Exploring the Interrelation between Urbach Energy and Dielectric Constant in Hf-Substituted BaTiO₃

Omkar V. Rambadey, Anil Kumar, Aanchal Sati, and Pankaj R. Sagdeo

ABSTRACT: The variation of dielectric constant ($\varepsilon_r$) in the low-frequency region ($\sim 10^6$ Hz) in Hf-substituted BaTiO₃ has been modelled considering the electronic disorder in the form of Urbach energy ($E_U$) with the help of a Bohr-like model. Optical absorption spectroscopy has been employed in order to estimate $E_U$ and also the band gap ($E_g$), which are found to scale systematically with Hf incorporation, whereas dielectric measurements reveal a decrease in the value of $\varepsilon_r$ observed in the frequency range up to $10^6$ Hz with Hf substitution in these prepared samples. The model predicts $E_U \propto 1/\varepsilon_r^2$ and $E_g \propto 1/\varepsilon_r^2$, which agrees with the variation of the corresponding experimental values. Thus, the present work contributes to understanding the interconnection between the optical and dielectric properties of such materials and successfully demonstrates the decrease in dielectric constant with increasing disorder.

1. INTRODUCTION

The field of materials science has undergone revolutionary research in the past few decades to understand the electronic, thermal, optical, magnetic, and dielectric properties of various materials. The knowledge of dependence of these properties on various factors has also been much fruitful for device fabrication that has enhanced the existing technologies. Out of these, optical and dielectric properties are of greater interest as they mainly involve the applications in solar cells, piezoelectric materials and devices, and charge storage capacitors. In addition to the device-based applications, the optical properties are useful in studying the electronic band structure, absorption characteristics, and the disorder (thermal, structural, and compositional) present in the materials. The disorder existing in a system may directly affect the electronic properties of the sample, which could determine the performance of a device prepared from such materials, and therefore, study of these disorders could have significant importance. From this view, optical absorption spectroscopy (OAS) is a useful tool to get the information of disorder in terms of a parameter called Urbach energy ($E_U$). The disorder is known to modify the bonding scheme of the host atoms/ions, thereby giving rise to onsite potential fluctuations. Consequently, some states near the conduction band (CB)/valence band (VB) could appear in the forbidden energy region due to the disorder, which are also known as Urbach tail states, which may be attributed to the exponential rise of the absorption coefficient rather than a sharp variation near the fundamental absorption region of the material, and the energy corresponding to width of these tail states is termed as $E_U$. A schematic diagram for manifestation of Urbach tail states is shown in Figure 1 to picturize the discussion.

The $E_U$ measures overall disorder present in a system. Further, the modified bonding scheme may also affect the induced polarization in the presence of an external electric field that could eventually alter the value of dielectric constant ($\varepsilon_r$). Thus,
Introduction of disorder into a system (could be due to doping ~ structural disorder) appears to alter both the dielectric and optical properties of the material, and such an interrelation between $E_U$ and $\epsilon_r$ may be modelled to investigate this correlation, which could be useful in understanding the properties of these materials and eventually helpful in determining the performance of the devices based on them.

Furthermore, titanate-based materials have been remarkably explored for a variety of applications like photovoltaics, water splitting, and energy storage.\textsuperscript{21-23} Also, belonging to the titanate family, BaTiO\textsubscript{3} (BTO) has been an interesting material due to its astonishing dielectric, piezoelectric, ferroelectric, optical, and structural properties.\textsuperscript{14,24-27} It has a perovskite-type (ABO\textsubscript{3}) structure where A = Ba, B= Ti. In addition, BTO exhibits crystal symmetries of four polymorphs in different temperature regions, namely, rhombohedral, orthorhombic, tetragonal, and cubic phases, from lower to higher temperatures (in a temperature range of $\sim$100 to 400 K). Interestingly, all these phases are ferroelectric, irrespective of the cubic phase.\textsuperscript{28} Moreover, the properties possessed by BTO can be tuned by substituting at A- or B-sites,\textsuperscript{24,29-31} which makes it an eligible candidate for exploring the correlation between $E_U$ and $\epsilon_r$ because being a dielectric material, BTO can be expected to exhibit significant variation in $\epsilon_r$ as a result of doping along with introduction of considerable disorder in the host system—altering $E_U$. Also, the frequency region of interest for variation of dielectric constant may lie in the range of MHz as this region is known to correspond to dipolar interactions.\textsuperscript{32}

