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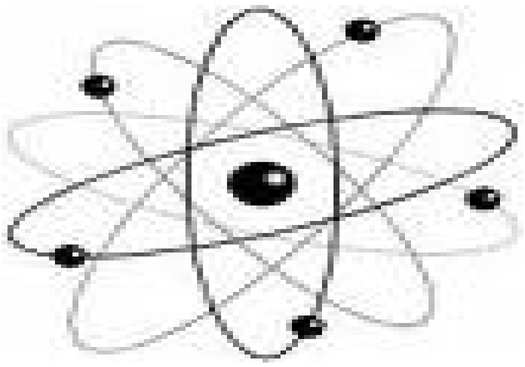

Final Dissertation in Master
Entitled:

Study of the mechanical, structural and thermal properties of dental ceramics

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Thanks

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Dedication

In the name of God the merciful and in terms of love

and fidelity,

I dedicate this present work:

To the two most precious beings in the world

My mother and my father

MAY GOD PROTECT THEM

To those who surrounded and supported me

My SISTERS

NADJETTE, HANA, CHAYMA and LOUBNA

My BROTHERS

DJAMEL, REDOUANE, ABDELHALIM, without forgetting SAMIR GH, HAMZA CH

and my BOBO

For their affection, support and understanding they gave me

during all these years of hard work

Moreover, to everyone I love

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General Introduction

The restoration of teeth has been used for more than three decades. This type of restoration has gained popularity from its expected performance and reasonable aesthetics. However, despite its success, the demand for improved aesthetics and concerns about the biocompatibility of the metal has led to the introduction of complete ceramic restoration.

To meet these growing demands, physics and dentistry have evolved considerably in recent years to achieve a true "silent revolution", especially for new, increasingly efficient and increasingly complex materials.

Ceramic is widely used as an indirect denture in dentistry due to its high biological compatibility and pleasant aesthetics. Dental ceramics are materials that are part of systems designed with the purpose of producing dental prostheses that in turn a used to replace missing or damaged dental structures. The latest developments involving dental ceramics are the entry of zirconium in this field, which is characterized by its important physical and aesthetic properties, which led to the increasing demand for it.

As part of our work, study of structural, mechanical and thermal properties of dental ceramics, several experimental methods were used:

- X-ray diffraction.

-Vickers microhardness

-The Scanning Electron Microscopy (SEM) + EDS

This manuscript is organized in three chapters:

The first chapter, which is an introduction to the dental ceramics, this introduction begins with the first materials used in the restoration of teeth, their types and their characteristics, to the use of zirconia in dentistry, which is the subject of our study.

The second chapter deals with the method of preparing the samples and the different characterization techniques used: X-ray diffraction, Vickers microhardness, The Scanning Electron Microscopy (SEM) + EDS.

In the third Chapter, we compile the various results obtained and their interpretation:

Finally, we conclude this research with a general conclusion.

Chapter I:

Dental materials

I.1. What is a biomaterial?

I.1.1. Introduction

Some of the earliest biomaterial applications were as far back as ancient Phoenicia, where loose teeth were bound together with gold wires for tying artificial ones to neighboring teeth. In the early 1900's, bone plates were successfully implemented to stabilize bone fractures and to accelerate their healing. While by the time of the 1950's to 60's, blood vessel replacement were in clinical trials and artificial heart valves and hip joints were in development [1].

I.1.2. Definition

A biomaterial can be defined as any material used to make devises to replace a part or a function of the body in a safe, reliable, economic, and physiologically acceptable manner. On the other hand, it is a synthetic material used to replace part of a living or to function in intimate contact with living tissue [2].

In general, a biomaterial may be described in or classified into representing the tissues responses in three terms. These are bioinert, bioresorbable, and bioactive [1].

- **Bioinert Biomaterials**

The term bioinert refers to any material that once placed in the human body has minimal interaction with its surrounding tissue; examples of these are stainless steel, titanium, alumina, partially stabilized zirconia, and ultra-high molecular weight polyethylene. Generally, a fibrous capsule might form around bioinert implants hence its biofunctionality relies on tissue integration through the implant.

- **Bioactive Biomaterials**

Bioactive refers to a material, which upon being placed within the human body interacts with the surrounding bone and in some cases, even soft tissue. This occurs through a time dependent kinetic modification of the surface, triggered by their implantation within the living bone. An ion exchange reaction between the bioactive implant and surrounding body fluids results in the formation of a biologically active carbonate apatite layer on the implant that is chemically and crystallographically equivalent to the mineral phase in bone. Prime examples of these materials are synthetic hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$], glass ceramic A-W and bioglass®.

- **Bioresorbable Biomaterials**

Bioresorbable refers to a material that upon placement within the human body starts to dissolve (resorbed) and slowly replaced by advancing tissue (such as bone). Common examples of bioresorbable materials are tricalcium phosphate [$Ca_3(PO_4)_2$] and polylactic–polyglycolic acid copolymers. Calcium oxide, calcium carbonate and gypsum are other common materials that have been utilized during the last three decades [1].

