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The Effect of Processing Parameters on the Mechanical Properties of Calcia-Stabilized Zirconia (CSZ) for Dental Use

M. Kannan [1,*], Satyendra Singh [2] and Raja Ram Prasad [3]

[1] Faculty of Technology, Uttarakhand Technical University, Deharadun 248007, India
[2] Mechanical Engineering Department, Bipin Chandra Tripati Kumaon Institute of Technology, Dwarahat 263653, India
[3] Mechanical Engineering Department, BSM College of Engineering, Roorkee 247667, India
* Correspondence: mkananm@gmail.com

Abstract: Three different compositions with 9%, 12%, and 15% of calcia-stabilised zirconia (CSZ) were prepared from commercially available submicron-sized powders by cryo-milling. The influence of the sintering conditions, temperature, and dwell time varied as 1400, 1500, and 1600 °C, at durations of 4, 3, and 2 h on mechanical properties is studied. SEM and XRD studies were performed on the pellets obtained by hydraulic pressing in a uniaxial press at 13 tonnes. The effect of sintering holding time and temperature on the mechanical properties, such as hardness, flexural strength, and compressive strength (in a universal testing machine), of CSZ is studied. It is seen that, with the increase in calcia, hardness, flexural strength, and compressive strength increase, until full stabilisation of zirconia is created due to calcium ion substitution in the ionic vacancies. An increase in sintering temperature and time has a positive effect until 1600 °C and 2 h on the flexural and compressive strengths of CSZ. Mechanical properties of CSZ obtained through cryo-milling and sintered at high temperature 1600 °C and shorter holding time is found suitable for dental applications.

Keywords: calcia-stabilised zirconia (CSZ); mechanical property; Vicker hardness; flexural strength; compressive strength; dental application

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1. Introduction

Zirconia ceramics have a wide application in dental restorations, such as crowns and bridges. Since pure zirconia is unstable at room temperature and the monoclinic phase does not have the properties required for zirconia to be used as a structural ceramic in dental implants, various oxides are used to stabilise the phase. Stabilised zirconia has been used in many applications, but phase stabilisation of zirconia is essential as the specialised properties are retained only in the cubic or tetragonal phase at all temperatures [1]. Stabilized zirconia powders are used in a wide variety of applications; hence, the development of a cost-effective method for their synthesis has been the subject of significant study in recent years. Sol-gel, spray pyrolysis, precipitation approaches, and rapid combustion pathways are some of the most effective techniques [2,3], although they take a long time and cost a lot of money. To make CSZ powder, mechanical alloying is used because it is the most economical synthetic method and provides minimal concessions in terms of properties. For stabilisation, various oxides have been researched, but calcia remains a preferred one due its low cost. For oxygen sensor applications, particularly for the detection of oxygen concentration in molten metals, CSZ solid electrolyte has been employed because of its high oxygen-ion conductivity and good thermochemical stability [4,5]. Solid-state reaction of component oxides, chemical pathways, sol-gel, and dc plasma process are common methods for preparing fully or partially calcia stabilised zirconia [6,7]. The addition of calcia is chosen over other oxides because the cubic phase is stable at all temperatures, in contrast to the magnesia or yttria-stabilisation, which reverts to the monoclinic structure at low temperatures [8,9]. Zirconia ceramic systems include yttrium doped tetragonal zirconium

polycrystals (3Y-TZP), magnesium stabilised zirconium (Mg-PSZ), zirconium-toughened alumina (ZTA), and ceria-stabilized zirconia-alumina (CeTZP/A). These are the types of zirconia ceramic systems that are most commonly used in dentistry [10,11]. These systems are comparatively costlier to calcia-stabilised zirconia and hence search is to improve properties of stabilized zirconia to replace ZTA/Mg-PSZ or 3Y-TZP. Low-temperature ageing degradation (LTAD) symptoms are seen in 3Y TZP due to phase transformation [12]. CeTZP/A reduces the LTAD problem but suffers from the wear of the milling machine. CSZ has reasonable fracture toughness (6 MPa/m^2) as reported by Nath et al. and found suitable for hip replacement implants, which is better than TZP or ZTA used commercially in present [13]. It is also reported that CSZ shows all polymorphism as seen in YZP ceramics at lower cost by Drazin and Castro [14]. Hence, calcia doped zirconia can be utilised in biomedical applications instead of yittrium or cerium, which are costlier and not found in abundance. Abbas Hussein et al. employ nano-CaO isolated from cockle shells to stabilise zirconia and compare it to commercial CaO sintered at varying temperatures. When compared to other materials, CSZ is determined to have desirable qualities for use in dentistry [15]. The mechanical properties of nano-CSZ obtained by size reduction from commercially available initial micron-sized powders under cryogenic circumstances have not been attempted or reported for suitability in dental applications.

The purpose of the present study is to prepare calcia-stabilised zirconia (CSZ) by mechanical means under controlled conditions from commercially available powders of zirconia and calcia. Effect of sintering temperature and holding time is varied to study the changes in mechanical properties with an aim to tailor the mechanical properties required for dental applications.

