 2.4: Block diagram of the major components in a micro-Raman spectrometer setup.

2.2.3 UV- VIS Spectroscopy

UV-vis spectroscopy or spectrophotometry is a quantitative analytical technique used to measure the absorption of near-ultraviolet (180- 400nm) or visible radiation (400- 800nm) of a chemical substance. The near-ultraviolet and visible regions provide energy that gives rise to electronic transitions. It is one of the most economical and simplified method to study the optical property of a given material. The UV-vis spectrophotometer measures the intensity of light passing through a sample (I) and compares it to the intensity of light before it passes through the sample (I₀). The ratio I/I₀ is known as the transmittance(T) and it is related to the absorbance (A) of the material by the formula[200]

$$A = -\log(T) = -\log\left(\frac{l_0}{L}\right) \tag{2.4}$$

The absorbance A of the material is a dimensionless quantity. In general, a UV-Vis spectrophotometer comprises a light source, sample

holder, monochromator, and a detector. In this technique, multiple sample types including liquids, solids, thin-films, and glass can be used. The schematic diagram of the working of the UV-Vis spectrometer is shown in fig.2.5. For powder samples, diffuse reflectance spectroscopy is used to estimate the absorbance because for the powder samples the transmission measurement is not possible.



Figure 2.5: Schematic diagram of UV-Vis spectrometer.

2.2.3.1 Diffuse reflectance spectroscopy

Diffuse reflectance spectroscopy (DRS) is a non-destructive technique that is used to analyze the optical properties of powdered samples. Since the powdered surface is oriented in all possible directions, so when the incident light interacts with the powdered sample it gets reflected in all possible directions. This kind of reflection is called a diffuse reflection, which is in contrast to the specular reflection, in which incident light gets reflected symmetrically with respect to the normal line, as shown in fig.2.6. Ideally, in diffuse reflection, the angular distribution of the reflected radiation is independent of the angle of incidence. In the present scenario, DRS has become one of the important tools to investigate the optical properties of solid samples.



Figure 2.6: Schematic of diffuse reflection and specular reflection, when a light incident on a rough surface or powder sample.

The theory of diffuse reflection has been investigated by numerous authors, but the Kubelka-Munk model is the most accepted model to interpret the diffuse reflectance spectra[201–203]. Originally, they proposed a model to describe the behavior of light traveling inside a light scattering specimen, which for the special case of an infinitely thick, opaque sample may be written as:

$$F(R_{\infty}) \approx \frac{(1-R_{\infty})^2}{2R_{\infty}} \approx \frac{K}{s}$$
 (2.5)

where $F(R_{\infty})$ is Kubelka-Munk function, K is the molar absorption coefficient, s is the scattering coefficient and $R_{\infty} = R_{sample}/R_{standard}$ is the relative diffused reflectance of the sample over a baseline of standard sample $R_{standard}$. The Kubelka-Munk function ($F(R_{\infty})$) represented in equation-2.3 can be written in terms of absorption coefficient (α) as

$$F(R_{\infty}) \propto \alpha \propto \frac{(hv - E_g)^{1/n}}{hv}$$
 (2.6)

Where α is the absorption coefficient of the material, E_g is the optical band-gap, hv is the photon energy and n denotes the nature of the transition between valance and conduction band, n can take two values i.e. n = 2 for direct band gap transition and n = $\frac{1}{2}$ for indirect band gap transition. The Tauc plot shows the quantity hv on the abscissa and the quantity $(\alpha hv)^{1/n}$ on the ordinate[204–206]. Thus, a plot between $(\alpha hv)^{1/n}$ and hv (energy) produces a straight line, and the intercept on the energy axis gives the value of the band gap of the sample.

Optical absorption spectroscopy has been widely used to probe the electronic structure of various materials. It is also known to probe the band gap as well as the disorder present in the sample [82,162]. The presence of an acceptor or donor level due to the defects/vacancies etc. in the sample gets reflected in the optical absorption spectroscopy. Thus, optical spectroscopy is also used for detecting such defect states present in the material[207,208]. Additionally, optical absorption spectroscopy has the potential to probe crystal field transitions. Recently, d-d transition in transition metal oxide complexes including 3d⁵ systems have been probed by this spectroscopic technique[209,210]. This spectroscopic technique has also been used to probe the dielectric behaviour of the materials[211]. Moreover, the temperature-dependent optical spectroscopy is used to calculate the electron-phonon coupling parameter and the localization/delocalization of the excitons[157,212].

In this present work, diffuse reflectance spectroscopy has been carried out using a commercial spectrometer Cary 60 from Agilent Technology, shown in fig.2.7(a). The internal ray diagram is shown in fig.2.7(b). In DRS measurement, when a broad range of UV-Vis radiation falls on a bulk sample through an optical fiber, then diffusely reflected light is collected using the ellipsoidal lens and guided to the detector, as shown in fig.2.7. Thus, a spectrum is obtained which contains all the information of the target samples. The DRS setup available in the lab can measure the bandgap with an accuracy of 0.001 eV and the detail about the calculation of optical bandgap and the data processing has been discussed in chapter-3.



Figure 2.7: *Experimental set up for Carry-60 UV-Vis spectrometer of (a) diffuse reflectance spectrometer (b) Internal optics of DRS setup.*

2.2.4 Dielectric Spectroscopy

Dielectric spectroscopy falls in the subcategory of impedance spectroscopy and it measures the dielectric properties of a material as a function of frequency. When the dielectric material is placed in the external electric field the material becomes polarized, which means it acquires a dipole moment. This property of dielectrics is known as polarizability. Depending on the structure of the molecules, there are different types of polarization processes in dielectric materials such as ionic, electronic, dipolar, or orientation and space charge polarization. In ionic polarization, the polarization is caused by the relative displacement between positive and negative ions in ionic crystals such as NaCl, KBr, etc. The electronic polarization occurs due to the shift of the electronic charge cloud of an atom with respect to the positive nucleus under the influence of the electric field. The dipolar or orientation polarization arises when the material has a permanent dipolar moment. Thus, when such materials are placed in the external electric field, the molecular dipoles begin to rotate and tend to align with the field, results in a net nonvanishing dipole moment. In space charge or interfacial polarization, when the material is placed in an external electric field the mobile positive and negative charge particles get separated which form positive and negative space charges in the bulk or at the interfaces between different materials[83,84].

The main objective of the present work is to measure the change in electrical polarization or indirectly the change in the capacitance properties of a material as a function of frequency by using an LCR meter. The electrical polarization is related to the dielectric susceptibility (χ) by $\frac{dP}{dE} = \varepsilon * \chi$. Thus, the dielectric constant of the material is proportional to the slope of a plot of P vs E, via $\varepsilon = 1+\chi$, which is proportional to the capacitance. For a parallel-plate capacitor filled with a dielectric, the capacitance becomes

$$C = \frac{\varepsilon_0 \varepsilon A}{d} \tag{2.7}$$

Where ε_0 is the permittivity of free space, ε is the dielectric constant, d is the thickness of the sample and A is the area of the contact plates as shown in fig.2.8.



Figure 2.8: Schematic of parallel plate capacitor geometry.

When a dielectric material is placed in an alternating electric field, a phase lead or lag may appear between the applied field (voltage) and the response(current) of the system, depending upon the type of the component (capacitor or inductor). The dielectric response of the material is recorded through an LCR meter. The phase difference between voltage and current for ideal capacitive, inductive, resistive, and arbitrary/unknown material is shown in fig.2.9.



Figure 2.9: *Examples of phase diagram between voltage and current, drawn individually for an ideal (a) resistive element, (b) inductive element, and (c) for an unknown element/material.*

It is important to note that the impedance analyzer measures the phase difference between the applied voltage and the measured current. When the alternative voltage is applied to a system, the impedance of the system obeys Ohm's law[213]:

$$V(t) = V_0 \exp(j\omega t)$$
(2.8)

$$I(t) = I_0 \exp(j\omega t - \varphi)$$
(2.9)

In complex plane representation, impedance can be expressed as

$$Z^* = Z' - jZ'' (2.10)$$

Where Z' and Z" are the real and imaginary parts of complex impedance. In the impedance technique, Z' and Z" for the sample under study can be measured simultaneously as a function of frequency. With the help of the measured impedance data, the complex permittivity (ε^*), complex admittance (Y^*), and complex modulus M^* can be calculated using the following conversion relations:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' = \frac{1}{j\omega C_0 Z^*}$$
(2.11)

$$Y^* = Y' + jY'' = \frac{1}{Z^*}$$
(2.12)

$$M^* = M' + jM'' = j\omega C_0 Z^*$$
(2.13)

Where, ε' is the real or dielectric constant or relative permittivity, ε'' is the imaginary equivalent or dielectric loss. C₀ is the capacitance of free space and ω is the angular frequency. Further, the imaginary part of dielectric loss can also be measured in terms of loss tangent (tan δ) which is defined as the ratio of ε'' and ε' or in other words the ratio of energy lost per cycle to energy stored per cycle. The loss tangent is parametrized by an angle δ which is either between the capacitor's impedance vector and the negative reactance axis or between the permittivity vector and lossless permittivity axis as shown in fig.2.10.



Figure 2.10: *Dielectric permittivity and impedance complex planes; defining angle* δ *.*

In the present work, the room temperature dielectric measurements were carried out using a precision impedance analyzer (LCR meter)-6500B of Wayne Kerr company with a measurement accuracy of $\pm 0.05\%$. A cryogenic temperature controller CTC100 was used to record the temperature-dependent dielectric response. The sample holder assembly is designed in our laboratory with the provision of cooling up to liquid nitrogen and vacuum up to 10^{-3} mbar (or even lower). The experimental arrangement used for dielectric measurement is shown in fig.2.11.



Figure 2.11: *Experimental arrangement used for temperature-dependent dielectric measurements.*

2.2.5 P-E loop tracer

A P-E loop is a plot of the charge or polarization (P) developed, against the field applied to that device (E) at a given frequency. The existence of the ferroelectric hysteresis loop is the hallmark evidence of ferroelectricity in materials. It is a very simple and effective tool to characterize the ferroelectric properties of ferroelectric materials such as spontaneous polarization (Ps), remnant polarization (Pr), and coercive field (E_c). A typical ferroelectric hysteresis loop is shown in fig.2.12. At the low and very high electric fields (E), the ferroelectric material behaves like an ordinary dielectric but in the vicinity of the coercive field (E_c), polarization reversal occurs and induces a large dielectric non-linearity. When the external electric field strength starts decreasing then some of the domains would back-switch, but at zero electric field, the net polarization is nonzero. The polarization even in zero electric field is known as retentivity (Er). Thus, an electric field with the opposite direction is required to obtain a zero polarization. The reverse electric field required to flip the domains, so that net polarization within the material is zero, is known as the coercive field (E_c) .



Figure 2.12: A ferroelectric hysteresis loop.

The Sawyer-Tower circuit is a frequently used method for study the P-E loop measurement[214]. This circuit is useful for the material having high polarization and low loss. The circuit consists of a signal generator

(E), an oscilloscope, a reference capacitor C_0 , and another capacitor C_x with the ferroelectric sample to be measured, as shown in Fig. 2.13. In this method, the ac electric signal generated by the signal generator changes the charge and current in the electronic devices. The $C_0 \mbox{ and } C_x$ are connected in series and the value of C_0 is chosen much greater than C_x so that the voltage drop across C_0 is less than that across C_x . Therefore, the drive voltage is almost equal to the voltage across the sample (C_x) . To measure the electric field across the sample, the drive voltage after safe attenuation is applied to the horizontal plates of the oscilloscope and the voltage across the reference capacitor (C_0) , which gives polarization of the sample, is applied to the vertical plates of the oscilloscope. There is a drawback in the Sawyer-Tower circuit that the reference capacitor C₀ induces a back voltage to the sample, due to which a parasitic capacitance C_p is generated during the charge and discharge process which perturb the ferroelectric hysteresis. Thus, to overcome these shortcomings, an integrated circuit with the virtual ground technique is implemented.

In the present work, Polarization Vs Electric field (PE) measurements at room temperature were carried out using a ferroelectric loop tracer system of Radiant Technologies (Precision Multiferroic Test System) at 50Hz.



Figure 2.13: Schematic diagram of Sawyer-Tower circuit for the P-E loop measurement.

Chapter 3

Synthesis and Characterization of Pure and Hf doped BaTiO₃

In this chapter, details about the synthesis of pure and Hf doped BaTiO₃ and its structural, optical, dielectric, ferroelectric, and Raman spectroscopy measurements have been provided¹.

3.1 Introduction

As discussed in chapter-1, BaTiO₃ ceramic has been investigated by various researchers to investigate the physics of structural phase transition and to improve its dielectric properties. It has been noticed during a detailed literature survey, that to study the optical properties of BaTiO₃ there are very scattered studies. The correlation between the dielectric and optical properties such as dependence of dielectric loss with optical band gap and electronic disorder (Urbach energy) has been found to be missing from the literature. A major portion of the literature reveals the correlation of temperature-dependent dielectric constant with optical properties but dielectric loss has been rarely discussed for BaTiO₃. Further in the literature, Shahid et. al [19] have shown that in BaTi_{1-x}Hf_xO₃ samples, a structural phase transition from tetragonal to cubic phase occurs at x=0.12 whereas Das et. al [21] have shown the ferroelectric loop for samples with x=0.15. It is also important to mention that the optical and Raman spectroscopy are known for their potential use to probe the electronic and structural disorder respectively. Therefore, in order to understand the possible correlation between the structural, dielectric, optical, and Raman

¹A. Sati et al. J. Mater. Sci. Mater. Electron. 2019, 30, 8064.

A. Sati et al. J. Mater. Sci. Mater. Electron. 2019, 30, 9498.

A. Sati et al. Mater. Chem. Phys. 257 (2021) 123792.

A. Sati et al. Communicated

measurements, Hf doped BaTiO₃ samples have been prepared and characterized these samples by various characterization techniques.

3.2 Experimental Detail

3.2.1 Synthesis of pure and Hf-doped BaTiO₃ samples

A series of polycrystalline BaTi_{1-x}Hf_xO₃ samples from x=0 to x=0.30 were synthesized *via* a solid-state reaction method by following the process described in section-2.1.1 (chapter- 2). For this, the high-purity powders of BaCO₃, TiO₂, and HfO₂ have been used. These starting reactants were mixed in proper stoichiometric amount and grounded thoroughly with propanol as a mixing medium. After mixing, these powders were calcined at 1100°C and 1200°C for 12 hours each. These calcined powders were once again grinded, remixed with polyvinyl alcohol as a binder, and then pelletized in a 10 mm diameter disc at 20 Ton/cm² pressure. The pellets were then sintered at 1300°C for 12h and cooled at the rage of 1°C/min to room temperature.

