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**Zirconia and Other
Advanced Ceramics**
Fabrication, Challenges and Applications

Edited by Alina Pruna



Zirconia and Other Advanced Ceramics - Fabrication, Challenges and Applications

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Materials Science

Volume 18

Aims and Scope of the Series

Materials science has always occupied an extremely high position in the human development process. As we explore the oceans of stars, various industries have put forward more stringent requirements for the performance of materials, forcing us to pay more and more attention to the development of new materials. At the same time, the formation of a data-driven scientific paradigm is dramatically shortening the development cycle of new materials. The huge data generated by synergistically combining theories, high-throughput experiments, high-throughput computation, and artificial intelligence is greatly contributing to our ability to utilize materials science to solve real-world problems. The three topics of this book series - Metals and Nonmetals; Composite Materials; and Surface Science - will address important areas of advancement in materials science. There will be a range of interesting works published under these topics.

Meet the Series Editor



Prof. Chonghe Li received his Ph.D. from the Chinese Academy of Sciences in 1995. From 1995 to 2000, he worked as a researcher at the Shanghai Institute of Metallurgy, Chinese Academy of Sciences, where he also served as director of the research laboratory. In 2000, he was appointed Professor at the Institute of High-Performance Computing in Singapore, where he worked on computation and simulation in materials science until 2004. Since then, he has been a professor at the School of Materials Science and Engineering, Shanghai University, China, as well as the director of the Shanghai Specialty Casting Engineering and Technology Research Center. Prof. Li's research focuses on titanium alloys, titanium-aluminum single crystals, intermetallic compounds, theoretical calculations, alloy design, and special refractory materials. His broad scientific expertise is well recognized by the scientific community around the world. He is a member of the editorial board of the journal *Metals*. As an author, he has published more than 200 peer-reviewed papers, 2 books, and over 40 patents.

Meet the Volume Editor



Dr. Alina Pruna is a Researcher at the University Institute of Materials Technology of the Polytechnic University of Valencia in Spain. Her research focuses on surface modification, with special emphasis on the fabrication of oxide and graphene-based materials by electrodeposition, hydrothermal synthesis, and solid-state synthesis. She authored approximately 60 papers in international scientific journals, three books, and seven chapters, in addition to disseminating results at 70 scientific events and performing various technology-transfer activities, resulting in three patents.

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Preface

Advanced materials benefit society through their improved performance. A wide range of applications has been the avenue for such materials, including biomedicine, automotive, aircraft, and military sectors. This book focuses on advanced ceramics, including zirconia and GaN, with an emphasis on the latest advances in synthesis, properties, and applications, and highlights the challenges involved in each.

The book begins with an Introductory chapter entitled “Introductory Chapter: Zirconia and Other Advanced Ceramics”, which presents the background and motivation behind the book project.

Chapter 2, entitled “Analytical Approaches to Characterizing Zirconia-Based Compounds for Advanced Applications”, overviews the structural, morphological, and compositional properties of zirconia for advanced applications, based on analytical approaches including X-ray diffraction, Raman spectroscopy, Electron Microscopy, X-ray Photoelectron Spectroscopy, and X-ray Fluorescence.

Chapter 3, entitled “Identification and Thermal Stability of Radiation-Induced Defects in Nanostructured Zirconia Ceramics”, further delves into the electron spin resonance characterization method applied for the identification and thermal stability of radiation-induced defects in monoclinic zirconia ceramics irradiated with heavy ions and electrons of different energies, with a focus on the impact of nanoparticle size.

Chapter 4, entitled “Upgrading the Acidity of Zirconia *via* Merging with Dilacunary Phosphotungstates: Synthesis, Characterization and Production of Alkyl Levulinates”, investigates the use of zirconia in catalyst fabrication by wet impregnation. The catalyst conversion rate and selectivity were obtained.

Chapter 5, entitled “Zirconia-Based Materials for Aerospace Applications”, discusses the importance of zirconia ceramics in the aerospace industry and identifies current challenges in their processability, cost, and long-term reliability.

Alina Pruna

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Section 1

Introduction

Introductory Chapter: Zirconia and Other Advanced Ceramics

Alina Pruna

1. Introduction

This book focuses on advanced ceramics that distinguish themselves from the traditional ones through their superior properties including particle size distribution, composition, grain size or purity. The materials included in this class refer to aluminates, titanates, zirconates, nitrides, borides and carbides [1].

While more complex synthesis approaches are applied for advanced ceramics, the demand for these has increased greatly in the last years. Considering their application field, the advanced ceramics may be classified into functional ones, structural, bioceramics, glasses and ceramic coatings.

Zirconia exhibits excellent attributes including mechanical properties, namely high hardness, fracture toughness and high strength as well as marked corrosion resistance, natural color, environmental friendly and biocompatibility. Other properties include a high dielectric constant, high refractive index, low thermal conductivity, high optical transparency, low coefficient of thermal expansion and chemical stability. All the above-mentioned properties made ZrO_2 one of the first candidates for advanced ceramic materials, a technologically significant material that attracted significant interest in sensing, cutting tools and thermal barrier coatings.

Due to the similarity between zirconia and titania, the former attracted remarkable interest in implantology, dentistry and orthopedics [2]. Nevertheless, their stiffness varies greatly, which results in differences in biomechanical interactions.

Zirconia is known to show polymorphism in a wide range of temperatures, namely monoclinic up to 1170°C , tetragonal between 1170 and 2370°C and cubic between 2370 and 2700°C . The key feature of zirconia is that it can shift from monoclinic to tetragonal structure under severe stress [3]. The tetragonal structure is known to show higher density and strength in comparison with the monoclinic one, but is less translucent than the cubic phase.

While having remarkable attributes, ZrO_2 is suffering from *in vivo* deterioration and shows a decay in its properties [4]. Its properties depend on its microstructure, grain size and defects. Stabilized zirconia can be obtained by the addition of yttria or magnesia to render it with improved stability and strength. Zirconia can be reinforced with alumina to obtain alumina-toughened zirconia, which offers marked superior hardness and wear. It was shown that the ZrO_2 's fracture strength also depends on the design, the composition and preparation of an implant abutment [5, 6].

The synthesis methods for zirconia are multiple and consider its characteristics and the performance prerequisites. Thus, typical approaches involve the compressing of the powders in hot press or isostatic press, followed by sintering, when the result is

a higher strength and toughness ceramic. The improvement in the zirconia strength and toughness is strongly related to its microstructure, which in turn depends on the synthesis and sintering approaches. Surface modification may affect the implant fracture toughness. On the other hand, cyclic loading and environmental conditions were indicated to contribute to the fatigue failure of ZrO_2 .

Therefore, a long-term dental performance of ZrO_2 calls for understanding and improving fatigue of the ZrO_2 [7].

There are several challenges related to the zirconia, namely the low temperature degradation and susceptibility to changes under ultraviolet light. Under these circumstances, the toughness needs to be balanced with the resistance to low-temperature degradation. Other challenges explore the relationship between the particle size and the thermal stability of paramagnetic radiation defects in ZrO_2 and the diffusion at the interface. Understanding diffusion processes is a pre-requisite to improve the advanced ceramics performance in varying applications including electrical and optoelectronic ones. On the other hand, there are challenges dealing with processability, the cost and long-term reliability of zirconia.

2. Synthesis

Powder processing of ZrO_2 by conventional methods is based on the subsequent stages of solidifying, shaping, machining and sintering. The resulting particle size and homogeneity will affect the final properties [8].

The uniaxial and isostatic compression yield a green body of ZrO_2 powder. The conditions of the compression will affect the body density, homogeneity and the microstructure [9]. This green body may be further machined to allow the fabrication of complex geometries.

Of high importance is the sintering stage when the green body is heated at given heating rate up to high temperatures. There are conventional sintering methods and advanced ones including spark plasma sintering and microwave sintering.

Post-treatments may be applied upon the sintering to optimize the ZrO_2 biocompatibility [10].

The characteristics of each method will affect the growth of the grain, the densification and mechanical properties [10]. Grains larger than 1 micron have been indicated to result in excessive phase transformation, while those smaller than 200 nm do not achieve transformation toughening [11].

3. Properties

Regarding biocompatibility, it has been indicated that zirconia does not exhibit adverse changes in the tissues where restorations made of this material are observed and the zirconia particles produced by wear have been indicated as no cytotoxic [12].

Thermal stress was evidenced to induce the transformation of metastable tetragonal phase to monoclinic one, which in turn aids in phase transformation toughening by arresting the crack growth because of the appeared compressive stress [13, 14].

In the absence of applied stress but in conditions of low temperature and humidity, zirconia transforms from tetragonal to monoclinic phase, which does result in crack propagation [15].

Zirconia offers corrosion protection; thus, it can stand harsh biological environments [16].

The choice of synthesis methods affects the particle size and morphology, which in turn affects the thermal conductivity of zirconia [17].

To explore zirconia benefits in customized restorations, 3D printed zirconia attracted an increasing interest; however, it is still in its infancy. The 3D printing technology involves disciplines of both engineering and materials science; therefore, it has great potential for the application of zirconia in dentistry.

Exploring ceramics such as zirconia and GaN as well as emerging technologies will be of high importance in overcoming the current challenges and advancing the field of highly performant ceramics.

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Section 2

Characterization of Zirconia for Advanced Applications

Analytical Approaches to Characterizing Zirconia-Based Compounds for Advanced Applications

Bincy Cyriac

Abstract

This chapter discusses the various characterization techniques employed to evaluate zirconia for different applications. The structural, morphological, and compositional properties of zirconia are crucial determinants in selecting its suitability for specific applications; therefore, it is essential to characterize synthesized zirconia thoroughly before its practical application. A comprehensive overview of structural (XRD, Raman spectroscopy, FTIR), morphological (SEM, TEM, AFM), and compositional characterization (XPS, ICP-AES, ICP-MS, LA-ICP-MS, XRF) techniques is presented. These methods enable systematic assessment of zirconia, ensuring that materials derived from particular synthesis routes meet the required criteria for targeted applications.

Keywords: zirconia, characterization techniques, structural analysis, morphological analysis, compositional analysis

1. Introduction

Zirconium oxide (ZrO_2), commonly named zirconia, mainly occurs naturally as the mineral baddeleyite [1]. However, the primary commercial source of zirconia is mineral zircon (ZrSiO_4), zirconium silicate. Zircon occurs abundantly in beach placer deposits, along with other economically significant minerals such as rutile, ilmenite, and monazite. The chemical composition of zircon is approximately 67% ZrO_2 , 34% SiO_2 (silica), and a minor fraction (0.2–0.4%) of hafnium oxide (HfO_2) [2]. Zircon undergoes a series of decomposition processes, which involve chemical, thermal, or mechanical treatment, and is converted to zirconia. The final refining of the resultant zirconia with specific purification methods is dictated on the basis of the intended application.

Zirconium dioxide (ZrO_2), is a prominent ceramic material extensively utilized in various fields due to its exceptional properties, promising a significant future in diverse

technological and biomedical fields. Zirconia is often referred to as ceramic steel owing to its superior mechanical properties, like intrinsic hardness, abrasiveness, and resistance [3]. Unlike other ceramic materials, zirconia's toughness and higher strength are attributed to the unique characteristic of transformation toughening. Zirconia is used as a structural material, thermal barrier coating, solid oxide fuel cell electrolytes, and semiconductor components due to its distinctive electrical, mechanical, optical, and thermal properties. Owing to its unique properties, high refractive index, high dielectric constant, ion exchange capacity, optical transparency, polymorphic nature, and chemical and optical stability, zirconia is widely used in photonics devices [4]. ZrO_2 is documented to function as an effective catalyst in various chemical reactions, including the isomerization of alkanes, the dehydration of alcohols, and the decomposition of nitrous oxide [5]. Zirconia has gained considerable attention as a bioceramic for use in biomimetic scaffolds due to its chemical stability, mechanical stability, and excellent biocompatibility [6]. Zirconia implants are gaining considerable importance in dentistry due to their favorable biomechanical properties, biocompatibility, and aesthetic advantage. This material holds considerable technological interest, characterized by its appealing natural coloration, inherent transformation toughness, robust chemical stability, and high strength. Its widespread application in bone tissue engineering is a testament to these properties, being employed in films or coatings on implants, bone cement, bone graft substitutes, dental prostheses, and general implants, thus establishing its preference as a critical bio-ceramic for bone repair. Zirconia-based nanocomposites are extensively incorporated into bone tissue materials, primarily due to their wear resistance, high mechanical strength, and low-temperature sintering characteristics.

The incorporation of ZrO_2 into dentistry is driven by its exceptional biocompatibility, biomechanical properties (including strength, toughness, fatigue resistance, low elasticity modulus, and fracture strength), excellent wear resistance, and its visual similarity to natural teeth [7]. Its ability to integrate morphologically with surrounding tissues, without requiring biological or chemical interactions, has been a subject of research for dental applications. With the mounting demand for cosmetic dental procedures, ZrO_2 has emerged as a favorable material due to its enhanced biocompatibility, aesthetic appeal, robust oxidation resistance, and improved mechanical properties. Besides, ZrO_2 has not been correlated with any allergic reactions. Recent advancements in artificial intelligence and machine learning have enabled the development of innovative applications for ZrO_2 in dental devices.

ZrO_2 is considered an attractive material for biosensing applications due to its increased stability across diverse environmental conditions, like pH, moisture, and temperature [8]. ZrO_2 nanoparticles (NPs) have acquired considerable interest in bio-analytical applications in the development of biosensors due to their chemical inertness and non-toxicity. Zirconia is often referred to “ceramic steel,” due to its inherent hardness, abrasiveness, high melting point, and low frictional resistance. Nano zirconia exhibits excellent antibacterial, antioxidant, and antifungal properties. Thus, the adoption of ZrO_2 -based nanomaterials for biomedical applications, especially in dentistry and drug delivery, represents an innovative approach due to their biocompatibility and reduced toxicity profile.

2. Zirconia-crystalline phases

Zirconium dioxide (ZrO_2) is a polymorphic material that exists in three different crystallographic phases—monoclinic, tetragonal, and cubic—each stable at

a different temperature range [9]. At ambient conditions, pure ZrO_2 assumes the monoclinic phase, which remains stable up to approximately 1170°C . Upon heating, it transforms slowly to the tetragonal phase and remains stable between 1170°C and 2370°C , and further transitions to the cubic fluorite structure above 2370°C [1]. Each phase transformation is accompanied by significant volumetric changes. Specifically, the monoclinic-to-tetragonal transformation involves a $\sim 5\%$ decrease in volume, while the reverse transformation leads to a 3–4% expansion, often resulting in structural degradation, such as cracking or splitting of ceramic components (**Figure 1**).

The monoclinic phase presents sevenfold coordination of Zr^{4+} ions, which is favored by the covalent nature of Zr-O bonds, leading to its thermodynamic stability at lower temperatures. However, both the cubic and tetragonal phases exhibit eightfold coordination and require the presence of oxygen vacancies for stabilization. These vacancies become more predominant at high temperatures or under lower oxygen partial pressures, enabling phase transitions.

To overcome the drawbacks associated with the thermal instability of tetragonal and cubic phases at room temperature, various metal oxides, such as yttria (Y_2O_3), magnesia (MgO), calcia (CaO), and ceria (Ce_2O_3), are introduced as dopants [1]. These dopants generate oxygen vacancies and alter the lattice structure of the cubic and tetragonal phases at ambient conditions. The morphology, crystal size, and defect structure of zirconia nanocrystals are affected by the extent and type of doping. The doped ZrO_2 materials are categorized based on their stabilized phases. For example, partially stabilized zirconia (PSZ) consists of a cubic matrix embedded with tetragonal and monoclinic precipitates, whereas tetragonal zirconia polycrystals (TZP) consist of fine tetragonal grains. Among the polymorphs, the tetragonal phase exhibits maximum mechanical strength and defect-induced reactivity, making it a suitable candidate for structural and catalytic applications.

Versatility of zirconia in diverse fields of application is strongly governed by its morphology, crystallographic phase, porosity, microstructure, and chemical composition. Hence, thorough characterization of the synthesized zirconia is indispensable to ensure that the material possesses the precise structural, chemical, and physical qualities required for specific applications. Raman spectroscopy and X-ray diffraction (XRD) spectroscopy are essential to identify the crystalline phases, lattice parameters, and grain size, which are critical for assessing the stability and performance of the final material. The synthesis conditions significantly influence the morphology, particle size distribution, and agglomeration behavior of zirconia powders. Characterization tools, such as nitrogen adsorption-desorption analysis (BET), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA), are crucial to evaluate pore size, pore volume, and metastable structures. Zirconia is

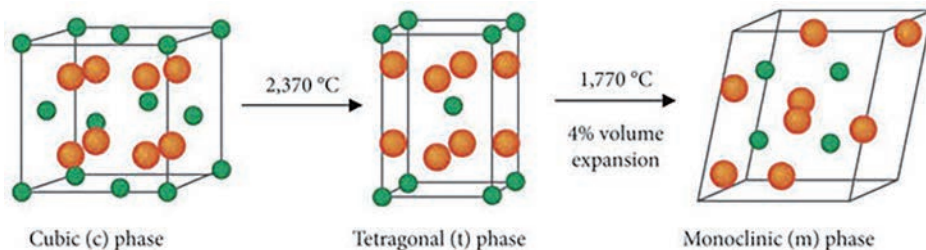


Figure 1.
Different crystalline phases of zirconia [10].

used as a catalytic support owing to its high melting point, low chemical reactivity, low thermal conductivity, and mesoporous nature. Surface compositions and dopant distribution can be evaluated using techniques such as X-ray photoelectron spectroscopy (XPS), UV–visible spectroscopy, and electron paramagnetic resonance (EPR). The characterization of zirconia materials is crucial not only to validate synthesis outcomes but also to ensure their long-term performance in real-world applications. A multi-technique approach to characterization of zirconia ensures zirconia-based materials meet the stringent functional requirements for their reliable deployment in advanced technological domains.

3. Characterization of zirconia

A wide range of advanced characterization tools is employed to investigate the morphological, structural, mechanical, and chemical properties of zirconia. XRD and Raman spectroscopy are used to determine its crystallographic structure and phase composition, while Fourier transform infrared spectroscopy (FTIR) provides an idea about the functional groups and bonding characteristics. SEM and transmission electron microscopy (TEM) offer high-resolution imaging of surface morphology, grain size, and particle distribution. Atomic force microscopy (AFM) further aids in evaluating nanoscale topography and surface roughness. For elemental and chemical analysis, energy dispersive X-ray (EDX) spectroscopy, XPS, inductively coupled plasma-atomic emission spectroscopy (ICP-AES), Inductively coupled plasma-mass spectroscopy (ICP-MS), laser ablation-inductively coupled plasma-mass spectroscopy (LA-ICP-MS), and wavelength dispersive X-ray fluorescence (WD-XRF) spectroscopy are employed. Mechanical properties such as hardness and modulus are typically assessed using nanoindentation techniques, while electrical conductivity and dielectric behavior are characterized using impedance spectroscopy and four-point probe methods.

3.1 Structural characterization

Structural analysis of zirconia includes the identification of its crystalline structure, phase composition, and surface features. Techniques such as XRD, Raman spectroscopy, and Fourier transform IR spectroscopy (FT-IR) are used to determine the crystalline phases and structural properties, which are critical for assessing the material's composition. These structural properties directly influence the mechanical, electrical, and biological performance of zirconia.

3.1.1 X-ray diffraction (XRD) spectroscopy

XRD is a powerful technique for determining the lattice parameters and crystal structure of zirconia. It enables the identification of various zirconia phases based on their distinct diffraction patterns. These phases exhibit different crystal structures, which are influenced by factors like temperature, dopants, and residual stress. By analyzing the diffraction data, one can identify the specific phase present, estimate the crystallite size and residual stress, detect phase transformations, and the presence of dopants.

The fundamental principle underlying XRD is Bragg's Law, which describes the condition for constructive interference of X-rays scattered by the periodic atomic

planes within a crystalline material. When a monochromatic X-ray beam interacts with a crystal, it is diffracted by the regularly spaced lattice planes. Constructive interference occurs when the path difference between the reflected rays satisfies Bragg's condition:

$$n\lambda = 2d\sin\theta$$

where n is the diffraction order, λ is the wavelength of the incident X-rays, d is the interplanar spacing, and θ is the angle of incidence. When this condition is satisfied, the diffracted beams are in phase, resulting in a peak in the diffraction pattern. By analyzing the positions (angles) and intensities of these peaks, one can determine the lattice parameters, crystalline phases, crystallite size, and phase composition of the material.

XRD patterns give crucial information regarding the crystal structure and lattice parameters of zirconia, enabling the identification and differentiation of its three primary polymorphic phases. Each of these phases possesses distinct crystallographic arrangements, which give rise to characteristic diffraction peak positions and intensities. By analyzing the diffraction data and comparing it with standard reference patterns, such as those from the JCPDS (Joint Committee on Powder Diffraction Standards) database, the presence, relative abundance, and phase composition of zirconia can be accurately determined. This information is essential for understanding the stability of zirconia phases under varying temperature conditions and in the presence of dopants.

The monoclinic phase typically exhibits diffraction peaks at lower 2θ angles compared to the tetragonal and cubic phases. The most prominent XRD peaks of monoclinic zirconia occur at approximately 28.2° , 31.5° , and 34.3° , corresponding to the (111), (-111) , and (111) planes, respectively. Additional peaks observed at 38.5° , 50.1° , and 59.8° are assigned to the (120), (022), and (131) planes [11]. The diffraction peaks for the tetragonal phase are typically located between those of the monoclinic and cubic phases. Characteristic peaks for the tetragonal phase are observed at 2θ values 30.48° , 35.36° , 50.97° , 60.49° , and 63.26° , corresponding to the (101), (110), (112), (211), and (202) crystallographic planes, respectively. The cubic phase exhibits diffraction peaks at high 2θ values due to its highly symmetrical structure. The major peaks for cubic zirconia are commonly observed at 30.06° , 34.97° , 50.42° , and 60.04° , corresponding to the (111), (200), (220), and (311) planes (**Figures 2 and 3**) [12].

Crystallite size can also be estimated from XRD data using the Scherrer Equation [14], which correlates peak broadening to particle dimensions:

$$D = (K\lambda) / (\beta \cos\theta)$$

where D is the average crystallite size, K is the Scherrer constant (~ 0.9), λ is the X-ray wavelength, β is the full width at half maximum (FWHM) of the diffraction peak (in radians), and θ is the Bragg angle. To evaluate unit cell parameters, lattice constants are calculated using Bragg's law from the peak position in the XRD spectrum. Deviations in lattice constants from standard values indicate unit cell distortions, often due to doping, oxygen vacancies, or thermal treatments.

XRD pattern is also utilized for the detection of dopants and impurities in the lattice [15]. Interstitial or substitutional doping often changes the unit cell dimensions, leading to systematic peak position shifts. Additional diffraction peaks are obtained in the case of the formation of secondary phases due to high dopant concentrations. Changes in peak

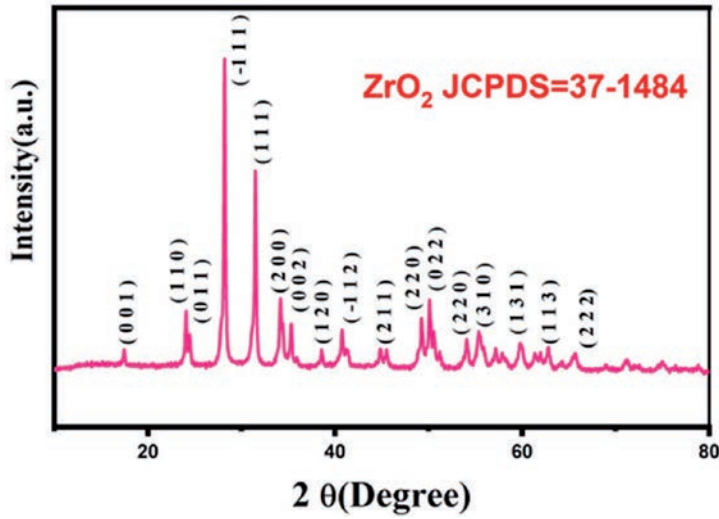


Figure 2.
XRD pattern of monoclinic zirconia [13].