2. Materials and Methods

Calcium oxide (CaO) (average size: 10 μm, anhydrous, 99.99% purity) and zirconium oxide (ZrO_2) (average size: 5 μm, powder, 99% purity) powders from Sigma Aldrich (St. Louis, MO, USA) were combined in varying concentrations to form zirconia oxide ceramics with calcia contents of 9%, 12%, and 15%, respectively. Mixing was performed in a high-energy planetary ball mill in cryogenic conditions, i.e., cryo-milling. Each composition's weighted powder combination was placed in a zirconium steel 500-mL jar and connected to a planetary ball mill equipped with 40 zirconium steel balls weighing 15 gms each, with the steel balls and powder maintaining a mass ratio of 10:1. Cryogenic conditions were maintained by liquid nitrogen produced by the machine procured from Retch firm (Haan, Germany). Separate jars containing the powder, grinding media, and water were operated at 300 rpm for 80 h, with short breaks in between.

The X-ray Diffractometer (HypIx 3000, Rigaku, Tokyo, Japan) was used to analyse the milled samples in the 2θ range 20–80° at a scanning speed of one degree per minute using Cu-K radiation (λ = 1.5406 Å, 40 kV). The investigation of the powder sample was conducted using scanning electron microscopy (SEM; Quanta 200 FEG, FEI, Hillsboro, OR, USA). All three powder compositions were compacted using a uniaxial pressing machine and 13 tonnes of pressure to create cylindrical green pellets. Before compaction to make cylindrical pellets using a cylindrical die punch system, weighed powders of each composition was combined rigorously with 3% binder, Polyvinyl alcohol (PVA). Stearic acid is used as a lubricant and applied to the die for easy removal of the pellets after compaction. Green samples of each composition were sintered in a box furnace for varying amounts of time and temperatures: 2,3, and 4 h at 1500 °C. Another set of samples was sintered for 2 h at 1400, 1500, and 1600 °C. Slow rates of 5 °C/min are used for both heating and cooling in the furnace. After the furnace cooled naturally for 24 h, the sample was taken out.

SEM is carried out to understand the physical surface topography after sintering. Density is measured using the Archimedes principle by measuring the weights of sintered

samples both before and after being submerged in double-distilled water. Density is calculated using the following equation:

$$\rho = \left[\frac{\text{actual weight}}{\text{actual} - \text{suspended}}\right]\rho_w$$

where sample density and water density are expressed as ρ and ρ_w, respectively, in gms/cc or g/cm^3. [15] Density was also calculated from mass-volume relationships and compared with the literature. The hardness of the sintered samples was measured using a computerised Vicker's hardness tester (Model: RVM-50PC, Ratnakar, Ichlakaranji, India). Average hardness values were calculated using Vicker's diamond pyramid indenter and a dwell time of 15 s. Hardness values obtained as Vicker's hardness number (VHN) were converted to SI units in GPa. Specimens' for flexural (according to ISO6872:2015) and compressive strengths (according to ISO9917-1:2007) were prepared and evaluated using a Universal Testing Machine (Instron, Norwood, MA, USA) operating at a crosshead speed of 0.75 mm/min for both tests [15].

Sizes of specimens were 20 mm × 2 mm × 2 mm for flexural test, with a span length of 12 mm, and for the compressive strength test, the sizes were 6 mm × 4 mm dia. Platens used in the compressive test were smooth stainless steel and the surfaces of the samples were polished using polishing disks with grits ranging from P400 to P1500. The formula used is as follows:

$$\text{Flexural strength} = 3\,PL/2\,bd^2$$

where P represents the greatest force that is exerted, L represents the length of the span, b represents the width, and d represents the thickness.

$$\text{Compressive strength} = 4\,P/\pi d^2$$

where P refers to the highest force that was applied and d represents the diameter of the specimen. Effect of varying compositions, sintering temperature, and dwell time on mechanical properties are discussed.

3. Results

Powder samples were obtained by cryo-milling of larger-sized commercial powders of CaO and ZrO_2 under controlled conditions for 80 h at 300 rpm. Powder morphology is studied for verifying the grain growth and phase transformation from monoclinic to tetragonal or cubic structure of zirconia in room temperature for better mechanical properties.

From the SEM and XRD studies, as shown in Figures 1–3, it is confirmed that nanograins and phase assemblages have been achieved in the samples prepared. Agglomeration is seen, with most of them being spherical-shaped and almost uniform in size. Table 1 shows the EDS analysis of the CSZ sample of all three compositions, indicating that mixing has been homogeneous to a great extent and that the chemical composition is similar to theoretical expectations depending on the mol%. Since the size of the grains influences their properties, the size of grains achieved is determined using Scherrer's formula [16]. Data from the joint committee on powder diffraction standards are compared to all peaks produced by XRD analysis (JCPDS). The average grain size, $D = (0.9\lambda)/(\beta\ \text{Cos}\theta)$, was estimated using Scherrer's formula. The X-ray wavelength (λ) of CuK radiation, which is equivalent to 0.154 nm, the Bragg diffraction angle (θ) and β is the FWHM (full width half maxima) of the XRD peak that appears at the diffraction angle θ, are all used in the formulas [9,17]. The average grain size was found to be approximately 21 nm, as tabulated in Table 2.