Earlier efforts have been successfully made by researchers to understand the behavior of Urbach energy (~electronic disorder) through suitable modelling and also to correlate it with optical band gap.\textsuperscript{33-38} Moreover, attempts in the direction to realize the interrelation of the dielectric constant ($\epsilon_r$) with the electrical, magnetic, and absorption-related properties for various materials have also been contributed by various research groups.\textsuperscript{39-42} In this, BTO has been a popular material for study of dielectric behavior of solids.\textsuperscript{25,28,43,44} However, reports that study the correlation of Urbach energy ($E_U$) with $\epsilon_r$ are limited. In the present work, barium titanate (BTO) has been subjected to Hf incorporation at Ti-sites—BaTi\textsubscript{1-x}Hf\textsubscript{x}O\textsubscript{3} (BTHO), for which optical and dielectric measurements have been performed at various compositions. Optical spectroscopic investigation provided the information of electronic disorder in the form of Urbach energy ($E_U$), whereas dielectric measurements provided the value of dielectric constant for these samples. The $E_U$ has been observed to scale, while $\epsilon_r$ is found to decrease systematically with Hf substitution in the present series of samples, which suggests that as the electronic disorder grows in this system, the ability of the material to store energy in the form of induced polarization under an applied electric field reduces, evident from the reduced values of $\epsilon_r$ with Hf incorporation. Apparently, the connection between the Urbach energy and the dielectric properties of such materials could be studied through a suitable model. It should be noted that introduction of disorder could affect the atomic arrangement in the lattice which may modify the coulombic interactions within the system, as a result of which not only the density of Urbach tail states but also the dipole moment corresponding to the bonding scheme and hence the dielectric constant are expected to alter. The appearance of disorder at local sites and their manifestation as Urbach tail states having localized nature could be seen as a system with the disorder center surrounded by the charge carriers lying in a medium offered by the host lattice. This picture resembles with a Bohr-like system immersed in a medium other than the free space (with permittivity $\epsilon_0 = 8.85 \times 10^{-12}$ Fm$^{-1}$), and therefore, in order to explore this correlation between $E_U$ and $\epsilon_r$, a Bohr-like model has been proposed in this study, which yields $E_U \propto \sqrt{\epsilon_r}$ like dependence between the two quantities. Furthermore, the same picture has also been extended to realize the correlation of band gap with dielectric constant, and the predicted proportionalities have been further validated with experimental values for the BaTi\textsubscript{1-x}Hf\textsubscript{x}O\textsubscript{3} series.

**2. RESULTS AND DISCUSSION**

**2.1. Variation of Urbach Energy with Composition.** As discussed earlier, the present study aims to explore the interrelation between dielectric constant and electronic disorder in BTHO. Therefore, in order to have insight of electronic disorder, OAS has been used as a tool for the present series of samples to estimate $E_U$ corresponding to each composition. The optical absorption coefficient $\alpha$ is related to incident photon energy as\textsuperscript{5,19,43}

$$\alpha = \alpha_0 \exp \left( \frac{(E - E_g)}{E_U} \right)$$ (1)

where $E = h\nu$ is the energy of the incident photon, $E_g$ is comparable to the band gap energy at temperature T, $\alpha_0$ is a material-dependent coefficient as is $E_g$, and the quantity $E_U$ is known as Urbach energy.

However, in this report, the optical absorption $\alpha$ has been obtained by converting the diffuse reflectance spectroscopy (DRS) data into the respective absorption spectra by using the well-known Kubelka–Munk relation\textsuperscript{40,46,47}

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

Here, $F(R_\infty)$ is the Kubelka–Munk function; $R_\infty = R_{\text{sample}}/R_{\text{standard}}$, $R_{\text{sample}}$ is the diffuse reflectance of the given sample, and $R_{\text{standard}}$ is that of a standard specimen.

As $F(R_\infty)$ is proportional to the absorption coefficient $\alpha$, ($F(R_\infty) \propto \alpha$), the logarithm of $F(R_\infty)$ can be considered to represent $\ln(\alpha)$, and therefore, rewriting eq 1\textsuperscript{41,46,47}

$$\ln(\alpha) = \ln(\alpha_0) + \frac{(h\nu - E_g)}{E_U}$$ (3)

Equation 3 implies that a plot between $h\nu$ and $\ln(\alpha)$, in the absorption edge region, should give a straight line, the inverse of
whose slope will give the information of Urbach energy \( (E_U) \) at constant temperature.

