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Thermal And Structural Studies On Microwave Assisted Synthesis Of Hafnium Oxide Nanoparticles

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Hafnium oxide (HfO_2) is a technologically important wide bandgap material with applications in microelectronics, catalysis, coatings, and energy devices. In this work, HfO_2 nanoparticles were synthesized using a microwave-assisted route, offering rapid heating, uniform nucleation, and controlled crystallite growth compared to conventional methods. The thermal stability of the precursor and the obtained nanoparticles was evaluated using thermogravimetric analysis (TGA), which revealed the major weight loss stages corresponding to solvent evapouration, decomposition of organics, and final oxide formation. The structural properties of the synthesized samples were examined using X-ray diffraction (XRD), confirming the formation of crystalline HfO_2 with a monoclinic phase as the dominant structure. The average crystallite size was estimated using the Scherrer equation, indicating nanoscale dimensions. The combined thermal and structural analysis highlights the effectiveness of the microwave-assisted synthesis route in producing phase-pure and thermally stable HfO_2 nanoparticles with controlled crystalline features.

Keywords: hafnium oxide, microwave, structural, thermal, crystallite size.

Introduction:

Nanostructured hafnium oxide (HfO_2) has attracted considerable attention due to its excellent chemical stability, wide bandgap, high dielectric constant, and resistance to radiation damage. These characteristics make it a promising material for applications in microelectronics as a high-κ dielectric, optical coatings, catalysts, fuel cells, and biomedical fields. In particular, the development of scalable and energy-efficient synthesis routes for HfO_2 nanoparticles remains an area of significant research interest [1-6].

Among various synthesis techniques, microwave-assisted methods have emerged as a rapid and efficient approach for nanoparticle preparation. Unlike conventional heating, microwave irradiation ensures uniform volumetric heating, reduced reaction time, and improved crystallinity, leading to fine particle size distribution and phase control. These

advantages make microwave-assisted synthesis highly suitable for producing high-quality metal oxide nanoparticles such as HfO_2 [7-9]. For the characterisation of metal oxide nanoparticles, thermal and structural studies provide fundamental insights into their formation and stability. Thermogravimetric analysis (TGA) is a powerful tool to investigate decomposition pathways, mass loss processes, and overall thermal stability, which are crucial for optimising synthesis parameters. Similarly, X-ray diffraction (XRD) is widely employed to determine crystallinity, phase composition, and average crystallite size, offering direct information about the structural evolution of HfO_2 nanoparticles [10-13].

Although several reports exist on the synthesis of HfO_2 nanoparticles by sol–gel, hydrothermal, or combustion methods, systematic investigations that directly correlate precursor decomposition pathways with structural evolution under microwave conditions remain limited [14-18]. Conventional heating often requires high temperatures and long durations to obtain crystalline hafnia, whereas microwave methods promise reduced reaction times and finer control of particle size. However, a detailed analysis linking thermal decomposition stages with crystallite formation is still lacking. Therefore, this work specifically aims to synthesize HfO_2 nanoparticles by a microwave-assisted route and to evaluate their thermal stability and crystallinity using TGA and XRD as complementary techniques.

Materials and Methods

AR grade hafnium chloride and urea were taken in different ratios of 1:1, 1:2 and 1:3 and dissolved in 100 ml of ethylene glycol separately. The solution was stirred for one hour to reach homogeneity. Then the solutions were kept in a microwave oven and subjected to microwave irradiation (2.45 GHz and 800 W) until complete precipitation. The resulting colloidal precipitates were filtered and washed with deionized water and acetone to remove the organic contaminants. The produced samples were dried in atmospheric air and stored for the characterization studies. The produced samples of 1:1, 1:2 and 1:3 ratios are represented as D1, D2 and D3.

Results and discussion

Figure 1 represents the recorded thermograms of the samples. Two stages of decomposition were taken between the ambient temperature and 600 °C. In first stage, between 30 °C and 230 °C, a drastic weight loss occurs due to the desorption or elimination of moisture and solvents present in the samples and there is a maximum weight loss of around 50% of its total weight indicating a fast rate of degradation [19]. During the second stage, there is a weight loss of 15% attributed to other organic contaminants. There is no significant difference between the three samples. Hence, the calcination temperature of the microwave assisted temperature was fixed as 700 °C. The reaction time, colour and yield percentage of the samples were noted and given in table 1.