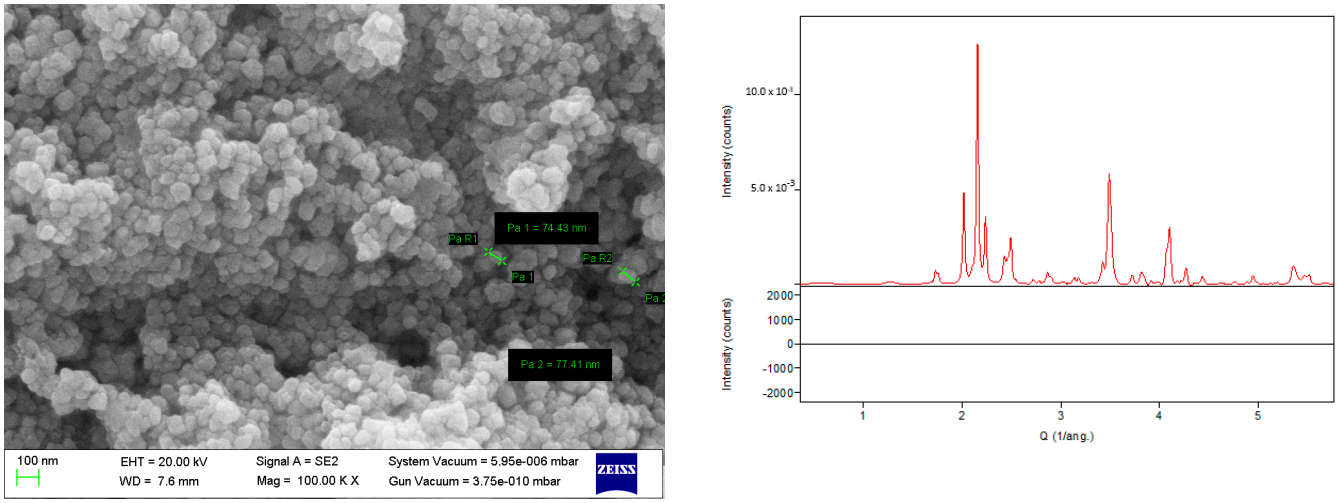


Figure 1. SEM and XRD of a CSZ powder sample with 9 mol% of CaO.

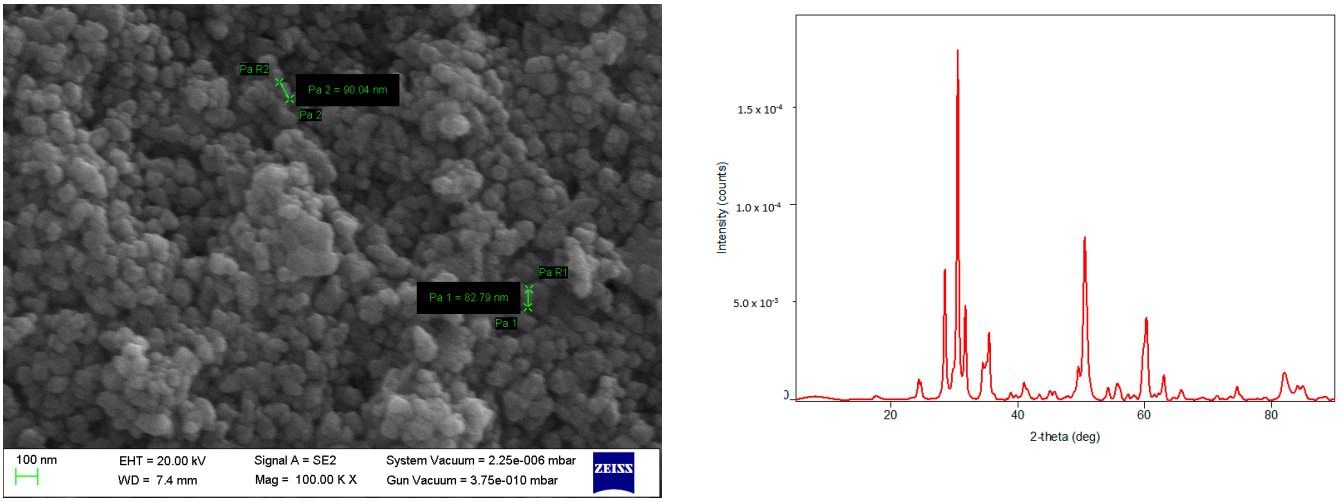


Figure 2. SEM and XRD of a CSZ powder sample with 12 mol% of CaO.

