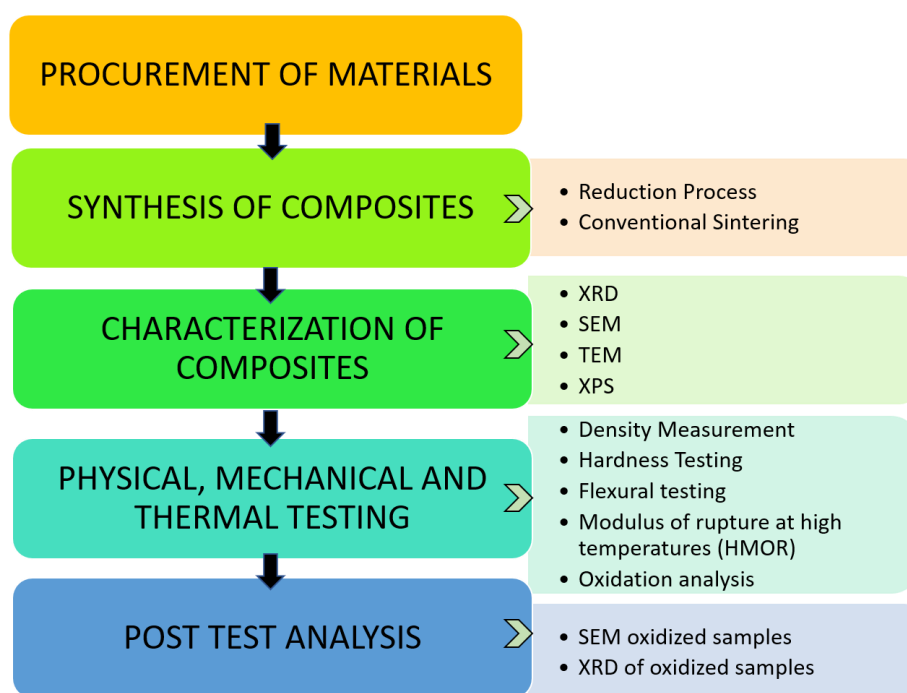


### 3.1 Introduction

This chapter discusses the materials selection process and characterization techniques employed in the study. A meticulous approach was taken to ensure that the chosen materials aligned with the research objectives and possessed the required properties and characteristics for the investigation. The chapter provides insight into the methods, instruments, and procedures used to thoroughly examine and analyze the selected materials.



*Fig. 3.1 Flow diagram for synthesis and characterization of ZrB<sub>2</sub>-based composite*

### 3.2 Raw materials

In this study, the synthesis of the composites involved utilizing a combination of specific starting reactants. These reactants included zirconia, which served as a source of zirconium, boron carbide as the boron source, silica as the silicon source, silicon as an additional silicon source, graphite as a carbon source, and carbon black to provide

carbonaceous material. Incorporating these reactants in the synthesis process initiated a controlled chemical reaction to form the desired ZrB<sub>2</sub>-based composites. Zirconia and boron carbide are essential for the formation of ZrB<sub>2</sub>. SiO<sub>2</sub> and Si acted as silicon sources, contributing to the composition of the composites. Carbon sources were introduced to provide an essential element for achieving the desired structure and properties.

The selection and combination of these specific reactants were crucial for achieving the desired synthesis outcome. Each reactant played a particular role in the overall chemical reaction, forming the ZrB<sub>2</sub>-based composites. The careful choice and combination of these starting reactants ensured the successful formation of the desired composite material with the selected properties. Table 3.1 provides details about all powders and their respective characteristics.