I.1.3.The different classes of biomaterials

The nature (metals, ceramics…), the biomedical applications, and the properties of biomaterials are very divers so there is a big diversity of biomaterials. We can classify biomaterials according to their nature in four categories [3]:

- Metallic Biomaterials: (pure metals, metal alloys);
- Ceramic Biomaterials: (bioinert ceramics, bioactive ceramics);
- Polymeric Biomaterials;
- Biomaterials of natural origin;

I.1.3.1. Metallic Biomaterials

The first biomaterials employed were metals. They are good conductors of the heat and of electricity, brilliances and opaque and can be deformed plastically. All these particular properties result from the existence of the metal connection.

The metals and metal alloys are among the first biomaterials used for biomedical applications. They are used mainly in orthopedy (articulations, plates, screw, nails), in stomatology (prostheses, parts of dentures, pivots, leading) and in surgery (instruments). The great diversity of metals and metal alloys allows following classification [3]:

I.1.3.1.1. Pure metals

Pure metals frequently used are:

- **Iron:** lack of corrosion resistance and present at the state isolated an unquestionable cytotoxicity (which disappears when it is put out of alloy).It should be noted that for the fixing of the fractures, the bindings containing wire were the first used and described already by Fabricius.

- **Copper:** is highly cytotoxic and misses mechanical properties necessary.

- **Nickel:** was regarded during long years as interesting in thin layer: in individual, Lambotte of Brussels recommended the use of nickel-plated steel in 1909. In 1924, Zierold has recognized that if nickel caused a light irritation of fabrics, it started on the other hand one acceleration of osteogenesis. However, the demonstration of carcinogenic effects and allergisants made it fall in discredit in this kind of application.

- **Silver:** was used successfully by Listing for the fixing of the fractures. It is not toxic for the bone, but its yield stress is insufficient. In intramuscular establishment, it causes one local answer similar to that produced by the stainless steel, with a light inflammatory reaction at the beginning and a thick vascular collagenic capsule after 5 months (active chemically).

- **Gold:** was used by Petronius as of the 16th century for the repair of the palatine slits. Its ductility is high. However, although it is resistant to the attack by the biological environment, it's very poor mechanical properties make it draw aside from materials intended for the establishment.

- **Platinum:** extremely corrosion resistant and among best is tolerated metals, but it has poor mechanical properties. It is primarily used with the alloy state. In addition to their high price, precious metals of the gold type or platinum present the disadvantage of an important density as well as strong electric and thermal conductivity.

- **Tantalum:** was considered for the realization of surgical implants by Burke by 1940, primarily because of its corrosion resistance, letting note a remarkable biocompatibility. Up to one recent time, its mechanical properties however had restricted its applications to the foldable wires, staples and sheets.

- **Zirconium:** was taken into account for surgical applications by 1950, because it have an excellent corrosion resistance and an absence of toxicity on the body tissues. It has mechanical properties close to those of tantalum, while being definitely less dense. An alloy with 2, 5 % of columbium (another denomination of niobium) was studied more recently to increase its resistance in fatigue.

- **Niobium (or columbium):** is a very similar metal. It should however be noted that tantalum and niobium do not offer good mechanical properties and an excellent corrosion resistance that if they are very pure (99, 90 % at least). Their high melting point require the recourse to the powder metallurgy or fusion by electron beam or arc under ultra-high vacuum (to avoid the contamination by hydrogen, carbon, oxygen, nitrogen).Their modulus of elasticity is closer to that of the bone than that of alloys containing cobalt. Their behavior in friction returns them however little indicated for articular surfaces.

With this category, most known is the use of gold in dentistry. The high cost of these materials their use makes increasingly rare [3].

I.1.3.1.2. Alloys

The combination of a metal with one or more other metallic or non-metallic elements makes an alloy [3].

I.1.3.1.2.a. Precious dental alloys

Precious alloys can be classified according to their field of use: alloys for metal-ceramic techniques, universal alloys and alloys conventional. Universal alloys can be ceramized with low ceramics fusions. The advantages of these alloys are numerous, in particular, on the biological level and for their corrosion resistance. Finally, the standards still recall the old classification (former AFNOR standard) in four types:

Soft (hardness Hv from 60 to 90)
Medium (hardness Hv from 90 to 120)
Hard (hardness Hv from 120 to 150)
Extra-hard (hardness Hv greater than 150 after casting and greater than 220 after hardening).

Some elements, with concentrations lower than the thousandths, have effects on the properties or the structure of the final alloy. It is therefore important to know all the components. The basic elements are added in varying proportions silver, copper and alloys, micro-additions of ruthenium, indium, iron, manganese, zinc, tantalum, tin, gallium, niobium .With six or more metal components, some alloys become complex.