In the present work, the \( E_U \) estimated for the prepared series of samples has been observed to increase systematically with Hf substitution (see Figure 2a). For the parent BTO sample, \( E_U \) has a value of \(~0.15\) eV, which increases with Hf inclusion and attains a value of \(~0.27\) eV at 30% Hf. The thermal contribution to \( E_U \) may be assumed to be constant as the experiments have been performed at room temperature (RT). Nevertheless, Hf substitution at the Ti-site introduces the onsite electronic disorder as well as structural disorder in the system. The random distribution of Hf ions in the lattice and the difference between ionic radii of \( \text{Hf}^{4+} \) and \( \text{Ti}^{4+} \) ions may result in potential fluctuations in the system that may introduce energy levels near VB/CB in the form of electronic disorder or \( E_U \), which could scale with higher substitution.

2.2. Effect of Hf Inclusion on Band Gap. In order to study the variation of band gap \( (E_g) \), which is another optical parameter, with the dielectric constant, the \( E_g \) values are estimated as a function of Hf content in the prepared samples. For this, the Tauc plot has been obtained from the OAS data. The discussed Kubelka–Munk (K–M) function also relates to the absorption coefficient as:

\[
\alpha(hv) = \frac{A(hv - E_g)^n}{\text{constant}}
\]

Here, \( A \) is the proportionality constant and \( n \) is a parameter that depends on the nature of the electronic transitions occurring in the system such that \( n = 1/2 \) for indirect band gap transition, whereas \( n = 2 \) for direct band gap transition. In the case of BTHO systems, being an indirect band gap material, \( n = 1/2 \) has been considered. Therefore, the intercept at the \( hv \)-axis for the plot between \((F(R_{\infty}) - hv)^2 \) vs \( hv \) would give the value of \( E_g \) for the respective sample.

In the case of the prepared series of samples, the values of \( E_g \) have been observed to scale with Hf incorporation into BTO and a comparative variation along with dielectric constant has also been shown with respect to Hf content in Figure 2b. Clearly, \( E_g \) values appear to have an inverse kind of correlation with the dielectric constant. The behavior of the two quantities will also be explained with the help of the Bohr-like model in the subsequent section.

2.3. Variation of Dielectric Constant with Hf Substitution. To explore the said relationship between \( \varepsilon_r \) and \( E_U \), information of dielectric properties for various compositions is further required. In this section, the dielectric behavior of the prepared series of samples is going to be discussed. BTO is well known for its tunable dielectric properties and high value of dielectric constant.\(^{14,26}\) Further, substituting at Ti-sites in the lattice can alter the properties of the system depending on the nature of the dopant.\(^{14,49}\) For the present study, dielectric properties of Hf-incorporated BTO at Ti-sites have been studied at RT in a wide range of frequencies \((\sim \text{MHz})\). The frequency-dependent variation of dielectric constant for different Hf contents at RT is shown in Figure 3, which reveals that the value of \( \varepsilon_r \) drops with frequency for a particular composition and attains a nearly stable value in the higher-frequency region \((\sim 10^9 \text{ Hz})\). This particular stable value in the higher-frequency region reduces with the increase in Hf content.

It is well known that at low frequencies, the ionic, interfacial, and dipolar contributions dominate, which may not be necessarily systematic. However, in the higher-frequency region, the space charges, dipoles, and ions are unable to respond to the oscillatory variations of the external electric field. Thus, their parts do not contribute to the overall dielectric constant in this range \((\sim 10^9 \text{ Hz})\), and in this case, electronic contributions persist at high frequencies and the \( \varepsilon_r \) becomes stable above a

![Figure 2](https://doi.org/10.1021/acsomega.1c05057)

**Figure 2.** (a) Plot of variation of dielectric constant \( (\varepsilon_r) \) and Urbach energy \( (E_U) \), showing an inverse kind of variation with Hf substitution; (b) plot of change in band gap \( (E_g) \) and dielectric constant with Hf content in \( \text{BaTi}_{1-x}\text{Hf}_x\text{O}_3 \) shown together.

