Investigation of the Impact of Calcinations Temperature on the Properties of Ba Doped HfO₂ Nano-rods

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Abstract: Barium doped hafnium oxide nanoparticles were synthesized by an easy co-precipitation method. FTIR analysis and EDX investigation shows the purity and stoichiometric composition of hafnium oxide nanoparticles. XRD investigation exhibit the as synthesized nanoparticles are amorphous in nature and calcined barium doped hafnium oxide nanoparticles have the monoclinic phase structure with the mean crystallite size was around 15 nm. TEM analysis shows the development of crystalline Nano-rods. The Nano-rod formations signify the possibility of its use in applications of sensor. Ultra violet visible spectroscopy investigation shows that the band gap of the nanoparticles is noticed between 5.4 -5.14 eV. The visible and NIR of barium doped hafnium oxide nanoparticles indicated high reflectance, which may possibly be employ as an antireflection coating in solar cells applications and high absorbance ultra violet region signify the viability of make use of the prepared nanoparticles could be used in Opto-electronic device applications.

Keywords: Co-precipitation; Ba-HfO₂ NPs; Nano-rods; XRD; Optical materials

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1. Introduction

Hafnium oxide is a suitable nominee for various industrial applications like electronics, structural ceramics, magneto-electronics, optics and optoelectronics because of their excellent properties such as chemical stability, good electrical, good mechanical, high dielectric constant, and wide band gap.¹² Hafnium oxide blended with graphene is able to produce hybrid structures, which is capable of suggest the chance to unite the multi functionalities of oxides through the outstanding electron transport in graphene, for the employment of the recent nanotechnology established high-speed electronics.³ Due to their remarkable optical properties like high refractive index and transmission in the visible spectrum, HfO₂ is used in antireflection coating. In addition, because of its elevated melting temperature (~2800°C) and thermal stability it has been used for thermal barrier coatings application in operating turbine blades.⁴ Also, due to its high transparency properties of HfO₂ in excess of a wide optical series from UV to mid-IR, these Nano-materials are employ in heat resistant and defensive optical coating applications.⁵ The merits of Nano-crystalline materials are enhanced phase structure, uniformity and sinter ability that leads to distinct properties such as mechanical, electrical, dielectric, magnetic, catalytic and optical. Also, nanoparticles has been used in optical systems due to their smaller size.⁶ Diverse preparation process of HfO₂ nanoparticles were accounted for example sol-gel,⁷ chemical solution method,⁸ precipitation method,⁹ solid-state reaction method,¹⁰ combustion reactions method,¹¹ reduction-oxidation synthetic route,¹² and one-pot synthesis route.¹³ The standard and successful approach to progress the achievement of the oxide materials depends on doping. Thus a suitable resistive method of the doped-oxide be required to progress the performance of the devices.¹⁴ The influence of dopant integration with calcinations temperature furnishes the crystal stability, fine crystal structure and controllable size.¹⁵ Based on the previous literature there is no information on Barium doped HfO₂ monoclinic structure Nano-rods. So, an opportunity has been made to prepare Barium doped HfO₂ Nano-rods, which could be used in optoelectronic and sensor device applications.
2. Experimental Techniques

2.1 Materials and Methods
The laboratory grade chemicals such as Hafnium tetra Chloride (HfCl₄) and Barium Chloride Dihydrate (BaCl₂.2H₂O) were obtained in Alfa Aesar.

2.2 Preparation Route
The barium doped HfO₂ NPs were prepared by an easy co-precipitation technique. Hafnium chloride (HfCl₄) and barium chloride dihydrate (BaCl₂.2H₂O) were used as starting precursors. An aqueous solution of 0.04M (50ml) BaCl₂.2H₂O further drop-by-drop addition into a 0.01M (50ml) aqueous solution of HfCl₄ kept at 55°C. This mixture was subsequently undergone forceful invigorating by a magnetic stirrer for 5 hours to make sure the whole dissolution of precursor. Then, white color Barium doped hafnium hydroxide resin was yielded by the addition of ammonia. The barium doped hafnium hydroxide mixture was methodically rinsed with distilled water. Then residuals were removed by centrifugation at 3000 rpm. The technique was redone for ten times to eradicate the contamination. The barium doped hafnium hydroxide precipitate was dehydrated by microwave oven kept at 75°C for three hours. Then calcinations at 600°C for 3 hours by muffle furnace using silica crucible to gain an unpolluted crystalline barium doped hafnium oxide nanoparticles.