- **Physical and mechanical properties**

The physical and mechanical properties of precious alloys are very variable according to the composition and the treatments used during processing. Precious alloys are of the ductile type. Their Vickers hardness (Hv) varies between 40 and 330 according to their nature, the shaping and the heat treatments undergone. The modulus of elasticity varies from 80 to 130 GPa. It is of the same order of magnitude as that of titanium and titanium alloys. On the other hand, it is much lower than that of non-precious alloys like Nickel-Chromium and Cobalt-Chrome.

For extra-hard alloys, the percentage of elongation can be relatively low. Hardness increases significantly after a treatment of hardening thermic, which complicates the polishing of the parts thus treated. Rigidity makes it possible to reduce the infrastructures in partial removable prosthesis and to refine the covers in the metal-ceramic technique. Cast metal plates and However, the bridge reinforcement for ceramization must be thickened when made of precious alloys compared to the Co-Cr or Ni-Cr infrastructures.

The run metal plates and they reinforcements of bridge intended for the ceramization must nevertheless be thickened when they are made out of precious alloys compared to the Co-Cr or Ni-Cr infrastructures.

- **Thermal properties**

Among the thermal properties, the coefficient of thermal expansion (TEC) more particularly interests alloys intended the metal-ceramic technique (Table I.2).

Table I.1: Thermal Expansion Coefficient of Precious Alloys (TEC) [4].

materials	**TEC (10^{-6} / °C)**
Gold	14.3
Dentine	8.4
Email	11.2
Commercially pure titanium	8 - 9
Precious alloys -Mixed precious dental alloys for casting and for low ceramics fusion. - Precious dental alloys for metal-ceramic restorations	15.3 to 16.8 13.9 to 15.7

I.1.3.1.2.b. Non-precious dental alloys

Two major classes of non-precious alloys can be distinguished: nickel and chromium-based alloys and cobalt and chromium-based alloys. To be standardized, an alloy must meet certain requirements as to their composition (Table I.2).

Table I.2: Normative requirements for cobalt-based and nickel-based alloys [4].

Cobalt base alloys	**Nickel base alloys**
Principal cobalt constituting **Chrome** equal or higher than 25 m% **Molybdenum** equal or higher than 4 m% **Cobalt** + **Nickel** + **Chrome** equal or superior than 85 m%	**Principal nickel constituting** **Chrome** equal or higher than 20 m% **Molybdenum** equal or higher than 4 m% **Cobalt** + **Nickel** + **Chrome** equal or superior with 85 m%

- **Mechanical and physical properties of Ni-Cr and Co-Cr alloys**

The properties of Ni-Cr and Co-Cr alloys are reported in Table I.3.These values, very variable from one alloy to another, have a primarily comparative interest. Users are therefore strongly advised to consult the technical sheet of the alloy for more precise information on these data. It should also be added that these are highly dependent on the conditions of development by foundry. This procedure combines a set of phenomena such as solidification, reflow, and possibly heat treatments. All these phenomena interfere with the microstructure and the mechanical properties of the castings.

Table I.3: Mechanical properties of non-precious alloys [4].

Alloy types	**Yield stress (MPa)**	**Rupture limit (MPa)**	**Modulus of elasticity (GPa)**	**Lengthening (%)**	**Hardness (Vickers)**
a) Alloys Co-Cr-Mo	496 - 690	640 - 825	186 - 228	1,5 - 10	300 - 380
b) Metal-ceramic technique					
Ni-Cr	255 - 730	400 - 1000	150 - 210	8 - 20	210 - 380
Co-Cr-Mo	460 - 640	520 - 820	145 - 220	6 -15	330 - 465

Among the thermal properties, the coefficient of thermal expansion (TEC) is of particular interest for alloys intended for the metal-ceramic technique (Table I.4). The TEC values are comparable to those of precious alloys and therefore allow the use of the same ceramics [4].

Table I.4: Thermal expansion coefficient (TEC) of non-precious alloys [4].

materials	TEC (10^{-6} / °C)
Gold	14.3
Dentine	8.4
Email	11.2
Co-Cr Alloys	13.9 to 15.5
Ni-Cr alloys 25 to 600 °C	13 to 15

I.1.3.2. Ceramic biomaterials and glasses

The term ceramic is a term for a non-organic and non-metallic solid elements (are polyphase solids) compounds of oxides, carbides, nitrides and borides. Ceramics and glass have in common to be, for the most part, made of mineral raw materials such as oxides or silicates, treated to varying degrees at high temperatures. Used for the first time in 1970 in France [3].

Ceramics and glasses are used as bone fillers, for hip prostheses, dental implants, inner ear implants and heart valves. This class of biomaterials can be divided into two sub-categories: inert bio ceramics and bioactive ceramics.

I.1.3.2.1. Inert organic ceramics

An inert biomaterial is a material endowed with a biological, chemical, physical and thermal inertia so as not to modify the normal physiological functions of the body. The most widely used inert ceramic as a biomaterial represented by alumina (Al_2O_3) and zirconia (ZrO_2), which are used for dental implants, for hip prostheses because of their low coefficient of friction.