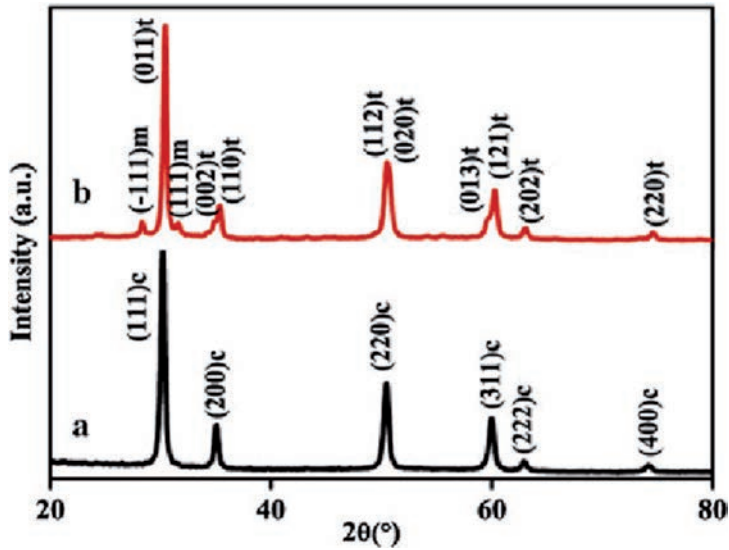


Figure 3.
XRD pattern for cubic and tetragonal zirconia [1].

intensity may also suggest modifications in phase distribution or crystallinity. Similar peak shifts can arise from thermal expansion, strain, or defects, warranting the use of complementary techniques to corroborate findings. From **Figure 4**, it is evident that yttria-doped zirconia exhibits an additional diffraction peak at 30.3 corresponding to the tetragonal phase, alongside the monoclinic zirconia phase at room temperature. Variations in peak intensities of the peaks at 28.3 and 31.6 of the monoclinic phase further indicate changes in crystallinity induced by yttria doping. Yttria (Y₂O₃) functions as a stabilizing dopant by producing oxygen vacancies in the zirconia lattice, which favor the retention of the high-symmetry cubic phase at lower temperatures. The degree of phase stabilization

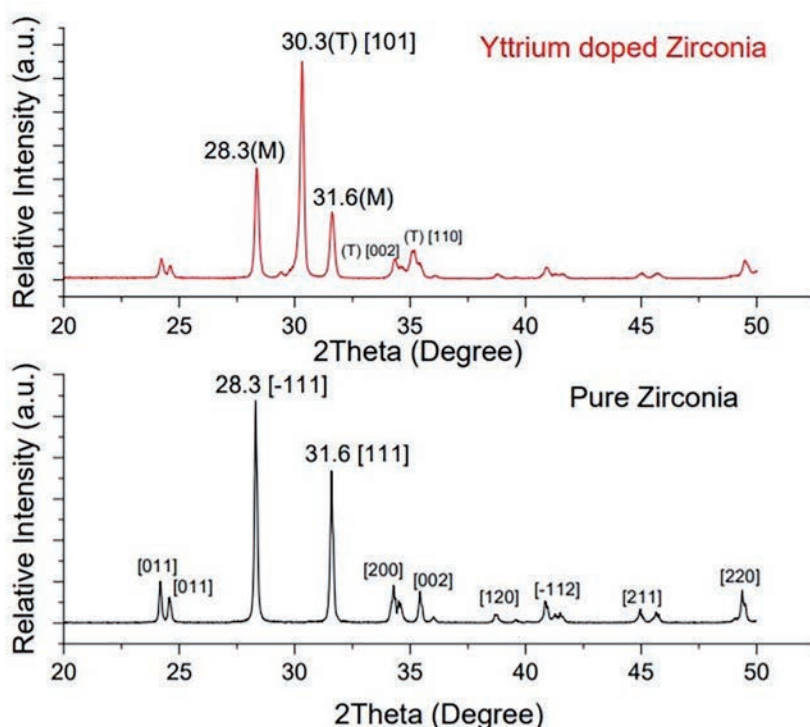


Figure 4.
XRD pattern of pure zirconia and yttria-doped zirconia [16].

is influenced by both the concentration of yttria and the sintering temperature employed during material processing.

Rietveld refinement of the XRD pattern is often used to gain quantitative insight into the structural details of the materials [17]. This method involves a least-squares fitting procedure that refines a theoretical diffraction pattern to match the observed data. The refinement gives an accurate determination of atomic positions, lattice parameters, phase fractions, occupancy factors, microstrain, crystallite size, and preferred orientation. By providing the ideal crystal structure and instrumental contributions, the technique enables the extraction of precise structural parameters even from complex powder diffraction data.

High-temperature X-ray diffraction (HT-XRD) extends the capabilities of conventional XRD by enabling *in situ* monitoring of structural evolution as a function of temperature [18]. Real-time observation of phase transitions, lattice expansion, sintering behavior, and thermal stability can be assessed by this technique, as it is equipped with specialized heating stages capable of reaching temperatures up to 1600°C. This is particularly important for the study of high-performance ceramics, refractory materials, and thermally stable oxides, including those used in nuclear and aerospace applications.

3.1.2 Raman spectroscopy

Raman spectroscopy is a complementary technique to XRD for the phase characterization of materials. It gives insights into phase transformations, stress, and the

presence of dopants by analyzing the vibrational modes of the crystal lattice. The basic principle of Raman spectroscopy involves the inelastic scattering of monochromatic light, typically from a laser source. When monochromatic light interacts with a material, a small portion is scattered with a shift in energy corresponding to the vibrational energy levels of the molecules or lattice, producing a unique spectral fingerprint.

Each polymorphic phase of zirconia—monoclinic, tetragonal, and cubic—exhibits characteristic Raman spectral peaks [19]. Monoclinic zirconia shows a complex vibrational structure, which is evident from the number of sharp Raman bands at approximately 183, 267, 301, 335, 381, 476, 536, 559, 613, and 636 cm^{-1} . Tetragonal zirconia shows fewer peaks, typically dominated by a strong band near 634 cm^{-1} , and lacks several of the weaker bands seen in the monoclinic phase. Cubic zirconia, due to its high symmetry and limited Raman activity, shows a broad, featureless spectrum, similar to that of an amorphous material [20]. By comparing the Raman spectrum obtained for a particular sample with reference data, the phase composition and structural changes in zirconia can be accurately identified, making Raman spectroscopy a powerful tool for monitoring phase stability and transformation behavior. Raman spectroscopy can also be used to analyze the phase transformations of zirconia due to stress, temperature, and presence of dopants (**Figure 5**).

Comparative analysis of XRD patterns and Raman spectra provides a comprehensive understanding of the phase composition, crystallinity, and structural changes in zirconia. These techniques employ fundamentally different principles for phase identification, which are often complementary. Raman spectroscopy is particularly useful in detecting minor or amorphous phases that may not be present in the XRD pattern. However, both techniques can be employed to assess strain, stress, and the presence of dopants—XRD through variations in d-spacing, and Raman spectroscopy through shifts in vibrational peak positions. In addition, peak broadening observed in both Raman spectra and XRD represents the reduced crystallinity or nanoscale grain structure. As illustrated in **Figure 6**, the XRD pattern and Raman spectra complement each other and together confirm the presence of monoclinic and tetragonal phases of zirconia.

3.1.3 Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy is a valuable characterization technique for the identification of the functional groups present on zirconia surfaces and for analyzing structural features at the molecular level. FTIR spectroscopy is an analytical technique used to identify functional groups and chemical bonds within a sample based on their characteristic vibrational modes. The method involves passing infrared radiation through the sample and measuring the amount of radiation absorbed at various frequencies. Each functional group absorbs IR radiation at specific frequencies, producing a unique absorption spectrum that serves as a molecular fingerprint. FTIR employs an interferometer, which splits the infrared beam into two paths, recombines them, and generates an interferogram. This interferogram is then mathematically transformed using Fourier analysis to produce the final infrared spectrum, typically represented as absorbance or transmittance versus wavenumber.

FTIR spectra of zirconia provide information regarding the presence of surface hydroxyl groups ($-\text{OH}$), adsorbed water, and metal-oxygen bonding environments [23]. Characteristic absorption bands observed in the 3000–3500 cm^{-1} region correspond to the stretching vibrations of surface $-\text{OH}$ groups, whereas a peak around

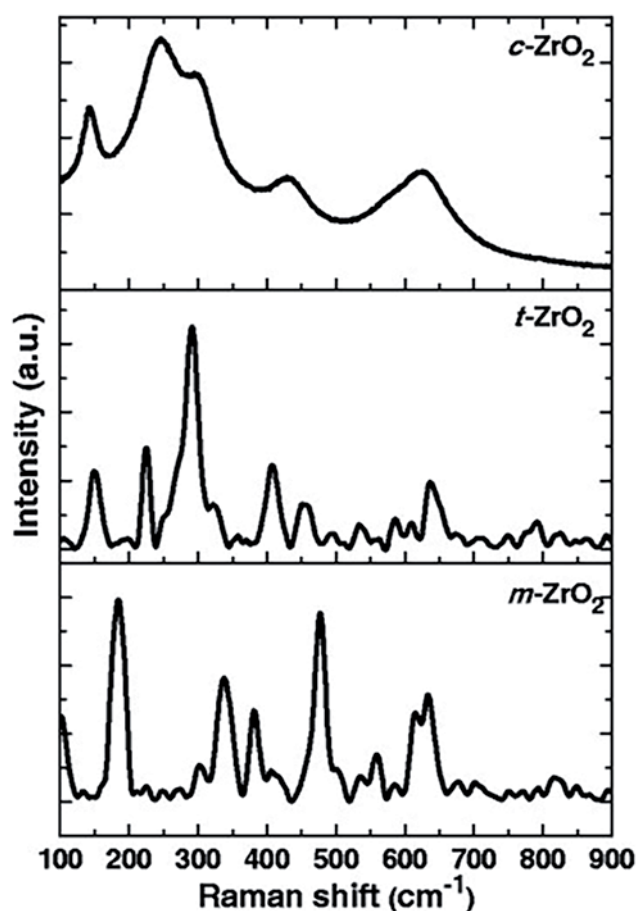


Figure 5.
 Raman spectra of monoclinic zirconia, tetragonal zirconia, and cubic zirconia [21].

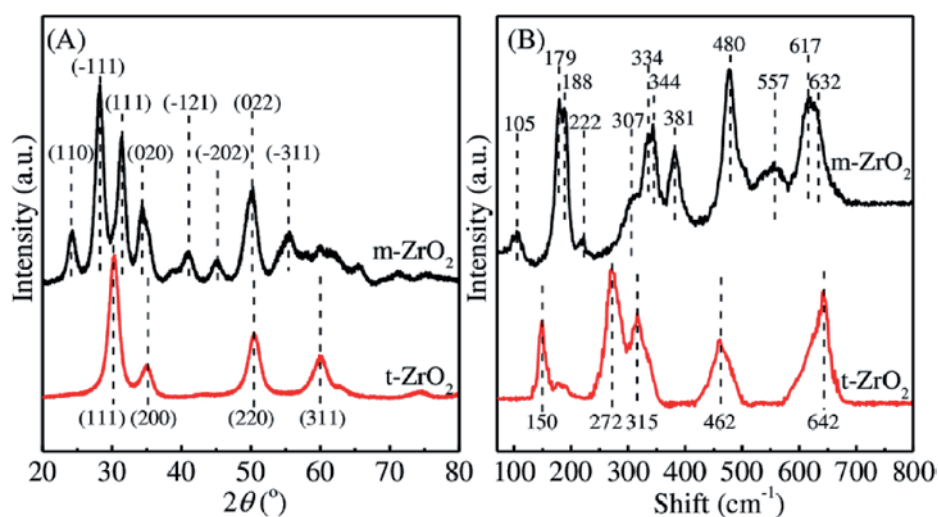


Figure 6.
 X-ray diffraction patterns (A), and Raman spectra (B) of ZrO_2 [22].

1642 cm^{-1} typically indicates the bending vibration of molecular water, confirming the presence of adsorbed water molecules. The region between 400 and 800 cm^{-1} is particularly significant for evaluating zirconium–oxygen (Zr–O) stretching vibrations. The absorption bands in this region are instrumental in distinguishing between different phases of zirconia. Monoclinic zirconia shows a broad absorption band near $435\text{--}440\text{ cm}^{-1}$ and a sharp peak around 755 cm^{-1} , while tetragonal zirconia gives a specific band around 600 cm^{-1} , and cubic zirconia is characterized by a peak near 400 cm^{-1} . A peak near 460 cm^{-1} is attributed to Zr–O bond stretching common to all zirconia phases. The exact position and intensity of these peaks may vary based on parameters such as particle size, dopant incorporation, and synthesis route, which influence crystallinity and surface chemistry. FTIR peaks are used to identify phase-related features that can reveal minute differences in local bonding environments. Comparative analysis of the experimental FTIR spectra with standard reference spectra of known zirconia phases enables reliable phase identification. Moreover, FTIR can elucidate surface modifications, detect adsorbed species, and assess changes in chemical bonding due to surface functionalization. Although FTIR provides critical information on the chemical structure and bonding environment, it is commonly used in conjunction with complementary techniques such as XRD to confirm phase purity and crystallographic information (**Figure 7**).

3.1.4 UV-visible spectroscopy

UV-Visible spectroscopic analysis provides insights into the absorption characteristics of materials within the visible and ultraviolet spectral regions. The intensity and position of absorption peaks are strongly influenced by factors such as particle size, crystallinity, and the synthesis method employed. Adsorption efficiency is diminished by structural defects and imperfections. Zirconia (ZrO_2) nanoparticles typically display a sharp absorption peak below 250 nm and a broader band around

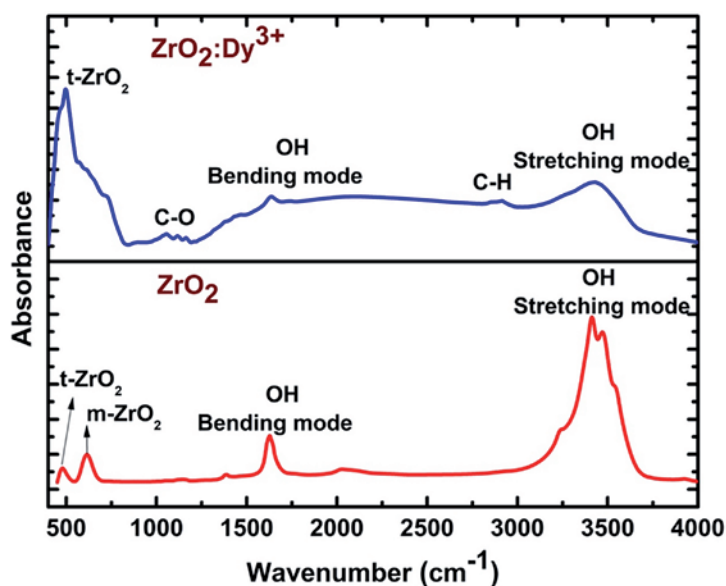


Figure 7. FTIR spectra of zirconia and dysprosium-doped zirconia [23].

280 nm [24]. A decrease in the particle size of the nanoparticle will cause an increase in scattering of light due to increased surface to volume ratio, resulting in a redshift (i.e., a move to longer wavelengths). However, upon further reduction in particle size, quantum confinement effects may induce a blueshift (i.e., shift to shorter wavelengths) in the absorption edge. Owing to the $4d^0$ electronic configuration of Zr^{4+} , d–d transitions are absent, and thus no absorption is observed in the visible region. Changes in crystalline phase also influence absorption features, as different phases (monoclinic, tetragonal, cubic) have distinct electronic structures (**Figure 8**).

3.2 Morphological characterization

Surface characterization of materials is commonly carried out using techniques such as SEM, EDX, TEM, and AFM, which provide detailed information on particle size, orientation, and surface roughness. To complement these methods, gas adsorption techniques, particularly Brunauer-Emmett-Teller (BET) analysis, are employed to evaluate pore characteristics, including pore size distribution and pore volume. Furthermore, thermal analysis techniques such as thermogravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC) are utilized to study phase transformations, thermal stability, and decomposition behavior of the materials.

3.2.1 Scanning electron microscopy (SEM)

SEM provides high-resolution images of surface topography of materials, enabling detailed visualization of microstructural features such as grain boundaries, cracks, and porosity. The underlying principle of SEM is the electron-matter interactions, wherein a focused high-energy electron beam strikes the surface of the sample, resulting in the emission of secondary electrons, backscattered electrons, and diffracted electrons. Secondary electrons, produced by inelastic scattering near the surface, are collected by scintillation detectors, which, in turn, produce flashes of light that are converted into electrical signals by a photomultiplier tube (PMT). These signals are transmitted to a cathode ray tube (CRT) or digital display to construct the image. The brightness of the

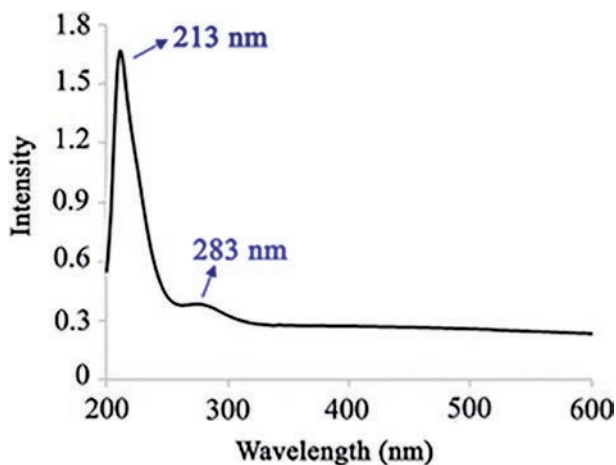


Figure 8.
UV-visible spectrum of zirconia nanoparticle [24].

image is determined by the intensity of the detected secondary electrons—elevated surface regions appear brighter as they emit more secondary electrons, while depressions emit fewer secondary electrons and appear darker. Inelastic scattering of the incident electron beam with atomic nuclei produces backscattered electrons, and they provide compositional contrast. Heavier elements scatter more electrons, appearing brighter in the image, while lighter elements scatter fewer electrons and appear darker. This contrast facilitates the identification of the elemental distributions across the sample surface.

SEM analysis of zirconia nanoparticles provides different morphologies, such as spherical, triangular, and irregular shapes, with particle sizes ranging between 10 and 90 nm, depending on the method of synthesis and processing conditions [25]. Agglomeration of nanoparticles, which is frequently observed in SEM micrographs, is a characteristic of nanoscale materials. The synthesis technique, along with the choice of precursors, surfactants, and processing parameters, significantly influences the size, shape, and distribution of zirconia nanoparticles (**Figures 9** and **10**).

3.2.2 Transmission electron microscopy (TEM)

TEM is a powerful characterization technique that provides detailed morphological and topographical information about materials by utilizing a beam of high-energy electrons. When an electron beam is transmitted through a thin section of a specimen, interactions between the electrons and the atomic structure of the material generate contrast, allowing for high-resolution imaging of internal features. When a high-energy electron beam passes through the sample, it interacts with the atomic lattice, undergoes scattering and diffraction, which depend on the orientation, thickness, and crystallography of the material. TEM images of zirconia samples provide magnification at a much higher level compared to other imaging techniques, making it possible to study fine structural details that are critical for understanding material behavior. The electron diffraction patterns differ across regions and orientations, highlighting variations in crystallographic alignment and phase distribution. This enables the correlation of microstructural features with macroscopic properties such as strength, toughness, and durability. Different regions of the crystal produce varied diffraction patterns, resulting in diffraction contrast. For spherical particles, electrons traveling shorter distances at the particle edges produce brighter regions, while longer paths through the particle center result in darker contrast areas (**Figure 11**).

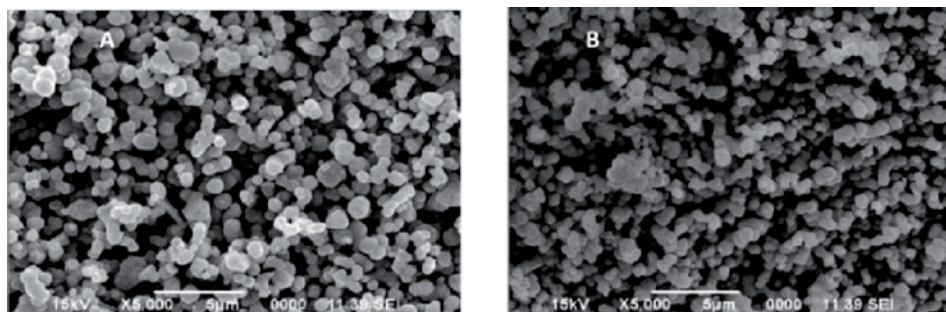


Figure 9.
SEM images of zirconia particles obtained by the homogeneous precipitation method [26].

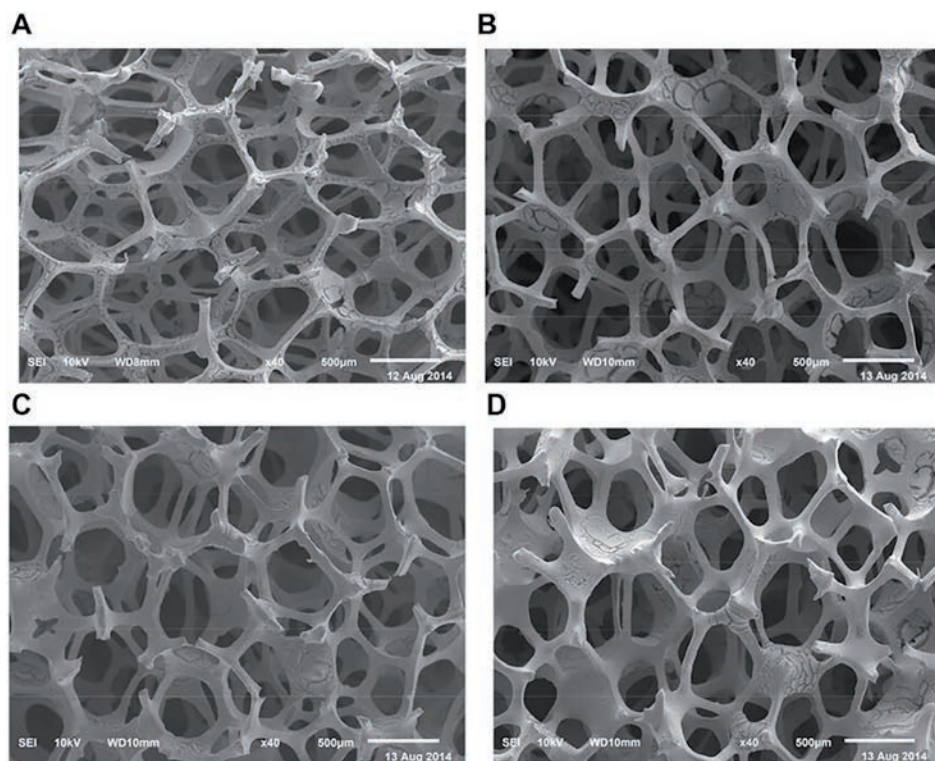


Figure 10. SEM images of zirconia scaffolds processed with (A) one sintering cycle, (B) three sintering cycles, (C) five sintering cycles, and (D) 7 sintering cycles [27].

3.2.3 Atomic force microscopy (AFM)

AFM is a crucial technique for surface characterization, as it provides valuable information on the nanoscale 3D topography of materials. 3D topography of materials obtained from AFM measurements allows the accurate characterization of surface roughness and texture to the nanometer scale. Surface roughness analysis is an important parameter for material characterization as it provides details about the surface topography, which directly influences functional, mechanical, and tribological properties. Surface roughness increases the coefficient of friction and minimizes the abrasive wear. Also, surface imperfections often act as stress concentrators where microcracks can initiate and progress. An optimal level of surface roughness increases the adhesive properties of the materials by increasing the area for surface interlocking. Surface imperfections can have a direct effect on the corrosion resistance of the materials by exposing a large surface area to aggressive environments. Surface roughness affects the electrical resistance and signal transmission by changing contact resistance and the heat dissipation in electronic materials by creating insulating pockets. Surface roughness is a critical parameter for implant materials as optimal surface adhesion is required to promote cell adhesion, and tissue growth.

Zirconia materials are widely employed as biocompatible components in prosthetic applications and in refractory ceramics. The analysis of surface roughness plays a crucial role in evaluating the performance and reliability of zirconia-based materials. The extent of surface roughness can be assessed from AFM images by evaluation

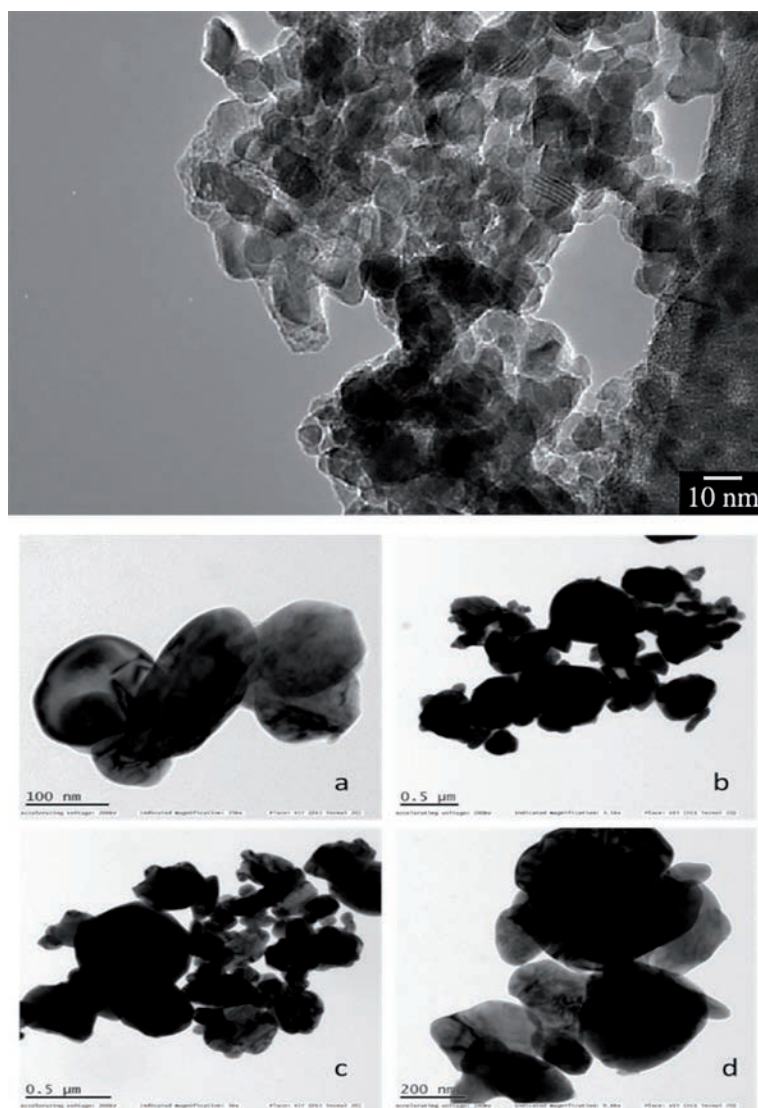


Figure 11. TEM image of zirconia nanoparticles synthesized by sol-gel method [28] and TEM images of Zirconia at different scales [29].

of roughness parametres R_a (arithmetic average roughness), R_q (root mean square roughness), and R_z (mean roughness depth) (**Figure 12**).