![Figure 3](https://doi.org/10.1021/acsomega.1c05057)

**Figure 3.** Frequency-dependent behavior of dielectric constant of \( \text{BaTi}_{1-x}\text{Hf}_x\text{O}_3 \) samples plotted for different Hf contents \( (x\%) \).
certain frequency value. This explains the frequency-dependent variation of $\varepsilon_r$ for a particular sample. Moreover, it could be observed that the stationary value of $\varepsilon_r$ around the frequencies $\sim 10^9$ Hz shifts downward with Hf content, which could be ascribed to the fact that Hf inclusion stabilizes the system toward a cubic structure near RT. This is further supported by the refined values for structural parameters obtained from the X-ray diffraction (XRD) analysis of these samples, reported in previous work. Clearly, the Ti–O–Ti bond angle ($\theta$(Ti–O–Ti)) has been found to approach 180° along with the increase in average Ti–O bond length.

Two possible inferences could be responsible for a decrease in the dielectric constant:

1. As $\theta$(Ti–O–Ti)$\rightarrow$180°, the dipole moments corresponding to in-plane Ti–O bonds tend to cancel each other, and therefore, the dipole moment reduces with Hf substitution.

2. The non-centrosymmetric TiO$_6$ octahedra, in which the Ti$^{4+}$ ion is displaced relative to its central position along the c-axis, possess a certain dipole moment. However, in BTHO samples, Hf replaces Ti-sites randomly, thereby increasing the effective distance between two successive TiO$_6$ octahedra, which weakens the dipole–dipole interaction corresponding to neighboring TiO$_6$ octahedra, leading to comparatively reduced polarization. It should be noted that HfO$_6$ octahedra may not necessarily occupy all the alternating positions with respect to the TiO$_6$ octahedra, but their (HfO$_6$) random occurrence within the lattice can affect the net dielectric behavior by weakening the local dipolar interactions which collectively may result as a decrease in the dielectric constant with a higher Hf content.

These inferences are also elucidated in Figure 4. Thus, it can be understood that incorporation of Hf into the BTO structure reduces the tendency to store the energy in the form of electric polarization which appears as lowering of the dielectric constant.

2.4. Model for Investigating Dependence of Dielectric Constant ($\varepsilon_r$) on Urbach Energy ($E_u$) and Band Gap ($E_g$)

Further, to investigate the correlation between $\varepsilon_r$ and $E_u$, a Bohr-like model will be discussed in this section and the same will be validated through the experimental data for $\varepsilon_r$ and $E_u$. It should be noted that introduction of a dopant into the host lattice could modify the bond angles, bond lengths, and the number of dangling bonds in the lattice that may appear as disorder centers and the associated energy levels may be assumed to lie within the forbidden gap of the semiconducting material. The current work aims to provide a picture toward how the disorder states obtain their localized nature and how dielectric constant would influence it. For this, we consider here the disorder centers so created due to the dopant incorporation—because of the onsite potential fluctuations which occur as a result of structural disorder, some energy levels (known as Urbach tail states) may appear in the forbidden gap of the semiconductor system that could localize the charge carriers; this could be visualized as the influence of the disorder centers over the charge carriers at different parts in the lattice. This situation has been compared with the Bohr-like model as the disorder center and the localized carrier may be looked as a Bohr-like system where the host lattice could provide the intervening medium and whose dielectric constant has been considered for the current study. Further, as the energy associated with the density of states of these localized carriers would correspond to the Urbach energy, the Bohr-like picture viewed for the combined disorder center—localized carrier system could be extended to explain the interrelation between the Urbach energy and the dielectric constant.

Considering these discussions, let us now consider a system of semiconductors containing dopants that can provide energy levels in the forbidden gap. These energy levels, in accordance with the Bohr-like model, can be given by the relation:

$$E_n = -\frac{R^*}{n^2}$$

where $n$ is some number and $R^*$ represents equivalent Rydberg constant expressed as

$$R^* = \frac{m^*}{m_0} \frac{1}{\varepsilon_r^2} R$$

where $m^*$ is the effective mass of the charge carrier, $m_0$ is the rest mass of the electron ($9.1 \times 10^{-31}$ Kg), $\varepsilon_r$ is the relative permittivity (or dielectric constant) of the medium surrounding the carriers, and $R$ denotes the Rydberg constant for the hydrogen atom given as
Here, $\varepsilon^*$ is the charge over an electron ($1.6 \times 10^{-19}$ C), $\varepsilon_0$ is the permittivity of free space ($8.85 \times 10^{-12}$ F/m), and $h$ is Planck’s constant ($6.626 \times 10^{-34}$ Js).