2.3 Characterization
Structural properties of the NPs was analyzed by powder XRD by Cu-Kα radiation (1.5406 Å) for the scale of 10° to 80°. The crystallite size and peak broadening of the nanoparticles investigated by FWHM (β) values and diffraction angles (θ). The stoichiometry compositions of Nano-particles were investigated by EDX -JEOL / JSM /6390/ Japan. FTIR - JASCO / FT / IR-680 was used to analyze the different functional, vibrational frequency molecules (groups) of the nanoparticles for the scale of 400 to 4000 cm⁻¹. The morphology and crystallite size of the prepared nanoparticles was obtained by using TEM – PHILIPS / CM 200 / 20-200kv / 2.3 Å. The phase structure and crystallinity of nanoparticles were achieved by SAED pattern investigation. Here diffraction rings are coupled with crystalline nature and X-ray diffraction. The Ultra visible spectroscopy-JASCO V670 / Japan, for the scale of 200 to 2000 nm was used to investigate the optical properties like Absorbance, Reflectance and band gap.

3. Results and Discussion

3.1 Structural Analysis
Figure 1 illustrates the XRD of barium doped HfO₂ NPs at different calcinations temperature. The XRD of as synthesized nanoparticles demonstrated a wide diffraction pattern observed within the diffraction angle 20° to 35°. It shows the obtained nanoparticles amorphous in nature and it reflects the premature period of crystallization. At 200°C calcined NPs exhibits several tiny peaks superimposed in the spectrum, which designate the establishment of crystallization. At 400°C calcined NPs exhibits limited high intensity narrow width peaks. It discovered that the crystallinity was significantly improved with increase in calcinations temperature. At 600°C calcined NPs exhibits high intense multi sharp peaks. It exposed that the grain development of NPs was thermally activated and also the XRD pattern of NPs at 600°C exhibits polycrystalline nature with structure of monoclinic. The better inclination plane and diffracting angle of monoclinic nanoparticles is (-111) at 2θ = 28.32°. The other peaks at 2θ values of 17.51, 24.62, 35.50, 41.22, 45.10, 56.32, 63.22, 71.54, 77.70 and 82.72° respectively corresponds to (100), (110), (200), (102), (112), (132), (311), (321), (410) and (024) orientation planes. The obtained diffraction pattern of barium doped HfO₂ NPs is good agreement with common JCPDS data file (78-0050). The peaks noticed in the diffraction pattern at an angle 12.72° and 32.41° corresponds to (111) and (331) inclination planes. It may possibly as a result of the doping of Barium (Ba). Also impurity peaks were absent. It indicates that the synthesized nanoparticles are of high purity and crystalline in nature. The monoclinic structure lattice geometry equations is obtained by using lattice parameters for example lattice constants (a, b, c), unit cell volume and the distance of neighboring planes in the Miller indices (hkl) given by the relation.

\[
\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left[ \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} - \frac{2hk \cos \beta}{a} \right] \quad \text{and} \quad V = abc \sin \beta
\]

(1)
The average lattice parameters values for example (a, b, and c) respectively 5.117 nm, 5.175 nm and 5.291 nm and \( \beta = 99.216 \) were used to estimate the \( d_{310} \) values of monoclinic phase structure. The obtained and estimated interplanar \( (d_{310}) \) distance values of barium doped \( \text{HfO}_2 \) NPs are consistent with each other and the interplanar \( (d_{310}) \) distance data are scheduled in Table 1 and 0.138 (nm)\(^3\) is the unit cell volume of barium doped hafnium oxide nanoparticles. The Debye-Scherrer equation was used to estimate the crystallite size.\(^{[21]}\)