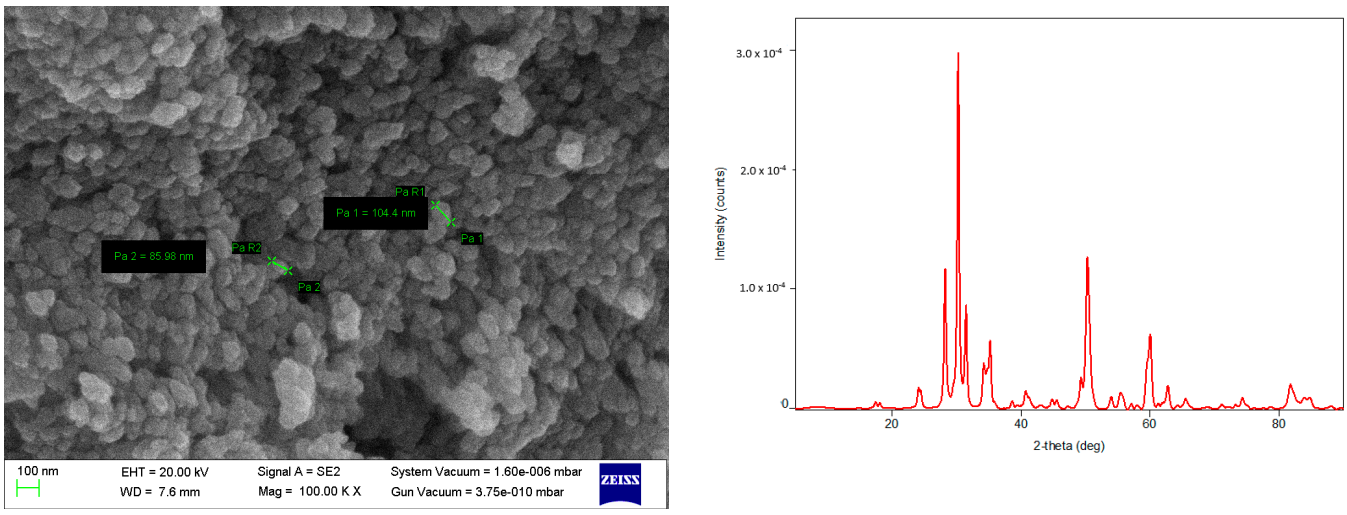


Figure 3. SEM and XRD of a CSZ powder sample with 15 mol% of CaO.

Table 1. EDS analysis of all three compositions.

	9 Mol%		12 Mol%		15 Mol%	
Element	**Wt.%**	**At%**	**Wt.%**	**At%**	**Wt.%**	**At%**
O K	31.28	71.14	31.28	71.14	31.28	71.14
Zr L	65.88	26.28	65.88	26.28	65.88	26.28
Ca K	02.85	02.58	02.85	02.58	02.85	02.58

Table 2. XRD grain size measurements in nanometers after 80 h milling.

CaO μm	ZrO_2 μm	9 Mol% CaO nm	12 Mol% CaO nm	15 Mol% CaO nm
10	5	21.07	21.69	22.15

Powders are pressed into cylindrical green pellets in a uniaxial press, and physical measurements, texture are noted. One set of samples (Group A) of all three compositions was sintered at 1400, 1500, and 1600 °C for 2 h in a muffle furnace. Another set (Group B) is sintered at 1500 °C for 2, 3, and 4 h in the furnace. Heating and cooling rates are kept the same at 5 °C/min. Samples are allowed to cool in the furnace and taken out within 24 h.

Density measurement was performed using the Archimedes principle, and the measurement of weights before and after submerging in double-distilled water were noted.

Density data listed in Tables 3 and 4, shows that the effect of sintering temperature on density is more dominant than the duration of sintering, and changes are mostly in the range of 40%–50% in case of temperature or dwell time variations. The theoretical density value of CSZ is 5.52 g/cm^3, and from experiments, it is noted that more than 90% of the theoretical density has been achieved with less porosity in both groups of samples.

Table 3. Density measurements for Group A CSZ samples with a dwell time of 2 h.

Mol %	Sintering Temperature (°C)	Density		% Change
		Before Sintering (g/cm^3)	After Sintering (g/cm^3)	
9	1400	3.55	5.21	46
	1500	3.55	5.23	47
	1600	3.55	5.28	48.5
12	1400	3.51	5.11	45
	1500	3.51	5.18	47.5
	1600	3.51	5.26	49.5
15	1400	3.68	5.19	41
	1500	3.68	5.26	43
	1600	3.68	5.29	43.5

Figures 4–6 represent SEM and EDS analyses of samples sintered for 4 h at 1500 °C.

SEM analysis of all the samples from both groups reflects good densification, little or no traces of pores, and grain growth, with phase transformation and stabilisation partial in 9 mol% and almost complete stabilisation in 15 mol%. This suggests that the best sintering conditions can be at 1600 °C and 2 h, as sintering time does not have much effect on pores or density. Phases present in samples sintered at 1400 and 1500 °C are composed of monoclinic and cubic phases, with monoclinic phases disappearing in the samples sintered at 1600 °C. Ref. [17] expected phases were obtained in the samples prepared by mechanical alloying or cryo-milling in our work. With an increase in calcia ions in the CSZ phase, stabilisation improves from partial to fully stabilised zirconia [18].

Table 4. Density measurements of Group B CSZ samples at sintering temperature of 1500 °C.

Mol %	Dwell Time (h)	Density		% Change
		Before Sintering (g/cm^3)	After Sintering (g/cm^3)	
9	2	3.55	5.21	46
	3	3.55	5.21	46
	4	3.55	5.22	47
12	2	3.51	5.11	45
	3	3.51	5.11	45
	4	3.51	5.12	45.5
15	2	3.68	5.17	40
	3	3.68	5.18	40.5
	4	3.68	5.19	41