One of the important applications of AFM in zirconia characterizations is in the study of the martensitic transformation of zirconia. The transformation of tetragonal zirconia to the monoclinic phase induces localized surface deformations known as “relief.” This relief can be measured by high-resolution AFM, offering insights into strain energy, crystallographic orientation, and transformation mechanisms. By observing phase changes under different conditions, such as applied stress or heating, AFM helps to understand the factors influencing the transformation and crack resistance (**Figure 13**). From AFM data, it has been confirmed that the

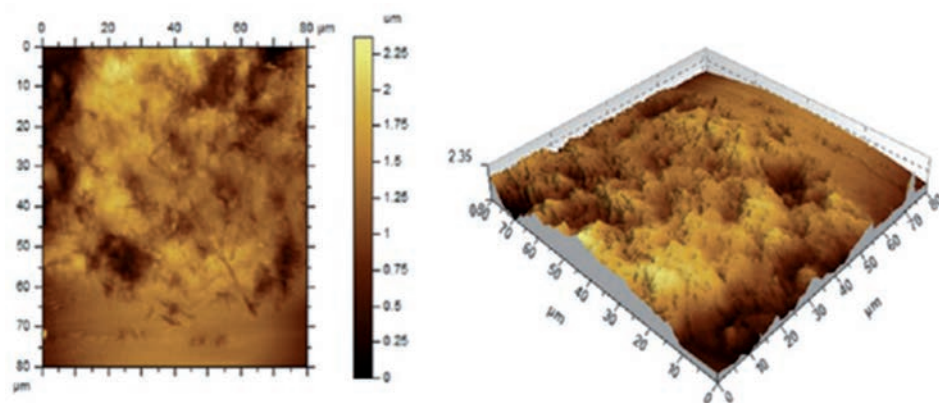


Figure 12.
Two-dimensional and three-dimensional topography images and roughness profile of Zirconia implants [30].

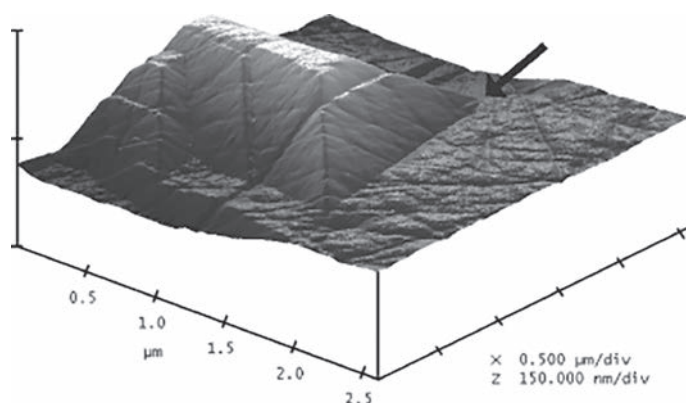


Figure 13.
Self-accommodating martensitic variant pair in Ce-TZP. The intersection of the habit plane and the surface (arrow) is clearly visible [31].

tetragonal-to-monoclinic (t-m) transformation is martensitic in nature and involves diffusionless, athermal processes dominated by shear and rapid structural rearrangements. When zirconia is doped with yttria (Y_2O_3) or ceria (CeO_2), it is retained in a metastable tetragonal phase post-sintering. Mechanical stress or hydrothermal exposure (e.g., water vapor at 140°C) may trigger the transformation into the stable monoclinic phase, contributing to transformation toughening by partially closing propagating cracks through volume expansion.

By enabling precise measurement and quantification of transformation mechanisms, AFM serves as a reliable tool for predicting long-term aging and performance degradation in zirconia ceramics. It has become indispensable in characterizing transformation toughening, elucidating microstructural changes, and supporting the design of durable, high-performance materials for advanced applications.

3.3 Compositional characterization of zirconia

Compositional characterization techniques evaluate the primary composition of zirconia materials, which involves the analysis of the concentration of zirconium

and oxygen, and also the presence of dopants and impurities in zirconia. XPS, ICP-AES, ICP-MS, Laser Ablation-Inductively Coupled Plasma-Mass Spectroscopy (LA-ICP-MS), and XRF spectroscopy are common techniques used to find the elemental compositions in zirconia.

3.3.1 X-ray photoelectron spectroscopy (XPS)

XPS is a powerful technique used to assess the surface chemical composition, bonding environments, and oxidation states of materials. In the chemical characterization of zirconia by XPS, core-level spectra of zirconia are examined as they serve as a critical indicator of zirconium's oxidation state and chemical interactions within the material. When zirconia material is irradiated with X-rays, core electrons are ejected from zirconium atoms. The binding energy of these electrons, especially from the Zr 3d orbitals, is influenced by the chemical environment, oxidation state, and local bonding. By evaluating these binding energies, XPS enables identification of zirconium's oxidation states and their distribution across the sample surface.

The zirconium 3d region of the XPS spectrum is typically analyzed by deconvoluting it into characteristic peaks corresponding to different oxidation states. The 3d spectrum shows a primary doublet in which peak at 181.5 eV arises due to the Zr 3d_{5/2} transition and the other peak at 183.9 eV arises due to the Zr 3d_{3/2} transition for fully oxidized zirconium oxide (Zr⁴⁺). Additional peaks at lower binding energies correspond to zirconium suboxides Zr1+, Zr2+, and Zr3+ states. Metallic zirconium (Zr⁰) is detected at even lower binding energies compared to the oxide states (**Figure 14**).

XPS is used to distinguish between stoichiometric zirconia (ZrO₂) and non-stoichiometric suboxides (ZrO, Zr₃O, etc.) by analyzing chemical shifts observed in the Zr 3d spectra. The suboxides are usually present in an interfacial layer beneath the bulk oxide and develop during early stages of oxidation or reactions. Their peaks appear at intermediate binding energies, between those of fully oxidized zirconia and metallic zirconium. This is indicative of oxygen diffusion and incomplete oxidation at the surface, which influences properties such as corrosion resistance, catalytic activity, and mechanical stability. The peak shifts observed in the Zr 3d binding energies reflect changes in the electron density around zirconium atoms. Higher oxidation states, like Zr⁴⁺, correspond to stronger metal-oxygen interactions and higher binding energies, while lower oxidation states indicate partial reduction or oxygen deficiency. Through careful spectral fitting, the coexistence of multiple oxidation states within the same sample can be resolved, providing valuable insights into surface chemistry, phase composition, and the nature of interfacial layers in zirconia-based materials.

3.3.2 Inductively coupled plasma-Atomic emission spectroscopy (ICP-AES)

Elemental characterization of zirconia is very important, as its properties vary with the presence of impurities and dopants, which influence its suitability for specific applications. Precise and accurate determination of trace elements such as Fe, Mn, Hf, Na, Ti and Si is crucial, since these elements are often present as impurities due to their natural association with zirconium minerals—the primary raw material for zirconia synthesis.

ICP-AES is a versatile and sensitive analytical technique for elemental characterization, capable of determining concentrations from percentage levels down to the nanogram range. Its advantages include multielement capability, high sensitivity to refractory elements, and a broad dynamic range. However, as a solution-based

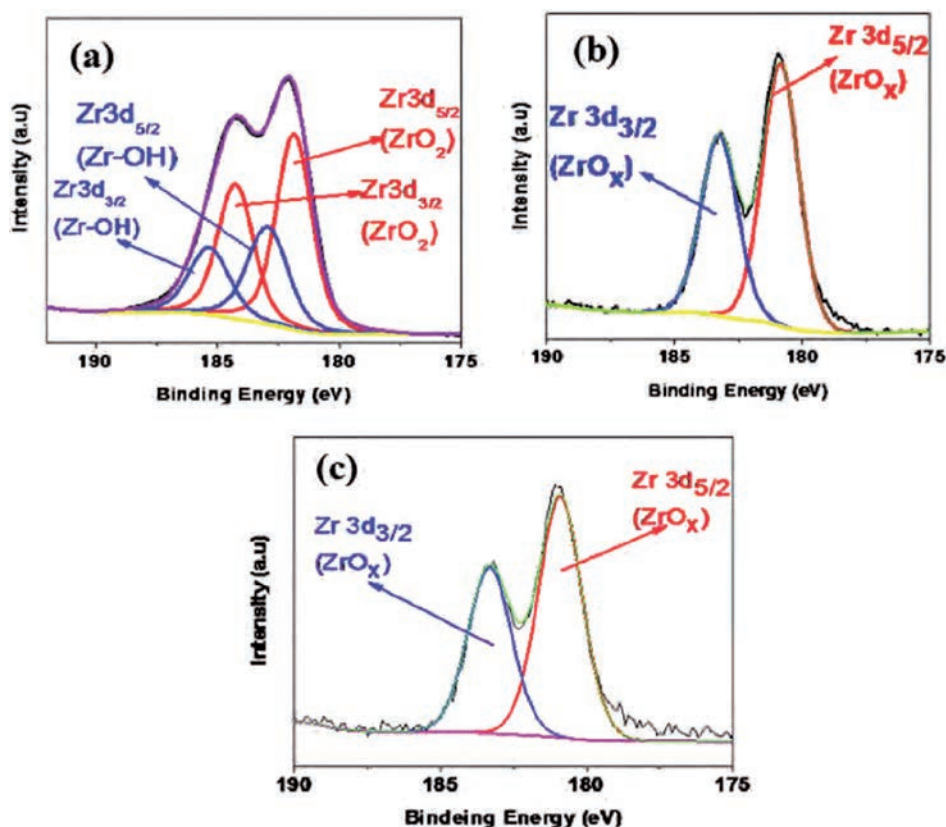


Figure 14.
 XPS spectra of Zr 3d spin-orbit doublet peaks of ZrO_2 nanoparticles synthesized in: (a) water (b) ethanol (c) acetone [32].

method, ICP-AES requires complete dissolution of the zirconia matrix before analysis. Several digestion methods have been employed for this purpose. Conventional techniques include dissolution using H_2SO_4 and HNO_3 under pressure, which is time-consuming, and fusion methods with fluxes such as sodium carbonate, sodium peroxide, sodium phosphate mixtures, sodium borohydride, or sodium fluoride-potassium bifluoride mixtures [33, 34]. Alternatively, microwave-assisted acid digestion under high pressure in closed vessels has proven effective for ZrO_2 powders and ceramics. Recently, microwave-assisted digestion using H_2SO_4 – $(\text{NH}_4)_2\text{SO}_4$ has been reported to provide improved accuracy and precision compared to open-system digestion [35].

Despite its strengths, ICP-AES analysis of zirconia faces significant challenges due to spectral interferences. Zirconium is a line-rich element, and its emission lines often cause severe spectral interference with those of trace analytes, thereby limiting the accuracy of quantification. Chemical separation of zirconium before trace element determination is a common strategy, but it involves toxic organic reagents and is labor-intensive. Improving the sensitivity and specificity of the analysis involves the elimination of spectral interference. High-resolution spectrometers can reduce line overlap, whereas mathematical correction methods offer alternative solutions. If the spectral background is flat or linear, the traditional background subtraction works well but may introduce incomprehensible errors under curved backgrounds. The use

of interference-free analytical lines of the trace elements with ICP-AES equipped with CCD detectors with high wavelength flexibility offers a solution for this problem [36]. Another innovative approach, liquid electrode plasma-optical emission spectrometry (LEP-OES), has also been proposed [37]. In this method, plasma is generated in a microchannel under a voltage pulse, producing emission spectra with relatively weak zirconium signals, thereby enabling highly sensitive measurement of trace impurities in zirconia matrices.

Dissolution of zirconia by fusion with different fluxes is very effective in the quantitative decomposition of zirconia materials. However, these methods introduce high salt concentrations that suppress impurity signals and cause clogging of the nebulizer and plasma torch, reducing sensitivity. Microwave-assisted digestion, by contrast, avoids these problems and is therefore considered the most suitable approach for zirconia sample preparation in ICP-AES analysis. Although ICP-AES is a destructive technique, its ability to provide accurate, multi-elemental quantification of trace impurities makes it an indispensable tool for assessing the purity of high-grade zirconia. When combined with optimized microwave-assisted digestion, it offers a reliable, sensitive, and relatively simple methodology for characterizing trace elemental impurities in zirconia materials.

3.3.3 Inductively coupled plasma--Mass spectroscopy (ICP-MS)

ICP-MS is a more sensitive technique for determining trace elements and characterizing zirconia compared to ICP-AES. The primary advantage lies in the measurement principle: ICP-AES quantifies elemental concentrations from atomic emission spectral intensities, while ICP-MS depends on mass-to-charge analysis of ions. Because of the minimal background for mass detection, ICP-MS is typically two to three orders of magnitude more sensitive than ICP-AES. However, ICP-MS faces practical limitations in the elemental characterization of zirconia. The design components—nebulizers, torch tubes, and ion extraction cones—are highly susceptible to clogging, restricting the limit of allowable salt content in solutions used for analysis. Even after microwave-assisted digestion, zirconia samples often contain salt concentrations that exceed the tolerance levels of ICP-MS. Diluting the digested solution can solve this issue, but risks lowering impurity concentrations below the detection limit. An alternative approach is to separate and preconcentrate trace elements before analysis using techniques such as ion exchange, solvent extraction, and solid-phase extraction. While effective, these methods are often time-consuming, labor-intensive, or reliant on hazardous chemicals. Consequently, despite its exceptional sensitivity, the operational challenges of sample preparation and matrix handling reduce the suitability of ICP-MS for routine elemental analysis of zirconia. As a result, it is less frequently employed than ICP-AES for this purpose.

3.3.4 Laser ablation-Inductively coupled plasma-Mass spectroscopy (LA-ICP-MS)

Drawbacks associated with ICP-MS analysis of zirconia can be overcome using laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS), which provides rapid, sensitive, and precise spot analyses of solid zirconia samples. LA-ICP-MS is a powerful analytical technique for elemental characterization, providing information on major, minor, and trace elements with excellent detection limits, broad elemental coverage, and a linear dynamic range of up to 10 orders of magnitude. The main advantage of LA-ICP-MS is its minimal sample preparation, which

reduces contamination risks, enhances sample throughput, and allows the analysis of both conductive and non-conductive, as well as opaque and transparent, materials. The method is based on converting solid material into a plume of vapor and microparticles by focusing a high-powered pulsed laser beam (commonly a Nd: YAG laser at 1064 nm) onto the sample surface. The ablated material is carried by argon gas into the ICP, where it undergoes atomization and ionization. The resulting ions are then analyzed by a quadrupole or high-resolution sector-field mass spectrometer.

During ablation, the laser-sample interaction produces particulates, ground-state atoms, excited atoms, and ions, all of which contribute to quantitative mass spectrometric analysis. Because the sample is introduced in a dry state (without solution components), atomization efficiency improves and matrix effects are reduced compared to solution-based ICP methods. Additional advantages of LA-ICP-MS include high spatial resolution (down to $\sim 20\ \mu\text{m}$), elemental mapping across surfaces, low background signals, detection limits below ppm levels, rapid analysis times (as short as ~ 2 minutes per spot), and minimal matrix effects across diverse materials. Moreover, its largely non-destructive nature and wide dynamic range allow the quantification of all elements in zirconia, from major constituents at percentage levels to dopants and impurities at microgram concentrations. Together, these features establish LA-ICP-MS as a highly effective and versatile technique for elemental characterization and trace impurity analysis of zirconia materials.

3.3.5 X-ray fluorescence spectroscopy

Wavelength-dispersive X-ray fluorescence (WD-XRF) Spectroscopy is a multi-element quantitative technique used for a wide concentration range, from percentage levels to trace levels. Its main advantages include simple and minimal sample preparation, simultaneous multi-element analysis, and long-term instrumental stability. These factors ensure that accuracy and precision are maintained over extended periods [38]. In WD-XRF, primary X-rays generated from an X-ray tube excite secondary X-rays from the sample. The emitted radiation contains the characteristic peaks of both major and trace elements present. These radiations are dispersed through specialized crystals into different wavelengths. The intensity (peak height) of each characteristic X-ray line is proportional to the element's concentration [39].

This method is particularly valuable for the analysis of ceramic oxide refractories like zirconia, offering faster, more reproducible results than other solution techniques like ICP-AES and ICP-MS [40]. Before analysis, samples are ground, and tungsten carbide mills are used as they avoid introducing contaminants. In WDXRF, an incident X-ray beam excites the sample, producing element-specific fluorescence radiation. Nevertheless, the analytical performance often depends on the availability of homogeneous calibration standards. While the method is largely non-destructive, it requires samples to be powdered and compacted with flux for analysis. A common approach involves borate fusion, in which samples are fused into pellets. This technique enhances sensitivity, allowing trace elements at very low concentrations to be determined with higher accuracy [41]. This method has been applied to estimate doped yttrium and lanthanum contents in zirconia ceramics [42].

Total reflection X-ray fluorescence (TXRF) is a complementary technique to WD-XRF, which is used for the elemental characterization of zirconia. TXRF is a microanalytical technique requiring only small sample quantities (2–100 μL or 20–1000 ng). It accommodates a wide range of sample types, including solutions,

suspensions, slurries, fine powders, metallic smears, thin membranes, and polished surfaces. The method, operating at grazing incidence with detection normal to the surface and tunable excitation energies, provides a highly sensitive and versatile approach for elemental determination.

4. Conclusion

Zirconia is a versatile ceramic material widely used in various applications owing to its unique structural, morphological, compositional, electrical, optical, and mechanical properties. The suitability of zirconia for specific applications is determined by its ability to meet the required set of properties, which can be systematically evaluated through comprehensive characterization techniques.

Structural analysis using XRD, Raman spectroscopy, and FTIR spectroscopy plays a crucial role in identifying the crystalline phases of zirconia, which commonly exists in monoclinic, tetragonal, and cubic forms. Comparative analysis of XRD and Raman data enables precise determination of the phase composition and phase transitions influenced by factors such as temperature, applied stress, or doping. This information is particularly useful in assessing the extent of stabilization of the cubic phase at ambient conditions through the use of dopants. FTIR spectroscopy complements this by providing insights into the molecular groups present, aiding in the evaluation of zirconia synthesized via different preparation routes.

Morphological characterization through SEM, TEM, and AFM offers detailed information on particle size, microstructure, and surface topography. SEM reveals the particle size distribution, surface morphology, and elemental distribution at the nanoscale, while TEM is particularly suitable for imaging zirconia nanoparticles smaller than 10 nm. AFM provides surface roughness measurements, a critical parameter in determining frictional and adhesive properties, which is highly relevant for applications in prosthetics, especially in dental implants.

The chemical state of zirconium in the zirconia matrix can be investigated using XPS, where analysis of the Zr 3d core-level peaks helps determine the oxidation state and electronic environment of zirconium atoms based on peak positions and shifts.

Elemental characterization, though challenging due to zirconia's refractory nature, can be effectively conducted using laser ablation inductively coupled plasma atomic emission spectroscopy (LA-ICP-AES) and XRF. These techniques provide compositional data without extensive sample preparation. Additionally, XRD remains a reliable method for assessing phase purity and structural characterization.

In contrast, destructive techniques such as ICP-AES and ICP-MS are less suitable for analyzing highly stable zirconia materials. Thus, a combination of advanced, non-destructive characterization methods enables thorough assessment of zirconia's properties, ensuring its targeted use in diverse applications.

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Identification and Thermal Stability of Radiation-Induced Defects in Nanostructured Zirconia Ceramics

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Abstract

The electron spin resonance (ESR) spectra of nanostructured monoclinic ZrO_2 (zirconia) ceramic samples subjected to irradiation with electrons (130 keV, 10 MeV) and 220 MeV Xe ions have been analyzed. It has been determined that exposure to 10 MeV electrons and Xe ions results in the creation of radiation-induced F^+ centers. The thermal degradation of these centers takes place between the temperatures of 375–550 K for samples irradiated with electrons, and between 500 and 700 K for those irradiated with Xe ions. It has been demonstrated that the reduction in F^+ center concentration correlates with the liberation of traps associated with thermoluminescence (TL) peaks within the specified temperature range. In samples subjected to ion irradiation, previously unrecognized paramagnetic centers with g-values of 1.963 and 1.986 were observed, likely involving Zr^{3+} ions and oxygen vacancies. The thermal degradation of these centers occurs within the temperature range of 500–873 K. Additionally, it was found that an increase in nanoparticle size reduces the radiation resistance of zirconium dioxide, while enhancing the thermal stability of the centers with $g = 1.963$ and 1.986 .

Keywords: ZrO_2 , nanostructured ceramic, ion and electron irradiations, radiation-induced defects, thermal stability, electron spin resonance, thermoluminescence

1. Introduction

It is well established that zirconium dioxide's optical and luminescent properties are primarily influenced by structural defects, which play a crucial role under high-radiation environments such as nuclear reactors and space electronics. Electron spin resonance (ESR) spectroscopy is among the most effective techniques for investigating radiation-induced defects in materials. The primary paramagnetic defects in zirconium dioxide are centers involving Zr^{3+} ions, including both surface and bulk Zr^{3+} (T-center). Also, noted are O $^{\cdot-}$ centers and F-type centers associated with positively charged

monovacancies (F^+ center) and divacancies (F_2^+ center). Zr^{3+} ions were detected previously in the original, heat-treated, and UV-irradiated ZrO_2 [1–3]. Radiation-induced T-centers were observed in ZrO_2 after electron and ion irradiation [4]. O $^-$ centers are formed in ZrO_2 after X-ray, ion, and gamma irradiation [5, 6]. The F^+ center was registered in ZrO_2 after gamma [7], electron, and ion irradiation [4, 8–11], and annealing of this material in a hydrogen atmosphere [1].

Despite the existence of several studies on paramagnetic radiation defects in ZrO_2 , their thermal stability has not been comprehensively explored. Understanding the thermal stability of these defects is essential, as thermal annealing is commonly employed to remove such defects and recover the functionality of ZrO_2 -based devices. The breakdown of paramagnetic centers during heating can result in thermoluminescence emission. Nevertheless, the correlation between TL peaks and the thermal decomposition of radiation-induced paramagnetic defects in ZrO_2 is still not fully understood.

The study of the correlation between paramagnetic defects and thermoluminescent properties of nanostructured zirconium dioxide is of considerable interest. Nanostructured materials have increased resistance to radiation-induced defect formation compared to their monocrystalline counterparts, which makes them promising candidates for applications in high-dose (more than 10 Gy) luminescence dosimetry.

This study aims to identify paramagnetic defects in monoclinic nanostructured ZrO_2 samples irradiated with heavy ions and electrons of different energies and evaluate their thermal stability.

2. The samples and experimental technique

Two types of monoclinic ZrO_2 ceramic samples made from two different nanopowders were used in this work. Nanopowder of type 1 was provided by the “Plasmotherm” company and was produced by plasma synthesis. Type 2 nanopowder was provided by the firm “ORMET.” The manufacturer did not provide information on the method of production of these powders. Samples in ceramic tablets with a diameter of 5 mm and a thickness of 1 mm were made by cold uniaxial pressing from nanopowders [5]. An X-ray phase analysis (XRF) of the samples was carried out using a Rigaku MiniFlex 600 diffractometer. It was found that the investigated tablets consist mainly of the monoclinic phase of zirconium dioxide. Section 3 presents studies on samples of type 1. The proportion of monoclinic ZrO_2 in the studied powder, according to XRF data, was at least 99.02%; the impurities were HfO_2 (0.331%), Cl (0.458%), K_2O (0.110%), TiO_2 (0.069%), PdO (0.009%), and Rb_2O (0.006%) [12].

The samples were irradiated with three different types of radiation:

- 220 MeV Xe ions generated by the DC-60 cyclotron (Astana, Kazakhstan).
- 130 keV electron beam generated by the pulse electron accelerator RADAN with pulse duration 2 ns, and current density 60 A/cm².
- 10 MeV electron beam from the linear electron accelerator (URFU) [5, 12].

Two electron beams with different energies were used due to their different interactions with the material: 10 MeV electrons can generate new F -type radiation

centers by the shock-induced mechanism, whereas 130 keV electrons mainly affect the charge states of already existing defects without creating new ones.

Thermoluminescence measurements were carried out using a photomultiplier with a peak spectral sensitivity in the range of 400–420 nm, under a linear heating rate of 2°C/s [5, 12, 13].

Electron spin resonance measurements were conducted using a Bruker ELEXSYS 580 spectrometer operating at a resonant frequency of 9.78 GHz, with the magnetic field varied from 50 to 600 mT. The ESR spectra were recorded at room temperature after the samples had been sequentially heated from 323 to 873 K with a step of 20 K [5, 14]. To assess the thermal stability of paramagnetic centers, the same heating regime used for TL measurements was applied.