**Table 1.** Interplanar Spacing’s Analysis of prepared samples

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<th>k</th>
<th>l</th>
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<td>7</td>
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</table>

**Figure 2.** EDX spectrum analysis of prepared NPs

**Table 2.** Crystallite Sizes Corresponding to Its Different Temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calculation temperature</th>
<th>Crystallite size</th>
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<tr>
<td></td>
<td>As prepared</td>
<td>12.12 nm</td>
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<tr>
<td>Ba doped ( \text{HfO}_2 )</td>
<td>200°C</td>
<td>13.30 nm</td>
</tr>
<tr>
<td></td>
<td>400°C</td>
<td>14.10 nm</td>
</tr>
<tr>
<td></td>
<td>600°C</td>
<td>15.11 nm</td>
</tr>
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</table>

**3.2 EDX Analysis**

Figure 2 shows the EDX spectrum of barium doped \( \text{HfO}_2 \) NPs for the calculations temperatures of (a) as prepared (b) at 200°C (c) at 400°C and (d) at 600°C. The prepared barium doped hafnium oxide nanoparticles proved the occurrence of Hf, O and Ba elements by EDX analysis. The weight and atomic percentage of the elements existing in the as prepared and various calcinations temperature of Barium doped Hafnium Oxide NPs are scheduled in Table 3. It exhibits that the cleanliness of synthesized NPs is increased with rising calcinations temperature.

**3.3 FTIR Analysis**

Figure 3 (a-d) illustrates the FTIR spectrum analysis of (a) as prepared (b) at 200°C (c) at 400°C and (d) at 600°C are respectively. The absorption bands at 850 and 450 cm\(^{-1}\), 860 and 450 cm\(^{-1}\), 760 and 510 cm\(^{-1}\), 760 and 510 cm\(^{-1}\) respectively for as prepared, calcined at 200°C, 400°C, 600°C nanoparticles revealed that the development of Metal-Oxide bonds (M=Hf, Ba) of IR range active phonon modes.\(^{[22]}\) The peak at 1367 cm\(^{-1}\) observed in the as prepared nanoparticles possibly caused by the bidentate carbonate symmetric stretching (O-C-O) and calcined nanoparticles does not shows such absorption band. The peaks at 1633, 1624, 1630 cm\(^{-1}\) noticed respectively for as prepared, calcined at 200°C, 400°C possibly due to H-O-H bending vibrations of adsorbed water whereas calcined at 600°C NPs indicates absence of the absorption band in this range. It also discovered that the absorption band in this range decreases with rising calcinations temperature. The peaks at 2365, 2360, 2376 cm\(^{-1}\) observed respectively for as prepared, calcined at 200°C, 400°C NPs possibly caused...
by CO$_3$ adsorption$^{[23]}$. The peaks at 3420 cm$^{-1}$ observed for the as prepared, calcined at 200$^\circ$C and 400$^\circ$C NPs probably by reason of stretching vibrations of hydrogen bond which provide evidence the occurrence of hydroxyl groups, while no absorption band noticed for the calcined at 600$^\circ$C NPs established the high purity and quality of nanoparticles. These observed bands are good agreement with earlier reports.$^{[24]}$

**Figure 3.** FTIR Spectrum Analysis of Prepared NPs

### 3.4 The SEM and TEM Analysis

Figure 4 (a) illustrates the surface morphology of as synthesized barium doped HfO$_2$ NPs. It exhibits lump like shape agglomeration. Figure 4 (b) shows patches like a shape agglomeration of calcined NPs at 200$^\circ$C. Figure 4 (c) shows spherical shape agglomeration of calcined NPs at 400$^\circ$C. Figure 4 (d) shows rock like shape agglomeration for NPs calcined at 600$^\circ$C. The agglomeration noticed in all the samples possibly on account of surface influence in the NPs with huge specific surface area and high surface energy.$^{[23]}$ Figure 5 illustrate the TEM image and SAED pattern of barium doped hafnium oxide nanoparticles. Figure 5 (a) is the TEM image of as prepared NPs. It exhibits amorphous nature. Figure 5 (c) is the TEM image of calcined amples at 600$^\circ$C, which exhibits the formation of Nano-rods. It revealed the improved crystallinity of calcined NPs. This is because of calcinations temperature and accumulation of barium ion. Figure 5 (d) is the SAED pattern of calcined NPs. It revealed that the bright and equally spaced parallel lattice points arranged periodically and it represents 2-fold rotation symmetry zone axis [110] plane of monoclinic structure. It also confirms that the NPs are crystalline in nature. This is probably attributable to the influence of barium dopants.