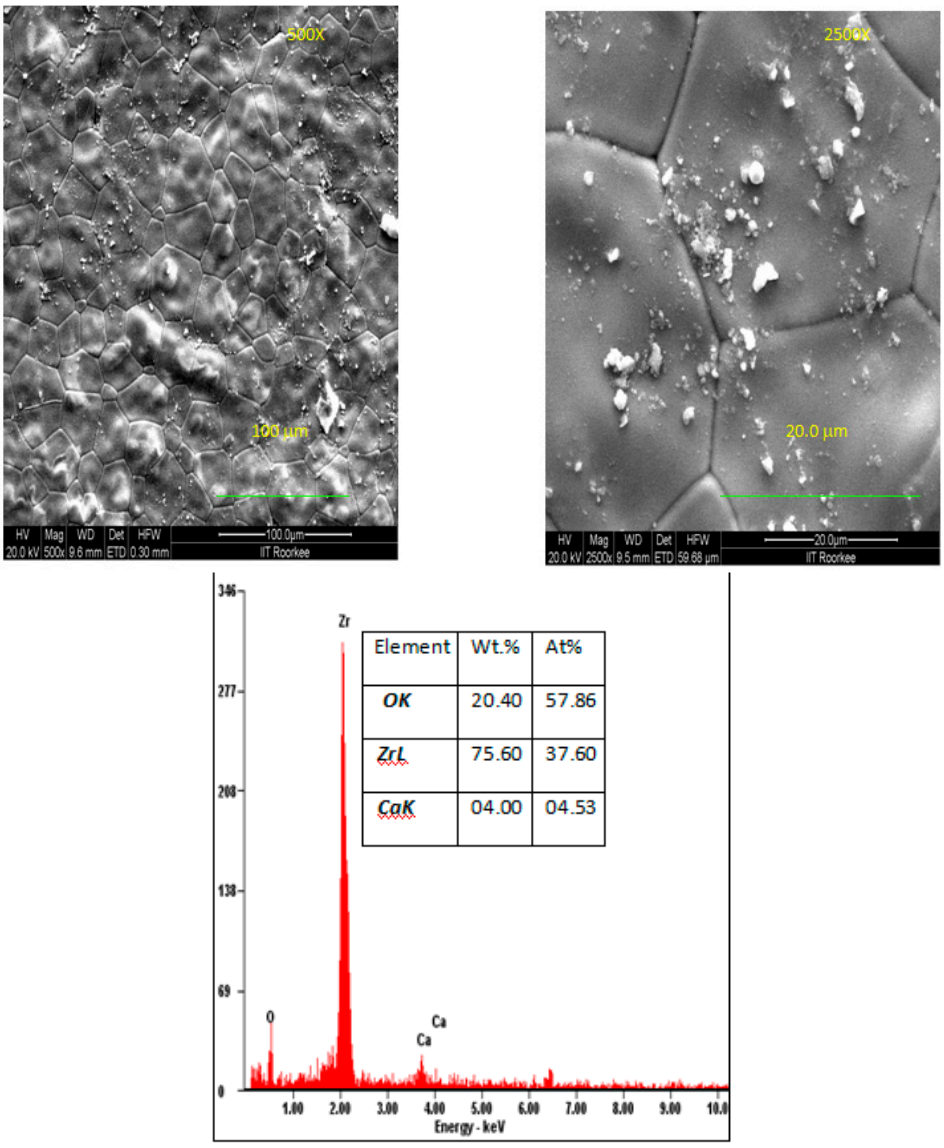


Figure 4. Nine mol% CaO-stabilised zirconia SEM and EDS.

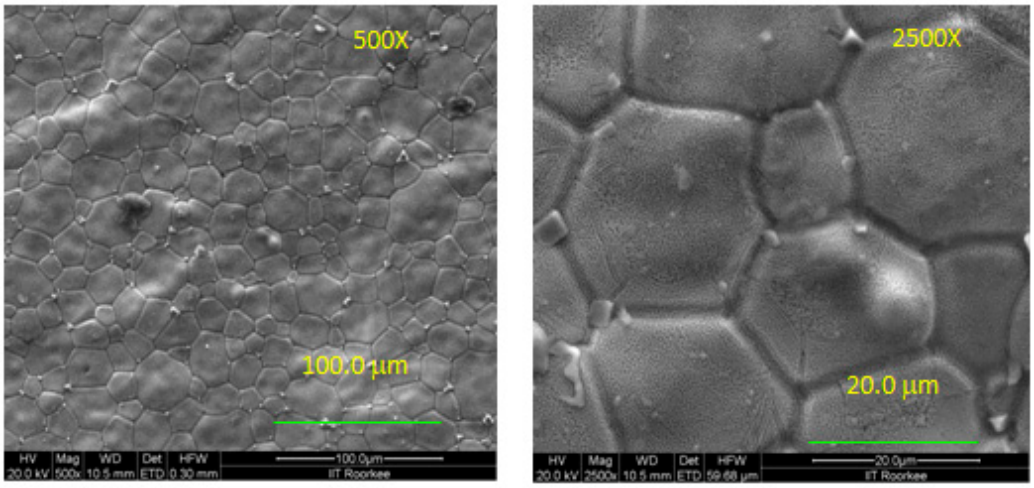


Figure 5. Twelve mol% CaO stabilised zirconia SEM and EDS.