- **alumina**

Alumina ceramics currently occupy a prominent place among the materials used in friction components for arthroplasty. Alumina indeed has many qualities:

Excellent resistance to all forms of corrosion, good bio-tolerance, a very fine crystalline structure allowing to have an excellent surface finish after polishing, a very low Ra roughness index of up to 0.01 μm, and purity 99.7%, a very high hardness (this is one of the hardest materials after diamond). A high modulus of elasticity (much higher than that of metal alloys), density greater than

3.93; grain size less than 6 µm, bending strength ≥ 500 MPa; compressive strength > 5000 MPa; impact strength: 45 N / cm^2 (0.50 MPa), Young's modulus (380 GPa). Alumina is a fragile material that is low in impact resistance and has poor support for non-uniform stress distribution.

- **The zirconia**

It is generally stabilized with additives (MgO, CaO, Y_2O_3, Al_2O_3, ...) whose rate varies between 5 and 10 %, it has a good resistance to all forms of corrosion, good mechanical characteristics (density: 6.02 g / cm^{-3}, flexural strength 1000-1500 MPa, modulus of elasticity: 210 GPa, compressive strength: (2500 MPa). Good resistance to wear and tear friction, their resistance to fatigue reaches 107 cycles on the test bench [3].

I.1.3.2.2. Bioactive ceramics and bioglasses

A bioactive material is a material that can create strong interactions with living tissue. There are essentially two categories of bioactive ceramics: phosphocalcic ceramics and bioglasses [3].

I.2. Dental ceramic

I.2.1. Definition

Dental ceramics are materials that are part of systems designed with the purpose of producing dental prosthesis that in turn are used to replace missing or damaged dental structures. The literature on this topic defines ceramics as inorganic, non-metallic materials made by man by the heating of raw minerals at high temperatures [5].

I.2.2. Historic

The word Ceramic can be traced back to the Greek term keramos, meaning "a potter" or "pottery". Keramos in turn is related to an older Sanskrit root meaning "to burn". According to a definition in 1967, a ceramic is an earthy material usually of silicate nature and may be defined as a combination of one or more metals with a non-metallic element usually oxygen. The American Ceramic Society had defined ceramics as inorganic, nonmetallic materials, which are typically crystalline in nature, and are compounds formed between metallic and nonmetallic elements such as aluminium & oxygen (alumina - Al_2O_3), calcium & oxygen (calcia - CaO), silicon & nitrogen (nitride- Si_3N_4) [6].

Dental ceramic materials can exist in a glass form (an amorphous solid), which has no crystalline phase; a glass with varying amounts and types of crystalline phase; a mostly crystalline material with small amounts of glass; all the way to a polycrystalline solid (a glass-free material). How ceramics are classified can be very confusing [7].

I.2.3. Classifications

I.2.3.1. Traditional classification

A first classification has been established, depending on the temperature of "fusion" or more properly called sintering. Sintering is a shaping process where an oxide-based powder is heated at high temperature, creating a bond between the grains at the contacts between the particles. Indeed the increase in temperature causes the diffusion of material through the "necks" of sintering. The cooling induces a retraction and a "polycrystalline" solid is obtained in a state of maximum compactness [8].

Table I.5: Classification of ceramics according to their melting range [8].

Ceramic type	Melting temperature	Indications
High fusion ceramics	1280 °C - 1390 °C	Assistant prosthesis
Average fusion ceramics	1090 °C - 1260 °C	“Jacket” or platinum matrix
Low fusion ceramics	870 °C - 1065 °C	Ceramometallic or enameling of metals
Very low fusion ceramics	660 °C - 780 °C	Ceramometallic for enameling of titanium and gold with low melting range

This classification is limited compared to modern ceramics, because the intrinsic properties of ceramics are a direct result of the chemical nature of the material as well as the shaping process used**.**