**Figure 4.** SEM Image Analysis of Prepared NPs

**Figure 5.** TEM Image Analysis of Prepared NPs

### 3.5 Optical Analysis

UV-Vis absorption spectra of BaHfO$_2$ NPs for different calcinations temperature are representation in Figure 6 (a). The characteristic peak observed between 230 – 240 nm for NPs (a) as synthesized (b) at 200$^\circ$C, (c) at 400$^\circ$C and (d) at 600$^\circ$C respectively revealed that the development of HfO$_2$ NPs.$^{[25]}$ It exhibits the calcinations temperature increased with the raise in wavelength peak. The wavelength range < 210 nm and between 260 nm to 380 nm
signify the higher absorbance of the nanoparticles which might be made use of for ultraviolet blocking contact lens and ultraviolet fascinating layer in optoelectronic devices. Figure 6 (b) demonstrate the reflectance spectra of nanoparticles (a) as synthesized and (b) at 200°C (c) at 400°C and (d) at 600°C respectively. It shows that the reflectance is about 90% in near infrared region and low in ultra violet region. This barium doped HfO2 might be utilized as antireflection layer in solar cells to get better efficiency. Meanwhile, plan for the assembly of roofs and walls of poultry forms because of high reflectance observed in the visible and near infrared region. Use such nanoparticles in poultry to minimize the cost of energy utilization coupled by the employ of electric bulbs, heater and stove. Use the plot (hv and Photon energy hv and to obtained band gap energy by the relation.\(^{[24]}\)

\[
E_g = \frac{1240 \text{ nm}}{\lambda_g} \text{ (eV)}
\]

Where \( E_g \) is the wavelength of the intercept intended from absorption spectra. The band gap of the NPs estimated for (a) as prepared, (b) calcined at 200°C, (c) calcined at 400°C and (d) calcined NPs at 600°C is discovered to be respectively \( E_g = 5.43 \text{ eV}, E_g = 5.39 \text{ eV}, E_g = 5.27 \text{ eV} \) and \( E_g = 5.16 \text{ eV} \). It is distinguished that the graphical and extrapolation methods are consistent with each other.

4. Conclusion

HfO2 were efficiently prepared by an easy and cost efficient co-precipitation method. XRD examination shows that the as prepared nanoparticles are amorphous in nature, while the calcined nanoparticles are polycrystalline in nature with monoclinic phase. The expected typical crystallite size was 15 nm. TEM and SAED pattern investigation of as prepared nanoparticles exhibits amorphous nature, which is verified by XRD pattern analysis whereas calcined nanoparticles discovered the formation of Nanorods and periodic arrangements of lattice bright spots of 2-fold rotation symmetry zone axis [110] of monoclinic phase. The evaluated band gap (\( E_g \)) of as synthesized NPs is 5.4 eV and for calcined NPs are 5.3 eV, 5.21 eV, 5.14 eV respectively for 200°C, 400°C and 600°C. This outcome was greatly consistent with extrapolation method. It also discovered that the transitional energy levels appear within the valence and conduction band by reason of the oxygen vacancy site. In the ultra violet region high absorbance indicated the possibility of employing these nanoparticles as ultra violet blocking layers in contact lens and ultra violet absorbing layer in optoelectronic devices and in the near infrared region high reflectance indicated that the nanoparticles might be apply as an antireflection layer in solar cells to advancement the efficiency.
References