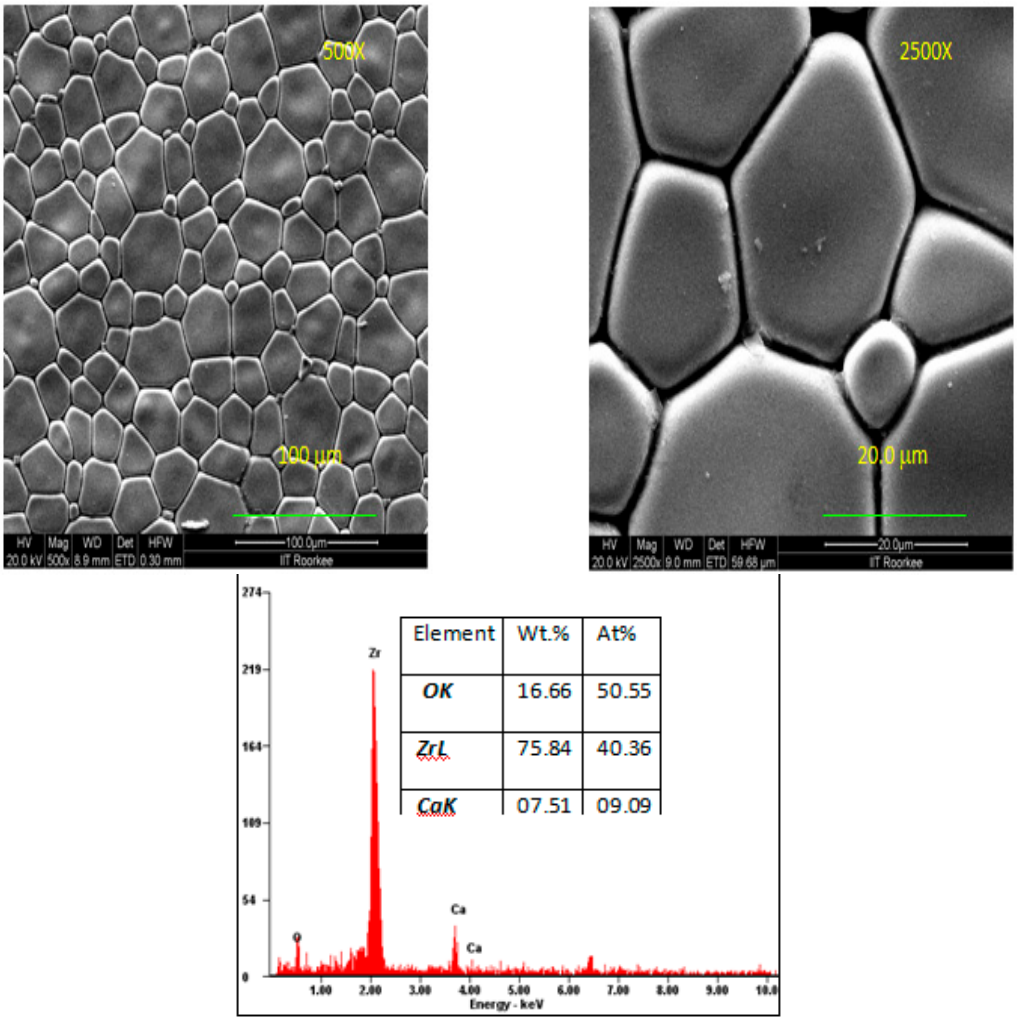


Figure 6. Fifteen mol% CaO-stabilised zirconia SEM and EDS.

The Vicker's hardness number was measured as it is one of the important characteristics in defining the use of material for load-bearing applications in dental implants [13,19]. Therefore, to understand the impact of CaO composition, sintering temperature, and holding time over hardness. Table 5 shows the values obtained from the Vicker's hardness test and the calculated values of flexural and compressive strength using the formulae.

Table 5. Vicker hardness, flexural strength, and compressive strength of CSZ samples.

S. No.	Mol% CaO		Sintering Temp (°C)	Holding Time (h)	Hardness (GPa)	Flexural Strength (MPa)	Compressive Strength (MPa)
1	9%	A	1400	2	8.42	1150	4650
2			1500	2	8.7	1181	4700
3			1600	2	10.56	1190	4700
4		B	1500	2	8.7	1180	4700
5			1500	3	8.8	1185	4720
6			1500	4	8.7	1192	4700
10	12%	A	1400	2	9.25	1214	4840
11			1500	2	8.52	1246	4860
12			1600	2	10.48	1262	4860
13		B	1500	2	8.52	1246	4860
14			1500	3	8.81	1248	4880
15			1500	4	8.84	1252	4880
19	15%	A	1400	2	8.92	1236	4890
20			1500	2	9.25	1268	4900
21			1600	2	11.88	1278	4910
22		B	1500	2	9.25	1268	4900
23			1500	3	9.34	1270	4910
24			1500	4	9.42	1282	4890

Group A samples test results indicate the effect of change in sintering temperature, while Group B samples reflect the effect of change in dwell time at constant sintering temperature. From the values, it is seen that sintering temperature has a significant effect initially, but beyond 1600 °C it has a negative effect on the mechanical properties as reported in the literature.

Figures 7–9 show that holding or dwell time has little effect in comparison to changes in sintering temperature, but it improves the mechanical properties (hardness, flexural strength, and compressive strength) to some extent. Hence, the effect cannot be completely ignored.