3. Identification and thermal stability of radiation-induced defects

3.1 Identification of radiation-induced defects

To detect radiation-induced defects in ZrO_2 , ESR spectra were recorded for both the original ZrO_2 tablets and those exposed to various radiation sources (**Figure 1**).

The ESR spectrum of the unirradiated ZrO_2 ceramic samples exhibits a signal at a magnetic field of $B = 356.0$ mT, with a g -factor of 1.965 and a maximum-to-maximum width of 3.7 mT. This signal is attributed to paramagnetic Zr^{3+} ions, which were likely formed during the synthesis of the initial ZrO_2 nanopowders.

The ESR of Zr^{3+} ions has previously been observed in unirradiated ZrO_2 [1, 12] and $\text{ZrO}_2\text{-Er}$ [7] nanopowders. In these studies, a spectrum characterized by $g_{\perp} = 1.975$ and $g_{\parallel} = 1.957\text{--}1.958$ was assigned to bulk Zr^{3+} . In contrast, other works [3, 7] discovered an ESR signal with the same $g_{\perp}$ but a different $g_{\parallel} = 1.905\text{--}1.928$, which was attributed to surface Zr^{3+} ions. The g -factor of paramagnetic Zr^{3+} detected in our initial tablets corresponds to bulk Zr^{3+} , supporting its identification as such.

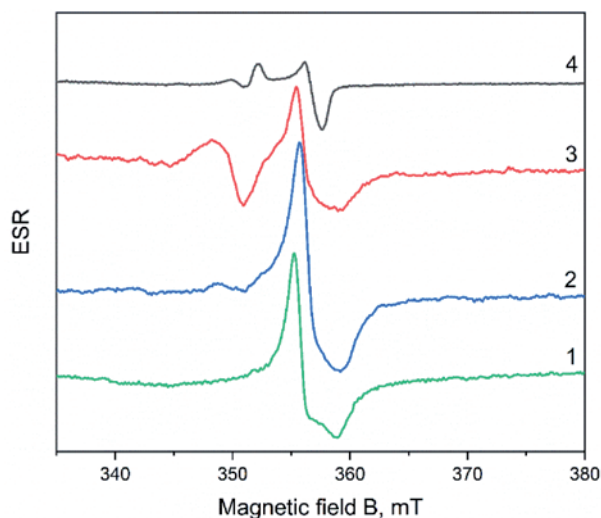


Figure 1.

ESR spectra of ZrO_2 : (1) unirradiated; (2) irradiated with 130 keV electrons to dose 15 kGy; (3) irradiated with 10 MeV electrons to fluence 10^{15} cm^{-2} (4) irradiated by 220 MeV Xe ions to fluence 10^{13} cm^{-2} [5].

In the ESR spectra of the samples irradiated with 130 keV electrons to a dose of 15 kGy, (**Figure 1**, curve 2), a Zr^{3+} signal with $g = 1.965$ and peak-to-peak width 3.2 mT is observed. Additionally, a weak signal with $g = 1.999$ emerges, indicating the presence of a trace amount of F^+ centers in the irradiated ceramics. Previously, the F^+ center was detected in ZrO_2 after electron and ion irradiation and represented a line with a small g -factor anisotropy ($g_{\perp} = 1.972$ and $g_{\parallel} = 1.996$) [4]. Some authors report that the F^+ center is characterized by an isotropic signal with a g -factor near the free electron value ($g_e = 2.0023$) [1, 7]. Earlier, it was reported in a study [12] by photoluminescence (PL) and pulsed cathodoluminescence (PCL) that the formation of F^+ centers upon irradiation with an electron beam with an energy of 130 keV could occur due to the capture of electrons by oxygen vacancies present in the initial samples. In the PL and PCL spectra of the samples studied in this work, a luminescence band at 480 nm was observed. Oxygen vacancies are involved in the formation of this luminescence band [12].

10 MeV electrons irradiation leads to an increase in the intensity of the ESR spectrum with $g = 1.999$ and a width of 2.7 mT of F^+ centers (**Figure 1**, curve 3). This suggests that high-energy electron impacts induce the formation of these centers in ZrO_2 ceramic through a collision mechanism. As notified in Costantini and Beuneu [15], the threshold energy for creating F -type defects in ZrO_2 is approximately 1 MeV. Therefore, 10 MeV electrons possess enough energy to displace oxygen atoms from the lattice sites [16]. At the same time, the ESR intensity of Zr^{3+} in ceramic samples irradiated by 10 MeV electrons is lower compared to the unirradiated samples. Further investigation is needed to determine the underlying reason for the decrease.

Irradiation of ZrO_2 ceramics with Xe ions at fluences lower than the fluence of 10^{13} cm^{-2} did not lead to noticeable changes in the EPR spectra compared to the unirradiated samples. These spectra still display a Zr^{3+} signal with $g = 1.963$, width 3.5 mT. However, at a fluence of 10^{13} cm^{-2} , the ESR spectrum undergoes a significant modification: The Zr^{3+} signal disappears, and new signals emerge at 356.8 mT ($g = 1.963$), 350.0 mT ($g = 1.998$), and 352.5 mT ($g = 1.986$) (**Figure 1**, curve 4). The signal with $g = 1.998$, width 1.2 mT, is likely associated with F^+ centers generated by swift heavy ion irradiation. Signals with $g = 1.986$ and 1.963, width 1.5 mT, may correlate to previously unreported radiation-induced defects.

3.2 Thermal stability of radiation-induced defects

The destruction temperatures of paramagnetic F^+ centers ($g = 1.999$) and Zr^{3+} ions ($g = 1.965$) in ceramic tablets exposed to a 10 MeV electron beam have been investigated. The temperature-dependent behavior of the ESR intensity for the F^+ defect is shown in **Figure 2**.

The ESR intensity begins to decrease at temperatures above 375 K, with a pronounced drop occurring between 375 and 550 K. As shown by curve 3 in **Figure 2**, the thermoluminescence of the samples exposed to 10-MeV electron irradiation exhibits two distinct peaks at 410 and 500 K.

Given that the samples were subjected to the same heating conditions during both the investigation of the thermal stability of paramagnetic defects and the thermoluminescence measurements, it can be inferred that the variation in the concentration of F^+ centers upon heating is likely linked to a change in their charge state caused by the capture of electrons released from traps responsible for TL. Previously, in work [17], the electronic origin of the TL maxima at 390 K and 485 K was proposed based on the analysis of TL quenching processes in monoclinic ZrO_2 .

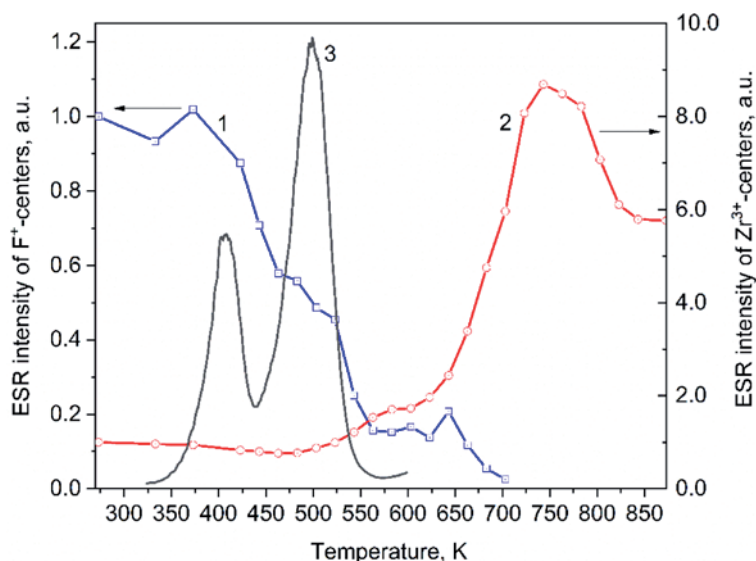


Figure 2.
 Temperature dependence of the ESR intensity for F^+ centers (1), Zr^{3+} ions (2), along with the thermoluminescence (3) of ZrO_2 samples irradiated with 10 MeV electron beam [5].

The thermal stability of radiation-induced F^+ defects has been studied in detail in Refs. [18–20]. In a combined analysis of TL and ESR data, the authors suggested that the gradual decrease in the concentration of F^+ centers up to 550–600 K could be attributed to their transformation into a diamagnetic state (F center) through the capture of electrons released from thermally stimulated traps. However, this hypothesis was challenged by two key observations. First, the peak temperature on the TL curve (550 K) was higher than the temperature at which 50% of the F^+ defects had already decayed (450 K). Second, the trap depth associated with the 550 K TL maximum, determined using the initial-rise method, was estimated to be 0.7–1.1 eV, somewhat higher than the activation energy for defect annealing (0.3–0.7 eV) obtained from ESR measurements.

Our results (**Figure 2**) demonstrate a correlation between the decreases in the ESR of F^+ defects within the temperature range of 375–550 K and the appearance of TL peaks in the same interval, thereby supporting the hypothesis proposed by the authors in Refs. [12–14]. It is also known that an alternative mechanism for the annealing of radiation-induced F -type defects in oxides involves the recombination of oxygen vacancies with oxygen interstitials, whose diffusion becomes feasible upon heating the crystal [21].

Previous studies [22] have shown that in zirconium oxide irradiated by neutrons with an energy greater than 0.1 MeV, the diffusion of interstitial oxygen becomes significant at temperatures above 500–600 K. In contrast, our samples exhibit a reduction in the concentration of F^+ defects at lower temperatures, specifically within the 375–550 K range. This observation supports the proposed mechanism in which the destruction of F^+ defects is attributed to their capture of charge carriers released from traps responsible for the observed TL peaks.

It is also important to point out that between temperatures of 550–700 K, the reduction in the concentration of F^+ centers decreases, and a modification in the ESR signal's shape can be observed in **Figure 3**. More comprehensive investigations have

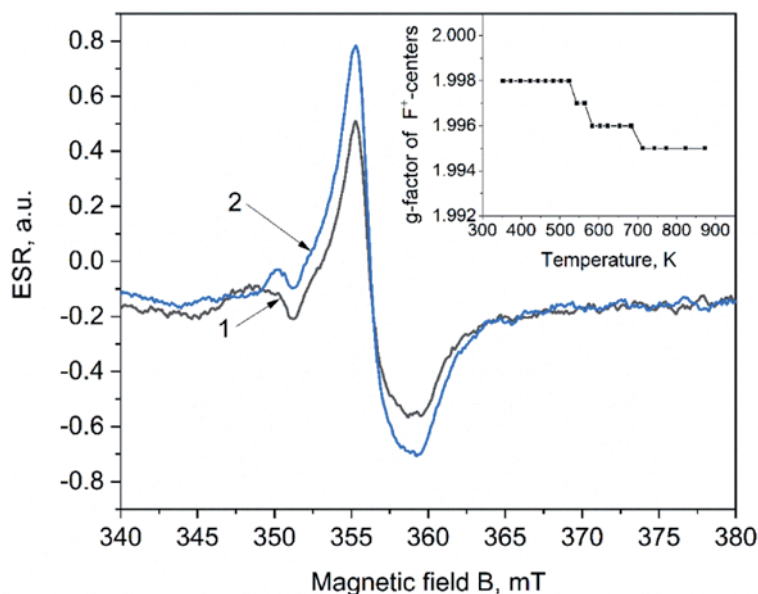


Figure 3.

ESR spectra of ZrO_2 ceramic tablets irradiated by 10 MeV electrons and then heated at temperatures of 540 K (1) and 580 K (2) [5].

revealed that at $T = 525\text{--}700$ K, the g -factor of the F^+ center shifts from 1.998 to 1.995 (see the insert in **Figure 3**). This change in the g -factor of the F^+ center might suggest an alteration in its local crystalline surroundings. The observed increase in the ESR intensity of Zr^{3+} ions within the same temperature range supports this idea. In this scenario, Zr^{3+} ions could influence the local environment of the F^+ centers. The thermal stability of Zr^{3+} ions was further examined. **Figure 2** illustrates that within the temperature interval of 280–525 K, the intensity of the ESR signal linked to Zr^{3+} remains constant. However, as the temperature rises to 750 K, there is an increase of 8.7 times.

When temperatures rise above 750 K, the intensity of the signal diminishes but does not revert to the level typical of the irradiated sample. The alteration in the ESR intensity of Zr^{3+} is not connected to the depletion of traps in the material being examined, as our experiments indicated that no TL peaks were detected within the 600–850 K temperature range. Simultaneously, the intensity values did not surpass the background levels attributed to the thermal radiation from the heating element.

The earlier studies noted an increase in Zr^{3+} concentration with higher annealing temperatures, as referenced in Bykov et al. [23]. The researchers explained this phenomenon as the conversion of Zr^{4+} ions to Zr^{3+} ions due to the capture of electrons. In this scenario, the sources of electrons may include oxygen vacancies that have gained one or two electrons, as well as O^{2-} ions, particularly if there is a lack of positive charge in the cationic sites near these ions. Similar processes may occur in the samples examined in this study, given that they contain defects related to oxygen vacancies.

Additionally, we examined the thermal stability of ESR signals in samples that were irradiated with ions. **Figure 4** illustrates how the intensity of the ESR signal for F^+ centers ($g = 1.998$) varies with the heating temperature in ZrO_2 samples that were exposed to a xenon ion beam with a fluence of 10^{13} ions/cm². The intensity of this signal starts to decline at temperatures exceeding 500 K, which is 125 K higher than

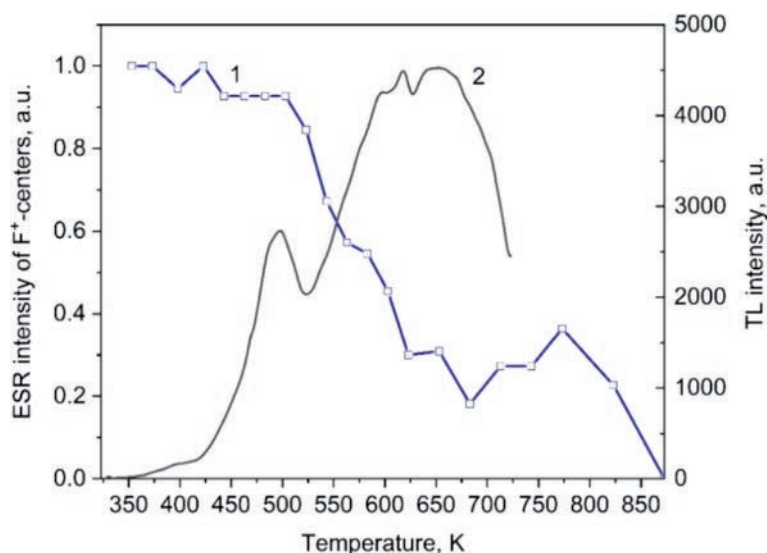


Figure 4.
 Dependence of the intensity of the ESR signal of F^+ centers on the heating temperature (1) and TL (2) of ZrO_2 samples irradiated with xenon ions [5].

what is observed in samples irradiated with electrons. Moreover, the intensity of the ESR signals for F^+ centers progressively diminishes until reaching 675 K.

Compared to samples that have been irradiated with electrons, the thermoluminescence emission maximum observed at 410 K in samples irradiated with ions exhibits a lower intensity. The variation in the temperature at which the annealing of F^+ centers initiates in ion- and electron-irradiated samples may be attributed to the difference in the intensity of this peak. The thermal dissolution of the trap linked to the low-intensity TL peak in ion-irradiated samples does not substantially influence the concentration of F^+ centers. The reduction in the concentration of F^+ centers in ion-irradiated samples begins when the trap associated with the intense TL peak at 500 K is emptied. This observation supports the notion that the thermal decay of F^+ centers is connected to the TL characteristics of ZrO_2 .

The information presented in **Figure 4** indicates that the reduction in the concentration of F^+ centers between 500 and 700 K is followed by an increase at elevated temperatures, which was not seen in samples subjected to electron irradiation. The range during which the concentration of F^+ centers increases may also be associated with the emptying of traps.

The thermoluminescence curve of samples subjected to ion irradiation exhibits, alongside the maxima at 410 and 500 K noted after electron irradiation, an extra maximum with a complicated structure between 550 and 750 K, which could comprise elements from both electrons and holes.

In this scenario, the reduction of electron traps will lead to a lower concentration of F^+ centers, while the reduction of hole traps results in their increase, which is seen at temperatures above 700 K. The rise in F^+ centers' concentration during the emptying of hole traps occurs because F-centers trap holes. A more detailed investigation of TL properties at temperatures exceeding 725 K is necessary to validate this hypothesis. However, measuring TL at these high temperatures is hindered by equipment limitations and the significant thermal background from the heating element.

The thermal stability of paramagnetic signals of unexplained origin, characterized by g -values of 1.986 and 1.963 (**Figure 1**), was investigated in samples exposed to Xe ion irradiation (**Figure 5**).

The dependence of ESR intensity on temperature for these two signals is the same and gradually diminishes to an undetectable level within the temperature range of 500–873 K. The correlation between the temperatures and the ESR intensity of these two signals is consistent, exhibiting a steady decline to a level that cannot be detected between 500 and 873 K. The relationship between temperature and ESR intensity for these two signals is similar. The similar behavior of signal intensities at $g = 1.986$ and 1.963 with varying heating temperatures indicates that these signals arise from the same paramagnetic center.

The characteristics of this center are probably associated with a complicated defect involving paramagnetic Zr^{3+} ions and oxygen vacancies. The role of Zr^{3+} ions in the creation of this defect is demonstrated by the simultaneous vanishing of their electron paramagnetic resonance along with the appearance of signals showing g -values of 1.986 and 1.963 in ZrO_2 tablets that were subjected to ion beam irradiation at a fluence of 10^{13} ions/cm². Furthermore, it is established that when ZrO_2 undergoes ion irradiation at energies exceeding the threshold, there is a notable increase in anionic vacancies, which may also play a part in the development of complex defects [4, 24].

It was found that unirradiated monoclinic ZrO_2 samples have paramagnetic Zr^{3+} ions, which are produced during the synthesis of the original nanopowders. Upon exposure to fast electrons at an energy level of 10 MeV, radiation-induced F^+ centers are created in the samples being studied.

The findings from the thermal stability investigation show that the concentration of F^+ centers diminishes within the temperature range of 375–550 K. This phenomenon is linked to the release of traps that are responsible for thermoluminescence during this temperature interval. Furthermore, the temperature-dependent behavior of

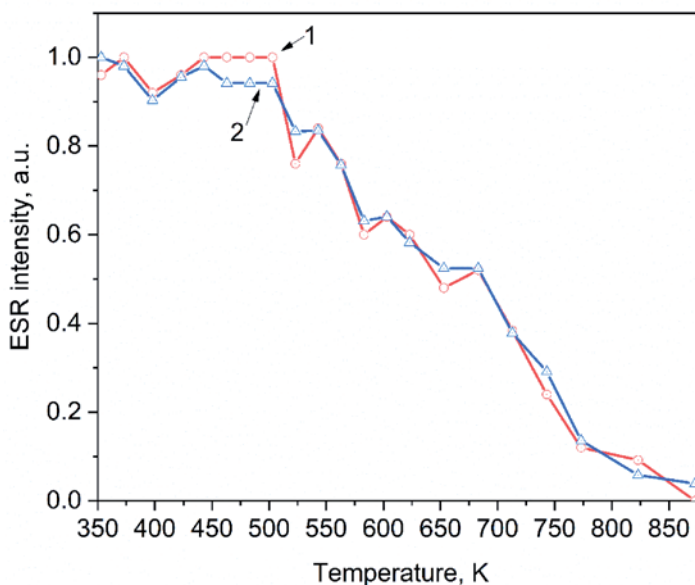


Figure 5. The relationship between the strength of ESR signals with $g = 1.986$ (1) and $g = 1.963$ (2) and the heating temperature of ZrO_2 samples irradiated by Xe ions [5].

the electron paramagnetic resonance signal intensity of Zr^{3+} ions exhibits a nonlinear trend, reaching a maximum at 750 K. Importantly, the variations in the ESR intensity of Zr^{3+} are not related to the TL observed in the material under examination.

Exposure of ZrO_2 ceramic samples to Xe ions at a fluence of 10^{13} ions/cm² leads to the formation of F^+ centers observed in ESR spectra, along with the emergence of two previously unreported signals characterized by g-values of 1.963 and 1.986. The concentration of F^+ centers decreases between 500 and 700 K, but begins to rise again at higher temperatures. These changes are likely associated with the release of charge carriers from traps responsible for thermoluminescence in ZrO_2 . The ESR signals at $g = 1.963$ and 1.986 exhibit identical temperature dependence, showing a steady decline in intensity from 500 to 873 K. The similarity suggests a common origin, most likely a paramagnetic center formed by a complex defect involving Zr^{3+} ions. Additional investigation is required to more accurately determine the nature of this defect center.

4. The impact of nanoparticle size on the creation and thermal stability of radiation-induced defects

Research indicates that the radiation resistance of zirconium dioxide-based materials is influenced by their morphological state, particularly the size of the crystallites [25]. Therefore, it is important to investigate the patterns of radiation defect formation in zirconium dioxide samples that vary in nanoparticle size.

The scanning electron microscopy (SEM) images of the surface of all types of samples are shown in **Figure 6**. Type 1 and type 2 samples have a porous structure, unlike type 3 samples, which are more densely packed and have clear grain boundaries. The nanoparticle shape for type 1 and type 2 is far from spherical due to the clumping of several particles into larger clusters.

The nanoparticle size is defined as the equivalent diameter, which is calculated as the arithmetic mean of the lengths of two mutually perpendicular segments. The analysis revealed that particles in type 1 samples ranged in size from 40 to 70 nm, type 2 samples ranged from 30 to 50 nm, and type 3 samples ranged from 80 to 140 nm.

Zirconium dioxide samples of type 2 with particle size 80–140 nm, more significant than type 1 (30–50 nm), were chosen for the studies. The samples were irradiated with a xenon ion beam with an energy of 220 MeV at the DC-60 accelerator.

To identify radiation defects in ZrO_2 , we measured the ESR spectra of both the original samples irradiated with a beam of xenon ions at varying fluences. The ESR

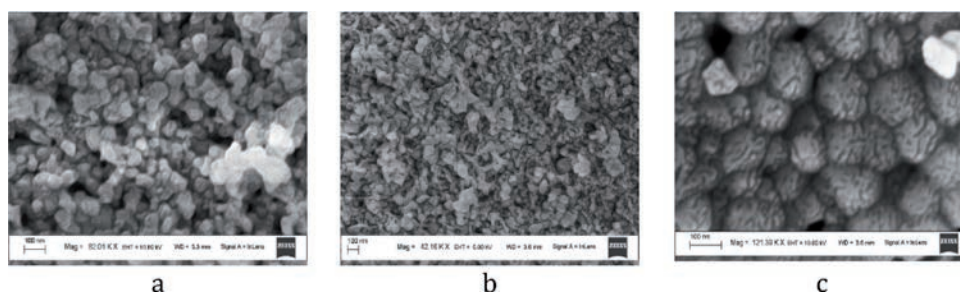


Figure 6.
SEM images of the surface of samples of type 1 (a), type 2 (b), and type 3 (c) [12].

spectrum of the unirradiated tablets shows no signals within the magnetic field induction range of 50–600 mT. As shown in **Figure 7**, irradiation of ZrO_2 with an ion beam at fluences below 10^{11} ions/cm² does not result in the formation of paramagnetic defects. However, when the fluence is increased to 10^{12} ions/cm², three signals appear in the ESR spectra of the samples: I ($g = 1.998$), II ($g = 1.985$), and III ($g = 1.963$). Further increases in fluence are accompanied by a rise in the intensity of these signals.

The presence of signal I in the ESR spectra of irradiated samples indicates the formation of F^+ centers, which are oxygen vacancies that contain one trapped electron [15]. Signals II and III, previously observed in nanostructured ZrO_2 type 1 irradiated with xenon ions at a fluence of 10^{13} ions/cm², were attributed to a new, previously unidentified center (see **Figure 1**).

Figure 7 illustrates the relationship between the normalized ESR intensity of all three signals and the annealing temperature. It was observed that the intensity of signals II and III begins to decline significantly when annealed at temperatures exceeding 670 K. At 820 K, these signals vanish from the ESR spectrum entirely. In contrast, the type 1 samples studied previously showed a decrease in the concentration of these centers starting at a lower temperature of 500 K (see **Figure 5**). This indicates that the thermal stability of these centers increases as the size of the nanoparticles increases.

Figure 8 demonstrates that the ESR intensity of F^+ centers exhibits a complex relationship with annealing temperature. The curve shows intervals where the signal intensity increases between 420–520 K and 670–570 K. In contrast, there is a decrease in signal intensity at temperatures ranging from 590 to 650 K and above 830 K [26].