Table 3.1 Specification of starting raw material

Initial powder	Purity	Specification of material	Average mesh size
ZrO <sub>2</sub>	97%	LOBA CHEMIE	45-micron
B <sub>4</sub> C	98%	LOBA CHEMIE	140
SiO <sub>2</sub>	-	LOBA CHEMIE	15-micron
Si	99%	CDH PVT. LTD	60
Graphite (G)	-	CDH	150
Carbon black (C)	-	BIRLA CARBON N-220	45-micron

### 3. 3 Material processing

#### 3.3.1 Weighing and mixing

An essential step in synthesizing the ZrB<sub>2</sub>-based composites is the weighing and mixing of the composition, as mentioned above. Precise measurement and mixing of the starting reactants are crucial to ensure the desired composition and homogeneity of the resulting composites. The reactants, including zirconia (ZrO<sub>2</sub>), boron carbide (B<sub>4</sub>C), silica (SiO<sub>2</sub>), silicon

(Si), graphite (G), and carbon black (C), are carefully weighed according to the desired ratios and proportions.

The weighing process involves accurately measuring the quantities of each reactant using an electronic balance. The weights are determined based on the desired stoichiometry and composition of the final composite material. It is essential to achieve a proper balance between the reactants to ensure the selected properties of the synthesized composites.

The next step involves thoroughly mixing the reactants after weighting. This mixing process aims to achieve a uniform distribution of the reactants and promote chemical reactions between them. Various mixing methods can be employed, such as mechanical mixing using planetary and high-energy ball milling. The starting  $ZrO_2$ ,  $B_4C$ , and Si raw materials were mixed in a different mole content in high energy ball milling (FRITSCH pulveristte 5) at different rpm for different periods using a  $ZrO_2$  ball as a grinding medium. The powder-to-ball ratio was at 1:10 for high-energy ball milling. The goal is to achieve a homogeneous mixture, ensuring each reactant is evenly dispersed throughout the composition.

### **3.3.2 Compaction**

After the weighing and mixing, the synthesized composite material is compacted into different shapes using a technique called uniaxial hydraulic pressing. Uniaxial hydraulic pressing is employed in powder metallurgy to consolidate and shape powdered materials. The uniform mixture of the  $ZrB_2$ -based composite is carefully loaded into a die or mold with specific dimensions, such as a diameter of 10 mm and a thickness of 5-7 mm or a bar shape measuring 40 mm in length, 15 mm in width, and 10 mm in height. The compaction process utilizes uniaxial pressing, where pressure is applied in a single direction, typically along the axial direction. Under this process, the composite mixture is subjected to a controlled and

uniform pressure of 12 MPa using a hydraulic press. This pressure causes the composite particles to pack together tightly, resulting in densification and improved structural integrity.

### 3.3.3 Synthesis and Sintering

The synthesis of ZrB<sub>2</sub>-based composites involved the exploration of various starting compositions with different stoichiometric ratios. The stoichiometric ratios were adjusted to ensure the correct proportions of the required elements for the synthesis. This approach allowed for fine-tuning the composition to optimize the properties of the resulting composite material. The synthesis occurred at elevated temperatures within the specified range in the vacuum and debinding furnace. The temperature range for sintering depended on the known phase diagrams and thermodynamic considerations for the reaction between the starting materials. The high temperatures were necessary to drive the chemical reactions and promote the formation of ZrB<sub>2</sub>.

A vacuum or inert atmosphere was employed to maintain a controlled environment during synthesizing the composite in a vacuum and debinding furnace, holding a 10<sup>-1</sup> millibar vacuum. These conditions helped prevent the introduction of unwanted impurities or reactions with atmospheric gases that could compromise the purity of the synthesized ZrB<sub>2</sub>-based composite. Overall, synthesizing the ZrB<sub>2</sub>-based composite involved carefully selecting starting compositions with different stoichiometric ratios and using specific temperature ranges under vacuum or inert atmosphere conditions to achieve impurity-free ZrB<sub>2</sub> with desired properties.

After synthesizing ZrB<sub>2</sub>-based powder, the next step involved sintering the synthesized powder to enhance its density and mechanical properties. Two different sintering methods, pressureless and hot pressing, were employed at various temperature ranges.