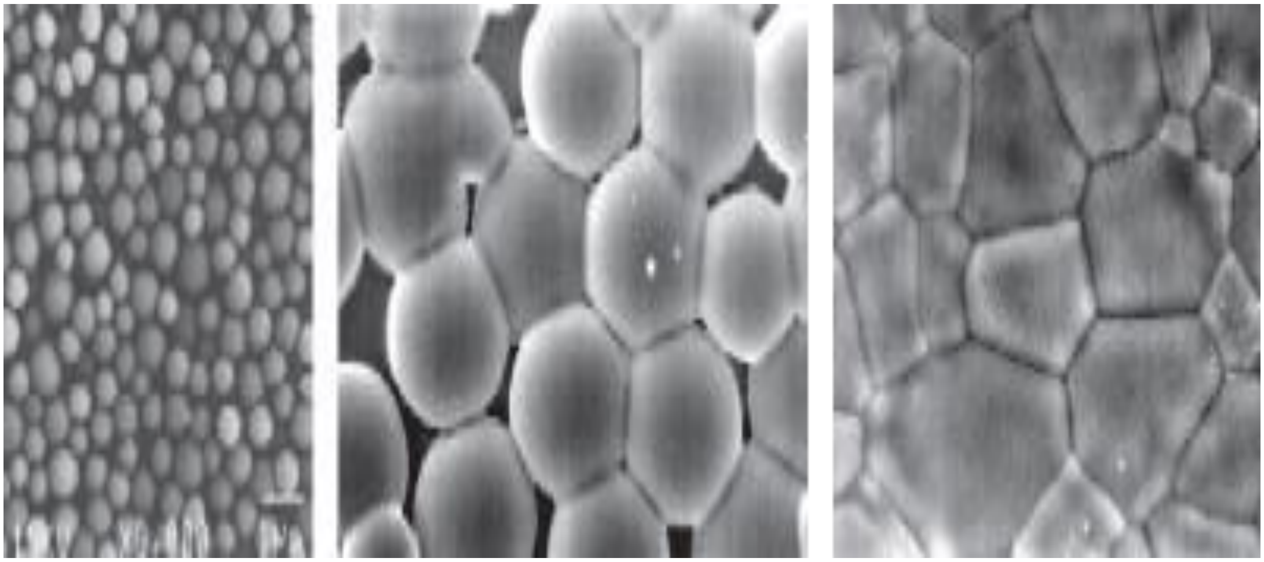


Figure I.1: Sintering of a ceramic powder (from left to right: particles in suspension, beginning of formation of the contacts, result, state of maximum compactness) [8].

I.2.3.2. Microstructural Classification

At a microstructural level, we can define ceramics by the nature of their composition of glass-to-crystalline ratio. There can be infinite variability of the microstructures of materials, but they can be broken down into four basic compositional categories, with a few subgroups:

I.2.3.2.1. Composition Category 1—Glass-Based Systems

Glass-based systems are made from materials that contain mainly silicon dioxide (also known as silica or quartz), which contains various amounts of alumina Alumino-silicates found in nature, which contain various amounts of potassium and sodium, are known as feldspars.

Feldspars are modified in various ways to create the glass used in dentistry. Synthetic forms of alumino-silicate glasses are also manufactured for dental ceramics. These materials were first used in dentistry to make porcelain denture teeth. More recently, powder-liquid versions were made for the specific veneering of alumina-based core systems, eg, In-Ceram® (Vita Zahnfabrik, distributed by Vident, Brea, CA) and NobelProcera™ (Nobel Biocare, Yorba Linda, CA). These materials have a low coefficient of thermal expansion (TEC) around 8 x 10^{-6}/K. These materials can also be used for porcelain veneers using either a refractory die technique or platinum foil.

I.2.3.2.2. Composition Category 2—Glass-Based Systems with Fillers

This category of materials has a very large range of glass-crystalline ratios and crystal types, so much so, that this category can be subdivided into three groups. The glass composition is basically the same as the pure glass Category 1.

The difference is that varying amounts of different types of crystals have either been added or grown in the glassy matrix. The primary crystal types today are leucite, lithium disilicate, or fluoroapatite. Leucite is created in dental porcelain by increasing the K_2O (potassium oxide) content of the alumino-silicate glass. Lithium-disilicate crystals are created by adding Li_2O (lithium oxide) to the alumino-silicate glass. It also acts as a flux, lowering the melting temperature of the material.

I.2.3.2.3. Composition Category 3—Crystalline-based Systems with Glass Fillers

Glass-infiltrated, partially sintered alumina was introduced in 1988, and marketed under the name In-Ceram. The system was developed as an alternative to conventional metal-ceramics, and has met with great clinical success. The system uses a sintered crystalline matrix of a high modulus material (85% of the volume), in which there is a junction of the particles in the crystalline phase.

This is very different than glass or glass-ceramic materials in that these ceramics consist of a glass matrix with or without a crystalline filler in which there is no junction of particles (crystals). The crystalline phase consists of alumina, alumina/zirconia, or an alumina/magnesia mixture appropriately named “spinel”. A process called slip casting fabricates that, or it can be milled from a pre-sintered block of either material.

I.2.3.2.4. Composition Category 4— Polycrystalline Solids

Solid-sintered, monophase ceramics are materials that are formed by directly sintering crystals together without any intervening matrix to from a dense, air-free, glass-free, polycrystalline structure (Figure 14). There are several different processing techniques that allow the fabrication of solid-sintered either aluminous-oxide or zirconia-oxide frameworks [5].

I.2.3.3. Classification Based on Processing Technique

Table I.6. Classification of Dental Ceramics [9].