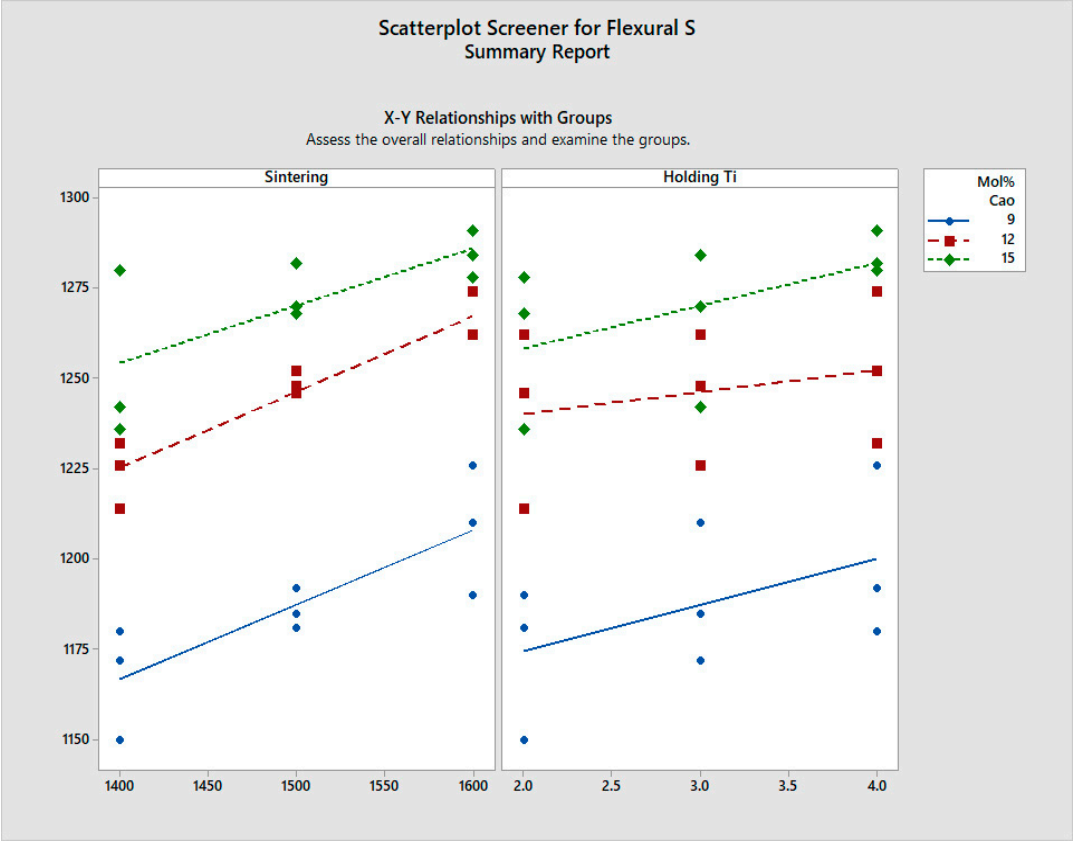


Figure 7. Effect of composition, sintering temperature, and holding time on flexural strength.

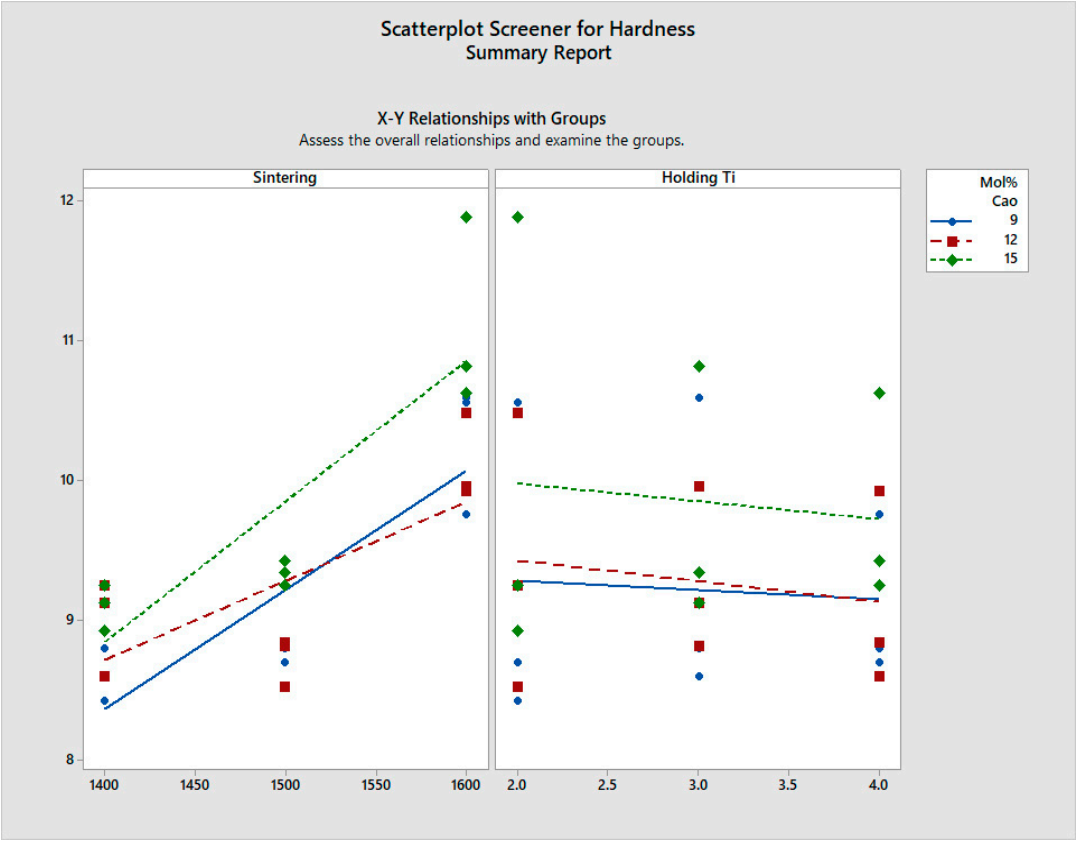


Figure 8. Effect of composition, sintering temperature, and holding time on hardness.