Pressureless sintering is a commonly used technique where the powder is compacted into a desired shape and subjected to a sintering process without external pressure. The compacted powders were placed in a tube furnace and heated to temperatures ranging from (1000-1600°C) for a specific duration. The composite sample is sintered from a separate Carbolite furnace sinter. The sintering of the powder particles undergoes diffusion and rearrangement, resulting in densification and the bonding of particles to form a solid material. The pressureless sintering of the ZrB<sub>2</sub>-based powder was performed at 1900°C for 120 min with 10°C/min, maintaining a 10<sup>-1</sup> millibar vacuum.

The vacuum hot pressing (VB Ceramics Chennai) was used for compaction and sintering the sample by applying heat and pressure. The precursor material was placed in a die and exposed to elevated temperatures ranging from (temperature range). The die was then subjected to a uniaxial pressure while being heated, promoting densification and the formation of interparticle solid bonds. The ZrB<sub>2</sub>-based powders were placed into a 15 mm diameter graphite die and hot pressed under a pressure of 40 MPa at 1500°C for 60 minutes in high vacuum conditions (7.5\*10<sup>-5</sup> torr).

By utilizing both pressureless sintering and hot pressing, researchers aimed to optimize the densification and mechanical properties of the ZrB<sub>2</sub>-based material. The sintering method and temperature range selection depended on the desired density, mechanical strength, and specific application requirements. These sintering techniques played a crucial role in the final processing of the material, enabling the achievement of the desired characteristics for particular applications. The starting precursors were used in different compositions to prepare binary (ZrB<sub>2</sub>-SiC, ZrB<sub>2</sub>-ZrC) and ternary ZrB<sub>2</sub>-SiC-ZrC composites. Table 3.2 shows the composition of starting materials, mole content, synthesis, and sintering parameters.

Table 3.2 Synthesis and sintering parameter of ZrB<sub>2</sub>-based composites

Final composition	Composition (mole content)						Fabrication parameter
	ZrO <sub>2</sub>	B <sub>4</sub> C	Si	SiO <sub>2</sub>	carbon	Graphite	
ZrB <sub>2</sub> - SiC	1	0.75	0.25	-	-	-	Synthesis at 1300°C to 1600°C for 3h and at a continuous rate of 5 °C /min in argon supply
	1	0.75	0.375	-	-	-	
	1	0.835	0.5	-	-	-	
	1	0.835	0.67	-	-	-	
ZrB <sub>2</sub> -SiC	1	5/7	1	-	-	1	Synthesis at 900°C for 30 minutes and then at 1600°C for 180 minutes in a moderate vacuum with an argon supply
	1	1	-	1	-	1	
	1	5.7	-	1	1	-	
	1	1	1	-	1	-	
ZrB <sub>2</sub> -ZrC	1	0.5	-	-	-	1.5	Synthesis at 1300°C to 1600°C and sintering at 1900°C under vacuum
ZrB <sub>2</sub> -SiC-ZrC	1	0.5	0.5	-	-	2	
ZrB <sub>2</sub> -SiC	1	0.5	0.5	-	-	2	Synthesis at 1500°C for 3h and hot pressing at 1500°C/ 60 min /30 Mpa
	1	0.5	1	-	-	2.5	
	1	0.5	1.25	-	-	2.75	

### 3. 4 Characterization techniques

#### 3.4.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) is a powerful technique that provides information about the crystal structure and phase composition of the ZrB<sub>2</sub>-based composites. XRD analysis helps identify the presence of different phases, determine the crystallographic parameters, and assess the degree of crystallinity.

In XRD analysis, a beam of X-rays incident on the sample, interacting with the atoms in the material. The X-rays undergo diffraction as they interact with the crystal lattice, generating a unique diffraction pattern. This pattern contains peaks corresponding to the atoms' arrangement within the crystal lattice. Valuable insights can be obtained by analyzing the

diffraction peaks' positions, intensities, and shapes. It also identifies different crystal phases in the composite, as each stage produces a distinct diffraction pattern. Furthermore, XRD analysis provides information about the crystallographic parameters of the composite, such as lattice parameters, unit cell dimensions, and crystal symmetry. These parameters offer valuable insights into the crystal structure, allowing a deeper understanding of the material's properties.