Since the motion of a hole (h)/electron (e) is not entirely free due to interactions with the lattice, its mass can be treated as the effective mass ($m^*$) to account for the boundedness with the lattice. Then, the charge carriers can be considered, under this approximation, as a free particle of mass $m_0$ and not the original mass ($m_0$), making movement across the lattice system. Further, the host lattice can be seen as a medium for motion of h/e with dielectric constant equal to $\varepsilon_r$. Now, considering the states near VB, $m^*$ in eq 5 represents hole effective mass, whereas it denotes the electron effective mass for states near CB. The energy associated with these states can be written by using eqs 5 and 6 in eq 4

$$\varepsilon_u = \frac{R}{\varepsilon_r} \frac{m^*}{m_0} \frac{1}{\varepsilon_r}$$

This implies that the defect energy level would lie deeper for a low-$\varepsilon_r$ medium that is ascribed to the weak shielding by the medium for the coulombic potential due to the disorder. It should be noticed that the energy ($\varepsilon_u$) associated with the dopant state depends inversely on $\varepsilon_r^2$. It is further noteworthy here that the states appearing due to interactions involving the disorder centers (arising due to doping in the present case) may have discrete nature, but the entire network as a whole could contribute to a number of such energy levels that lie along, and thus, it may lift the discrete nature of the levels when considered collectively. Therefore, in the case of doped systems, the overlapping of the dopant band with VB would result in the VB-tail width which is known to contribute to the Urbach tail states and thus, $\varepsilon_u$ should also depend on $1/\varepsilon_r^2$, in a similar way the dopant energy states ($\varepsilon_d$) do. Therefore, it can be inferred that Urbach tail width depends inversely on the square of $\varepsilon_r$ of the material, or $\varepsilon_u$ is $1/\varepsilon_r^2$.

Furthermore, considering the expression for $\varepsilon_u$ in eq 7, the same could be extended to elaborate the levels corresponding to the conduction band minimum ($\varepsilon_c$) and valence band maximum ($\varepsilon_v$), and the term ($\varepsilon_c - \varepsilon_v$) would give the band gap $E_g$ Following this discussion, eq 7 could be extended to express band gap as

$$E_g = E_u - E_v = -\frac{R}{m_0} \frac{m^*}{n^2} \frac{1}{\varepsilon_r^2}$$

$m^*$ and $n^2$ are the effective masses of charge carriers, whereas $n^2$ and $n^2$ are numbers corresponding to the conduction band minimum and valence band maximum energy levels, respectively; $R$ and $m_0$ are constants; moreover, in an approximation that the carrier effective masses do not vary much by a suitable substitution into a semiconductor lattice, it can be inferred from eq 8 that the band gap of a semiconductor material could have a correlation with dielectric constant of the form $E_g \propto 1/\varepsilon_r^2$ in addition to the Penn model. The discussion on the experimental investigation for these predictions will be carried out in upcoming sections.