	Fabrication technique	**Crystalline phase**
Metal-ceramics	Sintering	Leucite
	Heat-pressing on metal	Leucite, leucite & fluorapatite
All-ceramics	Sintering	Leucite
	Heat-pressing	Leucite, lithium disilicate
	Dry pressing and sintering	Alumina
	Slip-casting & glass infiltration	infiltration Alumina, spinel, alumina-zirconia (12Ce-TZP)
	Soft machining & glass-infiltration	Alumina, alumina-zirconia (12Ce-TZP)
	Soft machining & sintering	Alumina, zirconia (3Y-TZP)
	Soft machining, sintering & heat-pressing	Zirconia/fluorapatite-leucite glass-ceramic
	Hard machining	Sanidine, leucite
	Hard machining & heat treatment	Lithium disilicate

I.2.4. Physical and mechanical properties of dental ceramics

Dental ceramics exhibit excellent biocompatibility with the oral soft tissues and are also chemically inert in oral cavity. They possess excellent aesthetics. The structure of porcelain restoration is probably the most important mechanical property. The physical and mechanical properties are described in Table I.7. The strength is also depends on the presence of surface ingredients. The nature, amount, particle size and coefficient of thermal expansion of crystalline phases influence the mechanical and optical properties of the materials .Dental ceramics possesses very good resistance to the compressive stresses, however, they are very poor under tensile and shear stresses. This imparts brittle nature to the ceramics and tend to fracture under tensile stresses [10].

Table I.7: Physical and mechanical properties of dental ceramics [10].

Compressive strength	330 MPa
Diametral tensile strength	34 MPa
Transverse strength	62 - 90 MPa
Shear strength	110 MPa
Surface hardness	460 KHN
Specific gravity	2.2 - 2.3 gm/cm^3
Thermal conductivity	0.0030 Cal/Sec/cm^2
Thermal diffusivity	0.64 mm^2/sec
Coefficient of Thermal expansion	12 × 10^{-6}/ °C

Some mechanical properties exhibited by dental ceramic materials, table I.8 summarizes the results of some mechanical tests.

Table I.8. Reported values for ceramic systems, enamel and dentin subjected to several mechanical tests [11].

Material	**3point bending [MPa]**	**Hardness [GPa]**	**Fracture Toughness**
Feldspathic porcelain	98 – 101	712.9 - 763.9 kg/mm^2 6.98 - 7.48 GPa	1.0 - 1.49 MPa/m$^{0.5}$
Alumina-reinforced ceramic	116 - 117	3.7 - 5.2	1.95 MN/m$^{1/2}$
High-alumina content ceramic	155	5 - 10.8	4.58 MN/m$^{1/2}$

Glass-ceramic	239.2	3.4 - 4.1	1.28 MN/m $^{1/2}$
Leucite-reinforced glass-ceramic	78.37 - 133.56	6.53	1.26 MN/m $^{1/2}$
Lithium Disilicate-Reinforced glass-ceramic	na	5.6 - 6.2	na
Zirconium oxide ceramic	800 - 1590	1188 - 1274 Kg/mm^2 11.64 GPa	4.6 - 6.2 MPa.m $^{1/2}$
Dental enamel	na	343 kg/mm^2 3.36 GPa	0.70 - 1.16 MN/m $^{3/2}$
Dentin	137.9 - 220.63	64.75 - 73.75 kg/mm^2 0.63 - 0.72 GPa	3.08 MN.(m) $^{1.5}$

I.3. Glass ceramics

I.3.1. Historic and definition

Crystalline filler particles can be added mechanically to the glass, for example by mixing crystalline and glass powders before firing. In a more recent approach, the filler particles are grown inside the glass object (prosthesis or pellet for pressing into a mold) after the object has been formed. After forming, the glass object is given a special heat treatment causing the precipitation and growth of crystallites within the glass. Because these fillers are derived chemically from atoms of the glass itself, it stands to reason that the composition of the remaining glass is altered as well during this process termed ‘‘ceraming.’’ Such particle-filled composites are called glass-ceramics. The material Dicor (Dentsply), the first commercial glass-ceramic available for fixed prosthesis, contained filler particles of a type of crystalline mica (at~ 55 vol%) .More recently, a glass-ceramic containing 70 vol% crystalline lithium disilicate filler has been commercialized for dental use (Empress 2; Ivoclar-Vivadent) [12].

In principle, an article is formed while liquid and a metastable glass results on cooling. During a subsequent heat treatment, controlled crystallization occurs, with the nucleation and growth of internal crystals. This conversion process from a glass to a partially crystalline glass is called ceraming. Thus, a glass ceramic is a multiphase solid containing a residual glass phase with a finely dispersed crystalline phase. The controlled crystallization of the glass results in the formation of tiny crystals that are evenly distributed throughout the glass. The number of crystals, their growth rate and thus their size are regulated by the time and temperature of the ceraming heat treatment.

There are two important aspects to the formation of the crystalline phase: crystal nucleation and crystal growth. The thermal treatment known as creaming is composed of two processes: glass is heated up to a temperature where nuclei form (750 °C - 850 °C), and this temperature is kept for a period of time ranging from 1 to 6 h so that crystalline nuclei form in the glass (process known as nucleation). Then, the temperature is increased to the crystallization point (1000 °C – 1150 °C) and this temperature is maintained for a period ranging from 1 to 6 h until the desired level of glazing is obtained (process known as crystallization) [5].