The reaction taking place in this method for preparing BaTiO₃ can be written as:

$$BaCO_3 + TiO_2 + Heat \rightarrow BaTiO_3 + CO_2$$

Molar mass of BaTiO₃ = 233.191g/mol, BaCO₃= 197.334 g/mol, TiO₂ = 79.865 g/mol

Hence, for preparing 5gram of BaTiO₃;

 $\frac{5 \times 197.334}{233.191} = 4.2311 gm$ of BaCO₃ and $\frac{5 \times 79.865}{233.191} = 1.7124 gm$ of TiO₂ are required

Now, for preparing $BaTi_{0.70}Hf_{0.30}O_3$ the reaction taking place can be written as:

 $BaCO_3 + 0.70TiO_2 + 0.30HfO_2 + Heat \rightarrow BaTi_{0.70}Hf_{0.30}O_3 + CO_2$

Molar mass of $BaTi_{0.70}Hf_{0.30}O_3 = 272.377g/mol$ and Molar mass of $HfO_2 = 210.488g/mol$

Hence, for preparing 5gm of BaTi_{0.70}Hf_{0.30}O₃;

$$\frac{5 \times 197.334}{272.377} = 3.6224 gm \text{ of } BaCO_3, \quad \frac{5 \times 79.865 \times 0.70}{272.377} = 1.0262 gm \text{ of } TiO_2,$$

and
$$\frac{5 \times 210.488 \times 0.30}{272.377} = 1.1591 gm \text{ of } HfO_2 \text{ is required.}$$

Thus, by these proper calculations of stoichiometric followed by weighing with the accuracy up to five decimal points, the Hf amount has been controlled for all the prepared samples.

3.2.2 X-Ray Diffraction

X-ray diffraction measurement was carried out on the calcined powders using the Rigaku powder diffractometer, with Cu-K α radiation, operated at 40 kV, 30 mA in the Bragg-Brentano geometry. XRD data is recorded for ranging 2 θ of 20°- 120°. In this case, the sample stage is rotating to avoid the preferred orientation of a set of crystal planes. Further, Rietveld refinement of room temperature XRD patterns of ceramic samples is carried out using the Fullprof program to find out lattice parameter, phase purity, crystal symmetry, Wyckoff position of atoms, etc. Moreover, VESTA [134] software was used for visualization of the crystal structure of the refined pattern.

3.2.3 Diffuse Reflectance Measurements

Room-temperature (RT) and temperature-dependent (TD) variation of band-gap and electronic disorder in terms of Urbach energy (E_u) of prepared samples have been estimated using diffuse reflectivity measurements. These measurements have been performed in the 190 nm to 800 nm wavelength range using Cary-60 UV-VIZ-NIR spectrophotometer having Harrick Video-Barrelino diffuse reflectance probe[82,152,215].

3.2.4 Dielectric measurements

Frequency-dependent and TD dielectric measurements have carried out using a Wynne Kerr 65120 B precision impedance analyzer having an oscillator voltage of ± 1 V [70,84,85]. In this respect, single-phase powdered samples were pelletized at a high pressure of ~20 ton to form 1 mm thick circular discs having a diameter of 10 mm. The prepared pellet was sintered at 1250 °C for 24 h in the presence of air. Silver paint was coated on both sides of the prepared pellet and then heated for 60 min at 200 °C. The capacitance was measured from 350 K to 430 K at a rate of 1 K at various frequencies as a function of temperature.

3.2.5 Raman measurements

The Raman measurements were carried out on prepared pellets samples by using LABRAM HR dispersive spectrometer equipped with a 633nm excitation laser source and a CCD detector in backscattered mode. For TD Raman measurements THMS600 stage from Linkam having an accuracy of 0.1K was used[216,217].

3.2.6 PE measurements

Polarization Vs Electric field (PE) measurements at room temperature have been performed using a ferroelectric loop tracer system of Radiant Technologies (Precision Multiferroic Test System) at 50Hz. Silver paint was coated on both sides of the prepared pellet and then heated for 60 min at 200°C[190].

3.3 Results

3.3.1 Structural Properties via X-Rays Diffraction

In fig.3.1 the XRD pattern of the as-synthesized $BaTi_{1-x}Hf_xO_3$ (BHT) samples has been shown. XRD patterns reveal that BHT samples were synthesized in pure phase and there is no impurity present in these samples. In the inset of this fig., a systematic lower angle shift of all diffraction peaks has been observed with increasing Hf content. The systematic change in the diffraction corresponding to each composition of BHT clearly indicates that the substitution of Hf in BaTiO₃ has really taken place. The shifting of peaks to the lower angle side indicates that the lattice parameters are increasing due to the substitution of hafnium (Hf⁺⁴), which has a larger ionic size in comparison with the titanium cation (Ti⁺⁴). Further, to get accurate values of lattice parameters and also to confirm the tetragonal to cubic transition with increasing Hf concentration, Rietveld analysis has been carried out.

The XRD data of all the BHT compositions with $0 \le x \le 0.30$ were subjected to Rietveld refinement using Fullprof software [12], for

structural and phase purity characterizations. All the peaks of the XRD profiles were indexed and lattice parameters were determined. The data for x=0 (i.e. pure BaTiO₃) and x=0.06 have been refined on considering tetragonal structure having space group P4mm whereas, for x=0.15, 0.21, 0.27, and 0.30 is refined with considering cubic structure of space group *Pm3m.* The Rietveld refined XRD pattern is shown in fig. 3.2(a, b, c, d, e, f). The inset of fig.3.2 shows a magnified view to highlight the quality of fittings. The continuous line in fig.3.2 shows the Rietveld fit to the observed data, shown as circles. The quality of fit ensures the respective P4mm and Pm3m phase. The absence of any unaccounted diffraction peak and good agreement between the observed and calculated interplanar spacing (d-values) confirms that the synthesized BHT materials are single-phasic. The inset of fig.3.2(a)&(b) shows the splitting of some of the peaks, for example, 002/200 & 004/400, which is a clear signature of the tetragonal phase of BaTiO₃[82]while, the inset of fig.3.2 (c), (d), (e), and (f) show the merging of 002/200 & 004/400 peaks into a single peak with Hf doping. Merging of peaks indicates towards a gradual phase transformation of tetragonal phase into a higher symmetry phase, most probably cubic.

The refined tetragonal and cubic lattice parameters, bond-length, and bond-angles have been shown in table-3.1. From the lattice parameter variation as shown in fig.3.3 of synthesized compositions of BHT, it can be seen clearly that as x increases c decreases but a increases, and at x=0.15 both become equal leading to a tetragonal to cubic transformation. Above x=0.15 the lattice parameter of the cubic phase increases almost linearly with Hf concentration. Pure BaHfO₃ is reported [15] to be cubic with lattice parameter 4.17Å. Our result is in conformity with this.

Moreover, the ABO₃ types of perovskite transition metal oxides (such as BaTiO₃) are part of charge transfer insulators[218] where the bandgap ' E_g ' is related with the bond length and bond angle through;

 $E_g = \Delta$ -W; $W = \frac{Cos(K)}{d(Ti-O)^{3.5}}$; $K = \frac{180-\varphi(O-Ti-O)}{2}$, $\varphi(O-Ti-O)$ is the bond angle and Δ is the charge transfer parameter whose value almost remains constant for given series[219]. Moreover, it is important here to note that the c/a ratio is the measure of tetragonality and hence to the dipole moment associated with off-centered Ti atom. So, by the increasing and decreasing trend of c/a ratio, the value of the dielectric constant can be predicted. Thus, it signifies that there is a correlation between the structural parameters, band-gap, and dielectric constant.



Figure 3.1: Room temperature x-ray diffraction profiles for $BaTi_{1-x}Hf_xO_3$ ceramics for x = 0, 0.06, 0.12, 0.15, 0.21, 0.27 and 0.30. The inset of the figure shows a systematic lower angle shift of all diffraction peaks.



Figure 3.2(a): The XRD pattern with Reitveld refinement of pure BaTiO₃. The inset of the figure shows the splitting of (200)/(002) & 004/400 reflections.



Figure 3.2(b): The XRD pattern with Reitveld refinement of $BaTi_{1-x}Hf_xO_3$ sample for x=0.06. The inset of the figure shows the splitting of (200)/(002) & 004/400 reflections.



Figure 3.2(c): The XRD pattern with Reitveld refinement of $BaTi_{1-x}Hf_xO_3$ sample for x=0.15. The inset of the figure shows the merging of (200)/(002) & 004/400 reflections.



Figure 3.2(d): The XRD pattern with Reitveld refinement of $BaTi_{1-x}Hf_xO_3$ sample for x=0.21. The inset of the figure shows the merging of (200)/(002) & 004/400 reflections.



Figure 3.2(e): The XRD pattern with Reitveld refinement of $BaTi_{1-x}Hf_xO_3$ sample for x=0.27. The inset of the figure shows the merging of (200)/(002) & 004/400 reflections.



Figure 3.2(f): The XRD pattern with Reitveld refinement of $BaTi_{1-x}Hf_xO_3$ sample for x=0.30. The inset of the figure shows the merging of (200)/(002) & 004/400 reflections.

Hf content (x)	Space group	Lattice parameter (Å)			c/a ratio	<ti-o> Bond length (Å)</ti-o>	Ti-O-Ti bond angle (Degrees)	
		а	b	с			Ti- O1- Ti	Ti-O2-Ti
0	P4mm	3.9935(3)	3.9935(3)	4.0315(4)	1.009	2.001(2)	180 ⁰	179.74 ⁰ (2)
0.06	P4mm	3.9991(2)	3.9991(2)	4.0212(3)	1.005	2.007(3)	1800	179.78°(3)
0.12	P4mm	4.0148(4)	4.0148(4)	4.0189(5)	1.001	2.009(4)	1800	179.88°(3)
0.15	Pm3m	4.0289(3)	4.0289((3)	4.0289((3)	1.000	2.011(3)	180 ⁰	180 ⁰
0.21	Pm3m	4.0539(4)	4.0539(4)	4.0539(4)	1.000	2.014(6)	1800	180 ⁰
0.27	Pm3m	4.0790(2)	4.0790(2)	4.0790(2)	1.000	2.017(4)	180 ⁰	180 ⁰
0.30	Pm3m	4.0923(7)	4.0923(7)	4.0923(7)	1.000	2.020(3)	1800	1800

Table-3.1: Refined values of structural parameters for Hf doped BaTiO₃.



Figure 3.3: Variation of tetragonal and cubic phase lattice parameter with *Hf* concentration.

3.3.2 Dielectric Properties

The temperature dependence of the dielectric constant and dielectric loss of $BaTi_{1-x}Hf_xO_3$ for x = 0, 0.06, 0.21 and 0.30 samples are shown in fig.3.4(a)-(d). Moreover, the obtained dielectric data for pure and Hf doped BaTiO₃ as a function of frequency has been shown in fig. 3.5(a & b). The present results are consistent with those reported earlier by Anwar et al. [11, 22] and by Das et al. [21]. It is important to note that at lowfrequency regions the dielectric measurements have contribution due to the space charge regions i.e. due to the contact between metallic electrodes and sample or grain boundaries [10]. Hence, in order to examine only the grain contribution and to investigate the effect of Hf doping on the value of the dielectric loss, all the data have been collected at much higher frequency i.e. up to 5 MHz. The variation of dielectric constant and dielectric loss $(\tan \delta)$ at 5 MHz as a function of Hf doping has been shown in fig. 3.5(a) & fig. 3.5(b) respectively. As discussed in the earlier section, the variation of dielectric constant and dielectric loss as a function of temperature may be understood in terms of change in the c/a ratio and disappearance of electric dipole in the cubic phase of BaTiO₃. Further, the dielectric constant results from electronic polarization and electron migration from valence to conduction band therefore the dielectric constant of a semiconductor is directly related to the band gap. Thus, to understand the reason for the increase/decrease in the value of the dielectric constant in terms of bandgap, the Penn model has been studied. However, several models have been established to obtain an analytical formula for the linear dielectric function but the most fruitful and simplest one is that of Penn. Penn was probably the first to incorporate the effect of energy gap on dielectric constant which has been widely employed in the theory of solids because of its simplicity. The Penn model is an isotropic version of a nearly free electron model extended into threedimension and it mainly depends on a single parameter i.e. the bandgap. The relationship between the static dielectric constant and band gap is found to be

$$\varepsilon_1(0) \approx 1 + \left(\frac{\hbar\omega_p}{E_g}\right)^2$$
 (3.1)

where ω_p is the plasma frequency at which $\varepsilon_1(\omega)$ passes through zero. The above relation demonstrates an inverse relationship between dielectric constant and the energy bandgap. Thus, there is a systematic correlation between band-gap and dielectric constant.

Further, it is well known that the applicability of dielectric materials for charge storage applications is largely governed by the value of the dielectric loss. Hence, it is extremely important to understand the possible contributors to the 'dielectric loss' in greater detail. Some recent reports on perovskite oxides suggest that the value of the dielectric loss is critically controlled by the magnitude of bandgap (E_g) and electronic disorder i.e. Urbach energy E_u [34,35]. Since to understand the variation of dielectric constant there are well-accepted theories in literature; whereas to understand the variation of dielectric loss there exist some scattered studies. Therefore, in order to understand the variation of dielectric loss with doping a systematic correlation between the band-gap, dielectric constant, and dielectric loss has been studied in chapter-4.



Figure 3.4(a): *Temperature dependence of dielectric constant and dielectric loss of pure BaTiO₃ at various frequencies.*



Figure 3.4(b): *Temperature dependence of dielectric constant and dielectric loss of BaTi*_{0.94}*Hf*_{0.06}*O*₃ *ceramic at various frequencies.*



Figure 3.4(c): *Temperature dependence of dielectric constant and dielectric loss of BaTi*_{0.79}*Hf*_{0.21}*O*₃ *ceramic at various frequencies.*



Figure 3.4(d): *Temperature dependence of dielectric constant and dielectric loss of BaTi*_{0.70}*Hf*_{0.30}*O3 ceramic at various frequencies.*



Figure 3.5(a): Frequency dependence dielectric constant of $BaTi_{1-x}Hf_xO_3$ ceramics.



Figure 3.5(b): Frequency dependence dielectric loss of $BaTi_{1-x}Hf_xO_3$ ceramics.



Figure 3.6(a): The variation of dielectric constant (ε) at 5 MHz with Hf doping in BaTiO₃.



Figure 3.6(b): The variation of dielectric loss ($tan\delta$) at 5 MHz with Hf doping in BaTiO₃.