2.5. Comparison of Experimental Values of Urbach Energy and Dielectric Constant. To validate the discussed model, the experimental values of $\varepsilon_u$ and $\varepsilon_r$ are plotted as $\varepsilon_u$ versus $1/\varepsilon_r^2$ in Figure 5. It can be clearly seen that the $\varepsilon_u$ versus $1/\varepsilon_r^2$ plot is reasonably linear for Hf compositions > 6%, attributing to the systematic reduction in the ability of the medium to respond to the applied electric field through electric polarization. It also indicates the lower shielding of the disorder centers by the host lattice with dopant (Hf) incorporation that appears as the reduced dielectric constant of the medium. It is interesting to see that the pure BTO sample does not come into the linear trend exhibited by the Hf-doped samples and in this case, the graph may appear to show logarithmic behavior rather than linear. This inconsistency may be understood in terms of the effective mass of the charge carriers ($m^*$) that appears in eq 7. As substitution of Hf into the system introduces tail states near VB/CB and also tunes the optical band gap of the material,26 this may be further responsible for modifying the electrical properties of the system53 and hence the effective mass of the charge carriers. Thus, Hf substitution appears to significantly alter the effective mass only with respect to the pure BTO system; however, it appears to not vary much for higher Hf compositions. This can be further supported by the fact that the dielectric loss for these samples has been found to decrease with introduction of Hf, which shows a greater drop on the low Hf-content side and very less changes on the higher Hf-content side;36 also, the free carrier density may be assumed to remain unaltered since Hf$^{4+}$ inclusion at Ti$^{4+}$-sites in BTO is not expected to introduce any additional electrons/holes, thereby suggesting very small variation in the effective mass of the charge carriers for higher Hf contents (>6%), where the $\varepsilon_u$ versus $1/\varepsilon_r^2$ is clearly linear. Therefore, the linear behavior observed in accordance with eq 7 in Figure 5 advocates that the effective mass has not altered much for compositions above 6% Hf and the proposed Bohr-like model for this system still holds for the rest of the compositions too. It is noteworthy here that the slope of the corresponding linear plot may be assumed to provide information of the carrier effective mass in accordance with eq 7; however, it would not be appropriate to expect extraction of the exact value as it would require the information of number “n” as well, which may not be practically feasible. Further, since electron and hole effective masses are in general not equal, their influence could be different in the Urbach tail density of states near conduction and valence bands. Also, this study has been carried out neglecting the contribution of thermal fluctuations
with consideration that all the measurements were taken at (constant) room temperature; due to these reasons, exact and specific values of carrier effective mass cannot be expected to be found from the slope of the linear plot. However, these values can provide an approximate information in this regard, i.e., high slope values may correspond to higher effective masses and thus may be attributed to an insulating sample. Nevertheless, the current study is more focused on exploring the correlation between the Urbach energy and the dielectric constant, and in this regard, another view toward the slope of the linear plot could be the sensitivity of Urbach energy toward the change in the dielectric constant as the slope, in the experimental aspect, would correspond to the variation in Urbach energy per unit change in the inverse square of dielectric constant, which is found to be quite high as the estimated slope values obtained from linear fitting are large in magnitude.

Moreover, the linear behavior of the plot between experimentally obtained values suggests that the dependence of $E_U$ and $e_r$ is in agreement with that predicted by the discussed model in eq 7, implying that the proposed Bohr-like model is suitable for understanding the variation of dielectric constant with Urbach energy for the BTHO system in terms of interactions between the disorder centers and the charge carriers, and could be extended to similar doped semiconducting media.

### 2.6. Investigation on the Dependence of Dielectric Constant on Band Gap

So far, a correlation between the dielectric constant and the Urbach energy (~electronic disorder) has been successfully discussed and explored experimentally in the previous sub-sections. In the current sub-section, the correlation between band gap and dielectric constant will be investigated through the experimental values. The behavior of dielectric constant at intermediate frequencies (~5.2 MHz) with respect to band gap is plotted in Figure 6 as $E_g$ vs $1/e_r^2$.

![Figure 6. Plot of band gap with inverse square of dielectric constant for different HF compositions in BaTi$_{1-x}$Hf$_x$O$_3$ (slope of the linear fit = 36061.24 eV).](image)

Interestingly, the two quantities are observed to follow linear dependence. In addition, it is noteworthy here from the linear trend observed in Figure 5 that $m^*$ terms appearing in expression (8) do not alter much; also, the values of numbers $n_i^2$ and $n_i^*$ would be determined by the atomic species present in the system whose states contribute to the CB/VB which is not altered in the present series, that is, no elements other than Ba, Ti, Hf, and O are there. Hence, the proportionality predicted from eq 8, that is, $E_g \propto 1/e_r^2$, could hold for these samples, which is evident from Figure 6.

Thus, in addition to the correlation between dielectric constant and Urbach energy, this study also investigates the dependence of dielectric constant on band gap.

### 3. CONCLUSIONS

In conclusion, to understand the dependence of dielectric constant ($e_r$) on optical properties of Hf-incorporated BaTiO$_3$ samples, a quantitative correlation has been explored through a Bohr-like model considering the interaction between the disorder centers and the charge carriers and has been successfully validated for the Hf-substituted BaTiO$_3$ system. This study unravels that as the electronic disorder increases in a system with structural disorder as a consequence of doping, the bonding scheme of the host lattice atoms/ions could also be affected, which may ultimately modify the extent of polarization in the presence of an external electric field and hence the value of dielectric constant. Thus, the present work demonstrates, quantitatively, the interrelation between the optical and dielectric properties of semiconductor materials, explaining how a disordered system would tend to have a lower dielectric constant. The significance of the linear plot between Urbach energy ($E_U$) and $1/e_r^2$ is that its slope may suggest about the sensitivity of $E_U$ toward change in $e_r$.