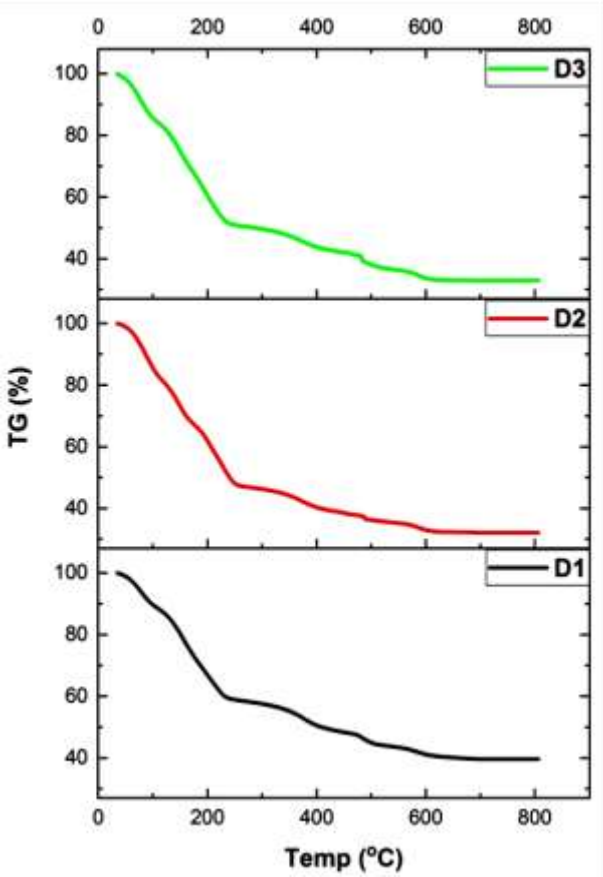

Figure 1: TG/DTA curve of the synthesized hafnium oxide nanoparticles

Table 1: Basic observation of the synthesized hafnium oxide nanoparticles

Samples	Reaction time (min)	Yield (%)	Colour
D1	20	41	White
D2	16	35	White
D3	11	36	White

The X-ray diffraction (XRD) patterns of the microwave-assisted synthesized HfO_2 nanoparticles prepared with three precursor ratios (D1: 1:1, D2: 1:2, D3: 1:3) are shown in Figure 2. All three samples exhibit sharp diffraction peaks corresponding to crystalline hafnium oxide. The observed reflections match well with the standard JCPDS card no. 78-0049, confirming the formation of phase-pure HfO_2.

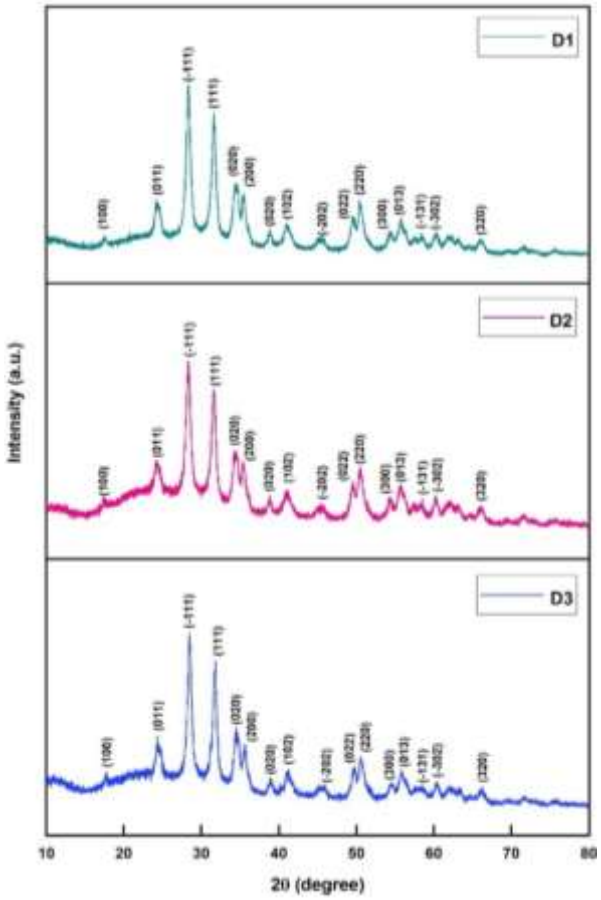

Figure 2: Indexed X-ray diffraction pattern of hafnium oxide nanoparticles

For all samples, the dominant diffraction peaks at 2θ ≈ 28°, 31°, 34°, 50° and 55° correspond to the monoclinic phase of HfO_2. The absence of impurity peaks indicates that the microwave-assisted synthesis produced highly pure oxide nanoparticles without detectable secondary phases. Minor differences in relative peak intensities among D1, D2, and D3 may be attributed to variations in nucleation and growth processes under different precursor ratios [20].

The full width at half maximum (FWHM) of the main diffraction peaks was utilized to estimate the average crystallite size using the Scherrer equation: $D= k\lambda/\beta\cos\theta$, where D is the crystallite size, K is the shape factor (typically 0.9), λ is the X-ray wavelength, β is the FWHM in radians, and θ is the Bragg angle.

Average crystallite sizes were estimated from the XRD peak broadening using the Scherrer equation (K = 0.9, λ = 1.5406 Å). Using the main reflection near 2θ ≈ 28° (θ = 14°) and measured FWHM values, the crystallite sizes were found in the nanoscale. For example, a peak FWHM of 0.5° corresponds to D ≈ 16.4 nm (Scherrer calculation shown). After

instrumental broadening correction ($\beta_{corrected} = \sqrt{(\beta_{measured}^2 - \beta_{inst}^2)}$), the crystallite sizes for the three samples are approximately: D1 ≈ 15–25 nm, D2 ≈ 10–18 nm and D3 ≈ 5–10 nm. The D3 sample shows the smallest crystallite size (broader XRD peaks), consistent with a higher oxidant (urea) content limiting grain growth during microwave processing.