3.3.3 Diffuse Reflectance spectroscopy (DRS)

Optical absorption for pure and Hf doped BaTiO₃ has been probed using diffuse reflectance spectroscopy. The obtained DRS has been converted into its corresponding absorption spectra by using the following Kubelka Munk relation[220,221]

$$F(R_{\infty}) = \frac{(1-R_{\infty})^2}{2R_{\infty}}$$
(3.2)

Where $F(R_{\infty})$ is the Kubelka-Munk function $R_{\infty} = \frac{R_{(sample)}}{R_{(standard)}}$, where $R_{(sample)}$ is the diffuse reflectance of the sample, $R_{(standard)}$ is the diffuse reflectance of the non-absorbing standard sample. Fig.3.7 shows the graph between the obtained Kubelka–Munk function as a function of wavelength for Hf doped BaTiO₃ at various Hf concentration. Kubelka-Munk function $F(R_{\infty})$ as represented above can be related/proportional to the absorption coefficient (α) as

$$F(R_{\infty}) \propto \alpha \propto \frac{(hv - E_g)^{1/n}}{hv}$$
 (3.3)

$$(\alpha h\nu)^n = \mathcal{A}(h\nu - E_g) \tag{3.4}$$

Here n=2 for direct bandgap transition, while n=1/2 for indirect bandgap transition. In the present case, n=1/2 has been chosen to determine the optical gap of pure and Hf doped BaTiO₃ samples as it is proposed to be an indirect bandgap material. The temperature dependence of the band gap of BaTi_{1-x}Hf_xO₃ for x = 0, 0.06, 0.21 and 0.30 samples are shown in fig.3.8(a)–(d). From the figure, it is clear that with an increase in temperature, the band gap systematically decreases. Further, fig.3.9 shows the variation of bandgap as a function of Hf concentration and with an increase in Hf concentration, the bandgap of Hf doped BaTiO₃ systematically increases. In literature, the variation of bandgap has been explained in terms of bowing parameter for standard semiconductors material such as Gallium Arsenide, Indium doped Gallium Arsenide[222–224], etc. Therefore, in order to understand the compositional dependence of band gap of BaTi_xHf_{1-x}O₃, the standing bowing equation has been used

$$E_{g}(BaTi_{1-x}Hf_{x}O_{3}) = (x) \times E_{g}(BaHfO_{3}) + (1-x) \times E_{g}(BaTiO_{3}) - b \times x \times (1-x)$$

$$(3.5)$$

Here, $E_g(BaHfO_3)$, $E_g(BaTiO_3)$, and $E_g(BaTi_{1-x}Hf_xO_3)$ are the energy bandgaps of BaHfO_3, BaTiO_3, BaTi_{1-x}Hf_xO_3 and b is a band bowing parameter which characterizes the degree of deviation from linearity[210,222]. The band gap data has been fitted using equation-1.8 as shown by the solid line in the inset to fig.3.8. The best fit has been obtained for a bowing parameter value of 0.187 ± 0.07 eV. The positive bowing parameter may be attributed to a repulsive interaction between the conduction band and the localized d-states of Hf.



Figure 3.7: *DRS spectra of* $BaTi_{1-x}Hf_xO_3$ *samples with* $0 \le x \le 0.30$.



Figure 3.8(a): Temperature-dependent band gap of pure BaTiO₃.



Figure 3.8(b): Temperature-dependent band gap of BaTi_{0.94}Hf_{0.06}O₃.



Figure 3.8(c): Temperature-dependent band gap of BaTi_{0.79}Hf_{0.21}O₃.



Figure 3.8(d): Temperature-dependent band gap of BaTi_{0.70}Hf_{0.30}O₃.



Figure 3.9: Variation of band gap as a function of Hf doping in BaTiO₃. In the inset, the solid line shows the fitting of experimental data with equation (3.5) to obtain the bowing parameter.

Further, as discussed in an earlier section that there is a systematic correlation between structural, dielectric, and optical measurements. Moreover, Kristoffel and Konsin [41] suggested that in the case of BaTiO₃ temperature dependence of the bandgap is best described by strong electron-phonon i.e. vibronic coupling. The electron-phonon coupling mainly controls the deformation arises due to change in the spontaneous polarization, as a result, the dielectric constant, and hence the bandgap changes systematically [41,42,98]. Similar arguments (based on the experimentally observed behaviour of the temperature-dependent optical band gap) have been proposed by Rössel et al. [42] and they suggested that the interaction of soft optical phonon mode with an electronic continuum is responsible for the observed temperature-dependent behaviour of bandgap. It is important here to note that E_g and λ_{e-ph} are known to be correlative. Therefore, this correlation needs to be studied in greater detail which has been discussed in chapter-5.

Further, the exponential variation of optical absorption near band edge (Urbach tail states/ Urbach energy) is one of the well-known features of optical absorption spectra. The Urbach energy (E_u) is a measure of total electronic disorder present in the system. In order to calculate the value of electronic disorder, the tail part of the absorption spectra (as marked in fig.3.10) has been used. It is important here to note that the optical absorption α is related to energy as[82,151,162,211,225,226];

$$\alpha(E,T) = \alpha_0 \exp\left[\sigma\left(\frac{E-\omega_p}{kT}\right)\right]$$
(3.6)

Where; α_0 and ω_p are the constants determined by extrapolating the linear region from ln (α) versus E curves at a given temperature T as shown in the inset of fig.3.10. The quantity $E_u = \frac{kT}{\sigma}$ is termed as Urbach energy ' E_u ' and the quantity σ is called steepness parameter. In order to estimate E_{μ} , logarithm of ' α ' (only the tail part near the absorption edge) is plotted as a function of 'E = hv' and fitted the same with the straight line, the inverse of slope represent E_u . Generally, it is believed that in various semiconductor oxide materials the Urbach energy always increases with temperature and structural disorder[179,225,227-229]. Fig.3.11 shows the representative temperature-dependent variation of E_u for BaTiO₃. Fig.3.12 shows the variation of E_u as a function of Hf concentration, and from the figure, it is clear that with an increase in Hf concentration E_u systematically increases. Further, Raman spectroscopy is known as an extremely powerful tool to probe the signature of structural disorder. So, keeping this in view, in chapter-6, both optical absorption spectroscopy and Raman spectroscopy has been used to probe the signature of electronic and structural disorder in the prepared samples. The knowledge of the electronic and phononic disorder and the possible correlation between these disorders is important for such materials in order to understand the physics of ferroelectric/dielectric relaxation and that of soft phonon driven structural phase transition observed in such ferroelectric materials.


Figure 3.10: Absorption spectra for $BaTi_{0.94}Hf_{0.06}O_3$. The region of Urbach tail states i.e., exponential decay, and the corresponding natural log of the same region is shown in the inset.



Figure 3.11: Variation of Urbach energy of BaTiO₃ as a function of temperature.



Figure 3.12: Variation of Urbach energy as a function of Hf doping in *BaTiO*₃.

3.3.4 Raman spectroscopy

It is known that the Raman spectroscopy is sensitive to probe the local symmetry[230], the effect of structural disorder on phonon spectra[199,217], and also provides information about the electron-phonon interaction[126,127]; therefore, the Raman spectroscopy has been carried out. Fig.3.13 (a-d) shows the temperature-dependent Raman spectra of BaTi_{1-x}Hf_xO₃ for x=0, 0.06, 0.21 and 0.30. Further from the figure, it is clear that the Raman spectra of pure BaTiO₃ show various Raman modes, out of which the prominent modes are at ~ 80 cm⁻¹ which is assigned to E(TO₁) phonon mode, a dip at 180 cm⁻¹ which is assigned to A₁(TO) phonon mode and broadband at 260 cm⁻¹ assigned to A₁(TO) mode which is due to BO₆ bending vibrations [20, 23, 31]. Another mode named as B₁ and E(TO+LO) mode associated with the tetragonal-cubic transition [65] was observed at 305 cm⁻¹. Since, the presence of vibrations of oxygen octahedral lies in the high wavenumber region (>500 cm⁻¹), in

which, an asymmetric broad mode near 520 cm^{-1} corresponds to E(TO) and A₁(TO) modes and the highest frequency peak near 720 cm⁻¹ corresponds to both A₁(LO) and E(LO) modes. Moreover, in the Raman spectra of pure BaTiO₃, the A₁(TO) phonon mode at 260cm⁻¹ is known as the polar Raman mode associated with the Ti-O vibrations. This mode is also known as a stiffened component of the soft mode phonon. In literature, it has been reported by various research groups that the polarization is proportional to the soft A₁(TO) mode displacement and thus also to the frequency of the soft mode. Thus by the displacement and frequency shift of soft phonon mode, the ferroelectric behaviour can be predicted by using Raman spectroscopy.

Furthermore, some interesting changes have been observed in the Raman spectra with the substitution of Hf at the Ti site as shown in fig. 3.14. The Raman spectra of BaTi_{1-x}Hf_xO₃ samples have some similarities as like the BaTiO₃ sample but with relevant differences. As x increases from 0.06 to 0.15, the intensity of the sharp mode at 310 cm^{-1} decreases, and the $A_1(TO)$ mode at 260 cm⁻¹ and 520 cm⁻¹ becomes asymmetric and broad. Moreover, a dip at 150 cm⁻¹ and a hump/shoulder at 190cm⁻¹ and 780cm⁻¹ also appear. Further, as x increases from 0.15 to 0.30, corresponding Raman modes at 310cm⁻¹ and 260cm⁻¹ almost get melted and the intensity of hump at 190 and 780cm⁻¹ gets increased. In addition, a sharp interference dip also gets appears at 125cm⁻¹ and the hump at 780cm⁻¹ becomes overlapped with the 715cm⁻¹ mode after a certain doping concentration. All these modes persist even in the as observed cubic phase of BaTi_{1-x}Hf_xO₃ where first-order Raman scattering is forbidden by symmetry/Raman selection rule. Since near phase boundary i.e. with x \approx 0.15 there may exist structural phase coexistence[231–235] which may be responsible for the persistence of Raman modes, but; the appearance of these Raman modes from beyond phase co-existence region, i.e. for higher Hf concentration i.e. even for x=0.30, where no structural phase co-existence is expected suggests that the origin of the observed Raman mode is something else which has been discussed in chapter-7.



Figure 3.13(a): Temperature-dependent Raman spectra of pure BaTiO₃.



Figure 3.13(b): *Temperature-dependent Raman spectra of BaTi0.94Hf0.06O3.*



Figure 3.13(c): *Temperature-dependent Raman spectra of BaTi*_{0.79}*Hf*_{0.21}*O*₃.



Figure 3.13(d): *Temperature-dependent Raman spectra of BaTi*_{0.70}*Hf*_{0.30}*O*₃.



Figure 3.14: Room Temperature Raman spectra of $BaTi_{1-x}Hf_xO_3$ ($0 \le x \le 0.30$) samples.

3.3.5 PE measurements

It is well known that the tetragonal phase of the BaTiO₃ is noncentrosymmetric and its cubic phase is centrosymmetric. In order to investigate the ferroelectric properties of Hf substituted BaTiO₃ samples, the PE measurements have been carried out. It should be noted that the PE measurements are very sensitive to the crystal structure i.e. the presence of non-centrosymmetry[236,237]. As in the cubic phase, no permanent dipole should exist, so the PE curve is expected to be linear[238]. PE data of all the prepared samples have been presented in fig.3.15 and from the figure, it is clear that all the samples including those having Hf concentration greater than 12% show a very clear hysteresis loop. This suggests the presence of dipole and hence non-centrosymmetry in the prepared. In chapter-7 the possible reason for polarization in the cubic structure of the Hf doped BaTiO₃ has been studied by using Raman spectroscopy.



Figure 3.15: Room temperature PE loop of $BaTi_{1-x}Hf_xO_3$ ($0 \le x \le 0.30$) samples.

3.4 Summary

Based synthesis of BaTi_{1-x}Hf_xO₃ on the and structural characterization through XRD, it can be concluded that the whole range of single-phase BHT ceramics from $0 \le x \le 0.30$ can be prepared using a solid-state reaction route. The Rietveld refinement of the XRD data of these ceramics clearly shows a tetragonal to cubic transformation at around Hf concentration of x=0.15. The dielectric, optical, and Raman behaviour of pure and Hf doped BaTiO₃ has been studied in a wide temperature and composition range (0 < x < 0.30). It has been observed with Hf doping, the value of band gap and Urbach energy systematically increases whereas the value of dielectric constant and dielectric loss systematically decreases. The Raman spectroscopy measurement on these samples suggests the presence of well distinct modes even in the cubic symmetry i.e. for x > 0.12 where the first-order Raman scattering is forbidden by symmetry/Raman selection rule. The PE measurement shows the well-defined ferroelectric PE hysteresis loop, including samples having Hf concentration greater than 12%. These characterization techniques reveal that all the results of pure and Hf doped BaTiO₃ samples can be correlated.

Chapter 4

Direct correlation between the band gap and dielectric loss in Hf doped BaTiO₃

In this chapter, the effect of Hf doping at Ti site in BaTiO₃ on the optical band gap (Eg), Urbach energy (Eu), dielectric constant (ε), and dielectric loss i.e. loss tangent (tan δ) have been investigated. It has been observed that with Hf doping, the value of Eg and Eu systematically increases whereas; the value of dielectric constant and dielectric loss systematically decreases. Present investigations clearly suggest that the value of dielectric loss is effectively controlled by Eg. Moreover, a possible correlation between the Eg and tan δ in terms of tunneling probability has been provided².

4.1 Introduction

Recently, efforts have been made to use BaTiO₃ as a multiferroic material by doing the magnetic impurity at Ba and Ti site, in this connection Yadav *et. al.*[239] investigated the effect of Mn doping at Ba site in BaTiO₃ and confirmed the role of Ba site on the ferroelectric properties of these materials, similarly the effect of Mn and Fe doping at B site has also been investigated[6,240]. In the case of doping magnetic impurity, it has been observed that the value of dielectric loss significantly increases. In these materials, it is believed that oxygen vacancies or defect significantly affects the dielectric properties of these materials. Experimentally it has been shown that these oxygen vacancies lead to the transition from insulator to metal[190,241–243]. Hence, it is believed that the dielectric loss (tan\delta) in these materials is essentially governed by

² A. Sati et al. J. Mater. Sci. Mater. Electron. 30, 8064 (2019).

oxygen defects[22,190,241,242,244]. In the case of BaTiO₃, the effect of Hf doping on the dielectric, ferroelectric, and piezoelectric properties have been investigated earlier [15,73,105,119,245-249]. Using ferroelectric studies, Das et al. have shown that the value of dielectric loss (measured through the area of ferroelectric hysteresis loop) decreases with Hf doping[119]. For any practical applications of these materials the value of tand must remain sufficiently small, hence; it is very important to know the possible contributing factors for dielectric loss. For any dielectric material, the dielectric loss consists of two parts (1) frequency dependent flipping of electrical dipole and (2) the leakage current[250]. For insulating materials, the leakage current is related to the band gap as; $\sigma =$ $\sigma_0 \exp\left(-\frac{E_g}{2kT}\right)$ (For intrinsic case E_a=E_g/2)[251]. The doping of any impurity atom at Ba or Ti site is expected to create some states within forbidden energy gap near valence and conduction band, which is possibly due to random distribution of defects and onsite potential fluctuation[252,253]. It is expected that the electronic disorder near band edge will also contributes to the leakage current/dielectric loss[252,253]. Hence, it is extremely important to investigate the possible correlation between band gap and dielectric loss in these types of materials. On examining these aspects regarding the said phenomenon, the effect of Hf doping to find the correlation between the optical and dielectric properties in case of BaTiO₃ has been investigated here. It is important here to note that the optical absorption spectroscopy is known for it's potential to probe the band gap and electronic disorder near band edge in the form of Urbach energy[82].