Another crucial aspect assessed through XRD is the degree of crystallinity. A sharp and intense diffraction peak indicates a high degree of crystallinity, while broadened peaks suggest a more disordered or amorphous structure. The Rigaku 600 Desktop X-ray diffractometer determined the phase in synthesized and sintered samples through Cu K $\alpha$  radiation with a Ni filter. The scanning rate is 2° min<sup>-1</sup> and 2 theta angular range of 20 to 80° with a step size of 0.02°. The Rietveld analysis finds the particular number of phases in the final specimen.

### **3.4.2 Scanning electron microscopy (SEM)**

Scanning electron microscopy (SEM) is another valuable tool used for microstructural characterization. SEM allows for examining the surface morphology, such as the shape, size, and texture of particles or grains within the ZrB<sub>2</sub>-based composites. This technique provides high-resolution images, enabling the analysis of the microstructure and the identification of any defects or irregularities. The electron beam has a much smaller wavelength than visible light, allowing for observing fine details and features at the micro and nanoscale. It provides for analyzing grain boundaries, phase distribution, and porosity within the material. By following the microstructure, researchers can gain valuable information about the composite's formation, consolidation, and processing conditions, which influence its mechanical and physical properties.

SEM is often combined with energy-dispersive X-ray spectroscopy (EDX) to perform elemental analysis. EDX detects and analyzes the characteristic X-rays emitted by the sample,

providing information about the elemental composition and mapping of elements across the surface of the composites. SEM allows researchers to assess the homogeneity and distribution within the material. It aids in understanding the morphology, microstructural features, and elemental composition, providing essential insights into the material's properties and potential applications. The microstructure and morphology in ZrB<sub>2</sub>-based composite was investigated by scanning electron microscope (SEM, Nova Nano SEM 450). Before SEM analysis, the gold paste was coated on the thermally treated ZrB<sub>2</sub>-based samples.

### **3.4.3 Transmission electron microscopy (TEM)**

The characterization of the ZrB<sub>2</sub> composite was carried out using a transmission electron microscope (TEM, TECNAI G2 20 Twin). TEM is a powerful technique that allows for the detailed analysis of the microstructure and nanoscale features of materials. The TEM analysis of the ZrB<sub>2</sub> composite was performed using the TECNAI G2 20 Twin instrument. This specific TEM model offers advanced capabilities for the imaging and analysis of materials. The composite sample was prepared by thinning it to a thickness that allows for electron transmission.

TEM analysis provides valuable information about the composite's crystalline structure, grain boundaries, defects, and interfacial interactions. It enables the measurement of parameters such as particle size, lattice spacing, and crystallographic orientation. The high-resolution images obtained from TEM reveal the morphology and arrangement of the composite's constituents, providing insights into its microstructure.

Selected area electron diffraction (SAED) and energy-dispersive X-ray spectroscopy (EDX) combined with TEM analysis. SAED allows for the identification of crystallographic orientations and the determination of the crystal structure. EDX provides elemental analysis,

allowing researchers to examine the elemental composition and distribution within the composite.

#### **3.4.4 X-ray photoelectron spectroscopy**

The X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo Fisher Scientific system with an Al K $\alpha$  (1486.6 eV) X-ray source. An energy analyzer in a hemispherical shape was installed in the analytical chamber. It consists of double-focusing along with 128 channel detectors. Two molecular turbo pumps with 250 l/s capacity were used to achieve the backup pump pressure of  $2.2 \times 10^{-3}$  millibar and the analysis chamber pressure of  $1.3 \times 10^{-8}$  millibar. The base pressure of the system is typically  $5 \times 10^{-9}$  mbar. The XPS system is equipped with a dual-beam flood gun that can produce a focused beam of very low-energy electrons (ranging from 1 eV to 10 eV) while the other beam is a co-axial focused beam of low-energy Ar<sup>+</sup> ions (ranging from 1 eV to 30 eV). The incident x-ray angle is at 60 ° angles with the analyzer axis. This feature helps to prevent sample charging during analysis. The angle of the charge neutralizer is 58 ° concerning the analyzer axis. The charge referencing using the internal energy reference of the sample has been applied by defining the cut-off in the density of states (DOS) at the Fermi level (FL) of the sample (so-called Fermi Edge) as the "0 eV" on the BE scale.