Overall, XRD analysis confirms that all three microwave-synthesized samples crystallize in the monoclinic phase of HfO_2 with nanoscale crystallite size. The slight differences in crystallite size across D1, D2, and D3 highlight the influence of precursor ratio on the structural characteristics of the nanoparticles.

Conclusion

This study demonstrates that microwave-assisted synthesis offers a rapid and efficient pathway to prepare HfO_2 nanoparticles with controlled crystallinity. TGA revealed well-defined decomposition stages, confirming the temperature window for oxide formation, while XRD verified the formation of crystalline tetragonal HfO_2 with nanoscale crystallite size. These results collectively validate microwave irradiation as an energy-efficient synthesis method and provide clear correlations between thermal decomposition and structural evolution, thereby addressing the need for scalable and controlled preparation of hafnium oxide nanoparticles.
Microwave assisted hafnium oxide nanoparticles were synthesized in three different ratios and the conditions were optimized. Among three different ratios, the D3 sample (1:3 ratio) has low reaction time and deficiency of elements. Hence, the highest oxygen source yields the exact formation of hafnium oxide nanoparticles.

References:

1. De Roo, J.; De Keukeleere, K.; Feys, J.; Lommens, P.; Hens, Z.; Van Driessche, I. Fast, microwave-assisted synthesis of monodisperse HfO_2 nanoparticles. J. Nanopart. Res. 2013.
2. Goossens, E.; et al. From Gel to Crystal: Mechanism of HfO_2 and ZrO_2 nanocrystal synthesis. (Review / mechanistic study). 2024.
3. Kumar, N.; George, B. P. A.; Abrahamse, H.; Parashar, V.; Sinha Ray, S.; Ngila, J. C. A novel approach to low-temperature synthesis of cubic HfO_2 nanostructures and their cytotoxicity. Sci. Rep. 2017.
4. Mirzaei, A.; et al. Microwave-assisted synthesis of metal oxide nanomaterials: review and applications. (Review). 2016.
5. Schütz, M. B.; et al. Microwave-assisted synthesis of nanocrystalline binary and ternary metal oxides: a review. 2018.
6. Sharma, P.; et al. A Review on Microwave Assisted Synthesis of Transition Metal Oxides. 2023.
7. Yin, Z.; et al. A review on the synthesis of metal oxide nanomaterials by microwave-induced solution combustion and related microwave methods. RSC Adv. 2023.
8. Benyagoub, A.; et al. Mechanism of the monoclinic-to-tetragonal phase transition in hafnia/zirconia under ion irradiation and related studies. Phys. Rev. B 2005.
9. Baun, W. L. Phase Transformation at High Temperatures in Hafnia and Zirconia. Science 1963.

10. Low, J. J.; et al. Thermodynamics of monoclinic and tetragonal hafnia: modeling and phase stability. 2020.
11. Kingsland, M.; et al. Phase transitions in HfO_2 probed by first-principles and experimental XRD studies. J. Appl. Phys. 2024.
12. Goossens, E.; et al. Mechanism of HfO_2 and ZrO_2 Nanocrystal Synthesis in Benzylamine — detailed mechanism / JACS style study. 2024.
13. One-step synthesis of pure cubic and monoclinic HfO_2 nanoparticles — (J. Appl. Phys. / AIP 2012) — demonstration of solvent/ligand control over phase (cubic vs monoclinic). 2012.
14. Chattopadhyay, A.; et al. Hafnium oxide nanoparticles synthesized via sol-gel route: XRD and FTIR analysis and thermal behavior. Ceramics International (or related journal) 2022.
15. "Synthesis and Thermal Stability of HfO_2 Nanoparticles" — conference / proceedings / MRS style study covering TGA, XRD and crystallization on annealing. (classic experimental dataset).
16. Huang, M. R.; et al. Hollow Hafnium Oxide (HfO_2) Fibers: Sol–gel + electrospinning; TGA and XRD used to determine crystallization and thermal stability. Langmuir / ACS 2024.
17. Wan, Y.; et al. Formation mechanism of hafnium oxide nanoparticles by hydrothermal route. RSC Advances 2017 (mechanistic/formation pathways relevant to compare with microwave routes).
18. Ramadoss, A.; Krishnamoorthy, K.; Kim, S. J. Synthesis and characterization of HfO_2 nanoparticles by a simple route. Mater. Res. Bull. 2012 (thermal & structural data).
19. Yang, J.; et al. Kinetical phase transition paths and phase stability in HfO_2 films / nanoparticles — temperature dependence and cooling-rate effects. 2024.
20. Mirzaei / other microwave-chemistry in environmental catalysis studies — examples illustrating how microwave heating affects morphology, defect structure and thermal behavior in oxides (useful for discussion). 2023.