4.2 Experimental

Polycrystalline samples of $BaTi_{1-x}Hf_xO_3$ ceramics, with x = 0, 0.06, 0.12, 0.15, 0.21, 0.27 and 0.30, have been prepared through conventional solid-state reaction technique by following the process described in section-2.1.1 of chapter-2. The phase purity of the as-prepared samples of $BaTi_{1-x}Hf_xO_3$ has been examined using powder x-ray diffraction (XRD) measurements carried out by Bruker D8 diffractometer equipped with Cu target. For dielectric measurements, the prepared pellets were coated with

high-temperature silver paint. These painted pellets were then dried at 300° C for 30 mins before proceeding with dielectric measurements. The frequency dependence of dielectric measurements on these pellet samples has been carried out at room temperature using a Wynne Kerr 65120B precision impedance analyzer with an oscillator voltage of ± 1 V[254]. The optical band gap and electronic disorder near band edge have been estimated using diffuse reflectance spectroscopy experiments carried out using Agilent Cary UV-VIZ-NIR spectrophotometer [82,211,215,225,255]. The details of estimating the band gap and Urbach energy has been discussed in section-3.3.3 of chapter-3.

4.3 Results and Discussions

4.3.1 Structural studies

Fig.3.1 of chapter-3 shows the X-ray diffraction data of $BaTi_{1-x}Hf_xO_3$ samples. The detailed X-ray diffraction analyses and the refined structural parameters of Hf doped $BaTiO_3$ have been discussed in section-3.3.1 of chapter-3.

4.3.2 Dielectric Measurements

Fig.3.5 (a) and (b) of section-3.3.2 of chapter-3 shows the variation of dielectric constant and dielectric loss at 5MHz as a function of Hf doping. From the figure, it is clear that the value of dielectric constant and that of dielectric loss systematically decreases with Hf doping. The present results are consistent with those reported earlier by Anwar et al. [73,105] and by Das et al.[119]. It is important here to note that Das et al.[119] have carried out ferroelectric studies on the Hf doped BaTiO₃ and observed that the value of polarization and area of the ferroelectric loop(which is a signature of reduced dielectric loss) decreases with Hf doping which is consistent with present results.

4.3.3 Diffuse Reflectance Spectroscopy (DRS)

Optical absorption for Hf doped $BaTiO_3$ has been probed using diffuse reflectance spectroscopy. Fig.3.8 of section-3.3.3 of chapter-3 shows the variation of band gap as a function of Hf concentration and

from the figure, it is clear that with an increase in Hf concentration, the band gap of Hf doped BaTiO₃ systematically increases.

Further, the exponential variation of optical absorption near the band edge (Urbach tail states/ Urbach energy) is one of the well-known features of optical absorption spectra. Generally, it is believed that Urbach energy (E_u) is a measure of total electronic disorder present in the system and the same scales with temperature and structural disorders. The variation of electronic disorder of all the prepared samples is shown in fig.3.10 in section-3.3.3 of chapter-3. From the figure, it is clear that the electronic disorder symmetrically increases with Hf doping. As optical absorption spectroscopy has been widely used by various researchers to probe the electronic disorder in the form of Urbach energy. These electronic disorders are due to various factors such as thermal disorder, structural disorder, compositional disorder, etc. In the present case, the contribution due to thermally induced disorder may be considered as constant, since all the measurements have been carried out at room temperature. Moreover, the doping of Hf at Ti site produces the structural and on-site electronic disorder in the system. The random distribution of Hf at lattice sites produces potential fluctuation in the system which creates energy levels within the forbidden energy gap in the form of Urbach tail states. Thus, in the present case, a systematic increase in the value of Urbach energy is possibly due to an increase in the structural disorder and on-site potential fluctuation due to Hf doping.

4.3.4 Systematic correlation between structural parameters, bandgap, and dielectric constant (by use of already existed literature)

As discussed in section-3.3.1 of chapter-3, that the ABO₃ types of perovskite transition metal oxides (such as BaTiO₃) are part of charge transfer insulators[218] where the band gap ' E_g ' is related to the bond length and bond angle through

$$E_g = \Delta - W \tag{4.1}$$

Where, $W = \frac{Cos(K)}{d(Ti-O)^{3.5}}$; $K = \frac{180-\varphi(O-Ti-O)}{2}$, $\varphi(O-Ti-O)$ is the bond angle and Δ is the charge transfer parameter whose value almost remains constant for given series[219]. In the case of tetragonal BaTiO₃, the $\varphi(O-$ *Ti-O*) bond angle is very close to 180° hence the bandgap is essentially controlled by \langle Ti-O \rangle bond length. From table-1 shown in chapter-3 it is clear that with Hf doping the average value of \langle Ti-O \rangle bond length increases, this may be responsible for the observed increase in the value of band gap. It is important here to note that the tetragonality i.e. c/a ratio decreases with Hf doping and the same may be is responsible for the decrease.

As discussed above it is known that Hf doping at Ti site reduces tetragonality [11, 22] which may lead to a decrease in the value of dielectric constant and the same is consistent with the earlier studies [8]. As discussed in chapter-3 that, D.R. Penn [51] theoretically derived the dielectric constant (ε') of semiconductors in terms of plasma frequency (ω p) and optical band gap (Eg), and represented the dielectric constant as

$$\varepsilon_1(0) \approx 1 + \left(\frac{\hbar\omega_p}{E_g}\right)^2$$
 (4.2)

Where ω_p is the plasma frequency at which $\varepsilon_1(\omega)$ passes through zero. The above relation demonstrates an inverse relationship between dielectric constant and energy band gap. Thus, it appears that in the current study the increase in the value of band gap leads to a decrease in the value of dielectric constant. These results are consistent with the studies reported earlier in the literature [52, 53].

4.3.5 Systematic correlation between optical and dielectric properties (a newly proposed model)

In the introduction part of this chapter; it has been discussed that for insulating/semiconducting system the dielectric loss i.e. leakage current is related to band gap as; $\sigma = \sigma_0 \exp\left(-\frac{E_g}{2kT}\right)$ (For intrinsic case $E_a = E_g/2$)[251,256]. Thus, it is natural to expect that with an increase in E_g the conductivity and hence, the dielectric loss should decrease. Exactly similar behavior has been observed in the present case. It is important here to note that P. Bräunlich *et al.*[257] discussed the tunneling i.e. escape probability of charge carriers from valence band to conduction band, in the terms of activation energy as[257],

$$Tij = C \exp\left[-\left(\frac{Ea}{kT}\right)\right] \tag{4.3}$$

Here T_{ij} is tunneling probability and *C* is constant and E_a is the activation energy. In the present case, the doping of Hf at Ti site is not expected to add electrons or holes to the system due to 4+ oxidation state of Hf and Ti both, hence one may replace E_a with E_g . Furthermore, doping of Hf at Ti site is expected to create the structural disorder due to differences in the ionic radii, also; the random distribution of Hf in the lattice may lead to the onsite potential fluctuation because of the difference in the atomic number (Z) of Ti(22) and Hf(72). This random distribution of Hf and hence, random strain fields at lattice sites, introduces potential fluctuations which are predicated to create energy levels within the forbidden energy gap or close to the valance/conduction band[253,258]. These energy levels are also termed as electronic disorders near band edge and are measured in the form of Urbach Energy[253,258]. This is shown schematically in fig.4.1 (a) and (b). Keeping this in view, equation (4.3) has been modified as follows:

$$Tij = C \exp\left[-\left(\frac{Eg-2Eu}{2kT}\right)\right]$$
(4.4)

Here, T_{ij} is tunneling probability and *C* is constant.



Figure 4.1: (*a*)*Schematic illustration of potential variation in Hf doped* BaTiO₃ and (b) corresponding band diagram for pure and Hf doped BaTiO₃. Magnified view of the encircled region is shown on the righthand side.

In the present case, all the experiments have been carried out at room temperature, hence the term 2kT is assumed to be constant. Further, using the obtained values of E_g and E_u , the values of T_{ij} have been calculated. Fig.4.2 represents the variation of T_{ij} as a function of Hf doping, this variation resembles with that of dielectric loss (Fig.3.5(b) of chapter-3). Thus, it appears that the band gap and Urbach energy of doped BaTiO₃ is effectively controlling the value of dielectric loss. Thus, the direct correlation between the optical band gap and dielectric loss is clear.



Figure 4.2: *The estimated values and variation of tunneling probability* T_{ij} *as a function of Hf doping.*

4.4 Summary

In this chapter, the origin of dielectric loss in Hf doped BaTiO₃ has been probed by using optical absorption spectroscopy. The present study suggests that there should be a direct correlation between the dielectric loss, band gap, and Urbach energy. In order to understand the possible correlation between these terms, the conductivity equation has been rewritten in the form of tunnelling probability. It has been observed that in BaTiO₃, both optical band gap and electronic disorder increases systematically with the inclusion of Hf. The increase in the optical band gap and electronic disorder leads to an overall increase in the tunnelling probability of electron and the same is responsible for the decreasing behaviour of dielectric loss. Thus, a strong correlation between the dielectric-loss measured in terms of loss tangent (tan δ), optical band gap E_g and electronic disordered term i.e. Urbach energy E_u have been observed and modeled with the modified equation of tunneling probability. In the present study, all the measurements have been carried out at room temperature, so to make this analysis complete it is equally important to do the temperature-dependent study.

Chapter 5

Correlation between the temperature-dependent dielectric loss and electron-phonon interaction in BaTiO₃

In this chapter, the possible correlation between dielectric loss measured in terms of loss tangent $(tan(\delta))$, band gap (E_g) , and electron-phonon coupling parameter (λ_{e-ph}) is presented. The observed temperaturedependent dielectric behaviour is understood by considering the competition between the tunnelling of electron from valence to the conduction band and electron-phonon coupling. This chapter provides a pathway for understanding the behaviour of temperature-dependent dielectric loss of fundamentally important material BaTiO₃³.

5.1 Introduction

It is well known that the applicability of dielectric materials for charge storage applications is largely governed by the value of the dielectric loss. Hence, it is extremely important to understand the possible contributors to the 'dielectric loss' in greater detail. In the previous chapter, a new methodology has been proposed for understanding the composition-dependent dielectric loss behaviour of BaTiO₃ in terms of band-gap and Urbach energy with a tunneling probability model. In the present study, same methodology has been used to understand the temperature-dependent behaviour of dielectric loss in BaTiO₃. But, there arises a discrepancy in the proposed model after the phase transition

³ A. Sati et al. Mater. Chem. Phys. 257 (2021) 123792.

temperature which suggests the presence of other controlling factors on deciding the temperature-dependent behaviour of the dielectric loss. In literature, some experimental and theoretical analysis suggests that the value of the dielectric loss is also governed by the strength of electronphonon interaction(λ_{e-ph})[120–124]. It is important here to note that Eg and λ_{e-ph} are known to be correlative [81,157,259,260]. However, experimentally it has been demonstrated that the value of the dielectric loss highly depends on stoichiometry i.e. lattice defects, etc.[261–263], these defects in turn will also affect the strength of electron-phonon coupling and the value of band gap too. On the other hand, the point group symmetry of the unit cell[264], phonon line width, and derivative of lattice potentials [265,266] have also been used to understand the frequency and temperature dependence of dielectric loss. The dependence of dielectric loss on the grain-boundaries, sample thickness, porosity, and the sample preparation technique of the materials has also been discussed in some literature [5,23,267–273], and these things may also affect the strength of electron-phonon coupling and the value of band gap.

It is now well established that the UV visible optical absorption and Raman spectroscopy measurements are potential techniques to determine band and strength of electron-phonon interaction gap respectively[82,125,127,141,144,152,207,212,215,217,255,274]. By using the temperature-dependent optical spectroscopy the strength of electron-phonon interaction may also be estimated [157,174,275]. In this respect, the Bose-Einstein model for the temperature-dependent band gap has been found to be very effective [157,159,276,277]. Moreover, Raman spectroscopy has been widely used to investigate the strength of electronphonon interaction in various materials qualitatively [144,217,278]. Fano model is found to be very successful for qualitative analysis of the electron-phonon interaction parameter and the corresponding asymmetry in the line shape also known as the Fano line shape of the Raman modes which is a signature of the electron-phonon interaction[82,125-128,141,144,145].

As discussed above there exist some scattered studies which suggest that dielectric loss is a function of various above-mentioned parameters. It is important here to note that in such materials the electron-phonon coupling has been predicted to play a very crucial role [75,81,170]. Further, in the previous chapter, the possible role of band gap on dielectric-loss is also discussed[279,280], therefore, to understand the possible correlation of dielectric loss with band gap, Urbach energy E_U and electron-phonon interaction, in the present studies a systematic investigation of temperature-dependent dielectric loss (using impedance spectroscopy), temperature-dependent band gap (using optical absorption spectroscopy) and temperature-dependent estimation of electron-phonon coupling parameter (using Raman spectroscopy) have been carried out.

5.2. Experimental

5.2.1. Dielectric measurements

Temperature-dependent dielectric measurements have carried out using a Wynne Kerr 65120B precision impedance analyzer having an oscillator voltage of \pm 1V [254,274,281,282]. In this respect, single-phase powdered samples were pelletized at a high pressure of ~ 20 ton to form 1mm thick circular discs having a diameter of 10mm. The prepared pellet was sintered at 1250°C for 24h in the presence of air. Silver paint was coated on both sides of the prepared pellet and then heated for 60 min at 200°C. The capacitance was measured from 350 K to 430 K at a rate of 1K at various frequencies as a function of temperature.

5.2.2. Raman measurements

The Raman spectroscopy measurements were carried out using Horiba (LABRAM HR) spectrometer having a 633 nm excitation laser source. The temperature-dependent Raman measurements were performed using a Linkam THMS600 temperature stage8[179,283].