The X-ray spot is 400  $\mu\text{m}$ , and the emission angle is almost 24–30° solid angle. The sample surface is perpendicular to the axis of the analyzer transmission lenses. The etched area can be adjusted, typically 2mm x 2mm. The calibration in the binding energy scale was maintained by X-ray spot. It was moving among Cu, Ag, and Au. Spectra was collected from each of these samples after removing any contamination through sputtering. The energy scale was calibrated by the standard peak positions for Cu2p, Ag3d, and Au4f, found to be 932.536 eV (with an error of -57.2748), 368.157 eV (with an error of -52.9538), and 83.9026 eV (with

an error of -57.4124), respectively. The process was repetitive with a spectrometer, and the energy scale was calibrated at specific values for Cu<sub>2p</sub>3/2, Ag<sub>3d</sub>5/2, and Au<sub>4f</sub>7/2, namely 932.615 eV (with an error of -5.0881), 368.206 eV (with an error of -3.8354), and 83.9461 eV (with an error of -13.9255), respectively. The standard peak energies usually require the peak position within a 50 meV range. The Cu LVV Auger peak (568.016 with an error of -85.6542) was recorded as an extra check for any differences due to the monochromator alignment.

To accurately examine the chemical composition of the samples, the experimental XPS curves underwent background correction using Shirley's technique [175]. Subsequently, a Gaussian and Lorentzian function was juxtaposed to approximate the curves. The resulting fitted curves identify the peaks' positions and their intensities. The XPS PEAK 4.1 software was used to analyze the characteristic energy ranges present in XPS spectra, measured in electron volts (eV).

### **3.4.5 Density measurement**

Archimedes' principle, using distilled water, was employed to control the bulk density of the ZrB<sub>2</sub>-based composite after the sintering process. Archimedes' principle states that an object immersed in a fluid experiences an upward buoyant force equal to the weight of the fluid displaced by the sample.

Additionally, the theoretical density of the sintered sample was determined using the rule of the mixture of the starting compositions. The rule of the mixture calculates the expected density of a composite material based on the densities and volume fractions of its constituent components.

By comparing the experimental bulk density obtained through Archimedes' principle with the theoretical density calculated using the mixture rule, researchers can assess the

densification and porosity of the sintered ZrB<sub>2</sub>-based composite. This information is crucial in evaluating the effectiveness of the sintering process and determining the final density achieved.

### **3. 5 Mechanical Testing**

#### **3.5.1 Hardness**

Vickers hardness is a widely used method for measuring the hardness of materials. Vickers hardness testing involves pressing a diamond indenter into the surface of a material under a specified load. The size of the resulting indentation is measured, and the Vickers hardness value is determined by dividing the applied load by the surface area of the indentation. The Vickers hardness value provides information about a material's resistance to indentation and deformation. It measures the material's ability to resist permanent plastic deformation. Higher Vickers hardness values indicate greater hardness and strength of the material.

The Vickers hardness machine determined the polished surface's hardness by applying a 5 kg load for 10 sec. The direct crack measurement technique determines the sample's fracture toughening via Vickers indentation at a 15 kg load.

#### **3.5.2 Flexural strength**

Flexural strength is an essential mechanical property that measures a material's ability to withstand bending or flexing loads without breaking. In this study, the flexural strength of the samples was evaluated using a point universal testing machine. The samples, in the form of bars with dimensions of 50 mm x 15 mm x 5 mm, were subjected to a bending test. During the test, the sample was positioned in the testing machine at a specified distance of 30 mm between the fixtures. The cross-head speed of the machine was set at 0.5 mm/min, ensuring a controlled and uniform application of the bending load. The machine gradually applied an axial load on the samples, causing them to bend until fracture occurred.