I.3.2. Biocompatible glass-ceramics

This is a new field of investigation of glass-ceramics: a use similar to that of biomaterials in dentistry or more generally in the field of human medicine.

These glass-ceramics can be produced according to the 'hydro plastic' formation, which consists in mixing heat-treated glass-ceramic powder with a liquid phase and baking this amalgam under pressure to form pellets. These pellets can be used in the dental restoration by various processes: thermal vaporization, molding and pressing (Empress II ® by crystallization of lithium disilicate), infusion and modeling (DICORR), polishing (CERECR by crystallization of leucite).

I.3.3. Properties of dental glass ceramics

Table I.9: Properties of dental glass ceramics [4].

Type	Thermal expansion 10^{-6} /C (25 - 500 °C)	Application	Mechanical resistance to bending (MPa)	Young modulus (GPa)	Chemical solubility (µg / cm^2)	Cooking temperature (°C)
Glass or Glass-ceramic	9-10	Titanium or zirconia	80-100	60-80	10-50	750-930
Glass or low fusion glass-ceramic	13-14	Precious non Precious	100-135	60-80	10-50	650-670
Glass-ceramic based on leucite	11,6-14,7	Precious non Precious	60-110	60-80	10-50	710-850
Glass-ceramic high expansion	15-16	High gold content	90-110	60-80	10-50	710-850
Glass-ceramic based on fluorapatite	9-10	Precious non Precious	80-120	60-80	10-50	800-900
Lithium disilicate	9-10,5	/	250-350	90-110	10-50	900-1000

I.4. A special ceramic: zirconia

I.4.1. Historical developments

Zirconium minerals were discovered decades ago but are still referred to as jargon, jacinth, and hyacinth. The metal zirconium (Zr) comes from the Arabic word zargon (golden in color), which in turn derives from two Persian words: zar (gold) and gun (color). The metal dioxide zirconia was discovered in 1789 and was isolated in 1824. Nowadays, zirconia is used extensively for industrial purposes. Research and development on zirconia as a biomaterial were started in the late sixties of last century when the first paper concerning different zirconia biomedical applications was published. Since then, research has focused on yttrium- oxide partially stabilized zirconia (YPSZ) ceramics, also known as yttrium tetragonal zirconia polycrystals (Y-TZP) that both exhibit high biocompatibility and improved fracture toughness. Since a work titled "Ceramic steel?"; zirconia has been considered a tough ceramic [13].

I.4.2. Definition

Pure zirconium exists in a crystalline form as a white and ductile metal and in an amorphous form as a blue-black powder. Among the elements in earth's crust zirconium is ranked 18th in abundance, however, this particular element does not occur in nature in a pure state but only in conjunction with silicate oxides (ZrO_2 x SiO_2) or as a free oxide(ZrO_2).

Zirconium dioxide (ZrO_2), known as zirconia, is a white crystalline oxide of zirconium. Although pure zirconium oxide does not occur in nature, it is found in the minerals baddeleyite and zircon ($ZrSiO_4$). At ordinary temperatures, it has a hexagonal close-packed crystalline structure and forms a number of compounds such a zirconate (ZrO_3^{-2}) and zirconyl (ZrO^{+2}) salts. Zirconia is obtained as a white powder and possesses both acidic and basic properties [13].

I.4.3. Crystallography

Zirconia is present in three allotropic forms under pressure atmospheric:

- Monoclinic ("m") at room temperature up to 1170 °C with reduced mechanical properties.
- Tetragonal or quadratic ("t") from 1170 °C to 2370 °C with consequent mechanical properties.
- Cubic ("c") from 2370 °C to 2680 °C (melting temperature) with moderate mechanical properties [14].

I.4.3.1. Monoclinic form

It is in this form that natural zirconia or baddeleyite is found. It is in a parallelepiped where the Zr^{4+} ions are bound to seven O_2 ions. Because of this arrangement of oxygen atoms, the structure of the oxygen ions is not quite flat. This partly explains the tendency of baddeleyite to form twins (association of several crystals of the same mineral species, but oriented differently, with partial interpenetration) [14].