5.3 Results and Discussions

5.3.1 Dielectric measurements

Temperature-dependent measurements of dielectric constant and dielectric loss have been carried out in the temperature range from 350K to 430K which is shown in fig.5.1(a) and (b) respectively. The signature of ferroelectric to the paraelectric phase transition is clearly visible and

exactly similar behaviour has been reported earlier [82,190]. The observed variation of dielectric constant as a function of temperature may be understood in terms of change in the c/a ratio and disappearance of electric dipole in the cubic phase of BaTiO₃[7,190]. It is clear from fig.5.1(b) that the value of the dielectric loss increases marginally up to ~ 405 K with increasing temperature, whereas; in the phase transition region the value of dielectric loss increased by almost two-fold and after structural phase transition i.e. in cubic phase the $tan(\delta)$ decreases with increase in temperature. It is important here to note that the theory which takes into account the phonon line width and derivative of lattice potentials has been successfully used to predict the correct order of dielectric loss as a function of temperature for Al₂O₃ and MgO[265,266]. Even though these theories do not explicitly consider electron-phonon interactions but consider phonon line width which is essentially governed by the electronphonon coupling[144,217]. Thus, it appears that the analysis of electronphonon interactions through phonon line shape/width may be useful to understand the behaviour of temperature-dependent value of dielectric loss, which will be discussed in the subsequent sections. Further, as discussed above; some recent experimental findings suggest that the value of the dielectric loss is also governed by the magnitude of band gap and electronic disorder i.e. Urbach energy E_u [211,284]. Keeping this in view, the temperature-dependent optical absorption spectroscopy and temperature-dependent Raman spectroscopy measurements have been carried out and the results of these measurements are discussed below.





Figure 5.1: *Temperature-dependent (a) dielectric constant (b) dielectric loss, for BaTiO₃ at a variable frequency range from 50kHz to 2MHz with respect to temperature, clearly showing the signature of high temperature structural and dielectric phase transition.*

5.3.2 Diffuse Reflectance Spectroscopy

The temperature-dependent estimation of band gap and Urbach energy has been carried out using temperature-dependent optical absorption spectroscopy[274]. The variation of E_g and E_u as a function of temperature is shown in fig.5.2(a) and fig.5.2(b) respectively. It is observed that the band gap decreases systematically with an increase in temperature. Interestingly, at around ~393K a sharp anomaly in the value of both E_g and E_u has been observed. This anomaly is a signature of tetragonal to cubic structural phase transition [79,82,190,283,285].



Figure 5.2(a): Variation of band gap of $BaTiO_3$ as a function of temperature.



Figure 5.2(b): Variation of Urbach energy of BaTiO₃ as a function of temperature.

The decrease in the behaviour of band gap with an increase in temperature may be understood as follows: (i) considering the change in electron-phonon interaction (which take cares of change in the value of lattice parameter/spontaneous polarization) (ii) considering change in the carrier concentration of electrons/holes (screening effect) or (iii) considering possible change in the grain/particle size [157,165,170,286,287]. Based on the already available and present experimental data, these conditions have been carefully analyzed and discussed below:

5.3.2.1 Effect of electron-phonon interactions

Kristoffel et.al[81] suggested that in the case of BaTiO₃ temperature dependence of the band gap is best describe by strong electron-phonon i.e. vibronic coupling. The said electron-phonon coupling mainly controls the deformation arises due to change in the spontaneous polarization, as a result, the dielectric constant, and hence the band gap changes systematically[81,259,288]. Similar arguments (based on the experimentally observed behaviour of the temperature-dependent optical band gap) have been proposed by Rossel et.al[259] and they suggested

that the interaction of soft optical phonon mode with an electronic continuum is responsible for the observed temperature-dependent behaviour of band gap. Based on the above studies, temperature-dependent band-gap data has been fitted using the Bose-Einstein model[276] which takes into account the electron-phonon coupling. According to the Bose-Einstein model, the temperature-dependent band gap may be written as[157,159,277];

$$E_g(T) = E_g(0) - a_B * \left[1 + \frac{2}{\{exp(E_{ph}/K_B T) - 1\}} \right]$$
(5.1)

Where, $E_g(T)$ band gap as a function of temperature, $E_g(0)$ is the energy gap at 0 K, E_{ph} represents the average energy of phonon which strongly coupled with electron and a_B represent the strength of electron-phonon interaction. Thus, temperature-dependent band gap data has been fitted by using equation (i) in both tetragonal and cubic phase, and the fitted curve is shown in fig.5.3. Extracting the value of electron-phonon interaction from fitting reveals that the electron-phonon interaction in the cubic phase increases two times than that in the tetragonal phase. The observed values of electron-phonon interaction are of the same order as predicted earlier[174,289,290]. Thus, it appears that the temperature dependence of band gap may be well described considering electron-phonon interactions.





Figure 5.3: *Fitting of temperature-dependent band gap data using the Bose-Einstein model for tetragonal and cubic crystallographic phase by origin.*

5.3.2.2 Effect of change in carrier concentration of electrons/holes (screening effect)

Berglund et.al [291] experimentally measured the Hall coefficient of BaTiO₃ over the temperature range from 293 to 473K and found that the Hall coefficient 'almost remains constant' over the said temperature range. Recently, these results are also experimentally verified by J. Fujioka et. al.[292] where the authors have observed the almost constant value of Hall coefficient in the temperature range of ~265 K to ~400K. It is important here to note that the change in the value of dielectric loss in the tetragonal phase is observed to be very small which further supports the above claim. Further, Wolf et.al [164] has derived an expression for the change in the band gap with carrier concentration as follows;

$$\Delta E_g = -\left(\frac{e}{2\pi\varepsilon_0\varepsilon_s}\right) \left(\frac{3}{\pi}\right)^{1/3} (\eta)^{1/3}$$
(5.2)

Where ε_0 the permittivity of free space, ε_s is relative static dielectric constant and η is the concentration of free electron/holes. According to

the above equation, ΔE_g is inversely proportional to static dielectric constant (ε_s). In the present case η almost remains constant and the value of the dielectric constant is of the order of 10^3 which implies that if ε_s is high and η is constant then; the corresponding change in the band gap (i.e. ΔE_g) will be very small i.e. of the order of $\sim 10^{-6}$ eV. It is important here to note that Kristoffel et.al. [81]also predicates the constant values of the Hall coefficient in wide band gap ferroelectric materials. This clearly indicates in the present case there is no significant change in the carrier concentration as a function of temperature and hence the screening effect may be neglected and the change in the value of band gap is essentially determined by change in the polarization through strong electron-phonon coupling[81].

5.3.2.3 Effect of change in the grain/particle size

In order to investigate the possible change in the value of grain/particle size (i.e. structural coherency), the temperature-dependent x-ray diffraction measurements have been carried out and the value of crystallite size is determined using Scherrer-formula[293,294]. According to this formula, the crystallite size (C.S) can be extracted from the peak width as $C.S. = (\frac{0.9 \lambda}{\beta \cos{(\theta)}})$. Here β is the width of the diffraction peak and θ is the half of diffraction angle. Fig.5.4 shows the temperature-dependent XRD data in the temperature range from 350K to 430K. In the case of BaTiO₃, it is well understood that the shape of the (111) peak remains unaffected during tetragonal to cubic phase transition hence the full width at half maximum (FWHM) of (111) peak has been investigated as a function of temperature. The inset of fig.5.4 shows the diffraction data of (111) peak collected at 350K and 414 K and the diffraction peak is shifting towards the lower angle which indicates that the lattice parameters are increasing with increasing temperature. Also from the figure, it is clear that there is no significant change in the value of FWHM of (111) peak as a function of temperature. This suggests that the effect of band gap due to structural coherency[165] must be neglected in the present case. Thus, from the above three analyses, it is clear that in the present case the band gap is essentially governed by strong electron-phonon coupling.



Figure 5.4: *Temperature-dependent X-ray diffraction of BaTiO₃. Inset of the figure shows the enlarged view of X-ray diffraction profiles of (111) peaks for different temperatures.*

5.3.3. Analysis of temperature-dependent Raman spectra:

As the Raman spectroscopy is known to provide information about the electron-phonon interaction[125,128,129,140] hence to estimate the variation of electron-phonon interaction with temperature, the temperature-dependent Raman spectroscopy measurements have been carried out. Fig.5.5 shows the representative temperature-dependent Raman spectra of the prepared sample. The details on various modes of Raman spectra of BaTiO₃ in tetragonal and cubic phases are already discussed in chapter-3. It has been observed that the Raman linewidth corresponding to various phonon modes such as ~520cm⁻¹ phonon mode etc. shows a systematic variation with temperature and increases drastically at the structural phase transition temperature, a representative variation is shown in fig.5.6. It is important here to note that, the Raman line width can be used to estimate the strength of electron-phonon interaction using Allen's formula[295,296] and also through the analysis of the asymmetry parameter of Raman peak termed as Fano resonance[128,129,140]. In the present study, the Fano equation[125,127,130,141] has been used to calculate the strength of the electron-phonon interaction.



Figure 5.5: Temperature-dependent Raman spectra of BaTiO₃.



Figure 5.6: The variation of FWHM of Raman mode at ~ 520 cm⁻¹ as a function of temperature.

For this purpose, the asymmetric Raman mode $[A_1(TO), E(TO)]$ corresponding to ~520 cm⁻¹ as shown in fig.5.7 has been used. Shifting of this mode towards the lower wave-number side i.e. a redshift has been observed with temperature (as shown in the inset), indicates the expansion of the material with temperature which is consistent with our diffraction studies. The electron-phonon coupling parameter has been calculated by fitting the asymmetric Raman mode $[A_1(TO), E(TO)]$ corresponding to ~520 cm⁻¹ using the Fano equation[128,146]. This Raman mode ~520 cm⁻¹ has been fitted by using the Fano equation given below[127]

$$I(\omega) = I_c \frac{|q+\varepsilon|^2}{1+\epsilon^2} + I_b(\omega)$$
(5.3)

Where q is asymmetry parameter, Γ is the Raman linewidth and ε is equal to $(\omega - \omega p)/\Gamma$, where; ωp is the renormalized phonon frequency. The inverse of the asymmetry parameter is proportional to the electron-phonon interaction i.e. a lower value of q means stronger electron-phonon

interaction[128,129,146]. As shown in fig.5.8, with an increase in the temperature, the electron-phonon interaction parameter increases gradually by 403K but around the structural phase transition temperature at ~ 413K a sharp change was observed and thereafter it increases further. This implies that there is a sharp increase in the electron-phonon interaction parameter around the phase transition temperature. These results are similar to the earlier reports for the case of polar materials (dielectric), where there is an enormous change in the electron-phonon interaction near the phase transition temperature[167].



Figure 5.7: Magnified view of shifting of $A_1(TO)$, E(TO) mode which is around 520cm-1 as a function of temperature. Inset of the figure shows the shifting towards the lower -wavenumber side i.e. a redshift.



Figure 5.8: The inverse of the Fano resonance parameter "q" as a function of temperature which determines the electron-phonon interaction. The value of q is extracted by fitting the $A_1(TO)$, E(TO) mode which is around 520cm⁻¹.

5.4 Correlation between the dielectric loss, band gap, and electron-phonon coupling

For non-polar insulating/semiconducting system the dielectric loss i.e. leakage current is related to band gap as; $\sigma = \sigma_0 \exp\left(-\frac{E_g}{2kT}\right)$. Thus, it is natural to expect that with the decrease in E_g , the conductivity and hence the dielectric loss should increase. Already in literature, P. Bräunlich et al.[257] discussed tunnelling probability of charge carriers from valence band to conduction band, in terms of activation energy. In chapter-4, we have modified this tunnelling probability equation in terms of band gap (E_g) and Urbach energy (E_u). According to this equation, the tunnelling probability of the charge carriers from valence to conduction band may be expressed as;

$$T_{ij} = C \exp\left[-\left(\frac{Eg-2E_U}{2kT}\right)\right]$$
(5.4)

Here, T_{ij} is the tunnelling probability and *C* is the proportionality constant. Using the obtained value of the band gap, Urbach energy and by equation (5.4), the value of T_{ij} has been estimated and plotted in fig.5.9.



Figure 5.9: The estimated value of tunnelling probability T_{ij} and its temperature variation.

The T_{ij} systematically increases with increasing temperature and shows a sharp anomaly around the transition temperature ~ 393K. However, the dielectric loss as shown in fig.5.1(b) increases marginally below the transition temperature and near structural phase transition shows a huge jump and decreases in the cubic phase. Thus, only tunnelling probability T_{ij} cannot explain the observed temperature-dependent behaviour of dielectric loss which suggests the presence of other controlling factors such as electron-phonon interaction on deciding the temperature-dependent behaviour of the dielectric loss as discussed below.

The Raman analysis clearly indicates that there is a sharp change in the electron-phonon interaction parameter across the phase transition temperature. Fig.5.7 shows that the rate of change of the electron-phonon coupling parameter is much larger in the cubic phase of BaTiO₃ than its tetragonal phase. Moreover, as discussed earlier the value of the electronphonon coupling parameter extracted by fitting the temperaturedependent optical band gap data using the Bose-Einstein equation also suggests that the value of the electron-phonon coupling parameter is increased by two-fold in the cubic phase as compared to the tetragonal phase as shown in fig.5.3. Thus, both Raman and optical spectroscopy techniques suggest that the strength of electron-phonon interaction is more in the cubic phase than that in the tetragonal phase. It is also to be mentioned here that the percentage change in the value of (E_g-2E_u) , which is controlling the value of tunnelling probability in the studied temperature range, is observed to be decreased by ~1.1% whereas the change in the value of electron-phonon interaction is observed to be increased by 343%. It is known that the electron-phonon coupling reduced the mobility factor and also leads to an increase in the effective mass of charge carriers [297]. Thus, it appears that the huge upturn in the value of the electron-phonon coupling parameter, after the phase transition temperature, is responsible for the decreasing behaviour of dielectric loss. Further comparing the rate of change of band gap and rate of change of electron-phonon coupling in tetragonal phase (see fig.5.2(a) and fig.5.7 and the corresponding slopes) it appears that there is a competition between the electronic tunnelling and electron-phonon coupling in the tetragonal phase. Further, a sudden rise in the value of dielectric loss near phase transition temperature may be due to an anomaly in band gap along with the disappearance of two strong phonon modes at 310cm⁻¹ and 715cm⁻¹ and a sudden rise in the pyroelectric current near phase transition[239]. Moreover, in the tetragonal phase, an increase in the value of dielectric loss with increasing temperature can be understood based on the delocalized nature of electronic wave function in high-dielectric constant material[298]. In order to further confirm the same, ac conductivity data of BaTiO₃ as a function of temperature at different frequencies has been carried out as shown in fig.5.10. The frequency-dependent conductivity data for prepared BaTiO₃ sample has been fitted using Jonscher's universal dielectric response model[299]

$$\sigma'(f) = \sigma_{dc} + \sigma_0 f^s , s \le 1$$
(5.5)

Where; σ_{dc} is dc conductivity, σ_0 and s are the fitting parameters. The value of 's' provides an idea about the delocalization/localization of electrons in the lattice². The 's' value closer to 0.5 indicates that electrons have a delocalized nature while 's' value higher than 0.8 specifies that the electron is localized[300]. Fig.5.11 shows the fitted frequency-dependent conductivity data of BaTiO₃ in the tetragonal and cubic phase along with the values of the above-mentioned fitting parameters. The value of parameters as extracted from fitting reveals that in the tetragonal phase the value of s is closer to 0.5 while that for the cubic phase is closer to 0.8 which signifies that in the tetragonal phase.