The changes in the concentration of F^+ centers in type 2 samples at temperatures up to 670 K show significant differences compared to those observed in type 1 samples with smaller nanoparticle sizes. These differences can be attributed to variations in the trap structure, as demonstrated by the analysis of thermoluminescence curves. In type 1 samples, a decrease in the concentration of F^+ centers occurs between 430 K and 520 K, which is linked to the appearance of a TL peak at 500 K. In contrast, type 2

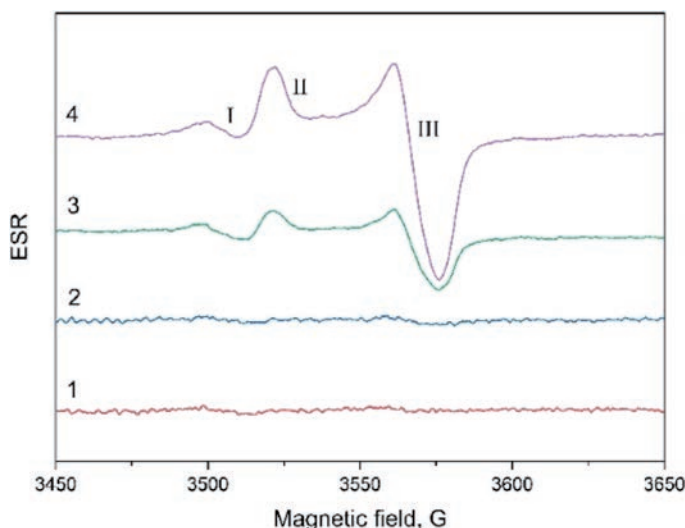


Figure 7. ESR spectra of initial tablets of type 2 (1) and tablets irradiated by ion beam with fluences 10^{11} ion/cm² (2), 10^{12} ion/cm² (3), 10^{13} ion/cm² (4).

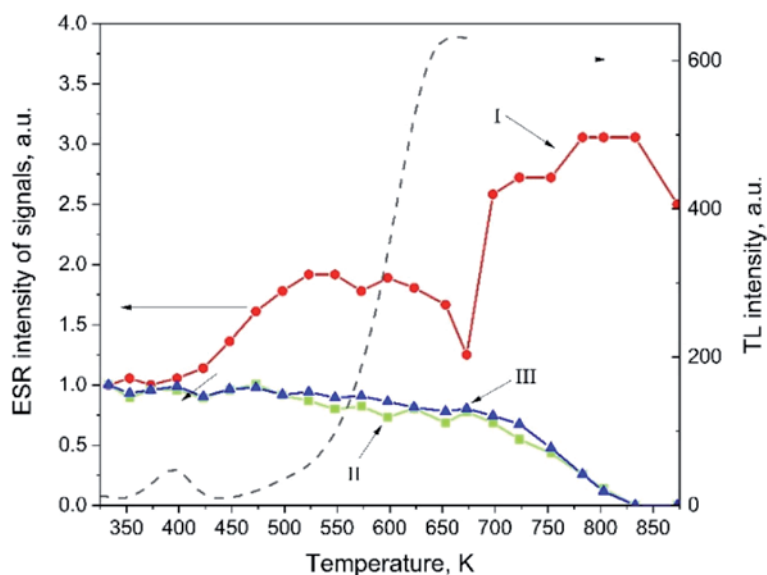


Figure 8.
 Dependence of ESR signal intensity on annealing temperature and TL of tablets irradiated with 220 MeV Xe ion beam to a fluence of 10^{13} ions/cm².

samples do not exhibit a TL maximum at this temperature. Instead, the increase in the concentration of F^+ centers between 430 and 520 K may be associated with the onset of a TL peak at 670 K.

The temperature dependence of F^+ center concentration for temperatures above 670 K is similar in both types of samples. In previous studies, the non-monotonic behavior of the F^+ center signal was explained by changes in its charge state, which occur due to the capture of electrons or holes released during the thermal emptying of deep traps within this temperature range. These processes may also occur in type 3 samples.

We discovered that irradiating ZrO_2 samples with nanoparticle sizes ranging from 80 to 140 nm using xenon ions at fluences of 10^{12} – 10^{13} ions/cm² results in the emergence of F^+ -center signals in EPR spectra, along with two additional signals of unknown nature at $g = 1.963$ and $g = 1.985$. In contrast, for samples with smaller nanoparticle sizes (30–50 nm), these signals were only detected at an irradiation fluence of 10^{13} ions/cm². This finding indicates a decrease in the radiation resistance of zirconium dioxide as the nanoparticle size increases. Furthermore, this increase in nanoparticle size also enhances the thermal stability of the centers with $g = 1.963$ and $g = 1.985$.

The concentration of F^+ centers in type 2 samples shows a more complex variation with temperature compared to type 1 samples, which have smaller nanoparticle sizes. This observed pattern may be attributed to differences in the nature and energy depth of the capture centers in ZrO_2 samples produced by different manufacturers.

5. Conclusions

1. It has been established that radiation-induced F^+ centers form in nanostructured monoclinic ZrO_2 tablets when exposed to fast electrons (10 MeV, fluence 10^{15} cm⁻²) and swift heavy Ve ions (220 MeV, fluence 10^{13} cm⁻²).

2. The reduction in decrease in the F^+ concentration during annealing is attributed to the release of charge carriers from traps responsible for thermoluminescence.
3. The variation in ESR intensity of Zr^{3+} during heating does not correspond to the thermoluminescence behavior of the studied zirconium dioxide samples.
4. Irradiation of ZrO_2 with swift heavy Xe ions to a fluence of 10^{13} cm^{-2} results in the emergence of new ESR signals with g-values of 1.963 and 1.986, whose origin remains unidentified; these signals remain stable up to 870 K.
5. Increasing the nanoparticle size leads to decreased radiation resistance of zirconium dioxide, while enhancing the thermal stability of the centers with g = 1.963 and 1.986.

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Conflict of interest

The authors declare no conflict of interest.

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Section 3

Advanced Applications of Zirconia

Upgrading the Acidity of Zirconia *via* Merging with Dilacunary Phosphotungstates: Synthesis, Characterization and Production of Alkyl Levulinates

Margi Joshi and Anjali Patel

Abstract

Zirconia-based materials have secured a prestigious position in the field of heterogeneous catalysis due to their exceptional thermal stability, tunable acidity and robust surface properties. Their synergy with heteropolyacids can be exemplified as “polishing the pearl”. This chapter elucidates upgrading the acidity of zirconia *via* the incipient wet impregnation method of dilacunary phosphotungstate and its characterization. The catalyst was examined in the esterification of levulinic acid with 1-butanol, which resulted in significant selectivity (>90%) of butyl levulinate and a high turnover number (1850) under mild reaction conditions. A kinetic study determined the activation energy and order of the reaction. The catalyst showcases its stability over multiple recycles, followed by its industrial relevance *via* successful scale-up trials. The versatility of the catalyst was also explored in the esterification of levulinic acid with bio-based alcohols, underscoring its broad applicability to alkyl levulinates, making this material a promising candidate for industrial applications.

Keywords: zirconia, heteropolyacids, heterogeneous catalysts, levulinic acid, alkyl levulinates

1. Introduction

Amongst all metal oxides, Zirconia (Zirconium dioxide— ZrO_2) emerges as the most important material, having exceptional scientific and industrial significance, owing to its excellent mechanical and chemical stability, high melting point, electrical resistivity and refractive index, along with a low thermal expansion coefficient [1]. It also stands out as promising in various applications, such as gas sensors [2], fuel cells [3], coatings [4] and insulators [5], and most importantly, it has been well demonstrated in heterogeneous catalysis [6–8]. In this context, the latest forecast

report predicts that the global zirconia market will expand to approximately USD 2.1 billion by 2030, with a compound annual growth rate of 6.4% (**Figure 1**).

It is interesting to note that amongst different types of sectors, alone the zircon-based chemicals sector has gained growing attention and reached USD 1.5 billion in 2024 with a 1.5 times increment compared to previous years, reflecting the rising demand as catalytic materials (**Figure 2**).

Despite having a number of advantageous properties, they exhibited only moderate activity, especially in acid catalysis, due to their low acidity [9]. This drawback can be addressed by combining it with strong acidic materials, which have the ability to upgrade the acidity of zirconia and make them compelling towards the same. In this regard, polyoxometalates (POMs) are evolving as excellent candidates, as they possess high Bronsted acidity. They are composed of early transition metal oxoanions linked by sharing a common oxygen atom. Amongst, Keggin-type POMs with a general formula $[XM_{12}O_{40}]^{n-}$, where X belongs to the heteroatom [P(V), Si(VI), or B(III)], M is the addenda atom [Mo(VI), W(VI), or V(V)] and O represents oxygen, are widely acknowledged from the viewpoint of their structural stability and acidity, making them strong contributor in different organic transformations [10–20]. In particular, they have been extensively explored in biomass conversion over the past decade owing to the above-mentioned unique properties [21–38]. POMs possess the remarkable ability to be designed at the molecular level, by removing one or more M-O units, resulting in a unique subclass recognized as mono lacunary polyoxometalates or poly (Di, tri) lacunary polyoxometalates, respectively, making them more adaptable for selective acid catalysis [39]. Amongst the available Keggin-type POMs, phosphotungstates have secured a top rank for possessing the highest Bronsted acidity. When looking at the detailed literature, to date, a very small number of investigations have been reported where the development of any type of lacunary phosphotungstates and zirconia as a support has been employed for biomass conversion. In 2008, Patel et al. published an article on esterification of acetic acid with n-butanol using a zirconia-supported mono lacunary phosphotungstates catalyst [40]. Further, in 2016, the same group introduced another catalyst,

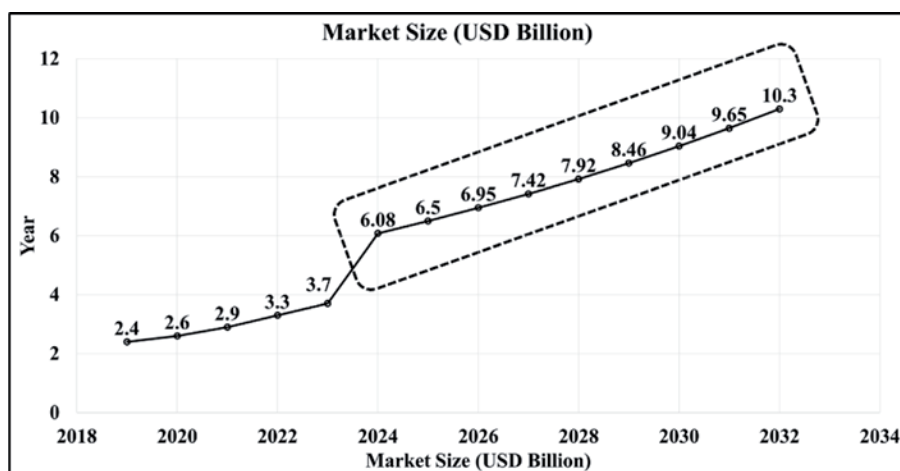


Figure 1.
Zirconia market size and forecast report (2025–2032).

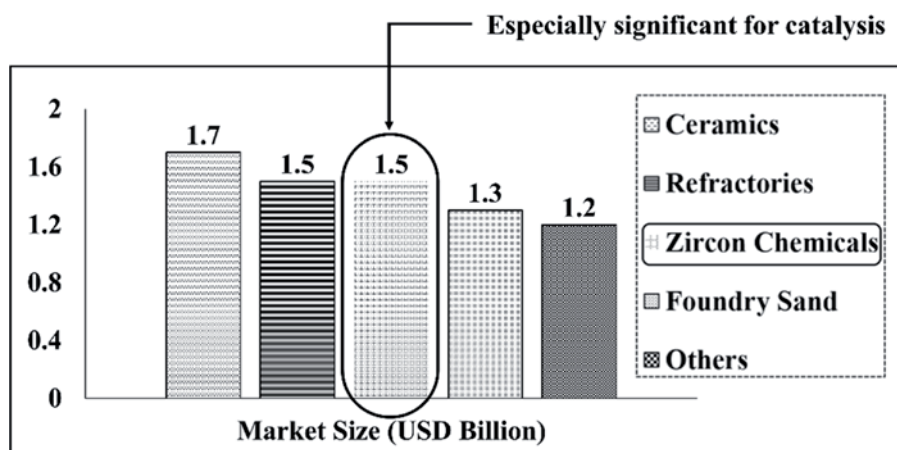


Figure 2.
 Distribution of the zirconia market by product type.

where a combination of zirconia and dilacunary phosphotungstates was used for the same reaction [41]. However, later on, the research involving such catalytic materials has been totally underrated, which highly encourages us to contribute in that direction, and we thought to resume the journey by further finding their application in a new domain that exclusively meets the latest demands of focusing on the invention of fossil fuel alternatives. For that, a primary effort was made, which involved the comparison of the activity of different supports such as zeolite HY and ZrO_2 on ester formation [42]. Now, building on that, the present work offers a deeper insight into the catalytic conversion of levulinic acid.

Amongst various biomass-derived chemicals, levulinic acid is the topmost choice to produce value-added chemicals *via* various organic transformations such as acetalization, aldol condensation, decarboxylation, esterification, hydrogenation, oxidation, reductive amination, dehydration, etc. [43, 44]. In particular, esterification has received significant attention as it leads to the formation of levulinate esters, versatile platform chemicals derived from biomass, widely used in flavours, fragrances, pharmaceuticals, plasticizers and eco-friendly solvents, and as fuel additives. The renewable origin, as well as chemical stability, render them attractive for sustainable industrial processes. Specifically, butyl levulinate is in greater demand, particularly as a biofuel additive, in view of its high oxygen content, significant miscibility with diesel, low viscosity and ability to lower the emissions, which drastically enhances the combustion efficiency and promotes the transition towards cleaner, renewable energy sources [45].

This book chapter aims to fill the existing research gap by reporting the development and evaluation of a strategy to increase the acidity of zirconia with a strong Bronsted acidic dilacunary phosphotungstates. The catalysts synthesis as well as characterization with various techniques and their catalytic application in the esterification of C5 bioplateform levulinic acid with 1-butanol, followed by the scale-up trials, have been employed. Additionally, the kinetic study was conducted to estimate the reaction order and activation energy. Moreover, the stability and recyclability of the catalyst were evaluated for multiple cycles to ascertain its industrial relevance. A broad substrate scope was also explored with different alcohols to understand the versatility of the catalyst.

2. Experimental

2.1 Materials

All chemicals used were of A.R. grade. Ammonium chloride (99%), dichloromethane (>99%), disodium hydrogen phosphate (>99%), ethanol (99%), isopropyl alcohol (>98%), methanol (99%), 1-butanol (>99%), sodium tungstate dihydrate (>99%), succinic acid (99.5%), zirconium oxychloride (ZrOCl_2) (%), 1-propanol (>99%), 1-pentanol (>99%), 1-hexanol (>99%) and 1-heptanol (>99%) levulinic acid (>99%) were used as received from Merck.

2.2 Catalyst synthesis

The catalysts were synthesized by following three steps.

2.2.1 Dilacunary phosphotungstate synthesis (PW_{10})

The dilacunary phosphotungstate was synthesized by following the reported method [41]. At first, the anhydrous disodium hydrogen phosphate (0.02 mol, 0.2 g) and sodium tungstate dihydrate (0.2 mol, 6.8 g) were completely dissolved in distilled water (~150–200 mL). Then, the solution was heated at 80 °C. After that, the pH was measured and adjusted to 6.5 with concentrated nitric acid. It is to be noted that this step is very important as the lacunary species formation is solely reliant on the pH. Once the volume was reduced to half, the product was extracted *via* a liquid-liquid extraction, using about 80 to 100 mL of acetone. The extraction was repeated until the complete removal of nitrate ions. The resulting white material was air-dried and designated as PW_{10} .

2.2.2 Synthesis of zirconia (ZrO_2)

Hydrous zirconia was synthesized by following the reported method by our group [40]. The solution of zirconyl chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) was prepared in distilled water, in which an aqueous solution of ammonia was added dropwise to form the precipitates which were then agitated for 1 hour in a 100 °C set water bath. Further, it was filtered and washed repeatedly with deionized water until the complete removal of chloride ions, dried at 100 °C for 10 hours and designated as ZrO_2 .

2.2.3 Supporting of PW_{10} on ZrO_2 : Upgrading the acidity of ZrO_2

The merging of PW_{10} and ZrO_2 was carried out *via* the incipient wet impregnation method. For that, 1 g of ZrO_2 support was impregnated with an aqueous solution of PW_{10} (0.1 g in 10 mL of distilled water). The mixture was stirred and dried at the same temperature for 10 hours. The resulting solid was treated with 0.1 N HCl, filtered, washed thoroughly with distilled water and dried again at 100 °C. The final material was designated as $(\text{PW}_{10})_1/\text{ZrO}_2$. Likewise, the catalysts based on different PW_{10} loadings (0.2–0.4 g in 20–40 mL of distilled water) were synthesized and designated as $(\text{PW}_{10})_2/\text{ZrO}_2$, $(\text{PW}_{10})_3/\text{ZrO}_2$ and $(\text{PW}_{10})_4/\text{ZrO}_2$, respectively.

2.3 Characterizations

2.3.1 Acidity measurements

2.3.1.1 Potentiometric titration

In this procedure, at first, the dispersion of 0.25 g of the sample and 25 mL of Acetonitrile was prepared and stirred for about 12–15 min. Then, an initial electrode potential was measured, which denotes the acidic strength of the material. After that, 0.1 mL of 0.05 N n-Butylamine (n-BA) solution prepared in Acetonitrile was added. The dispersion was then stirred at 25°C for about 3 h. Lastly, it was potentiometrically titrated against the same solution of n-Butylamine, and the variation in electrode potential was recorded with a digital pH metre. The acidic sites were estimated using the scale, very strong sites ($E_i > 100$ mV), strong sites ($0 < E_i < 100$ mV), weak sites ($-100 < E_i < 0$ mV) and very weak sites ($E_i < -100$ mV) [46].

2.3.1.2 n-butylamine titration

In this, solutions of 0.025 M n-butylamine and 0.025 M Trichloroacetic acid (TCA) were prepared in Toluene. After that, a 0.25 g sample was dispersed in a 25 mL n-butylamine solution for 24 h. At last, the excess base was titrated against Trichloroacetic acid using neutral red as an indicator [47].

2.3.2 Physicochemical techniques

^{31}P solution and NMR (161.97 MHz, external 85% H_3PO_4) was recorded on the BRUKER instrument. The cyclic voltammetry experiment for PW_{10} was performed on the CH 620A system at room temperature by using a glassy carbon working electrode and an Ag/AgCl reference electrode. The Shimadzu instrument (IRAffinity-1S) was used to record FTIR spectra between 4000 and 400 cm^{-1} using a KBr disc. The thermogravimetric analysis (TGA) was operated under nitrogen atmosphere applying a flow rate of 2 mL min^{-1} and a ramp rate of 10°C min^{-1} in the temperature range of 25–600°C on Mettler Toledo Star SW 7.01. The Brunauer–Emmett–Teller (BET) surface area and N_2 adsorption-desorption isotherms were determined on a volumetric static adsorption instrument, Micromeritics ASAP 2010 (USA). The pore size distributions were measured using the BJH adsorption-desorption method. The X-ray diffraction (XRD) pattern was recorded in a 2θ range of 5–90° using Cu $\text{K}\alpha$ radiation at $\lambda = 1.54$ Å, on a Philips PW-1830 instrument.

2.4 Catalytic activity

The esterification of levulinic acid with 1-butanol was performed in a batch reactor (50 mL), loaded with levulinic acid (10 mmol), 1-butanol (20 mmol), catalyst and the magnetic stirring bar. The system was kept closed with an air condenser along with a guard tube. The reactor was placed in an oil bath and heated at a desired temperature with continuous stirring. Upon completion of the reaction, first, the reaction mass was allowed to cool at room temperature and then diluted with dichloromethane (~15 mL), which was further centrifuged. The analysis of the reactants, products and standards was carried out on a gas chromatograph GC-FID (Shimadzu-2014), which

has a capillary column RTX-5 with an internal diameter of 0.25 mm and a length of 30 m. The GC temperature profile for identification is mentioned here; the initial temperature was set to 35°C, which was then elevated up to 300°C. The hold time for ramp rate was initially 2 min at 80°C (equilibration time = 1.0 min), and then the ramp rate was increased to 10 until 300°C with a 6-minute hold time. Throughout the analysis, pressure (100 kPa), total flow (50.0 ml/min), column flow (1.19 ml/min), linear velocity (31.1 cm/sec) and purge flow (3.0 ml/min) remained constant. The products were confirmed with the standards. The % conversion and % selectivity were calculated by using the formula,

$$\% \text{ Conversion} = \frac{(\text{initial mol \%}) - (\text{final mol \%})}{(\text{initial mol \%})} \times 100, \quad (1)$$

$$\% \text{ Selectivity} = \frac{\text{moles of product formed}}{\text{moles of substrate consumed}} \times 100 \quad (2)$$

2.5 Leaching test

In order to assess the leaching of PW₁₀ from the support, a reported method was employed [48], in which 1 g of catalyst was suspended in 10 mL of distilled water for about 24 hours. It was further treated with an ascorbic acid solution after decanting the supernatant solution. As a result, no blue colour was observed, which is strong evidence of the absence of leaching. Further, the leaching can also be tested *via* the hot filtration test. In which, after the completion of the reaction, the reaction mass was filtered hot, and the obtained filtrate was treated with ascorbic acid solution. Here also, no blue colouration was observed, confirming that no leaching of PW₁₀ from ZrO₂.

3. Results and discussion

3.1 Characterization

3.1.1 Characterization of PW₁₀

³¹P NMR, emerging as the most significant and reliable technique to analyze and understand the chemical environment around the central phosphorus atom present in the polyoxometalate-based materials. It was reported that removing one WO unit from PW₁₂ (12-tungstophosphoric acid) significantly impacts the chemical shift value [49]. Thus, an observed shift of 4.5 to 10.5 ppm from PW₁₂ is likely for mono lacunary PW₁₁, and the same is anticipated for dilacunary species PW₁₀. The solution ³¹P NMR spectrum of PW₁₀ exhibited a peak at 10.88 ppm (**Figure 3a**); this value of chemical shift is in good accordance with the existing literature and indicates the successful lacuna formation in the parent Keggin structure with the formula [PW₁₀O₃₆]⁻⁷. An additional peak observed with a low intensity at 1.37 ppm is attributed to the [PW₁₀O₃₇] species [50]. The presence of various counter ions may cause a minor change in the value of. The counterions have a significant impact on

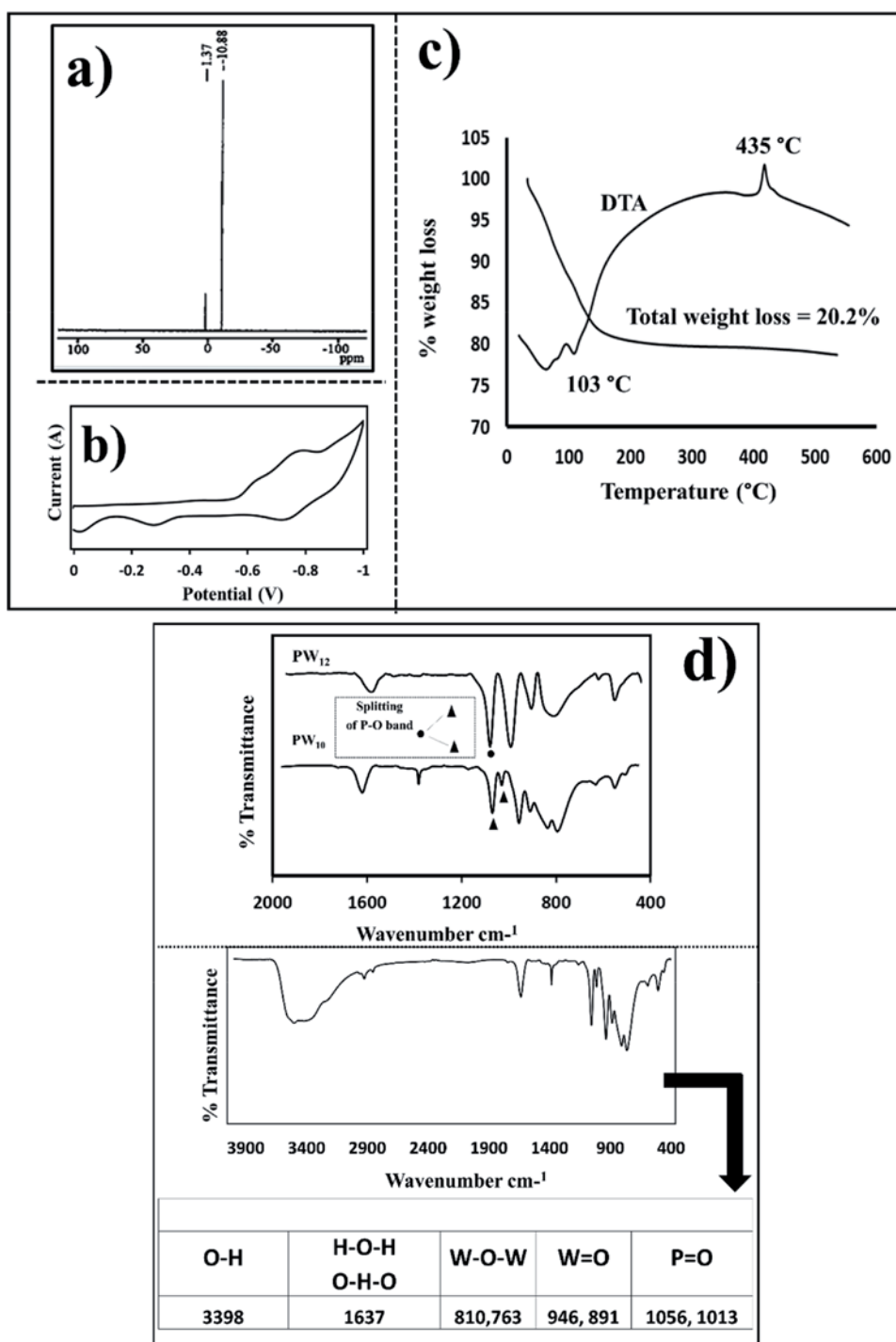


Figure 3.
 a. ^{31}P solution NMR of PW_{10} in D_2O . b. Cyclic voltammogram of PW_{10} in citrate buffer. c. TG-DTA of PW_{10} . d. FTIR of PW_{10} .

the NMR resonances, causing slight variations in the NMR values. Here, the observed $\delta = 10.88$ ppm confirms the formation of dilacunary phosphotungstate moiety.