### 4. EXPERIMENTAL METHODS

#### 4.1. Sample Synthesis and Characterization

The synthesis of Hf-incorporated barium titanate BaTi$_{1-x}$Hf$_x$O$_3$ (BTHO) was carried out with a solid-state route for compositions—$x = 0.06, 0.12, 0.15, 0.18, 0.21, 0.27,$ and $0.30$. For this purpose, high-purity HfO$_2$, BaCO$_3$, and TiO$_2$ were taken in stoichiometric ratios as precursors and ground to obtain fine particles. The mixture was then subjected to calcination at 1100 °C for 6 h, followed by further heat treatment at 1250 °C for 12 h. The phase purity of the synthesized samples was confirmed by XRD measurements. In order to further characterize the prepared samples, room-temperature Raman spectra in the spectral range from 100 to 1000 cm$^{-1}$, in the backscattering geometry, have also been recorded by the micro-Raman analysis using a high-resolution dispersive Raman spectrometer equipped with a 633 nm excitation laser source and a charge-coupled device detector. The detailed discussion on sample preparation, XRD data, and Raman analysis for the present series of samples have been reported in our previous report.

#### 4.2. Optical Measurements

The optical measurements of prepared samples have been performed using DRS on a UV–VIS–NIR spectrophotometer in the photon energy range of 2–4 eV. The DRS data have been converted into the corresponding absorbance with the help of the K–M function, which provides a quantity proportional to the absorption coefficient of the material. In order to obtain Urbach energy ($E_U$), the variation of absorption coefficient (~K–M function) has been observed with respect to the energy of the incident photon for the prepared series of samples and the energy range, in which the K–M function exhibits exponential behavior, is considered. A brief description of the methodology has been given in Section 2.1 regarding the extraction of $E_U$ from the experimental data. Further, optical band gap values have also
been obtained from the OAS data of present series of samples by using the Tauc equation.\(^{27}\)

### 4.3. Dielectric Measurements

In order to study the dielectric properties, the samples have been obtained in the form of pellets of a diameter of \(\sim 10\) mm and a thickness of \(\sim 1\) mm at a 20 Ton/cm\(^2\) pressure sintered at 1300 °C for 12 h. The density of pellets is found to be \(\sim 93\%\), which were then coated with silver paint in order to make electrodes on the opposite surfaces, thereby preparing a capacitor with the prepared sample as a filling material. Since the capacitance \((C)\) for a parallel plate capacitor is given by\(^{12,56}\)

\[
C = \frac{\varepsilon_r \varepsilon_0 A}{d}
\]

where \(\varepsilon_r\) is dielectric constant or the relative permittivity of the filling material between the parallel plates, \(\varepsilon_0\) is the permittivity of free space, \(A\) is the area of cross-section of the parallel plate, and \(d\) is the thickness of the capacitor; hence, by measuring the capacitances of the obtained capacitors, one can obtain the dielectric constant \(\varepsilon_r\) of the filling material, that is, the prepared samples, provided the other parameters in the expression are known. The dielectric measurements have been performed at RT on these pellets using a precision impedance analyzer with an oscillator voltage of \(\pm 1\) V\(^{15,28}\) in the frequency range of 10 Hz to \(10^7\) Hz.

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**Notes**

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

SIC IIT Indore is acknowledged for providing some of the experimental facilities. The authors sincerely thank the Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, for providing synchrotron radiation facilities. The authors sincerely thank DST-SERB for financial support through sanction number CRG/2018/001829. The authors sincerely thank DST-FIST (SR/FIST/PSI-225/2016) for providing funding for the Raman spectrometer. The authors A.K. and O.V.R. acknowledge IIT Indore for providing financial support through Teaching Assistantship. Author A.S. acknowledges CSIR New Delhi for providing Junior Research fellowship through grant no. 1061651837 and IIT Indore for allowing pursuing research activity through Ph.D. program.

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