Figure 5.10: Temperature-dependent ac conductivity of BaTiO₃ at a variable frequency range from 50kHz to 2MHz with respect to temperature.





Figure 5.11: *Fitting of temperature-dependent conductivity data using Jonscher's universal dielectric response mode for(a) tetragonal and (b) cubic crystallographic phase of BaTiO₃.*

It is important here to mention that, this study also fits perfectly for explaining the temperature-dependent dielectric loss behaviour of Hf doped BaTiO₃ samples. As shown in fig.3.3 of chapter-3, that the temperature-dependent behaviour of Hf doped samples is the same as that of pure BaTiO₃ but instead of a sharp transition, the doped samples show the diffuse transition. Moreover, the temperature-dependent band gap data, as shown in fig.3.7 of chapter-3, shows that the band gap decreases systematically with an increase in Hf concentration and as the tunneling probability is dependent on the band gap, therefore the tunneling probability will also show the decreasing behaviour. Furthermore, in the Raman spectra of Hf doped samples, as shown in fig.3.12 of chapter-3, the asymmetry in the Raman mode is clearly visible and the asymmetry is the direct consequence of increased electron-phonon coupling. Thus, the electron-phonon coupling in the Hf doped samples will play a crucial role to explain the temperature-dependent behaviour of dielectric loss.

5.5 Summary

In the present chapter, the temperature-dependent dielectric loss of $BaTiO_3$ is interpreted by using the temperature-dependent optical and Raman spectroscopy. The outcomes of two different spectroscopy are being helpful to explain the temperature-dependent behaviour of dielectric loss. Further, these spectroscopy techniques deliver the two times larger electron-phonon interaction parameter in the cubic phase compared to the tetragonal phase. The temperature-dependent behaviour of dielectric loss in the present case appears to be governed through strong electron-phonon interaction. Thus, there exists a strong correlation between the dielectric loss and electron-phonon coupling. This study provides a new way to analyze the temperature dependence of dielectric loss in BaTiO₃. In the present study, as the electron-phonon coupling is increasing, so it becomes important to understand the origin of the increased value of electron-phonon coupling.
Chapter 6

Effect of structural disorder on the electronic and phononic properties of Hf doped BaTiO₃

In this chapter, the classical ferroelectric material BaTiO₃ has been doped with large cation i.e. Hf at Ti site in order to understand the effect of structural disorder in electronic and phononic state. The Raman spectroscopy measurement on these samples indicates an increase in the structural disorder with Hf doping. The detailed analysis of the Raman spectroscopy data clearly suggests the appearance of a new Raman mode at ~780cm⁻¹ and the presence of an asymmetry in almost all Raman modes. The appearance of the new Raman mode has been attributed due to the structural disorder induced phonon modes. The systematic increase in the intensity of disorder phonon mode and that of the electronic disorder has been observed. This suggests that structural disorder not only affects phonons but electronic state of the system as well⁴.

6.1 Introduction

At room temperature, $BaTiO_3$ has a tetragonal structure and it is characterized by sharp peaks at $80cm^{-1} E(TO_1)$, $180cm^{-1} A_1(TO_1)$ and $305cm^{-1}B_1$, E(TO+LO), and asymmetric broad bands at $260 A_1(TO_2)$, $520 A_1$, E(TO) and $720cm^{-1}E(LO)$, $A_1(LO)[301-303]$. In pure $BaTiO_3$, numerous independent investigations have shown that the two broad asymmetric modes at 275 and 514 cm⁻¹ in the Raman spectrum persist

⁴ A. Sati et al. J. Mater. Sci. Mater. Electron. 30, 9498 (2019).

well into the cubic paraelectric phase. In the cubic paraelectric phase ideally, no Raman mode is allowed by selection rule[5,304,305] but the local disorder/strain fields are believed to be responsible for observed modes[20,301,306]. It is important here to note that in the case of pure BaTiO₃ the Raman mode (peak) near 720cm⁻¹ at room temperature is found to be asymmetric[301,307]. It has been reported in the literature that, with a decrease in the sample temperature (within the same crystallographic phase) the peak becomes symmetric[132]and with an increase in the sample's temperature this peak becomes broader. In some cases, a broad peak appears as a hump/shoulder around ~ 780 cm⁻¹ i.e. on the higher frequency side of 720cm⁻¹ [308]. Importantly, the doping of isovalent impurity at Ba site does not affect the intensity of peak around ~780cm⁻¹ to the large extent[34,309] whereas the intensity of said hump ~ 780cm⁻¹ significantly enhances with doping concentration, at Ti site[100,309,310]. Based on these observations, it has been proposed that the peak at ~ 780 cm⁻¹ is due to the asymmetry in the breathing mode (A_{1g}) which arises due to dis-similar ions in the center of the octahedra[34,309].

Thus, it is clear that the shoulder peak around~780cm⁻¹ appears in pure as well as in doped BaTiO₃, and the intensity of this peak scales with temperature and doping concentration at Ti site[100,309–311]. Further, Raman spectroscopy is known to be an extremely powerful tool to probe the disorder phonon modes, which has been shown by the appearance of very clear distinct phonon modes in structurally disordered i.e. ion irradiated and doped nano-crystalline systems. There exists a mixed opinion about the Raman mode adjacent to ~780cm⁻¹ i.e. it appears due to the asymmetry in the breathing mode (A_{1g}) which arises due to dissimilar ions in the center of the octahedra[34,309] or structural disorder[305]. The present study is aimed to remove this ambiguity and to understand the origin of the said hump in greater detail and to understand the possible correlation between the electronic and phononic disorder.

Keeping this in view, in the present study Hf has been doped at Ti site in BaTiO₃. It has already been shown in chapter-3 that with Hf doping BaTiO₃ leads to the structural phase transition from tetragonal to cubic[73,105,245]and during this phase transition (higher

crystallographic symmetry to lower crystallographic symmetry) it is expected that the Raman mode will disappear and no extra peak should appear in Raman spectra. Further, doping of Hf at Ti site in BaTiO₃ is expected to modify the local strain field due to a significant difference in the ionic radii of Hf^{+4} (1.42 Å) as compared to that of Ti^{+4} (1.21Å)[312]. Such type of doping is also expected to modify the on-site potential due to a huge change in the atomic number of Hf (Z=72) as compared to that of Ti (Z=22)[225]. Hence, the doping of Hf at Ti site is expected to create both structural as well as electronic disorder [225]. It is important here to note that, optical absorption spectroscopy is known for its potential to probe the electronic disorder in the form of Urbach energy[151,225,313-316]. From chapter-3, it has been observed that with an increase in the Hf concentration the electronic disorder calculated in the form of Urbach energy systematically increases. Further as discussed above, Raman spectroscopy is an extremely powerful tool to probe the signature of structural disorder. Keeping this in view, in the present investigation, optical absorption spectroscopy, and Raman spectroscopy has been used to probe the signature of electronic and structural disorder in the prepared samples. The knowledge of electronic and phononic disorder and the possible correlation between these disorders is important for such materials in order to understand the physics of ferroelectric/dielectric relaxation and that of soft phonon driven structural phase transition observed in such ferroelectric materials.

6.2 Experimental

6.2.1 Raman measurements

The Raman measurements were carried out on prepared samples using; LABRAM HR dispersive spectrometer equipped with 633 nm excitation laser source and a CCD detector in backscattered mode.

6.3 Result and Discussion

6.3.1 Raman analyses

In order to investigate the effect of structural disorder on phonon spectra; Raman spectroscopy has been carried out. Fig.6.1 shows the Raman spectra for the studied samples. The various modes of the Raman spectra are marked in the figure and these modes are discussed in detail in section-3.3.4 of chapter-3. The observed Raman peaks of the polycrystalline sample of BaTiO₃ is in agreement with the Raman spectra reported by various researchers [134,309,317]. Meanwhile, a change in spectra has been obtained by increasing the B-site substituent content in BaTi_{1-x}Hf_xO₃ and the same is discussed in detail in chapter-3. In the cubic (paraelectric) phase of Hf doped BaTiO₃, there exist only 12 optical modes (3F_{1u}+1F_{2u}) which are not Raman active[301]. Hence, in the cubic paraelectric phase ideally, no Raman modes are allowed by selection rule[5,304,305]. But in some of the cases, few modes in the Raman spectra may be present, even in the cubic phase. The origin of Raman modes in the cubic phase has been discussed in detail in chapter-7. Hence, in order to confirm the presence of disorder in our samples, the peak width of Raman modes have been investigated. Fig.6.2 shows the variation in the FWHM (peak width) for a peak at 520 cm⁻¹ and 310cm⁻¹.



Figure 6.1: Room Temperature Raman spectra of $BaTi_{1-x}Hf_xO_3$ ($0 \le x \le 0.30$) ceramics. Expanded view of the disorder mode presented in (a), (b), (c), and (d) for different doping percentage shows a clear view on the increasing behaviour of disorder mode intensity in a finite range of Raman spectroscopy.

From fig.6.2, it is clear that the peak width systematically increases with Hf doping which further confirms the presence of structural disorder in the present case[150,318,319]. Thus, it appears that the huge difference in the ionic radii of Hf⁺⁴ (1.42 Å) as compared to that of Ti⁺⁴ (1.21 Å)[312] is responsible for the observed structural disorder.



Figure 6.2: The variation of the Raman line width for (a) $310cm^{-1}$ mode and (b) $520cm^{-1}$ mode as a function of Hf content in BaTiO₃. Figure (a) and (b) clearly signifies as a doping percentage increases Raman line width also increases.

Further, from fig.6.1 it is clear that with Hf doping, a broad peak appears as a hump/shoulder at around ~780cm⁻¹. This broad mode around ~780cm⁻¹ ¹ is also present in pure BaTiO₃ but with very little intensity[308]. As reported in the literature, it is important here to note that the doping of isovalent impurity at Ba site does not affect the intensity of peak around ~780cm⁻¹ to the large extent [34,309] whereas the intensity of said hump ~ 780cm⁻¹ significantly enhances with doping concentration, at Ti site[100,309,310]. Based on these reported observations, it has been proposed that the peak at ~ 780 cm⁻¹ is due to the asymmetry in the breathing mode (A1g) which arises due to dissimilar ions in the center of the octahedra[34,309]. It is also worth pointing out that, the Hf doping in BaTiO₃ results in a structural phase transition from tetragonal to cubic phase[73,105,245], and during the said phase transition (higher crystallographic symmetry to lower crystallographic symmetry) it is expected that in the cubic phase due to O_h^1 symmetry the Raman mode will disappear and no extra peak should appear in Raman spectra[320]. Hence, the presence of other high-intensity Raman modes and appearance of almost a new Raman mode around ~780cm⁻¹ is not due to structural phase transition but due to structural disorder. This is consistent with the eight minimum site model proposed by Comes et al.[321], which says that in the cubic phase the Ti/Hf atom does not have the minimum in potential energy at the center of octahedral but has eight almost equipotential minima around [111] direction of disordered pseudocubic cell[305]. It is important here to note that various researchers have studied the effect of structural disorder on the phonon modes and very clear distinct phonon modes have been observed in structurally disordered i.e. ion irradiated and doped nano-crystalline systems [199,318,322-326]. Thus, it appears that the new phonon modes do appear as a result of the structural disorder[199,318,322–326].

Moreover, as shown in fig.3.10 of chapter-3, that the electronic disorder measured in terms of Urbach energy systematically increases with an increase in Hf concentration. A systematic increase in the width of Raman modes and that of electronic disorder clearly suggests an increase in the structural disorder in the prepared samples[150,225,318].

Hence, the appearance of mode ~780 cm⁻¹ may be possibly due to the breakdown of the Raman selection rule due to disorder in B-site, so that contribution from some point in the Brillouin zone and infrared active and silent modes becomes possible[307,328,329]. Further, the loss of the translation symmetry due to disorder of the B-site initiates some contribution to Raman scattering from the Brillouin zone[330]. Therefore, the enhancement of the intensity of ~780 cm⁻¹ mode in Raman spectra is proposed here due to the structural disorder induced by the doping of Hf at Ti site in BaTiO₃.

Hence, in the light of the above discussion, it can be concluded that the introduction of structural disorder, results in the disorder phonon modes around ~780cm⁻¹. Thus, from both Raman and optical spectroscopy measurements, it becomes clear that the structural disorder affects phonons as well as the electronic state.

6.4 Possible Correlation between electronic and phononic disorder (electron-phonon coupling)

In order to investigate the possible correlation between the electronic and phononic disorder, the Urbach energy and intensity of disorder phonon mode have been plotted in fig. 6.3. From the figure, it is clear that both the quantities increase with an increase in Hf concentration. It is important here to note that the broadening of electronic and phononic disorder in energy scale may enhance the electron-phonon coupling[318,319,331,332]. In the presence of strong electron-phonon interaction, the phonon spectra lead towards the asymmetry line shape, implying a Fano resonance. Therefore, the strong electron-phonon coupling is accompanied by an asymmetry in the Raman line shape[126-128,141,145–147]. It has been observed that the $A_1(TO)$, E(TO) mode has an asymmetry line shape, which implies a Fano resonance. The detail of the Fano equation has been discussed in section-5.3.3 of chapter-5. Using the Fano equation, the peaks corresponding to $A_1(TO)$, E(TO) mode has been fitted, the fitted curve has been shown in fig.6.4. The variation of 1/qas a function of Hf doping in BaTiO₃ has been plotted in fig.6.5. From the figure, it appears that electron-phonon coupling increases with the

structural disorder. Moreover, as shown in fig.6.2 that the Raman line width is increasing with Hf doping which will decrease the phonon lifetime and enhance the electron-phonon coupling. [145,326,333,334]. These results are consistent with the theoretical predictions on disorder semiconductors[157,335].



Figure 6.3: The systematic correlation between the intensity of disorder phonon mode and electronic disordered term i.e. Urbach energy as a function of Hf content.



Figure 6.4: Fitting of Raman spectra using Fano function for $A_1(TO)$, E(TO) mode for few doped samples. The decrease in the value of q indicates an increase in the value of electron-phonon coupling.



Figure 6.5: The Fano resonance parameter "q" known as asymmetry parameter obtained from fitting the $A_1(TO)$, E(TO) mode which is around 520 cm^{-1} . The inverse of "q" determines the electron-phonon coupling.