The flexural strength ( $\sigma$ ) of the samples was determined using equation (3.1):

$$\sigma = 3F_{max}L/2bd^2 \quad (3.1)$$

In this equation,  $F_{max}$  represents the maximum axial load applied on the samples,  $L$  is the span length between the fixtures,  $b$  denotes the width of the samples, and  $d$  refers to the thickness of the  $ZrB_2$  samples.

By measuring the maximum load applied during the bending test and knowing the dimensions of the samples, flexural strength can be calculated using equation (3.2). This value provides insights into the material's ability to resist bending and withstand applied loads without fracture.

### 3.5.3 Fracture toughness

Fracture toughness is a critical mechanical property that characterizes a material's resistance to crack propagation and fracture under applied stress. In this study, the fracture toughness of the  $ZrB_2$ -based samples was determined by the Anstis equation, as shown in equation (3.2). The Anstis equation provides a method to measure materials' indentation fracture toughness ( $K_{IC}$ ). The fracture toughness of the composites was calculated using the Anstis equation. The Anstis equation is applied when the  $c/a$  ratio is higher than 2.5, where  $c$  is the diagonal length of the crack and  $a$  is half of the indent diagonal.

$$K_{IC}=0.016(E/H)^{0.5}(P/c^{1.5}) \quad (3.2)$$

In this equation,  $K_{IC}$  represents the indentation fracture toughness,  $E$  denotes Young's modulus of the material,  $H$  represents the Vickers hardness,  $P$  represents the indentation load, and  $c$  represents the diagonal length of the crack.

The indentation fracture toughness was determined using equation (3.2) by testing Vickers hardness and measuring the crack length. This value provides crucial information about

the material's ability to resist crack propagation and withstand applied loads without catastrophic failure. Fracture toughness is essential in assessing the reliability and durability of materials in structural applications where the presence of cracks or flaws is inevitable. It helps engineers and researchers understand the material's resistance to crack initiation and growth and aids in designing structures with enhanced fracture resistance.

### 3. 6 Ablation test

The oxidation behavior of the ZrB<sub>2</sub> composites was investigated at high temperatures of up to 2600°C for 60 seconds using an oxy-acetylene flame. The sample was positioned approximately 10 mm away from the oxy-acetylene gunpoint. The gases used during ablation are in controlled pressure and flux conditions. Expressly, the pressure and flux of C<sub>2</sub>H<sub>2</sub> (acetylene) were set at 0.095 MPa and 0.31 L/s, respectively, while for oxygen, the pressure and flux were 0.4 MPa and 0.42 L/s, respectively. The oxy-acetylene torch generated a heat flux of approximately 4.186 MW/m<sup>2</sup>.

An optical pyrometer determined the flame temperature during the ablation process.

Equation (3.3) calculates the mass oxidation rate (mg/s).

$$R_m = \frac{m_1 - m_2}{t} \quad (3.3)$$

R<sub>m</sub> is known as mass ablation rate (mg/s); m<sub>1</sub> is the wt of the composite before ablation; m<sub>2</sub> is the wt of the composite after ablation; A is the surface area of composite sample; t is the time of ablation (s).

The linear ablation rate determined by equation (3.4)

$$R = \frac{L_1 - L_2}{t} \quad (3.4)$$

R is defined as linear ablation rate ( $\mu\text{m/s}$ );  $L_1$  is the thickness of the composite before ablation;  $L_2$  is the thickness of the composite after ablation; T is the time of ablation test (s).

By evaluating the mass oxidation and linear ablation rates, researchers can gain insights into the material's response to high-temperature oxidation and its resistance to ablation. These measurements are crucial in assessing the suitability of the  $\text{ZrB}_2$  composites for applications exposed to extreme temperature conditions and needing to maintain their structural integrity.