The reduction potential of dilacunary species was measured in citrate buffer, as shown in **Figure 3b** obtained from a cyclic voltammetric experiment, in which glassy carbon Ag/AgCl was used as a working and a reference electrode, respectively. To prepare a buffer solution, 0.1 M KCl (electrolyte) was added to the 0.1 M freshly prepared citrate buffer [51]. The lacunary anion, consisting of a formal charge of (-7) , is said to undergo two processes in an aqueous buffer medium. The polyanion showed only one electron reduction in a water medium. However, it underwent a two-electron reduction process in an acidic medium. It was observed that, with a rising pH, the E° values for the reduction of $[\text{PW}_{10}\text{O}_{36}]^{-7}$ are shifted towards a more negative potential. In the case of a citrate buffer of pH 3.1, the E° value was changed from -0.8 V in water to -0.62 V. The dilacunary, being an electron-deficient species, accepts the electron, which results in the reduction potentials.

Further, the TGA analysis demonstrated the weight loss mainly in two stages (**Figure 3c**). An initial weight loss (19.1%) was observed from 50 to 250 °C, corresponding to the loss of adsorbed water as well as coordinated water from the polyanion structure. The DTA exhibited a broad endothermic peak followed by a sharp exothermic peak, corresponding to the degradation of the dilacunary species. Further, only 1% weight loss was observed and stable up to 550 °C, indicating its excellent thermal stability.

FTIR spectrum of PW_{10} (**Figure 3d**) showed the significant vibration of W-O-W at 810, 763 cm^{-1} and W = O terminal stretching vibrations at 946, 891 cm^{-1} . The prominent P-O band from parent phosphotungstate (PW_{12}) 1080 cm^{-1} was split into two new bands at 1056 and 1013 cm^{-1} , indicating the in-situ formation of dilacunary phosphotungstate. The observed band values of IR found a good agreement with the reported ones [50].

3.1.2 Characterization of the catalyst

As discussed earlier, the acidity was measured by two types of titrations. At first, the acidic strength along with nature as well as type of acidic sites of ZrO_2 and all the catalysts were determined by the potentiometric titration, and the obtained observations are given in **Table 1**. As evident from the table, after supporting with different %loading of PW_{10} to the support, the acidic parameters were increased progressively, which indicates the effective impregnation with the zirconia. This resulted in the main objective of the catalyst synthesis in the present work, i.e., upgrading the acidity, mainly *via* the Bronsted acidity available in the phosphotungstates. However, beyond 30% loading, only a slight increase in acidic properties was observed, which may be due to the blocking by excess loading, ultimately decreasing the number of availabilities of accessible active sites. Therefore, 30% was selected. Further, the strong correlation between results from potentiometric titration and n-butylamine titration validated that 30% loading of PW_{10} was appropriate. Therefore, $(\text{PW}_{10})_3/\text{ZrO}_2$ was optimized for detailed characterization and renamed as $\text{PW}_{10}/\text{ZrO}_2$.

The FTIR spectra are presented in **Figure 4a**. FTIR of ZrO_2 exhibited a broad band around 3500 cm^{-1} associated with an asymmetric stretching of $-\text{OH}$ (hydroxyl groups on surface) and aquo species. The H-O-H and O-H-O bending vibrations were observed at 1600 cm^{-1} and 1370 cm^{-1} , respectively. An additional band at 600 cm^{-1} of Zr-O-H bending vibration was also observed [40]. While the FTIR of $\text{PW}_{10}/\text{ZrO}_2$ demonstrated retention of significant peaks of PW_{10} at 885 cm^{-1} and 1043 (W=O), 1012 cm^{-1} (P-O), even after supporting on ZrO_2 .

Potentiometric titration					n-Butylamine titration	
Support/ Catalysts	Acidic strength (mV)	Types of acidic sites (meq/g)			Total no of acidic sites (meq/g)	Total acidity (mmol/g)
		Very Strong	Strong	Weak		
ZrO ₂	18	—	0.1	2.1	2.2	0.55
(PW ₁₀) ₁ /ZrO ₂	180	—	0.3	2.3	2.6	0.86
(PW ₁₀) ₂ /ZrO ₂	248	0.1	0.3	2.3	2.7	0.90
(PW10)3/ ZrO2	278	0.2	0.5	2.2	2.9	0.93
(PW ₁₀) ₄ /ZrO ₂	280	0.2	0.7	2.1	3.0	0.97

Table 1.
Acidity measurements of support and catalysts.

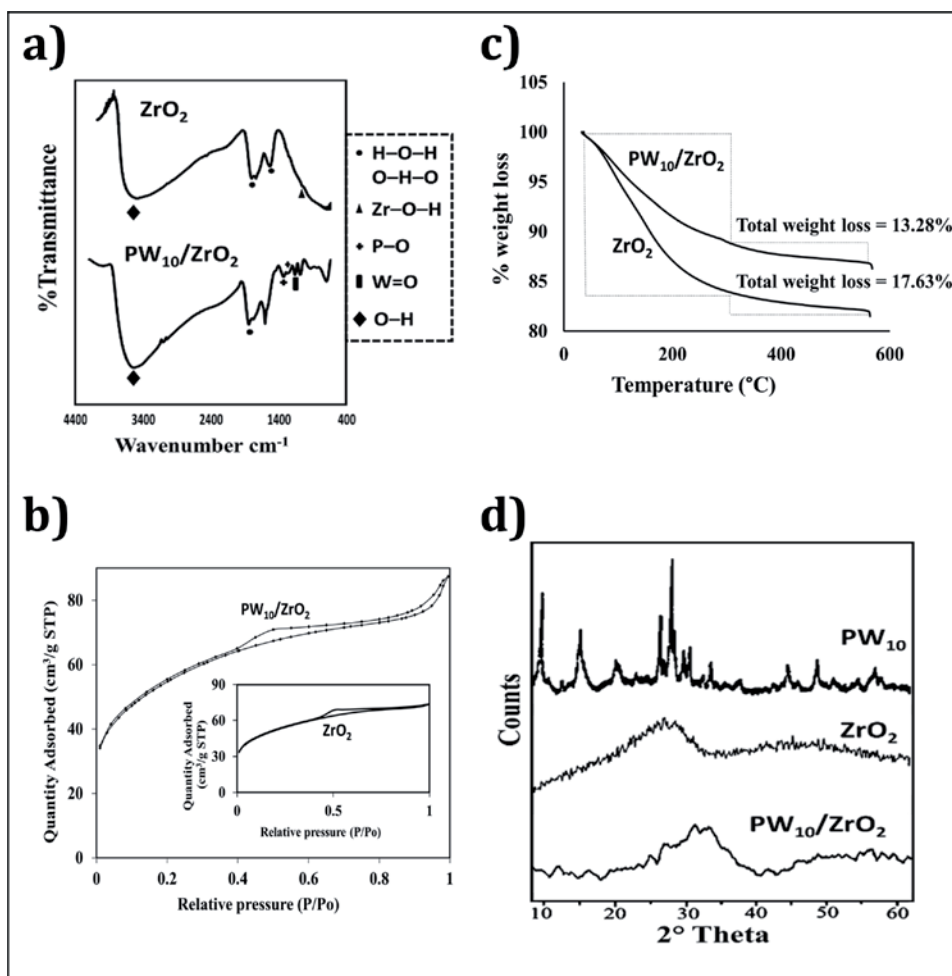
The surface area was measured by BET analysis, and the obtained surface area of ZrO₂ is 170 m²/g, whereas PW₁₀/ZrO₂ exhibited an increased surface area of 228 m²/g. This increase in the value clearly indicates the presence of PW₁₀ on the surface of zirconia, ensuring effective support. This is attributed to the good dispersion of dilacunary heteropoly species over the support surface without a significant pore blockage. Further, the N₂ adsorption-desorption isotherm of ZrO₂ (**Figure 4b**) exhibited a type IV isotherm with H₃ hysteresis loops. The material shows mesopores due to the occurrence of conspicuous hysteresis loops at high relative pressures and non-rigid aggregates of plate-like particles (slit-shaped pores) that exhibited weak interaction and capillary condensation associated with large pore channels [52]. The catalyst showed a similar isotherm type, which indicates the basic structure of zirconia is intact even after being supported with dilacunary species.

The TGA curves of support and catalyst are presented in **Figure 4c**. TGA of ZrO₂ showed the first weight loss observed around 15.4% up to 180°C due to the loss of physisorbed water molecules. Further, a second weight loss of 2.2% was observed because of dehydroxylation of zirconyl hydroxide, and it is stable up to 550°C. TGA of PW₁₀/ZrO₂ showed a total weight loss of 13.28%, in which the initial weight loss of 11.2% due to loss of adsorbed water molecules, and the final weight loss of 2.08% subjected to the loss of crystallization water, and further no weight loss was observed, making it stable up to 550°C.

The XRD patterns of PW₁₀, ZrO₂ and PW₁₀/ZrO₂ are given in **Figure 4d**. The characteristic crystalline diffraction peaks of PW₁₀ appeared in the 2θ range of 25°–35°, revealing the formation of dilacunary species and the observed peak values are in good agreement with the reported literature [50]. When looking after supporting with ZrO₂, there was a loss of crystallinity observed in PW₁₀/ZrO₂, resulting in an amorphous nature, which is identical to the XRD pattern of ZrO₂. This is also evident by another observation that the absence of all the characteristic peaks of PW₁₀ strongly reveals its homogeneous well dispersion on the surface of zirconia.

3.2 Catalytic evaluation

The esterification of levulinic acid with 1-butanol over PW₁₀/ZrO₂ was carried out to produce butyl levulinate (BL). However, it is well known and reported in literature

**Figure 4.**

a. FTIR spectra, b. N_2 adsorption-desorption isotherms, c. TGA curves, d. XRD patterns.

that initially, the reaction undergoes to form pseudo butyl levulinate, which is a cyclic intermediate that is further converted into butyl levulinate as a final product. The existence of strong Bronsted acidity in the catalyst contributes prominently towards the ester formation, which was reflected mainly in terms of selectivity from the detailed optimization presented in **Figure 5**.

At first, the set of experiments was performed by varying the amount of catalyst from 25 to 75 mg, keeping other parameters constant (**Figure 5a**). It was observed that with a minimum amount of catalyst (25 mg), the maximum conversion as well as selectivity of BL was achieved. However, further increasing the amount reduced the activity along with an increase in the pseudo butyl selectivity, which is subject to the blocking of active sites of the catalyst that hinders the reactants. To get the accurate findings by minimizing the personal error, each experiment throughout the optimization was carried out three times, and the observed errors are ± 1 .

Further, the influence of reaction time was monitored by varying it from 2 to 14 h in intervals of every two hours (**Figure 5b**). From the obtained data, it was found that

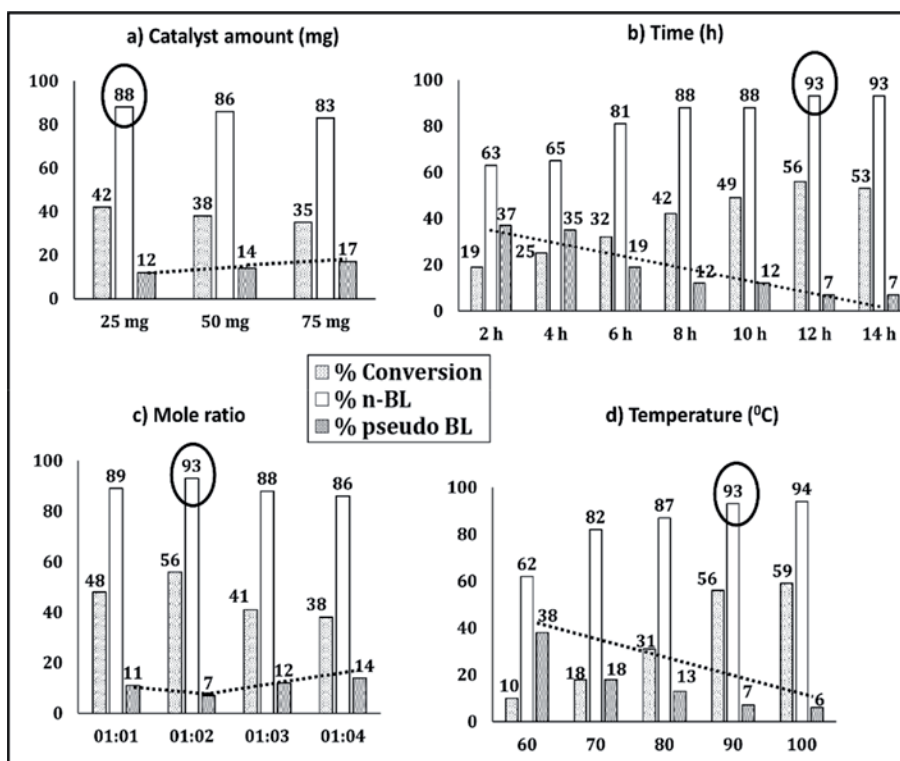


Figure 5.

a. Effect of catalyst amount. Mole ratio: 1:2, Temperature: 90°C, Time: 8 h; b. Effect of time. Mole ratio: 1:2, Catalyst amount: 25 mg, Temperature: 90°C; c. Effect of Mole ratio. Catalyst amount: 25 mg, Temperature: 90°C, Time: 12 h; d. Effect of temperature. Catalyst amount: 25 mg, Mole ratio: 1:2, Time: 12 h.

for 2 to 12 hours, the reaction proceeds gradually. Also, the decreased %selectivity of pseudo-BL decreased with an increase in time, highlighting the crucial impact of time on the reaction progression. However, upon further increasing the time, no change in the selectivity was observed as the reaction reached an equilibrium state.

The effect of the levulinic acid:1-butanol mole ratio was presented in **Figure 5c**. By increasing from 1:1 to 1:2, the conversion as well as BL formation increased. Further increasing the mole ratio led to a decrease in the pseudo-BL selectivity along with lower conversion rates, subject to the dilution of the reaction media, which decreases the overall activity.

By keeping the above optimized parameters, the role of temperature was observed. It is clearly seen from **Figure 5d** that by increasing the temperature from 60 to 70°C, the formation of pseudo-BL was decreased from 38 to 18%, which means the reaction is progressing towards the final step more effectively. Likewise, the maximum conversion as well as BL production was achieved by increasing the temperature up to 100°C. However, while keeping in mind the green parameters, 90°C was optimized since there is only 1% difference in the selectivity.

After careful evaluation of all the parameters, a maximum 56% conversion of levulinic acid and 93% selectivity of BL were achieved under the following optimized parameters: 25 mg (catalyst amount), 12 hours (time), 1:2 (mole ratio), 90 °C (temperature). The turnover number (TON) and turnover frequency (TOF) were found to be 1850 and 154 h⁻¹, respectively, which effectively lie within the industrial standards.

Further, industrial adaptability of the catalyst was studied *via* the scale-up trials up to 2,3,4 and 5 times, by keeping the same mole ratio, reaction time and temperature. The obtained results are summarized in **Table 2**.

3.3 Kinetics: Estimation of activation energy

In this study, the reactions at different temperatures (343, 353, 363, 373 K) with different times (4, 6, 8, 10, 12 hours) were carried out. Then, the graph of $1/(a-x)$ vs. time was plotted for all four temperatures, which gave the rate constant values and is summarized in **Table 3**. The obtained R^2 value and linear graph confirm the second-order kinetics. With these data, the activation energy was calculated from the obtained k values by the plot of $\ln k$ vs. $1/T$ (**Figure 6**). The obtained value confirms the truth of the reaction, as it exceeds the typical range, i.e., 25 kJ/mol observed for diffusion-controlled regime [53].

3.4 Control experiments

The control experiments were conducted to investigate the specific contribution of individual components present in the catalyst, and the resulting data are enumerated in **Table 4**. It was observed that, alone, ZrO_2 is not active for the product formation as it lacks the acidity, which is especially required in the esterification, which was already discussed in the introduction section. Herein, the catalytic activity of zirconia alone is obtained as expected. On the other hand, PW_{10} exhibited better activity with a significantly enhanced selectivity, as it possesses Bronsted acidic sites. Therefore, it is clear from both the data that, alone, PW_{10} and ZrO_2 are giving almost opposite results. Now, their combination PW_{10}/ZrO_2 showed the retained activity of PW_{10} .

	Reaction conditions			Results	
	Levulinic acid (ml)	1-butanol (ml)	Catalyst amount (mg)	%Conversion	%BL
Optimized Batch scale	1.09	1.83	25	56	93
Scale up (x2)	2.18	3.66	50	56	93
Scale up (x3)	3.27	5.49	75	56	93
Scale up (x4)	4.36	7.32	100	54	93
Scale up (x5)	5.09	9.2	125	54	93

Table 2.
Scale-up experiments.

Temperature (K)	Rate constant k ($M^{-1} \text{ min}^{-1}$)	R^2 value	Activation energy E_a (kJ/mol)
343	$4.12 \times 10^{-5} M^{-1} \text{ min}^{-1}$	0.9897	117
353	$5.30 \times 10^{-4} M^{-1} \text{ min}^{-1}$	0.9980	
363	$6.35 \times 10^{-5} M^{-1} \text{ min}^{-1}$	0.9905	
373	$4.23 \times 10^{-3} M^{-1} \text{ min}^{-1}$	0.9987	

Table 3.
Rate constants and activation energy.

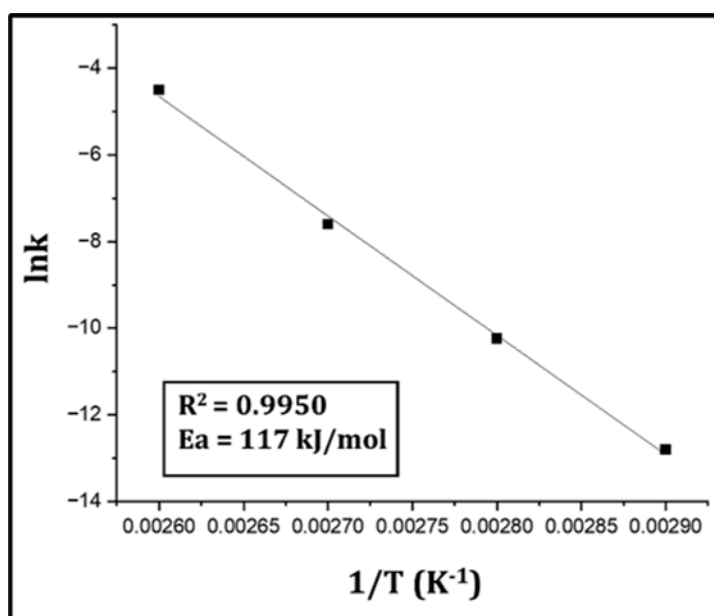


Figure 6.
lnk vs. 1/T graph.

Material	Amount (mg)	%Conversion	%BL	%pseudo-BL
ZrO ₂	19	12	25	75
PW ₁₀	5.8	60	93	07
PW ₁₀ /ZrO ₂	25	56	93	07

**Reaction conditions: 1:2/12 h/ 90°C.*

Table 4.
Control experiments with PW₁₀ ZrO₂ and PW₁₀/ZrO₂.*

It is important to note that the systematic design of a catalyst by keeping in mind important facts such as the selection of suitable support, method of supporting and leaching, can lead to a targeted as well as successful catalyst synthesis. Hence, it can be stated that we have successfully upgraded the acidity of support, and that confirms the true heterogeneous nature and successful synthesis of PW₁₀/ZrO₂. It must be noted that the strong acidic sites are the major active component that promotes the reaction in the forward direction and hence effectively converts the intermediate into the final product.

3.5 Regeneration and recycling of the catalyst

The catalyst was regenerated by following this procedure. After the completion of the reaction, the reaction mixture was diluted with dichloromethane and allowed for the centrifugation. The catalyst was separated, filtered and washed with double-distilled water with an ethanol wash to completely remove any adsorbed impurities over there. After that, the obtained residue was dried at 100 °C for 2 hours, further designated as R-PW₁₀/ZrO₂ and reused for another catalytic run. It exhibited excellent

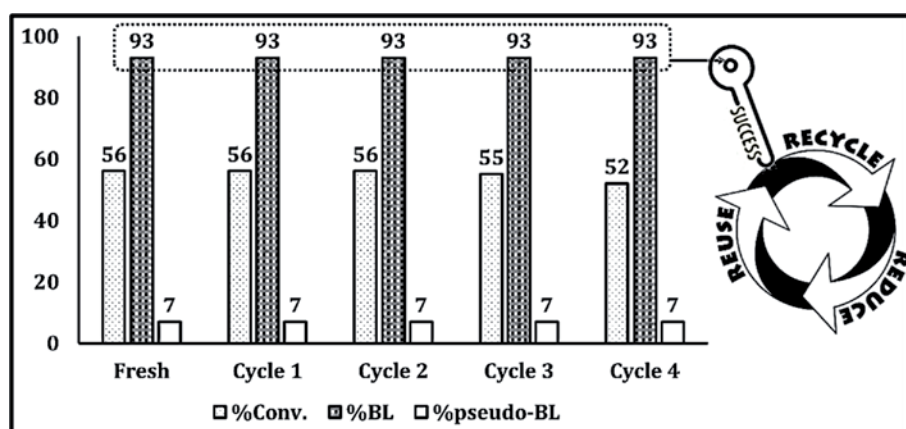


Figure 7.
Recycling experiments.

activity and stability up to four catalytic cycles (Figure 7), confirming the intact, sustainable nature of the catalyst that can be economically viable.

3.6 Characterization of R-PW₁₀/ZrO₂

The regenerated catalyst was further characterized by XRD, FTIR and acidity measurements, and presented in Figure 8a, b and c, respectively. A similar pattern observed from XRD, as well as the retention of characteristic peaks in FTIR, clearly depicts that there are no structural changes after regeneration. Also, the obtained acidic parameters are in good agreement with the fresh catalyst.

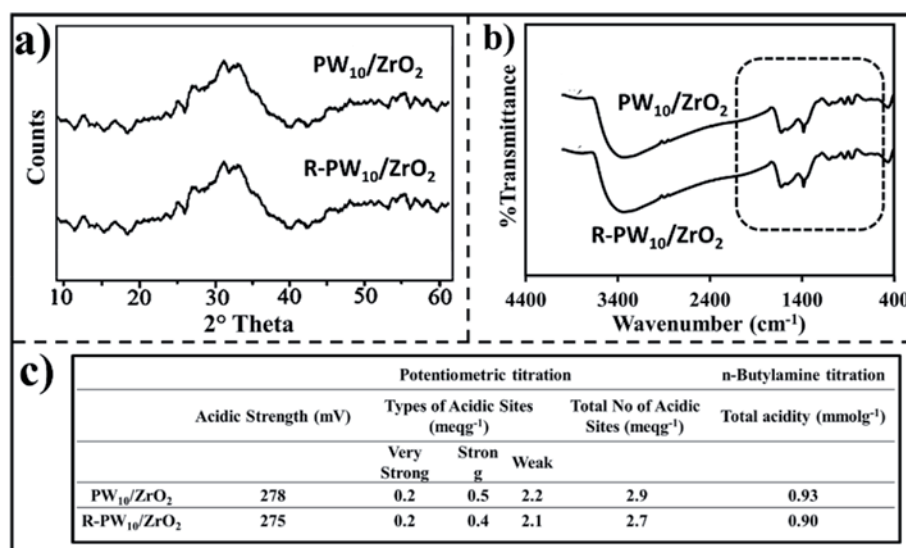


Figure 8.
a. XRD of fresh and regenerated catalysts; b. FTIR of fresh and regenerated catalysts; c. Acidity measurements of fresh and regenerated catalysts.

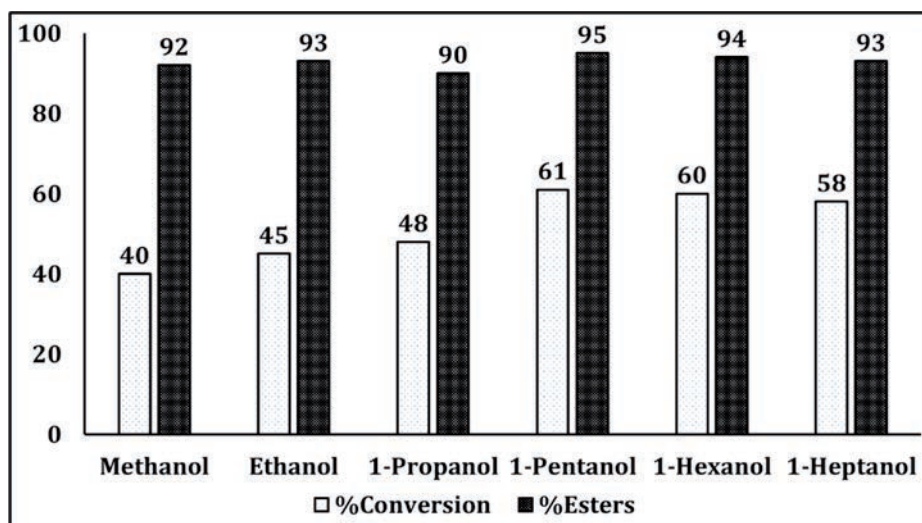


Figure 9.
 Esterification of levulinic acid with different alcohols.