6.5 Summary

The doping of Hf at Ti site leads to structural disorder which might be due to the significant difference in the ionic radii of Hf (1.42 Å) as compared to that of Ti (1.21 Å). A new mode appears in the Raman spectrum around 780cm⁻¹ that has been understood in terms of structural disorder produce by Hf doping. A systematic correlation between Raman line width, intensity of disorder phonon mode, and Urbach energy have been observed, which implies that structural disorder affects phonons as well as electronic states of the system. The analysis of the Raman peak profile using the Fano model suggests that the strength of electron-phonon coupling also increases with Hf doping in BaTiO₃. Thus, it appears that the increase in the width of electronic and phononic disorder is responsible for an increase in the electron-phonon coupling. In the present study, the Raman spectra of Hf doped samples is showing strong Raman lines even in its cubic phase where symmetry precludes the observation of first-order spectra. Therefore, it is important to understand the origin of the Raman lines in the cubic phase of Hf doped BaTiO₃ samples.

Chapter 7

Possible signature of structural disorder induced polarization in the cubic phase of Hf doped BaTiO₃

In this chapter, the origin of polarization in the cubic phase of Hf doped BaTiO₃ samples has been investigated. The presence of well-defined ferroelectric PE hysteresis loop in the samples with global cubic symmetry suggests the presence of 'local polar regions', induced possibly due to the huge difference in the electronegativity and also difference in the ionic radii of Hf⁺⁴ and Ti⁺⁴ ions, which may lead to local structural disorder. The presence of polar regions is also supported through the appearance of $A_1(TO)$ polar mode in Raman spectra which in principle should be absent in the samples with cubic symmetry. The results are discussed in terms of disorder-induced local dipoles due to the electronegativity difference between Hf and Ti ions.⁵

7.1 Introduction

The observation of ferroelectricity in the samples with cubic symmetry has been explained in literature by considering the vibronic theory of phase transition[75]. According to vibronic theory i.e. pseudo-Jahn Teller effect (PJTE), the vibronic coupling (electron-phonon coupling) creates local dipolar distortions of dynamic nature, resonating between two or more equivalent orientations resulting in spontaneous symmetry breaking[75,76,169]. The origin of all the four phases in BaTiO₃ is explained by the adiabatic potential energy surface (APES) induced by the PJTE[75]. Since the trigonal well is the only minima of

⁵ A. Sati et al. (Communicated).

APES, thus depending upon the off-center displacement of the transition metal ion along one of the eight equivalent trigonal directions the resulting phase is identified. As the PJTE is of local origin therefore in the macroscopic picture, the paraelectric cubic phase of $BaTiO_3$ is centrosymmetric. As per the prediction of the vibronic theory, all the eight adiabatic potential energy surface (APES) minima are found to be equivalent, and hence cubic phase is a paraelectric phase. A small perturbation to the system in form of doping, strain, etc. makes the abovementioned eight minima non-equivalent, which may lead to finite local dipole-moments.

It is important here to note that as per the selection rules of Raman spectroscopy for the samples with cubic symmetry first-order Raman modes are not allowed[320]. In literature, it has been observed that the appearance of the Raman line in cubic samples is due to the structural disorder present in the sample[74,308,321,336,337]. Thus, it appears that the Raman spectroscopy is very sensitive to probe the structural disorder. It is known that the doping of Hf at the Ti site leads to the short-range polar disorder[73,105] which is also believed to be responsible for observed relaxor behaviour[338]. Further such short-range disorder is also known to show the ferroelectricity in pure and doped SrTiO₃[183,184]. Thus, it will be interesting to investigate the structural and ferroelectric properties in cubic samples of Hf doped BaTiO₃.

7.2. Experimental details

7.2.1 PE measurements

Polarization Vs Electric field (PE) measurements at room temperature have been performed using a ferroelectric loop tracer system of Radiant Technologies (Precision Multiferroic Test System) at 50Hz. Silver paint was coated on both sides of the prepared pellet and then heated for 60 min at 200°C[339].

7.3. Result and discussion

7.3.1 X-ray diffraction analysis

It has already been shown in chapter-3, that the inclusion of Hf in BaTiO₃ leads to the structural phase transition from tetragonal to cubic phase after 12% Hf doping. The substitution of Hf⁺⁴ for Ti⁺⁴ in BaTiO₃ introduces structural disorder because of the mismatch in the size of Ti and Hf ions, causing perturbations like local electric and strain fields[73]. From the XRD experiments, it has been observed that with Hf doping FWHM of the diffraction peaks systematically increases as shown in fig.7.1 which confirms the decrease in structural coherency or increase in the structural disorder. Moreover, to estimate the grain size and straininduced with the inclusion of Hf doping, the Williamson Hall plot[185] has been plotted. It is observed that with Hf doping the strain in the sample increases, whereas the value of structural coherency decreasing. The variation of strain and grain size as a function of Hf doping is shown in fig.7.2. The finite value of strain in pure undoped BaTiO₃ could be due to the presence of natural defects such as; point and line defects, stacking faults, dislocations, etc. which are generally present in the prepared samples[178,340,341]. Thus, the X-ray diffraction analysis clearly suggests the increase in structural disorders in the form of crystallographic strain with Hf doping.



Figure 7.1: *X-ray diffraction peak width (full width at half maxima, i.e., FWHM) for prepared* $BaTi_{1-x}Hf_xO_3$ samples.



Figure 7.2: Variation of strain and grain size with Hf doping in BaTi₁₋ $_xHf_xO_3$ from x=0 to x=0.30.

7.3.2 PE measurements

It is well known that the tetragonal phase of the BaTiO₃ is noncentrosymmetric and its cubic phase is centrosymmetric. In order to investigate the ferroelectric properties of Hf substituted BaTiO₃ samples, the PE measurements have been carried out. It should be noted that the PE measurements are very sensitive to the crystal structure i.e. the presence of non-centrosymmetry[236,237]. As in the cubic phase, no permanent dipole should exist, hence the PE curve is expected to be linear[238]. PE data of all the prepared samples have been presented in fig.7.3 and from this figure, it is clear that all the samples including those having Hf concentration greater than 12% show a very clear hysteresis loop. This suggests the presence of dipole and hence non-centrosymmetry in the prepared samples. To further confirm the existence of ferroelectricity, PUND (positive up negative down) measurement on BaTi_{0.70}Hf_{0.30}O₃ sample has been carried out to capture the true polarization. This method was initially reported by Scott et al.[342-344], and now being used to measure the FE properties of leaky multiferroic samples [345-348]. It is important to note that the PUND measurement provides the true FE switched charge density (Q_{SW}) as compared to that of conventional P-E loops by removing the contribution of leakage current[345–348]. Fig.7.4 shows the PUND data of $BaTi_{0.70}Hf_{0.30}O_3$ sample by which the Q_{sw} is obtained as $Q_{sw} = P_1 - P_2[345, 349, 350]$. The existence of Q_{sw} depicts that some dipoles are switched at room temperature. Therefore, as suggested by Xie et al.[351], the existence of the switching charge may be due to the presence of static polar nano-regions. Apart from this, fig.7.5 shows that the maximum polarization decreases with an increase in doping concentration. As the polarization is related to the dielectric constant and which is decreasing with an increase of Hf concentration. These results are consistent with the result of the dielectric constant as shown in fig.3.5 of chapter-3. It must be noted here that, the c/a ratio decreases with Hf doping (as clear from the present diffraction studies) and the same is responsible for the decreased value of polarization in the present case. The correlation between the c/a ratio and the polarization is already well addressed in the available literature [175,190,352-354] as the c/a ratio is

the measure of tetragonality and hence to the dipole moment associated with the off-centered Ti atom. With Hf substitution, it is observed that c/a ratio and near neighbor correlation between Ti dipole due to the presence of randomly distributed Hf ions both get modified which results in a decrease in the net value of polarization in the present case. Moreover, the observation of a well-defined PE loop i.e. polarization in the Hf doped BaTiO₃ samples, which appears to possesses cubic symmetry via x-ray diffraction, is the direct evidence of the presence of local dipolar regions with short-range correlation. Thus, the inclusion of Hf at the Ti site in BaTiO₃ produces local polar regions even in the average cubic symmetry.



Figure 7.3: Room temperature PE loop of $BaTi_{1-x}Hf_xO_3$ ($0 \le x \le 0.30$) samples.



Figure 7.4: *PUND result of BaTi*_{0.70}*Hf*_{0.30}*O*₃ *sample with pulse width and pulse delay of 10ms.*



Figure 7.5: Variation of maximum polarization with temperature as a function of Hf concentration.



Figure 7.6: Room Temperature Raman spectra of $BaTi_{1-x}Hf_xO_3$ ($0 \le x \le 0.30$) samples.

7.3.3 Raman Measurements

It is known that the Raman spectroscopy is sensitive to local symmetry[230]; therefore, to get more insight into the local symmetry, the Raman spectroscopy has been carried out. Fig.7.6 shows the room temperature Raman spectra of all the prepared samples and the obtained spectra are consistent with the earlier reports[144,307,308,336]. The main spectral feature in the Raman spectra of the ferroelectric tetragonal phase of BaTiO₃ has been discussed in section-3.3.4 of chapter-3.

The Raman spectra of $BaTi_{1-x}Hf_xO_3$ samples have some similarities as like the $BaTiO_3$ [301,308,336,355] sample but with relevant differences, as stated below.

- a) As Hf concentration increases from 0.06 to 0.30, the intensity ratio i.e. I_{max}/I_{min} of 305 cm⁻¹ mode decreases as shown in the inset of fig.7.6.
- b) The A₁(TO) mode at 260 cm⁻¹ and 520 cm⁻¹ becomes asymmetric and broad as shown in fig.7.8 and fig.6.2 of chapter-6.

- c) A dip at ~ 125 cm⁻¹ and 150 cm⁻¹ becomes more prominent with Hf substitution as shown in the rectangular box in fig.7.6.
- d) A hump/shoulder at 190cm⁻¹ and 780cm⁻¹ appears as shown in fig.7.8 and inset of fig.7.6 respectively.
- e) Further, as x increases from 0.15 to 0.30, corresponding Raman modes at 310 cm⁻¹ and 260 cm⁻¹ almost get melted as shown in the inset of fig.7.6 and fig.7.8 respectively.
- f) With further increase in x, the hump at 780cm⁻¹ becomes overlapped with the 715cm⁻¹ mode after a certain doping concentration as shown in fig.7.9.

In the following we have discussed the Raman data systematically for observed features:

7.3.3.1 Appearance of Raman spectra

The Raman spectroscopy experiment clearly suggests the presence of well distinct modes persist even in the samples with cubic symmetry i.e. for $x \ge 0.12$ where first-order Raman scattering is forbidden by symmetry/Raman selection rule[320]. Near phase boundary i.e. near $x\approx 0.12$ there may exist structural phase coexistence[231–235] which may be responsible for the persistence of Raman modes, but; the appearance of these Raman modes much beyond the possible phase co-existence region, i.e. for higher Hf concentration i.e. even for x=0.30, where no structural phase co-existence is expected clearly suggests that the origin of the observed Raman modes is something else and the possible origin of the same is discussed below.

The persistence of Raman modes in the cubic phase can be understood either due to the strong second-order Raman scattering or disorder-induced first-order scattering associated with local deviations from cubic symmetry[356,357]. In pure BaTiO₃, numerous independent investigations have shown that the two broad asymmetric modes at 275 and 514 cm⁻¹ in the Raman spectrum persist well into the cubic paraelectric phase even though symmetry precludes the observation of first-order spectra[358–362]. The appearance of first-order Raman modes in the paraelectric phase of BaTiO₃ can be understood based on the disordered structure model proposed by Comes et al.[321]. Further, Ouni et al.[363] have shown the coexistence of first and second-order Raman lines in pure BaTiO₃ and concluded that all the Raman modes in BaTiO₃ are of first-order but second-order processes lying close to these positions contribute to a broadening of these peaks. In the present case like BaTiO₃, the persistence of Raman modes in the cubic phase of Hf doped samples is considered to be of first-order that arises due to the structural disorder [307,309,357,364]. It is important here to note that the presence of ferroelectric microregions, performing as symmetry-breaking defects, may also lead to the first-order Raman scattering in the cubic phase[355,365–367]. Further, as per x-ray diffraction investigations, the samples having Hf concentration higher than 12% possesses cubic symmetry but these samples also show clear Raman modes, in the following we have discussed this issue in detail.

For the cubic phase of BaTiO₃, 12 optical modes labelled by $3F_{1u}+F_{2u}$ are possible according to the irreducible representation of the crystallographic space group Pm3m, in which F_{1u} modes are only infrared active and F_{2u} mode is silent[336,368]; therefore, for perfect cubic symmetry, there should be no first-order Raman active mode. It is known that structural disorder relaxes the Raman selection rule and the phonons Brillouin slightly out of the zone center may also get detected[301,369,370], thus the presence of strong Raman lines and absence of any impurity peaks in x-ray diffraction data suggests the presence of structural disorder in the prepared samples [301,359,369]. We believe that the substitution of Hf at the Ti site can modify the local structure possibly due to the difference in the ionic radii, electronic density, and electronegativity of Ti and Hf ions.[144,279]. Thus the local small structural distortion may be responsible for the observed Raman modes in these samples.

7.3.3.2 Analysis of Raman mode appeared at 780cm⁻¹

In the Raman spectra of Hf doped BaTiO₃ samples, an additional hump/shoulder at ~780cm⁻¹ appears and the intensity of this hump increases with increasing the Hf concentration. In literature, it has been proposed that this hump is due to the asymmetry in the octahedra breathing mode (A_{1g}) which arises because of the dissimilar ions in the center of the octahedra[307-309]. Sati et al.[144] suggested that the presence of this hump is a consequence of structural disorder that has occurred by doping. The relative intensity ratio of these two modes i.e. I715/I780 can be used as an indication of the ferroelectric state of the material[198,371]. The values of (I715/I780) much higher than unity specifies the long-range ordered ferroelectric phase[198]. Values less than or equal to 1 indicates the disruption of long-range ferroelectric order[198]. Fig.7.7 shows that as the Hf concentration increases the I₇₁₅/I₇₈₀ intensity ratio decrease which clearly signifies the disruption of long-range ferroelectric order, which may be responsible for the observed ferroelectric relaxor behaviour[73,133]. The overall intensity ratio of I_{715}/I_{780} observed for x= 0.27 and 0.30 doped BaTi_{1-x}Hf_xO₃ samples are much lower than for x=0.15, indicates a lower degree of ferroelectricity in the former as compared to the latter samples respectively. This indicates that Hf substitution disrupts the long-range ferroelectric order, which may be responsible for the observed decrease in the value of maximum polarization with Hf substitution as shown in fig.7.5.



Figure 7.7: Variation of I715/I780 intensity ratio with Hf concentration.