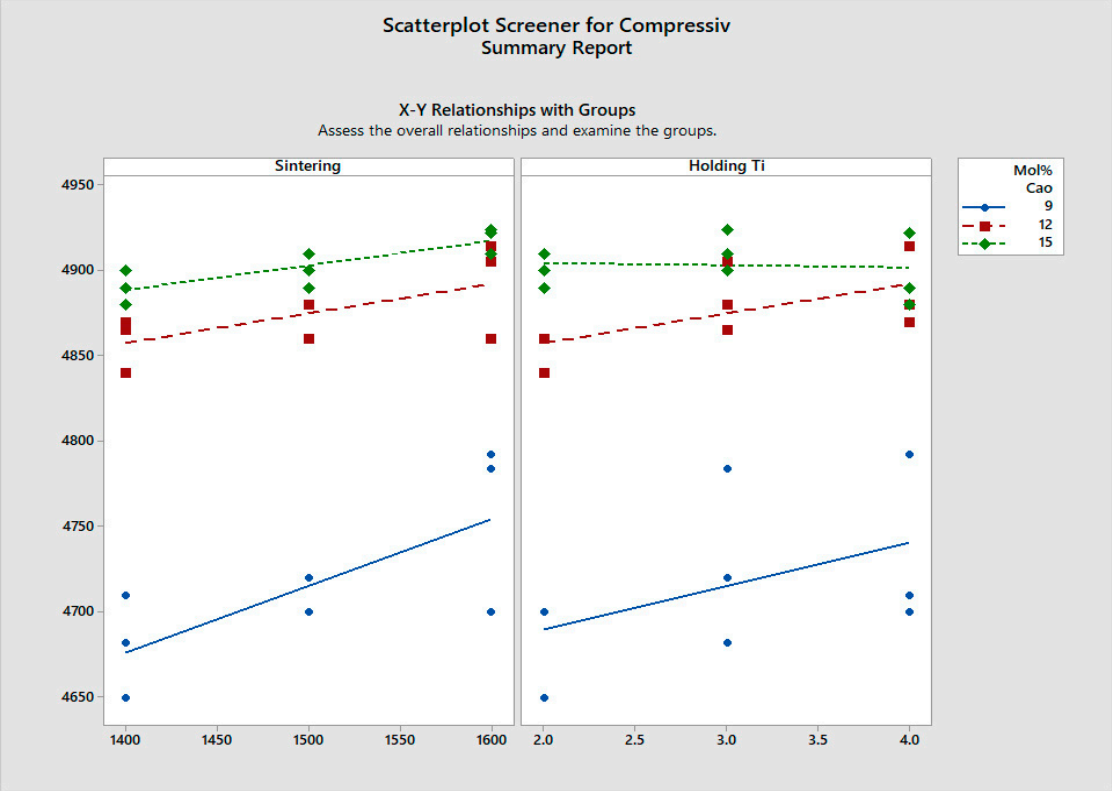


Figure 9. Effect of composition, sintering temperature, and holding time on compressive strength.

4. Discussion

Zirconia's stabilisation goes from being partially stabilised to fully stabilised as the composition of the material was raised, and the microstructure's ability to retain its transformation hardening also improves. A higher temperature during the sintering process results in a higher density, which in turn leads to improvements in the material's hardness, flexural strength, and compressive strength. An increase in the holding time during the sintering process has only a negligible effect; as a result, a shorter duration is recommended [19–23]. Different researchers have reported that the results also vary with respect to the testing method and the samples' processing, such as the fact that the biaxial flexural strength displays roughly a 10% greater value than the three-point bending strength [24]. The boundary conditions used were friction free during compression tests to ensure uniaxial loading [25]. The strength limits achieved in the CSZ sample were comparable to YSZ, Ceria-doped zirconia, or ZTA, which are used in general for dental applications [6,7,9,10,13]. The maximum strengths achieved using the mechanical route under cryo-milling conditions for the CSZ sample were 11 GPaof hardness, 1280 MPa of flexural strength, and 4.9 Gpa of compressive strength, which is in the acceptable limits for being used as a dental material [13]. Higher sintering temperatures, shorter holding times, and fully stabilised (higher composition) zirconia are suitable for achieving the required strength. Biocompatibility and tribology studies were not part of our study, which can be carried out as future work.

5. Conclusions

It can be concluded that:

(1) Mechanical alloying of larger-sized commercial powders (ZrO_2 and CaO) was successfully carried out in a cryogenic environment and micron-sized powders were reduced to nanosized grains.

(2) SEM, XRD, and EDS studies on the powders prepared were carried out to validate the presence of nanograins by calculating size using Scherrer's formula and also validated that powders retained the cubic structure at room temperature.

(3) Density is measured for various sintered samples and found as above 90% theoretical density for samples of all conditions.
(4) Vickers hardness of 11.88 GPawas found for the 15 mol% CaO-stabilised zirconia sintered at 1600 °C and 2 h. Flexural strength varied between 1.1 GPa and 1.3 GPa for all the samples, showing an increase in strength with an increase in sintering temperature. A very marginal increase in flexural strength is noted with increased dwell time.
(5) Compressive strength also reflects similar trend as flexural strength.
(6) From the literature, it is known that sintering temperatures beyond 1600 °C and longer dwell times are not suitable for improving mechanical properties, as samples may get burnt out and become brittle.
(7) Mechanical properties achieved by cryo-milling are comparable to the already in use materials, such as ZTA or ceria-doped zirconia. Low-cost CSZ obtained by cryo-milling can be utilised as an alternative, cheaper dental material.

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