3.7 Catalytic versatility of PW_{10}/ZrO_2 towards renewable C_1 - C_7 alcohols

The dynamic catalytic activity of PW_{10}/ZrO_2 towards the C_1 - C_7 bio-based linear alcohols was evaluated by conducting the esterification with levulinic acid. The obtained results are presented in **Figure 9**. With an increase in the carbon chain length, the conversion increases up to C_5 . Further, for C_6 and C_7 , the obtained results

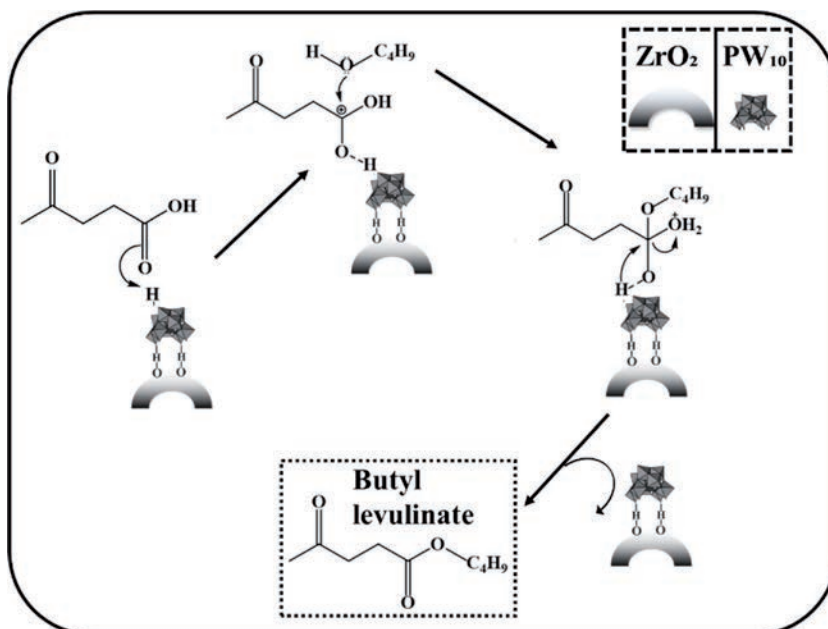


Figure 10.
 Probable mechanistic pathway for the formation of BL.

were off-trend, still significant, which corresponds to the steric effect that restricts the nucleophilic attack and the slower diffusion of molecules. But these findings are from the optimized conditions of the levulinic acid and 1-butanol system. So, further modification in optimization can lead to better conversion rates. In this regard, the preset catalyst can be a good contributor to the industrial sectors.

3.8 Reaction mechanism

The esterification of levulinic acid with n-butanol proceeds *via* the traditional Fischer mechanism [42], and we have anticipated the same mechanistic pathway here. According to this, at first, the levulinic acid gets adsorbed on PW_{10}/ZrO_2 , resulting in the formation of a protonated acid intermediate. This then increases the electrophilicity of the carbonyl carbon. Consequently, the carbonyl carbon is attacked by the nucleophilic oxygen of n-butanol to form a tetrahedral oxonium ion intermediate. Which then loses a water molecule and produces n-butyl levulinate. The reaction scheme is given in **Figure 10**.

4. Conclusion

The present study is a successful attempt to upgrade the acidity of zirconia by the addition of PW_{10} , for the efficient synthesis of biofuel additives, *via* esterification. Further, its careful evaluation revealed the 56% conversion along with 93% selectivity of butyl levulinate, under the mild reaction conditions (1:2, 25 mg, 12 hours, 90°C). The control experiments further substantiated the importance of acid site tuning in driving the esterification process. To validate its applicability, the catalyst was also tested under different scale-up trials. Based on cumulative findings, PW_{10}/ZrO_2 proves to be a promising candidate for commercialization due to the following main key points: (i) its stable activity over four catalytic cycles with minimal loss, (ii) the excellent scalable approach from 2 to 5 times and (iii) its applicability in converting biomass-derived acids to fuel-range esters under varied operating conditions. In summary, this work affirms that the rational design of lacunary phosphotungstates-based catalysts supported on metal oxide supports can lead to efficient, scalable and sustainable chemical processes.

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Conflict of interest

The authors declare no conflict of interest.

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Zirconia-Based Materials for Aerospace Applications

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Abstract

This chapter discusses the importance of zirconium-based materials in the aerospace industry, highlighting their need for high-performance applications due to their properties, such as low weight, good resistance to high temperatures and corrosion. The basic aspects of zirconium and its compounds are analyzed and the crystal structure, physical and mechanical characteristics important for severe applications are highlighted. A detailed description is dedicated to specific applications, illustrating the use of zirconium-based materials in critical components of aircraft engines, thermal protection systems for space vehicles, high-performance sensors, and equipment for hostile environments. Potential emerging applications, such as lightweight structural elements and components for braking systems, are also explored. Finally, the chapter identifies current challenges related to cost, processability, and long-term reliability. Research and development directions aimed at improving performance and expanding the scope of applicability are presented, along with anticipated future trends in the use of advanced ceramic materials in the aerospace sector.

Keywords: zirconia, PSZ, TSP, turbojet engines, TBCs—Thermal barrier coatings

1. Introduction

The aerospace industry, perpetually advancing and propelled by increasingly stringent requirements regarding performance, safety, and efficiency, has always been a driving force for innovation in the field of materials. In this context, ceramic matrix composites (CMCs), thermal barrier coatings (TBCs), and environmental barrier coatings (EBCs) are increasingly used in high-temperature applications in the energy and transportation industries [1], offering novel solutions to address the challenges imposed by traditional metal alloys. In recent years, there has been an increased need for these materials that exhibit remarkable properties in sensitive technological contexts, from jet engine components subjected to extreme temperatures to thermal protection systems (TPSs) for space vehicles. Zirconium (Zr) and its compounds are unique in the high-performance materials market, and their distinct characteristics make them significant candidates for advanced aerospace applications. The chemical reactivity of zirconium, a transition metal, is moderate; it creates a diverse range of compounds, particularly ceramic oxides, which have the most

desirable properties for the severe operational environments encountered in the aerospace industry.

The ability of zirconia (zirconium oxide, ZrO_2) to exist in different crystalline forms (allotropic phases) and to be stabilized in specific structures by doping with other metal oxides opens up a wide horizon of possibilities for optimizing mechanical, thermal, and chemical properties. From significantly increasing toughness through phase transformation mechanisms to providing effective thermal barriers against extreme temperatures, zirconia-based materials demonstrate a remarkable balance between performance and versatility [2].

This chapter presents a thorough scientific review of zirconium-based materials, focusing on their applicability and use in the field of aerospace engineering. The first stage of this study will involve a thorough analysis of the intrinsic physicochemical characteristics of elemental zirconium and its various chemical compounds, in order to develop a complete understanding of the fundamental qualities that make these materials extremely beneficial for this technologically demanding industry. The different types of zirconium-containing materials that are either in use or have a great deal of potential for use in aerospace applications will then be systematically reviewed. These materials include protective surface treatments, zirconium matrix composites (ZMCs), tetragonal zirconia polycrystal (TZP), and partially stabilized zirconia (PSZ). Last but not least, we will pay special attention to presenting specific applications in the aerospace industry, illustrating how these materials are integrated into components and subcomponents of aircraft and space vehicles prone to thermal shock. Finally, we will discuss current challenges and future prospects in the use of zirconium-based materials, highlighting research and development directions that could further expand the impact of these materials in tomorrow's aviation and space exploration.

2. Zirconia: Features, applications, and challenges

2.1 Fundamental properties of zirconium and zirconium-based materials

Zircon (ZrSiO_4) typically occurs as well-defined crystals, especially in igneous rocks, although it can occasionally be found as aggregates of irregular grains in sedimentary or metamorphic rocks. Its crystal structure belongs to the tetragonal system, being classified in the ditetragonal-bipyramidal ($4/\text{mmm}$) class. X-ray diffraction analyses have elucidated its internal structure, revealing an ionic network consisting of SiO_4^{4-} anionic groups and Zr^{4+} cations, each zirconium ion being coordinated by eight oxygen ions. The crystal habit of zircon is predominantly short prismatic or isometric, rarely developing tetragonal-bipyramidal forms, from a crystallographic point of view denoted by the symbols $\{111\}$ and $\{101\}$ [3].

It is a nonsilicate mineral (more precisely, an orthosilicate) containing zirconium (Zr) in the +4 oxidation state. It crystallizes in the tetragonal crystal system and is the main representative of a group of minerals called the zircon group. This group includes structurally and chemically related minerals, in which Zr^{4+} may be partially replaced by Th^{4+} (tetravalent thorium cation), Hf^{4+} (tetravalent hafnium cation), and sometimes U^{4+} (tetravalent uranium cation) [4]. Chemically, zircon is composed mainly of zirconium (Zr), representing about 49.5% by mass, and silicon in the form of silicon dioxide (SiO_2), constituting about 32.9%. Impurities are almost always present, including frequently iron (III) oxide (Fe_2O_3) in small proportions (around 0.35%), often calcium oxide (CaO) with a variable concentration (between 0.05 and

4%), and sometimes aluminum oxide (Al_2O_3). A constant presence, but in significant quantities (between 4 and 16%), is hafnium oxide (HfO_2). Also, yttrium oxide (Y_2O_3) and, sometimes, rare earth oxides can be frequently found in the composition of zircon, and their concentration can reach up to 16% in certain cases. In some specific varieties, other chemical elements can also be identified in minor quantities [5].

Zircon can occur in a variety of colors, depending on impurities and the radiation-modified crystal structure. It is colorless when very pure (in this form, it is a substitute for diamond, known as “Matura diamond”). It is typically yellow in color but can also appear orange or red. Very rarely, it is green and usually occurs due to natural radiation (thorium (Th) and uranium (U) content) [6].

Zirconium is a highly active metal which, like aluminum, seems quite passive because of its stable, cohesive, protective oxide film, which is always present in air or water. Massive zirconium does not burn in air, but oxidizes rapidly above 600°C. Clean zirconium plate ignites spontaneously in oxygen of approximately 2 MPa, but the autoignition pressure drops as the metal thickness decreases. It is resistant to corrosion by water and steam, mineral acids, strong alkalies, organic acids, salt solutions, and molten salts. This property is attributed to the presence of a dense adherent oxide film that forms at ambient temperatures. Any break in the film reforms instantly and spontaneously in most environments [7]. **Table 1** shows the physical properties of zirconium.

Property	Value	Unit
Atomic weight	91.22	g/mol
Density at 25°C	6.5107	g/cm^3
Crystal structure of α -Zr – Type	Hexagonal close-packed (HCP)	—
Crystal structure of α -Zr – Space group	$P6_3/mmc$	—
Crystal structure of α -Zr – Lattice parameter a	0.3231	nm
Crystal structure of α -Zr – Lattice parameter c	0.5146	nm
Crystal structure of α -Zr – c/a ratio	1.5927	—
Crystal structure of β -Zr – Type	Body-centered cubic (BCC)	—
Crystal structure of β -Zr – Space group	$Im3m$	—
$\alpha \rightarrow \beta$ phase transition temperature	862.85 ± 5	°C
Melting point	1851.85 ± 10	°C
Boiling point	4303.85 ± 100	°C
Vapor pressure – α -Zr	$\log_{10}P = 8.956 \pm 0.080 - (30,810 \pm 240)/T$	$\log_{10}(P \text{ in kPa}), T \text{ in K}$
Vapor pressure – Liquid Zr	$\log_{10}P = 8.547 \pm 0.080 - (29,940 \pm 240)/T$	$\log_{10}(P \text{ in kPa}), T \text{ in K}$
Heat of $\alpha \rightarrow \beta$ transition	3.89 ± 0.08	kJ/mol

Property	Value	Unit
Heat of fusion (melting)	18.8 ± 2.1	kJ/mol
Heat of boiling	573.2 ± 4.6	kJ/mol
Heat of sublimation at 25°C	600.8	kJ/mol
Molar heat capacity – α -Zr	$C_p = 22.857 + 8.970 \times 10^{-3} \cdot T - 0.69 \times 10^{-5} T^2$	J/(mol·K), T in K
Molar heat capacity – β -Zr	$C_p = 21.493 + 6.586 \times 10^{-3} \cdot T + 36.718 \times 10^{-5} T^2$	J/(mol·K), T in K
Entropy at 25°C	38.99 ± 0.46	J/(mol·K)
Thermal conductivity 0–10 K	$\kappa = 1.08189 \times 10^{-1} \cdot T + 1.65524 \times 10^{-3} \cdot T^2 - 2.63239 \times 10^{-4} \cdot T^3$	W/(m·K), T in K
Thermal conductivity 10–25 K	$\kappa = 0.94865 + 0.344316 \cdot T - 1.79663 \times 10^{-2} \cdot T^2 + 2.82821 \times 10^{-4} \cdot T^3$	W/(m·K), T in K
Thermal conductivity 25–80 K	$\kappa = 1.80754 - 5.50950 \times 10^{-2} \cdot T + 7.61839 \times 10^{-4} \cdot T^2 - 3.72006 \times 10^{-6} \cdot T^3$	W/(m·K), T in K
Thermal conductivity 80–500 K	$\kappa = 0.518009 - 2.36738 \times 10^{-3} \cdot T + 6.28905 \times 10^{-6} \cdot T^2 - 5.58159 \times 10^{-9} \cdot T^3$	W/(m·K), T in K
Thermal conductivity 500–1900 K	$\kappa = 0.244486 - 2.3982 \times 10^{-4} \cdot T + 2.27218 \times 10^{-7} \cdot T^2 - 6.24923 \times 10^{-11} \cdot T^3$	W/(m·K), T in K
Electrical resistivity at 5°C	43.74 ± 0.08	$\mu\Omega\cdot\text{cm}$
Temperature coefficient of resistivity (0–200°C)	42.5×10^{-4}	per °C
Elastic modulus – C_{11}	143.5 ± 0.2	GPa
Elastic modulus – C_{12}	72.5 ± 0.2	GPa
Elastic modulus – C_{13}	65.4 ± 0.2	GPa
Elastic modulus – C_{33}	164.9 ± 0.2	GPa
Elastic modulus – C_{44}	32.07 ± 0.03	GPa
Polycrystalline – Young's modulus	97.1	GPa
Polycrystalline – Shear modulus	36.5	GPa
Polycrystalline – Bulk modulus	95.4	GPa
Poisson's ratio	0.33	—
Brinell hardness number	90–130	HB
Thermal expansion $\perp$ c-axis	$LTC = L_0 \cdot (1 + 5.145 \times 10^{-6} \cdot T)$	T in °C
Thermal expansion $\parallel$ c-axis	$LTC = L_0 \cdot (1 + 9.213 \times 10^{-6} \cdot T - 6.385 \times 10^{-9} \cdot T^2 + 18.491 \times 10^{-12} \cdot T^3 - 9.856 \times 10^{-15} \cdot T^4)$	T in °C
Volumetric expansion (single crystal)	$VTC = V_0 \cdot (1 + 19.756 \times 10^{-6} \cdot T - 7.023 \times 10^{-9} \cdot T^2 + 19.146 \times 10^{-12} \cdot T^3 - 9.980 \times 10^{-15} \cdot T^4)$	T in °C
Thermal expansion (polycrystalline)	$LTC = L_0 \cdot (1 + 6.499 \times 10^{-6} \cdot T - 2.096 \times 10^{-9} \cdot T^2 + 6.108 \times 10^{-12} \cdot T^3 - 3.259 \times 10^{-15} \cdot T^4)$	T in °C

Adapted after Stefan [5] and Nielsen et al. [7].

Table 1.
Specific properties of zirconium.

Chemically, zirconium crystals are insoluble and do not melt in acids. However, in powder form, they can be decomposed by melting with sodium carbonate (Na_2CO_3), and the resulting solution in dilute hydrochloric acid (HCl) produces a reaction specific to zirconium, coloring litmus paper orange. It reacts with oxygen and nitrogen in the atmosphere, forming thin layers of oxides and nitrides on the surface, which give it good corrosion resistance. Interestingly, zirconium becomes superconductive when alloyed with niobium, an important property for certain technological applications.

Figure 1 shows the solid-state structure of zirconium.

Zirconium has both stable and radioactive isotopes. The latter have specific half-lives. **Figure 2** shows the radioactive isotopes of zirconium and their half-lives.

Due to its specific characteristics, zirconium is a perfect candidate for nuclear applications, being used especially in the production of nuclear reactor cores because it is corrosion resistant and does not absorb neutrons rapidly. On the other hand, it is used as a thermal barrier in turbojet engines due to its low thermal conductivity, high melting point, and thermal stability, protecting components from extreme temperatures and improving engine efficiency [9].

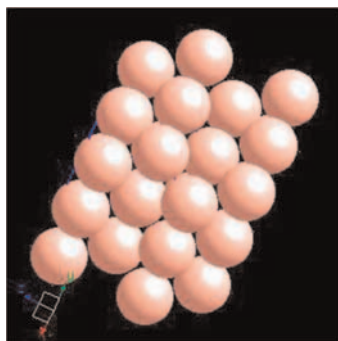


Figure 1.
 Solid-state structure of zirconium [8].

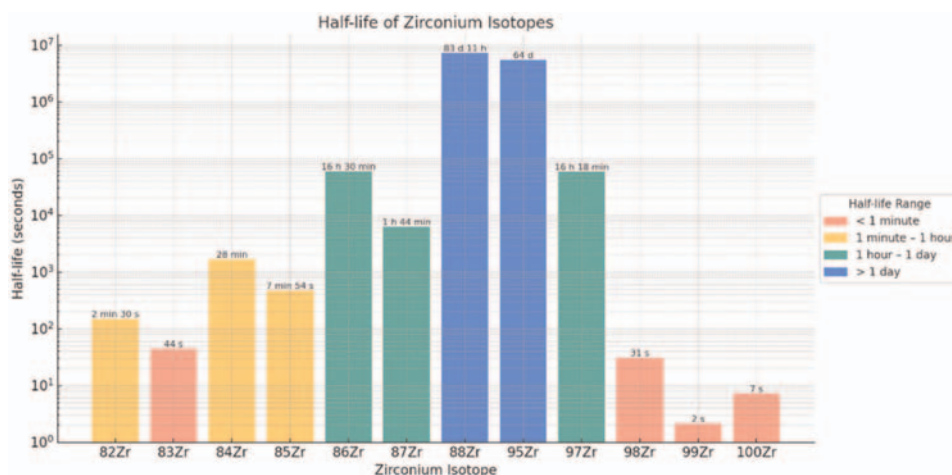


Figure 2.
 Radioactive isotopes of zirconium and their half-lives.

2.2 Zirconium and its compounds: Essential mechanical and chemical properties

Zirconium-based materials are valuable candidates for structural and functional applications in the aerospace industry due to their remarkable mechanical properties. These materials have the ability to be formulated to achieve high tensile, compressive, and bending values, which is essential for components that are subjected to intense stress during flight or under extreme operational conditions. Furthermore, their significant hardness allows them to resist abrasion and wear, extending the components' service life. A particularly important aspect is toughness, the ability of the material to resist crack propagation. Through advanced processing and alloying techniques, the toughness of zirconia can be significantly improved, making it suitable for applications where reliability is critical. In terms of creep behavior, i.e. slow plastic deformation under constant load at elevated temperatures, zirconium-based materials demonstrate superior strength compared to many metal alloys, maintaining their structural integrity in demanding thermal environments [10, 11].

In addition to superior mechanical properties, zirconium and its compounds also excel in terms of chemical properties, an essential factor in the aggressive environment encountered in aerospace applications [2]. Also, a defining characteristic is resistance to corrosion and oxidation at high temperatures, allowing zirconium-based materials to maintain their performance in contact with hot gases and oxidizing environments, such as those found in jet engines. This type of resistance is crucial for the durability of components directly exposed to the flue gas flow. Furthermore, chemical compatibility with other materials used in the aerospace industry, such as nickel-based superalloys or other ceramic materials, is an important aspect for ensuring the integrity of complex assemblies. Undesirable chemical interactions at interfaces can compromise the performance and reliability of aerospace systems, and zirconium and its compounds demonstrate good compatibility in many relevant material combinations [12, 13].

The overall physical properties of ceramics are closely related to these atomic bonds. Because all valence electrons are involved in ionic or covalent bonds, ceramics generally have low electrical and thermal conductivity, often being used as dielectrics and thermal insulators. However, there are notable exceptions, such as silicon carbide (SiC) or gallium arsenide (GaAs), which can exhibit semiconducting properties, or materials with piezoelectric properties [14]. Strong covalent bonds make ceramics ideal as refractory materials by imparting them high melting temperatures, often exceeding metals. The chemical stability of the bonds provides them with high chemical inertness and superior corrosion resistance compared to metals. In the case of ionic bonds, the stability varies with the charge of the ions and the distance between them, revealing significant differences in properties, such as melting point and chemical reactivity (for example: NaCl vs. Al_2O_3).

The strong nature of the atomic bonds determines a high rigidity of ceramic materials. Except in the temperature range close to the melting point, ceramics are brittle and fracture without significant plastic deformation. Surface or internal defects, such as cracks or porosities, can significantly reduce the tensile strength, while the compressive behavior is generally much better. An important category is represented by refractory oxide ceramic materials, whose intrinsic stability is governed by the free enthalpy of the dissociation reaction of the oxide into its component elements ($\text{MO}_2 \rightarrow \text{M} + \text{O}_2$ (metal + oxygen)). The material's high enthalpy values (ΔH) indicate that it has good thermal stability at low temperatures, and positive free reaction enthalpy Gibbs free energy change (ΔG) values indicate that it resists atmospheric reduction for most oxides until around 1800°C [15]. Oxides like

ZrO₂ and HfO₂ can undergo polymorphic transformations at specific temperatures, which require stabilizing additives to ensure a favorable crystalline structure [16].

Refractory oxides have low coefficient of thermal expansion (about 7–10°C) and low thermal conductivity, making them excellent thermal insulators. Thermal conductivity is determined by the microstructure and the interaction of phonons with the vibrations of the crystalline grid. Due to their insulating nature, refractory oxides' electrical resistivity can vary based on the oxide's nature, temperature, porosity, impurities, and environmental conditions. It is a combination of ionic and electronic conductivity. The fragility and microhardness of these materials are also influenced by porosity, microstructure, and the presence of impurities [17, 18].

2.3 Zirconia structure: Characteristics

ZrO₂ has been extensively investigated and analyzed due to its variety of applications, related to its chemical and physical properties, including mechanical properties, high resistance to high temperatures, low electrical conductivity, permeability, and biocompatibility. Zirconia is widely used, among other things, as a transparent optical component and electrochemical capacitor [5].

ZrO₂ is obtained from Zr by acid or coke reduction and is an extremely refractory material. The structure of zirconia or baddeleyite, as it is called, is of type C 43. Other compounds with this structure are HfO₂, cobalt antimonide (CoSb₂), and silver telluride (Ag₂Te) [20]. **Figures 3 and 4** show the crystal structure of baddeleyite (ZrO₂ in its monoclinic form).

Simple monoclinic primitive vectors [5, 19]:

$$A_1 = a \hat{X}$$

$$A_2 = a \hat{Y}$$

$$A_3 = c \cos(\beta) \hat{X} + c \sin(\beta) \hat{Z}$$

Basis vectors [5, 19]:

$$B_1 = +x_1 A_1 + y_1 A_2 + z_1 A_3 = +[x_1 a + z_1 c \cos(\beta)] \hat{X} + y_1 b \hat{Y} + z_1 c \sin(\beta) \hat{Z} \quad (\text{Zr}) \quad (4e)$$

$$B_2 = +x_1 A_1 + (\frac{1}{2} - y_1) A_2 = +[x_1 a + (\frac{1}{2} + z_1) c \cos(\beta)] \hat{X} + (\frac{1}{2} - y_1) b \hat{Y} + (\frac{1}{2} + z_1) c \sin(\beta) \hat{Z} \quad (\text{Zr}) \quad (4e)$$

$$B_3 = -x_1 A_1 - y_1 A_2 - z_1 A_3 = -[x_1 a + z_1 c \cos(\beta)] \hat{X} - y_1 b \hat{Y} - z_1 c \sin(\beta) \hat{Z} \quad (\text{Zr}) \quad (4e)$$

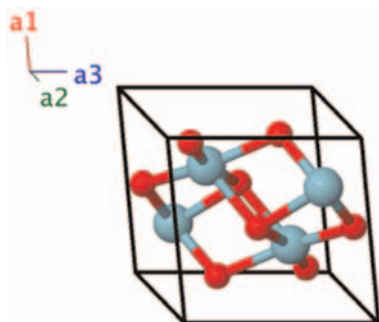


Figure 3.
Zirconia structure [19].