7.3.3.3 Analysis of Raman modes around 260 and 520cm⁻¹

Furthermore, in the Raman spectra of BaTi_{1-x}Hf_xO₃ samples, modes around 260 and 520cm⁻¹ have a dominant $A_1(TO)$ character and are associated with the Ti-O vibrations[198,336,372]. With an increase in the Hf substitution, the Raman spectrum ranging from 180 cm⁻¹ to 300 cm⁻¹ transforms its nature with the disappearance and appearance of peaks in the said range. The peak at 260 cm⁻¹ (polar $A_1(TO)$ mode) disappears gradually and correspondingly a new peak at around 190 cm⁻¹ generates, as is clear from fig.7.8. Since the ionic radii of $Hf^{4+}(0.71\text{\AA})$ is larger than $Ti^{+4}(0.605\text{\AA})[312]$, which may cause the elastic interaction between polar Ti⁴⁺ rich regions and non-polar Hf⁴⁺ regions, which may further results in the appearance of random strain fields in the samples which is also supported through the analysis of x-ray diffraction data using Williamson-Hall method. The 190cm⁻¹ A₁(TO) mode is the result of strain-induced polar mode that generates due to the Hf doping [372]. The intensity of this new polar mode increases with Hf substitution. This increase in the intensity of 190cm⁻¹ A₁(TO) polar mode even in the cubic phase indicates

the presence of localized polar regions in the prepared samples which is consistent with earlier results[73,133]. Since this mode is known to be the polar Raman mode associated with the Ti-O vibrations so its presence will affect the ferroelectric property of the prepared samples.



Figure 7.8: Polar A₁(TO) phonon mode for various Hf concentration.

7.3.3.4 Analysis of other phonon modes and possible evidence of structural disorder through Raman Spectroscopy

The disappearance of 305cm^{-1} and 725cm^{-1} i.e. B₁ and E(TO+LO) modes represent the structural phase transition from tetragonal to cubic phase[336]·[260,337,362], but the presence of other Raman phonon modes indicates the presence of structural disorder[198]. It would be imperative to mention here that in a 30% Hf doped sample, out of the above mentioned two characteristics modes, the B₁, E(TO+LO) mode almost gets melted as shown in the fig.7.9 but A₁(LO) mode overlapped with the disorder-induced band which is shown in the inset. The increase

in the intensity of the disorder phonon mode and its overlapping with A₁(LO) mode clearly indicates that the disorder is being responsible for the local distortion of Hf doped samples in the globally appeared cubic phase. The same is also reflected through the presence of a very prominent dip at~125 cm⁻¹ in the Raman spectra which is a signature of highly disordered cubic structure, reported earlier [198,371]. With Hf substitution, this dip gets more prominent which indicates an increase in the structural disorder of the cubic phase of $BaTi_{1-x}Hf_xO_3$ (i.e. x > 0.12) samples. The same can also be explained by the broadening of the Raman line width of these phonon modes and x-ray diffraction investigations. Fig.6.2 of chapter-6 shows the variation in the Raman line width corresponding to 520cm⁻¹ phonon mode. The increase in the Raman linewidth is basically an immediate effect of the positional disorder[144,217,295].



Figure 7.9: Raman spectrum of $BaTi_{0.70}Hf_{0.30}O_3$ polycrystalline sample. The inset of the figure shows the overlapping of $A_1(LO_3)$ mode with the disorder phonon mode.

Moreover, in the Raman spectra of Hf doped BaTiO₃ samples, the interference dip around 125cm⁻¹ and 150cm⁻¹ is a signature of two different types of oxygen octahedra (i.e., Ti-based and Hf based)[198,364,371] as shown in fig.7.6. The random distribution of these two different types of the octahedral environment may produce random strain fields which may be responsible for the polarization in the globally appeared cubic phase[183]. In literature, it has been shown that the strain field produced in the sample is responsible for the ferroelectric polarization in centrosymmetric structures [373,374] and also affects the polarization in non-centrosymmetric structures[175,176,352,375].

To get more insight into this, we consider a one-dimension chain of Ti and Hf atoms connected to each other through oxygen (O) by a spring with spring constant k_1 (for Hf-O bond) and k_2 (for Ti-O bond) as shown below in fig.7.10.



Figure 7.10: Formation of local dipolar regions in a one-dimensional linear chain of Ti/Hf–O atoms.

Since Hf is randomly distributed in the BaTiO₃ lattice and the electronegativity of Hf (1.33) is smaller than Ti (1.54) [376,377], therefore in the region where Hf replaced the Ti atoms, the O atom which is attached to the Ti atom will attract more towards the Hf atom and Ti atom will attract towards O atom as shown in fig.7.10, which disturbs the position of Ti atom locally resulting in local non-centrosymmetry in the crystal structure and hence local dipole, such local dipoles will be distributed randomly throughout the sample even in the globally appeared cubic phase. The signature of polar regions appears in the Raman spectra of all Hf doped samples with an interference dip around 125cm⁻¹ [198,364,371]. In literature, this interference dip is due to the presence of non-polar HfO₆ in polar TiO₆ atoms and indicates the presence of nano-sized polar regions in the perovskite structure[371,378]. The increase or

decrease of the size of polar nano regions can also be determined by the integrated intensity of the phonon modes[198,378,379]. Present investigations also suggest that integrated intensity increases with Hf substitution as shown in fig.7.11. The increasing intensity indicates that the number density of local polar nano-regions increases with Hf concentration. The formation of polar nano regions is due to the off-center displacement of Ti ions arising because of the difference in the sizes of Hf and Ti cations and due to the difference in the electronegativity of these atoms. This off-centering displacement of Ti atom affects the polarization and hence the ferroelectric property of the prepared samples. Therefore, in light of the above discussion, it can be concluded that the inclusion of Hf at Ti site in BaTiO₃ relaxes the Raman selection rules i.e. phonons slightly out of the Brillouin zone center may also get detected[301,369,370] and generates several modes that influence its ferroelectric properties. The main features are as follows:

1. The sharp interference dip generated at about 125 cm⁻¹ and 150cm⁻¹ provide information about the polar nano-regions and its presence is a sign of two different types of oxygen octahedra.

2. The new mode generated at 190cm⁻¹ is the result of strain-induced polar mode and the intensity of this polar mode grows with an increase in Hf content.

3. An additional hump appears at 780cm⁻¹ whose intensity increases with an increase in Hf content and at 30% Hf doping it gets overlapped with the 715cm⁻¹ mode.

Thus, the presence of different radii ions at the B-site of the composition i.e. Hf⁴⁺ ions as well as Ti⁴⁺ ion may result in a kind of distortion in the cubic phase or off-centering some of the B-site cations from their centrosymmetric position which influences the ferroelectric property of the samples.

Further, it is imperative to mention here that the ferroelectric phase is always called the ordered state. However, the inclusion of Hf⁴⁺ ions for Ti⁴⁺ ions modifies the ferroelectric phase and the structure of the parent matrix, because Hf⁴⁺ ion possesses larger ionic radii than Ti⁴⁺ ions. The substitution of Hf at Ti sites increases the distance between the offcentered Ti dipoles and thus weakened the correlation between these dipoles. The random distributions of these Hf ions at Ti sites break the translation symmetry and hence the long-range ferroelectric order gets disrupted and nano-polar regions are formed with increasing Hf concentration. Thus, the doping causes local symmetry fluctuation that induces non-centrosymmetry in the short-range. Therefore, due to the short-range ordering, the ordered ferroelectric features with less intensity is observed even in the globally appeared cubic phase. In the present case, the terminology disorder applies to the said local fluctuation in symmetry due to Hf substitution.



Figure 7.11: The intensity of the Raman mode at $520cm^{-1}$ for $BaTi_{1-x}Hf_xO_3$.

7.3.3.5 Analysis through vibronic (electron-phonon) coupling

It is important here to note that, according to the vibronic theory [75,76,169,170,380] the presence of strong electron-phonon coupling initiated by the pseudo-Jahn-teller effect(PJTE) is required to produce the above-mentioned structural distortion. Hence to investigate the presence of strong electron-phonon coupling in the present case, the Raman spectra of the prepared samples have been analyzed considering Fano resonance. In many earlier reports, the interference dip around 180-200cm⁻¹ is known to be attributed due to the Fano interference[360,381]. But, in the present study, the Raman modes around 180-200 cm⁻¹ are not present in all the prepared samples, hence it is not possible to consider these modes for estimation of electron-phonon coupling using Fano fitting. It is important here to note that, the Fano effect is characterized in terms of asymmetric Raman line shape along with antiresonance peak[125,128]. Since the Fano effect is caused by interference of electronic and phononic continuum which results in Fano line shape. It has been observed that the 520cm⁻¹ mode has an asymmetry line shape as well as a well-defined dip in the form of antiresonance before the same peak, which implies a Fano resonance. Therefore, this mode has been fitted by the Fano equation. The detail of the Fano equation has been discussed in chapter-5.

It has been observed that the electron-phonon coupling parameter increases with an increase in the Hf concentration as shown in fig.6.5 of chapter-6. The electron-phonon coupling parameter extracted by fitting the Raman mode has been found to be higher in the cubic phase than that of the tetragonal phase which indicates that the vibronic coupling is playing a significant role in distorting the cubic phase of Hf doped BaTiO₃ samples. Thus, considering the above, it can be concluded that the Hf doped samples after 12% are not truly cubic as inferred by the x-ray diffraction data but there are some regions with local deformations that break the symmetry rules and responsible for the observed Raman spectra in the globally appeared cubic phase. This implies that vibronic coupling and structural disorder are responsible for the instability arising in the cubic phase of Hf doped samples.

7.4 Summary

The existence of polarization in the cubic phase of Hf doped BaTiO₃ is demonstrated by using Raman and PE measurements. The persistence of local polar bands in the Raman spectra of BaTi_{1-x}Hf_xO₃ samples even in the cubic phase indicates the presence of short-range correlated displacements of the Ti ions. The PE data shows that all the samples including those having Hf concentration greater than 12% show a very clear hysteresis loop. This confirms the presence of dipole and hence non-centrosymmetry in the prepared samples. Moreover, the vibronic (electron-phonon) coupling parameter increases with increasing Hf content which also signifies the existence of local dipolar regions in the perovskite structure. Thus, this study provides a way to understand the possible reason for polarization in the cubic structure of the perovskites.

Chapter 8

Conclusion and Future Perspectives

This chapter includes the overall conclusion of this work which are listed below. Also, the possible future scope of the work that can be carried out for further development in this field are discussed.

8.1 Conclusion

- ✤ In the present work, we studied the well-known classical ferroelectric material BaTiO₃ in its pure and doped form. A detailed structural, dielectric, optical, and Raman study of BaTi₁₋ _xHf_xO₃ was presented. For this various composition of BaTi₁₋ $_{x}Hf_{x}O_{3}$ ceramics with x=0.06, 0.09, 0.12, 0.15, 0.18, 0.21, 0.27 & 0.30 were prepared following the conventional solid-state reaction technique. The dielectric and optical properties of BaTi_{1-x}Hf_xO₃ samples have been investigated using impedance and diffuse reflectance spectroscopy respectively. In the present investigations, a new methodology has been proposed for understanding the origin of dielectric loss in terms of band-gap and Urbach energy. Thus, a possible correlation between E_g and tan δ in terms of tunneling probability was established.
- Further, the temperature-dependent dielectric loss behaviour of pure BaTiO₃ is understood by using the temperature-dependent optical and Raman spectroscopy. The dielectric study reveals that in the tetragonal phase of BaTiO₃ dielectric loss increases marginally, whereas in the cubic phase it shows a decreasing trend with increasing temperature. The optical and Raman spectroscopy techniques deliver the two times larger electron-phonon interaction parameter in the cubic phase compared to the tetragonal phase. The marginal increase in the value of dielectric

loss with temperature in the tetragonal phase is understood by considering the competition between the tunnelling of electron from valence to the conduction band and electron-phonon coupling, whereas; decrease in the value of $tan(\delta)$ in the cubic phase as a function of temperature may be due to the dominating contribution of electron-phonon coupling. Present investigations clearly establish the strong correlation between the temperature dependence of dielectric loss, the value of band gap, and electron-phonon interaction.

- The vibrational properties of BaTi_{1-x}Hf_xO₃ samples have been investigated using Raman spectroscopy. The Raman spectroscopy data suggests the appearance of a new Raman mode at ~780cm⁻¹ and the presence of asymmetry in almost all Raman modes. The intensity of this new phonon mode increases systematically with Hf doping; indicating an increase in the phononic disorder. The value of electronic disorder probe by diffuse reflectance spectroscopy in the form of Urbach energy has been estimated and the same is observed to scale with Hf doping. The systematic increase in the intensity of disorder phonon mode and that of electronic disorder suggests that structural disorder not only affects phonons but electronic state of the system as well.
- Further, the origin of polarization in the cubic phase of Hf doped BaTiO₃ samples has been investigated by using Raman and PE measurements. Study reveals that the inclusion of Hf⁴⁺ ions for Ti⁴⁺ ions modifies the ferroelectric phase and the structure of the parent matrix because Hf⁴⁺ ion possesses larger ionic radii than Ti⁴⁺ ions. The random distributions of these Hf ions at Ti sites break the translation symmetry and hence the long-range ferroelectric order gets disrupted and nano-polar regions are formed with increasing Hf concentration. Thus, the doping causes local symmetry fluctuation that induces non-centrosymmetry in the short-range. The presence of polar regions is supported through the appearance of A₁(TO) polar mode in Raman spectra which in principle should be absent in the samples with cubic

symmetry. The presence of a well-defined ferroelectric PE hysteresis loop in the samples with global cubic symmetry also confirms the presence of local polar regions. Thus, this study provides a way to understand the possible reason for polarization in the cubic structure of the perovskites.

8.2 Future Perspectives

- ✤ In this work, a new methodology has been proposed for understanding the origin of composition-dependent dielectric loss in terms of band-gap and Urbach energy with a proposed tunneling probability model. However, it has been observed that only tunneling probability fails to explain the observed temperaturedependent behaviour of dielectric loss in pure BaTiO₃. The temperature-dependent Raman and optical analysis indicate that there is a sharp change in the electron-phonon interaction parameter across the phase transition temperature. Therefore, as a further scope, the tunneling probability model can be further modified by incorporating the electron-phonon coupling parameter.
- As the Hf doped BaTiO₃ samples are known to show dielectric relaxation and during relaxation, it is believed that the system goes to the metastable state. The presence of the metastable state can be understood using the time-dependent optical and Raman spectroscopic measurements.
- In Hf doped BaTiO₃ samples, the Raman and PE measurements predict the presence of local polar regions. The presence of nanopolar regions can be further verified by extended x-ray absorption fine structure (EXAFS) measurement.
- In the present study, it has been observed that the electron-phonon coupling increases in the cubic phase of pure and Hf doped BaTiO3 samples. To check whether the increasing behaviour of electron-phonon coupling in the cubic phase is of universal nature or not, the electron-phonon coupling can also be calculated on other sets of cubic samples.

- It has been reported in literature that the relaxor ferroelectrics are useful in energy storage applications. So, the energy storage performance of Hf doped sample can be explored.
- It would be interesting to grow thin films of pure and Hf doped BaTiO₃ systems for device applications.
- The structural, optical, dielectric, and vibrational properties can be explored by using theoretical DFT codes.
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