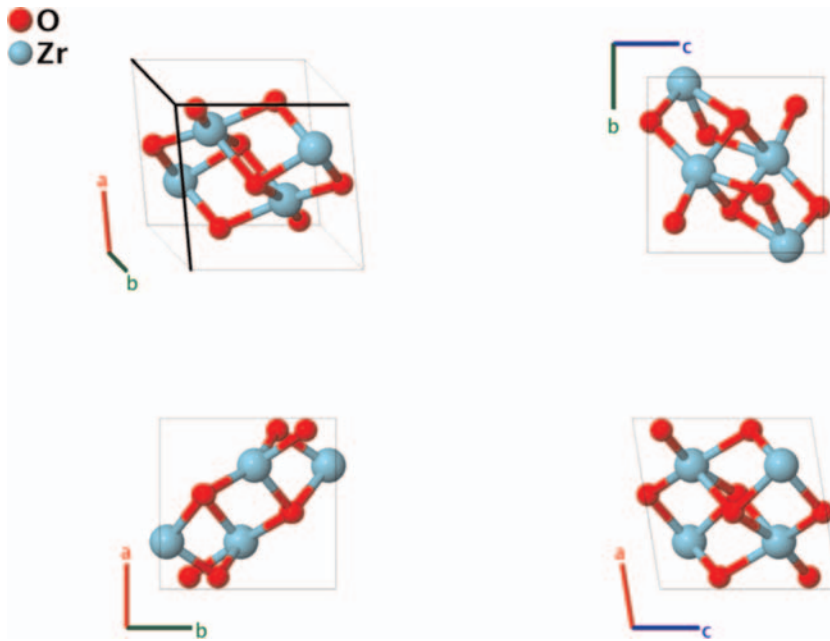


Figure 4.
Isometric views of the crystal structure of baddeleyite [19].

B_4	$= -x_1A_1 + (\frac{1}{2} + y_1)A_2 =$	$-[x_1 a - (\frac{1}{2} - z_1) c \cos(\beta)] \hat{X} + (\frac{1}{2} + y_1) b \hat{Y}$	(Zr)	(4e)
	$+ (\frac{1}{2} - z_1)A_3$	$+ (\frac{1}{2} - z_1) c \sin(\beta) \hat{Z}$		
B_5	$= +x_2A_1 + y_2A_2 + z_2A_3 =$	$+ [x_2 a + z_2 c \cos(\beta)] \hat{X} + y_2 b \hat{Y}$	(O-I)	(4e)
		$+ z_2 c \sin(\beta) \hat{Z}$		
B_6	$= +x_2A_1 + (\frac{1}{2} - y_2)A_2 =$	$+ [x_2 a + (\frac{1}{2} + z_2) c \cos(\beta)] \hat{X} + (\frac{1}{2} - y_2) b \hat{Y}$	(O-I)	(4e)
	$+ (\frac{1}{2} + z_2)A_3$	$+ (\frac{1}{2} + z_2) c \sin(\beta) \hat{Z}$		
B_7	$= -x_2A_1 - y_2A_2 - z_2A_3 =$	$-[x_2 a + z_2 c \cos(\beta)] \hat{X} - y_2 b \hat{Y} - z_2 c \sin(\beta) \hat{Z}$	(O-I)	(4e)
B_8	$= -x_2A_1 + (\frac{1}{2} + y_2)A_2 =$	$-[x_2 a - (\frac{1}{2} - z_2) c \cos(\beta)] \hat{X} + (\frac{1}{2} + y_2) b \hat{Y}$	(O-I)	(4e)
	$+ (\frac{1}{2} - z_2)A_3$	$+ (\frac{1}{2} - z_2) c \sin(\beta) \hat{Z}$		
B_9	$= +x_3A_1 + y_3A_2 + z_3A_3 =$	$+ [x_3 a + z_3 c \cos(\beta)] \hat{X} + y_3 b \hat{Y}$	(O-II)	(4e)
		$+ z_3 c \sin(\beta) \hat{Z}$		
B_{10}	$= +x_3A_1 + (\frac{1}{2} - y_3)A_2 =$	$+ [x_3 a + (\frac{1}{2} + z_3) c \cos(\beta)] \hat{X} + (\frac{1}{2} - y_3) b \hat{Y}$	(O-II)	(4e)
	$+ (\frac{1}{2} + z_3)A_3$	$+ (\frac{1}{2} + z_3) c \sin(\beta) \hat{Z}$		
B_{11}	$= -x_3A_1 - y_3A_2 - z_3A_3 =$	$-[x_3 a + z_3 c \cos(\beta)] \hat{X} - y_3 b \hat{Y} - z_3 c \sin(\beta) \hat{Z}$	(O-I I)	(4e)
B_{12}	$= -x_3A_1 + (\frac{1}{2} + y_3)A_2 =$	$-[x_3 a - (\frac{1}{2} - z_3) c \cos(\beta)] \hat{X} + (\frac{1}{2} + y_3) b \hat{Y}$	(O-I I)	(4e)
	$+ (\frac{1}{2} - z_3)A_3$	$+ (\frac{1}{2} - z_3) c \sin(\beta) \hat{Z}$		

Zirconia exhibits polymorphism, adopting different crystal structures depending on temperature. Up to 1100°C, the stable phase is monoclinic. With increasing temperature above this threshold, ZrO_2 undergoes a rapid and reversible phase transformation to a tetragonal structure. At an even higher temperature, around 2370°C, a new structural transition to a cubic form occurs. This stability of the cubic structure at extreme temperatures contributes to the high strength of ZrO_2 under such conditions. The phase transformation from monoclinic to tetragonal is an instantaneous and reversible process, characterized by a volume contraction upon heating and a corresponding expansion upon cooling. This volume variation, estimated to be

between 3 and 5%, generates significant internal stresses in the material, representing a major challenge as it can lead to the appearance and propagation of cracks, affecting the structural integrity of components manufactured from pure ZrO_2 [5].

This structural instability, caused by volumetric phase transformations, has a negative impact on the mechanical properties of the material, leading to its degradation. An effective strategy to circumvent this problem consists in the controlled addition of stabilizing oxides into the zirconia crystal lattice, resulting in what is called partially or fully stabilized zirconia. Common additives include calcium oxide (CaO), magnesium oxide (MgO), and yttrium oxide (Y_2O_3), whose metal ions (cations) have ionic radii similar to that of the Zr^{4+} ion [21, 22]. The ionic radii of Mg^{2+} (0.78 Å), Ca^{2+} (1.06 Å), and Y^{3+} (1.06 Å) are close enough to the ionic radius of Zr^{4+} (0.87 Å) to allow the formation of solid solutions by isomorphic substitution between these oxides and ZrO_2 . This substitution favors crystallization in a cubic system, resulting in stabilized cubic zirconia. Such a ceramic material is distinguished by its refractory and inert character, since destructive phase transitions that occur upon heating and cooling are eliminated [21, 23].

Interestingly, the volume expansion associated with the structural transformation of ZrO_2 from the monoclinic to the tetragonal phase is exploited in the production of certain types of ZrO_2 with superior strength and hardness, intended for structural and mechanical applications. This transformation mechanism, controlled by microstructure and additives, is the basis for the increase in toughness of the material. There are several mechanisms by which the presence of particles with a tetragonal structure in a zirconia matrix can lead to an increase in the hardness of the material. These complex mechanisms are mainly influenced by the specific size of these particles, the heat treatment regime applied to the material, and the nature of the stabilizing additives incorporated into its structure [5].

2.4 Types of zirconia-based materials used in aerospace applications

Zirconia is used for thermal barriers because it has a high melting point (approximately 2700°C), low intrinsic thermal conductivity (approximately 2.0–2.5 W/m-K), and a relatively high coefficient of thermal expansion, making it an ideal ceramic material for protecting nickel-based superalloy components for high-temperature TBC applications. Dopants in oxide alloys, such as Y_2O_3 or rare earth oxides (e.g., ytterbium (III) oxide (Yb_2O_3) and gadolinium (III) oxide (Gd_2O_3)), are added to stabilize zirconia and preserve the phases at high temperatures, a particularly favorable metastable tetragonal or cubic phase structure, which suppresses the deleterious transformation of the tetragonal martensitic phase to the monoclinic phase during operation [24, 25].

Partially stabilized zirconia (PSZ) represents an important class of advanced ceramic materials, obtained by the controlled addition of stabilizing oxides, such as yttrium oxide (yttria-stabilized zirconia (YSZ)), calcium oxide (calcia-stabilized zirconia (CSZ)), or magnesium oxide (magnesia-stabilized zirconia (MSZ)), into the zirconia crystal lattice [26, 27].

Given the specific characteristics of this class of oxides, the stable ZrO_2 -based compounds used in protective systems, ZrO_2 -CaO, ZrO_2 -MgO, and ZrO_2 - Y_2O_3 , are presented later. Ceramic layers based on ZrO_2 partially stabilized with CaO, MgO, or Y_2O_3 exhibit remarkable properties of resistance to temperature, thermal fatigue, and corrosion [5, 26].

These additives have the role of maintaining part of the tetragonal structure of zirconia at ambient temperature, preventing the complete transformation to the monoclinic phase and, implicitly, the negative effects associated with volume changes. One of the key mechanisms that contributes to the significant increase in toughness in PSZ is phase transformation. When a crack propagates through the material and reaches a metastable tetragonal particle, the energy associated with the crack tip induces its transformation to the monoclinic phase, accompanied by a local volume expansion. This expansion generates compressive stresses around the crack tip, obstructing its advancement and thus increasing the material's resistance to fracture. Due to the combination of improved toughness and high-temperature resistance, PSZ finds important applications in the aerospace industry, being used in the manufacture of gas turbine components, such as blades or valves, and as a constituent material for effective thermal barriers, protecting critical components from extreme temperatures in engines. On the other hand, tetragonal zirconia polycrystal (TZP) is distinguished by its microstructure characterized by an extremely fine grain size and an advanced level of densification. By rigorously controlling the manufacturing process, a ceramic with a very high relative density and a grain size on the nanometric or submicrometric scale is obtained. This fine microstructure has a direct impact on the mechanical properties, giving TZP high mechanical strength and toughness. Unlike PSZ, in TZP, the dominant mechanism of toughness increase is often associated with microcracking or the deflection of cracks at grain boundaries due to their small size and uniform distribution. Although not as commonly used as PSZ in current aerospace applications due to challenges with long-term stability at very high temperatures, TZP shows significant potential for a number of applications, including as lightweight structural elements, where a high strength-to-weight ratio is crucial, and in the manufacture of advanced cutting tools, due to its toughness and wear resistance. Research continues to explore ways to improve the thermal stability of TZP to expand its application in the aerospace sector [28].

2.5 Zirconia-based coatings

Zirconia-based coatings play a crucial role in protecting critical aerospace components exposed to extremely severe operational conditions. Due to its intrinsic high-temperature resistance and outstanding chemical stability, zirconia (ZrO_2) is a material of choice for creating effective thermal barrier coatings (TBCs). These coatings function as an insulating protective layer, significantly reducing heat transfer to the metal substrate of components, such as gas turbine blades or combustion chambers. By maintaining substrate temperatures within safe limits, TBCs help extend component life, improve engine efficiency, and enable operation at higher temperatures, which translate into superior aircraft performance.

Zirconia-based coatings are applied using various advanced deposition techniques, tailored to ensure optimal adhesion, controlled microstructure, and uniform thickness of the protective layer. Among the most widely used method is plasma spraying, a versatile technique that allows the rapid deposition of thick ceramic layers by projecting molten or partially molten particles onto the substrate surface [29]. Another important method is chemical vapor deposition (CVD), which involves the chemical reaction of gaseous precursors at the heated surface of the substrate [30], resulting in a dense and homogeneous ceramic layer. Variants of CVD, such as physical vapor deposition (PVD), are also used for specific applications. In this case, despite the optimization of the coating parameters, the PVD deposits exfoliate due to

the insufficient surface properties of the substrate. Thus, the influence of surface properties on the adhesive film of PVD coatings with carbides is investigated [5]. The choice of deposition technique depends on the specific requirements of the application, such as the desired layer thickness, the complexity of the component geometry, and the required coating performance. A similar method is sputtering, which is a coating process that offers the possibility of transporting practically any metal, alloy, or compound from a source called a target to any substrate. The ejection of the material from the target to the support is accompanied by the bombardment of its surface with ion gas, accelerated by a high potential difference. The principle is the same as that of high-voltage glow discharges, with cathode sputtering, and is the basis of both metallic coatings and ion nitriding [5].

Current compositions of TBC ZrO_2 -(6–8) wt% Y_2O_3 have metastable tetragonal (t') phase structures, which possess high toughness and excellent cyclic [31, 32]. Early development of TBC coatings by the National Aeronautics Space Administration (NASA) showed the best over cycle life and durability for TBC coating systems with a composition range of ZrO_2 -6 to 8 wt% Y_2O_3 . Microstructures of plasma-sprayed and electron beam physical vapor deposition (EB-PVD) thermal barrier coatings are shown in **Figure 5**. A more recent work by Mercer et al. [34] showed that the metastable tetragonal coating composition 7YSZ (ZrO_2 -7 wt% Y_2O_3) has a higher fracture toughness value ($3.0 \text{ MPa m}^{0.5}$), compared to another commercially available TBC composition with a higher Y_2O_3 content, 20YSZ (ZrO_2 -20 wt% Y_2O_3) (1.0 – $1.2 \text{ MPa m}^{0.5}$).

The performance and durability of zirconia-based coatings under extreme aerospace conditions are critical aspects that are being rigorously evaluated. These coatings must withstand intense thermal cycling, particle impact (erosion), chemical attack from hot gases, and mechanical stress. Factors, such as the coating microstructure (porosity, density, grain morphology), adhesion to the substrate, and the stability of the zirconia phase at high temperatures, directly influence the lifetime and thermal barrier efficiency. Ongoing research focuses on optimizing the chemical composition of zirconia (e.g., by doping with other oxides), improving deposition techniques, and developing multilayer architectures to enhance the crack resistance, adhesion, and overall performance of TBCs in increasingly demanding aerospace applications.

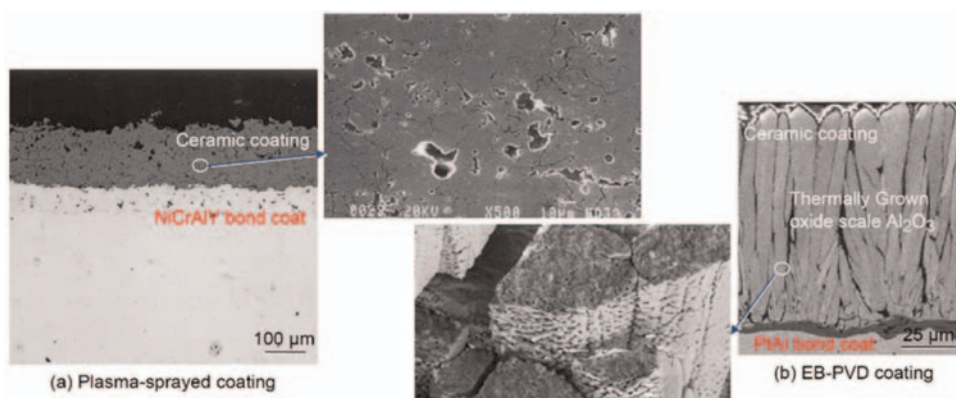


Figure 5. Microstructures of thermal barrier coatings (TBCs) on metal substrates. (a) A plasma-sprayed TBC system; (b) an electron beam physical vapor deposition (EB-PVD) TBC system [33].

2.6 Specific applications of zirconia-based materials in the aerospace industry

Numerous critical aerospace applications have demonstrated the invaluable quality of zirconia-based materials, due to their unique combination of high-temperature resistance, hardness, toughness, and chemical stability.

Their ability to function effectively in extreme operational environments makes them essential for the performance, safety, and durability of aircraft and space vehicles.

2.6.1 Components for aircraft engines

Modern jet engines operate at higher and higher temperatures to achieve superior thermal efficiency and increased traction. In this context, zirconia-based materials are indispensable for the manufacture of components directly exposed to the hot gases flow.

The turbine blades (stators and rotors): The turbine blades are subjected to extreme mechanical and thermal stresses. Zirconia-based materials, especially partially stabilized zirconia (PSZ) and tetragonal polycrystalline zirconia (TZP) with improved toughness, are used for the manufacture of these components. Their high-temperature creep resistance, combined with thermal shock resistance, allows them to maintain structural integrity under severe operational conditions. Zirconia-based thermal barrier coatings (TBCs) are also applied to metal blades to reduce substrate temperature and extend their lifespan [33, 35].

Combustion chambers and exhaust nozzles: The temperatures reached in the combustion chambers of jet engines are extremely high, and the materials used here must withstand oxidation, corrosion, and thermal shock. The zirconia-based ceramic liners provide effective thermal insulation and protect the metal structure of the combustion chamber. In exhaust nozzles, where hot gases are accelerated, the erosion and high-temperature resistance of zirconia are crucial for maintaining optimal geometry and performance [33].

Thermal insulation and linings: Zirconia-based materials are used in various sections of the engine as thermal insulators to protect heat-sensitive components and improve overall engine efficiency by reducing heat loss. Zirconia-based ceramic linings can be applied to the internal surfaces of engine housings or other components to resist high temperatures and corrosion [36].

2.6.2 Thermal protection systems for space vehicles

Spacecraft face extreme temperatures during launch and, especially, upon reentry into the atmosphere. Zirconia-based materials are crucial for the thermal protection systems (TPSs) of these vehicles.

Thermal tiles for atmospheric reentry protection: During reentry, friction with the atmosphere generates intense heat. Zirconia-based ceramic tiles, such as those used on the space shuttle, provide exceptional thermal insulation, protecting the vehicle's internal structure from temperatures that can exceed thousands of degrees Celsius. These tiles are designed to have not only low density to minimize vehicle weight, but also high thermal shock resistance to survive rapid heating and cooling [37, 38].

Components exposed to extreme temperatures during *launch and reentry*: Other spacecraft components, such as nose cones, control fins, and structural elements directly exposed to the rocket engine jet or the plasma flow generated upon reentry, may use zirconia-based materials or zirconia-based coatings to resist extreme temperatures and erosion [38, 39].

2.6.3 Sensors and instrumentation

Zirconia's unique properties also make it suitable for applications in sensors and instrumentation used in hostile aerospace environments.

High-performance temperature sensors: Zirconia can be used as a material for manufacturing temperature sensors capable of operating accurately at very high temperatures, such as those found in jet engines or exhaust systems. Its chemical stability and corrosion resistance ensure long-term reliable operation [40–42].

Components for measurement systems in hostile environments: In various measurement systems used in the aerospace industry, components exposed to extreme temperatures, vibrations, or corrosive environments can be manufactured from zirconia-based materials to ensure durability and measurement accuracy [43].

2.6.4 Other potential applications

In addition to established applications, research continues to explore new ways to harness the properties of zirconia-based materials in the aerospace industry.

Lightweight structural elements: Due to its relatively low density and the potential to achieve high mechanical strength (in particular, TZP), zirconia could be used to manufacture lightweight structural elements, helping to reduce the overall weight of aircraft and improve fuel efficiency [44].

Components for braking systems: The high-temperature resistance and hardness of zirconia could be exploited in the development of components for advanced aircraft braking systems, providing reliable performance and superior wear resistance [45].

2.7 Challenges and perspectives in the use of zirconia-based materials in the aerospace industry

Despite the outstanding performance demonstrated by zirconia-based materials in various aerospace applications, their wider use faces a number of significant challenges. One of the major obstacles is the relatively high production costs. The final cost is significant due to the complex processes of zirconia powder synthesis, advanced techniques for processing and manufacturing complex geometric components, and rigorous quality controls required for critical applications. To compete with advanced metal alloys, zirconia-based materials must develop more efficient synthesis routes, optimize forming and sintering processes, and implement large-scale manufacturing strategies to reduce production costs [11, 46].

Another important challenge concerns the processability of these materials. Due to the inherent hardness and fragility of ceramics, the final mechanical processing of zirconia components can be difficult and expensive, requiring specialized grinding and finishing techniques. The development of new additive manufacturing (AM) technologies (three-dimensional (3D) printing) adapted for ceramic materials could provide solutions for the creation of complex geometries with a minimum need for further processing, thus reducing costs and production time. Also, improving sintering techniques to achieve full densification at lower temperatures could contribute to more efficient processability. Techniques, such as ceramic-based lithography (Ceramic Stereolithography) or selective laser sintering (Selective Laser Sintering), allow the creation of components with complex and custom geometries, reducing material waste and production time. The current research aims to refine

these technologies to ensure the density, homogeneity, and mechanical properties necessary for aerospace applications [47].

Another major concern is the long-term reliability of zirconia-based materials under extreme aerospace operating conditions. Although zirconia exhibits outstanding resistance to high temperatures and corrosion, prolonged exposure to severe thermal cycles, complex mechanical stresses, and aggressive media can lead to microstructural degradation, the appearance of cracks and, ultimately, the failure of components [39].

With regard to research and development directions, current efforts are focused on overcoming the mentioned challenges and exploring new possibilities for performance improvement and expansion of applications of zirconia-based materials. An important direction is aimed at developing new compositions of doped or allied zirconia with other elements to optimize specific properties, such as high-temperature tenacity, oxidation resistance in aggressive environments, or thermal conductivity for specific applications [48].

Another active area of research is nanoscale microstructure control. The aim is to create materials that have enhanced properties like superior mechanical strength and toughness, and maintain stability at high temperatures by manipulating grain size, phase distribution, and nano-inclusions. The development of new advanced characterization techniques plays a key role in understanding the relationship between microstructure and properties, thus guiding optimization efforts [49].

Also, a priority in the aerospace sector is exploring new applications for zirconia-based materials. In addition to well-established uses in motors and thermal protection systems, the potential of zirconia in the development of advanced sensors for structural condition monitoring, high-performance actuators, components for electric propulsion systems, and even materials for energy storage is being investigated [50, 51].

A future trend in the aerospace sector is the continued growth in the use of advanced ceramic materials based on zirconia. Constant pressure to reduce aircraft weight, improve fuel efficiency, and operate at higher temperatures will drive the adoption of high-performance materials. The expectation is that ceramic materials will be integrated more closely into multifunctional structures, allowing them to perform both structural and thermal functions, as well as integrate sensors, actuators, or self-repair capabilities. A priority to ensure the structural integrity of complex assemblies will be the development of optimized interfaces between ceramic and metallic or composite components.

In addition, the adoption of digital manufacturing technologies for ceramic materials is expected to accelerate, allowing for more flexible design, faster production, and greater customization of components for specific aerospace applications. The aerospace industry's future with zirconia-based materials is promising, if current challenges are overcome through sustained research and development efforts.

3. Conclusion

Zirconia-based ceramics stand out as highly promising materials for aerospace applications, particularly as thermal barrier coatings. Owing to their specific properties, such as low thermal expansion coefficients and low thermal conductivity, zirconia materials offer excellent thermal insulation performance, making them ideal for protecting components exposed to extreme temperatures.

Beyond their thermal advantages, zirconia-based ceramics exhibit remarkable mechanical properties. They can withstand high tensile, compressive, and flexural

stresses, and their significant hardness ensures resistance to abrasion and wear, thereby extending the service life of critical components. Their favorable creep behavior, characterized by slow plastic deformation under constant load at elevated temperatures, demonstrates superior structural stability compared to many conventional metal alloys.

In addition to these superior mechanical characteristics, zirconia and its compounds also excel from a chemical point of view, a property demonstrated in the harsh environments encountered in aerospace applications. Their resistance to corrosion and oxidation at high temperatures allows zirconia-based materials to maintain their performance in contact with hot gases and oxidizing environments, such as those found in jet engines. In addition, their chemical compatibility with other materials commonly used in the aerospace industry, such as nickel-based superalloys and other ceramics, is important for ensuring the structural integrity of complex assemblies. A major challenge for ongoing research is the development of advanced additive manufacturing solutions tailored to zirconia-based ceramics. Such technologies would enable the fabrication of complex geometries with minimal post-processing, leading to significantly reduced production costs and shorter manufacturing times.

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Appendices and nomenclature

Ag ₂ Te	silver telluride
Al ₂ O ₃	aluminum oxide
AM	additive manufacturing
CaO	calcium oxide
CMCs	ceramic matrix composites
CoSb ₂	cobalt antimonide
CSZ	calcia-stabilized zirconia
CVD	chemical vapor deposition
EB-PVD	electron beam physical vapor deposition
Fe ₂ O ₃	iron (III) oxide
GaAs	gallium arsenide
Gd ₂ O ₃	gadolinium (III) oxide
Hf ⁴⁺	tetravalent hafnium cation
HfO ₂	hafnium oxide
MgO	magnesium oxide
M ₈₉	MO ₂ → M + O ₂ metal + oxygen
MgO	magnesia-stabilized zirconia
NaCl	sodium chloride
PSZ	partially stabilized zirconia

PVD	physical vapor deposition
SiC	silicon carbide
SiO ₂	silicon dioxide
SLS	selective laser sintering
TBCs	thermal barrier coatings
Th	thorium
Th ⁴⁺	tetravalent thorium cation
TPSs	thermal protection systems
TZP	tetragonal zirconia polycrystal
U	uranium
U ⁴⁺	tetravalent uranium cation
Y ₂ O ₃	yttrium oxide
Yb ₂ O ₃	ytterbium (III) oxide
YSZ	yttria-stabilized zirconia
Zr	zirconium
ZrO ₂	zirconium oxide
ZrSiO ₄	zircon
G	gibbs free energy
ΔG	gibbs free energy change
ΔH	high enthalpy values

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