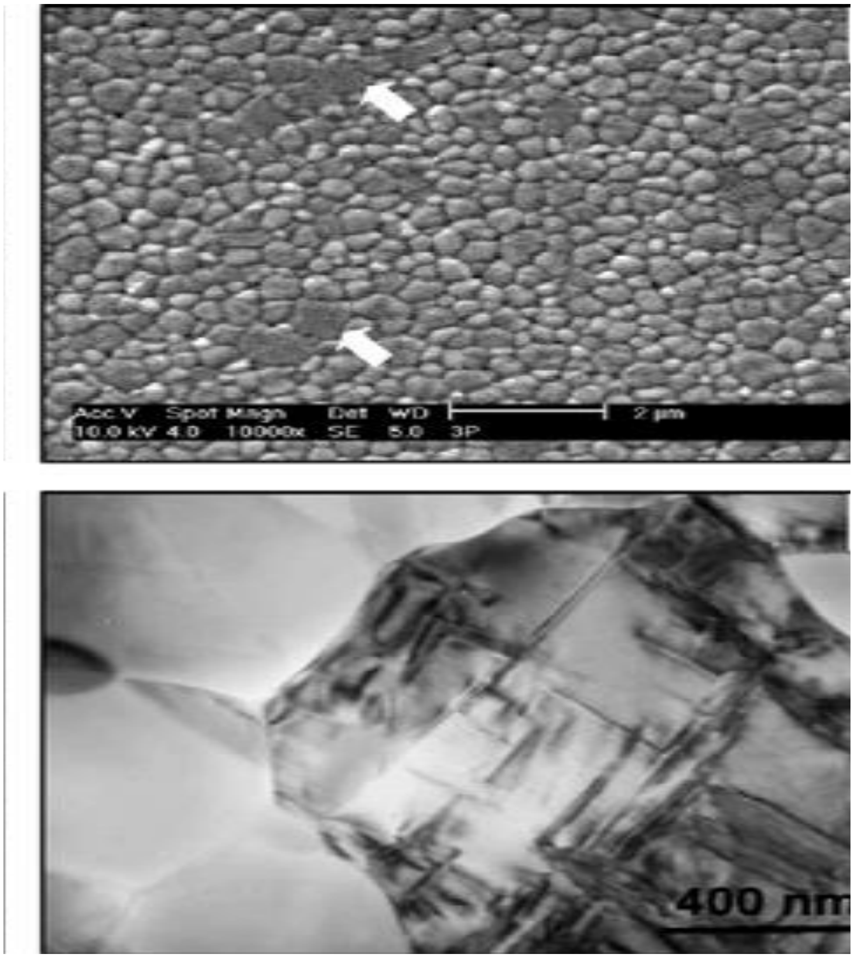


Figure I.2: Electron microscopic observation of the zirconia Y-TZP surface, the white arrows indicate the larger monoclinic grains (A), a monoclinic zirconia grain (B) [14].

I.4.3.2. Tetragonal or quadratic form

Zirconia is organized into a metastable structure between 1170 °C and 2370 °C with tetragonal crystals at right angles. The grains of zirconium oxide have a size, which is between 300 nm and 500 nm. In this arrangement, the Zr $^{4+}$ ions are bound to eight O $^{2-}$: four O $^{2-}$ ions form a flattened tetrahedron and are located at 2,065 Ǻ of the Zr $^{4+}$, four O $^{2-}$ ions form an elongated tetrahedron located at 2,455 Ǻ zirconium and angulated by 90 ° compared to the first tetrahedron.

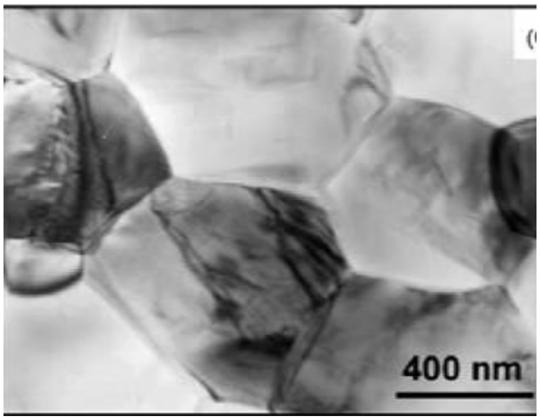


Figure I.3: Quadratic phase stabilized Y-TZP zirconia [14].

I.4.3.3. Cubic form

From 2370 °C appear the cubic crystals: it is the cubic phase, which is maintained until the melting point at 2680 °C. Cubic zirconia has a face-centered cubic structure, and each Zr $^{4+}$ ion is surrounded by eight O $^{2-}$ ions forming two regular tetrahedra [14].

Figure I.4: Example of cubic zirconia [14].

I.4.4. Different types of zirconia ceramics available for dental applications

Although many types of zirconia-containing ceramic systems are currently available, only three are used to date in dentistry. These are yttrium cation-doped tetragonal zirconia polycrystals (3Y-TZP), magnesium cation-doped partially stabilized zirconia (Mg-PSZ) and zirconia-toughened alumina (ZTA) [15].

I.4.4.1. 3Y-TZP

Biomedical grade zirconia usually contains three-mol % yttria (Y_2O_3) as a stabilizer (3Y-TZP). While the stabilizing Y^{3+} cations and Zr^{4+} are randomly distributed over the cationic sites, electrical neutrality is achieved by the creation of oxygen vacancies. 3Y-TZP has been used to manufacture femoral heads in total hip replacement prostheses since the late eighties but its use in orthopedic surgery has since been reduced by more than 90 %, mostly due to a series of failures that occurred in 2001. 3Y-TZP is available in dentistry for the fabrication of dental crowns and fixed partial dentures. The restorations are processed either by soft machining of Presintered blanks followed by sintering at high temperature, or by hard machining of fully sintered blocks [15].

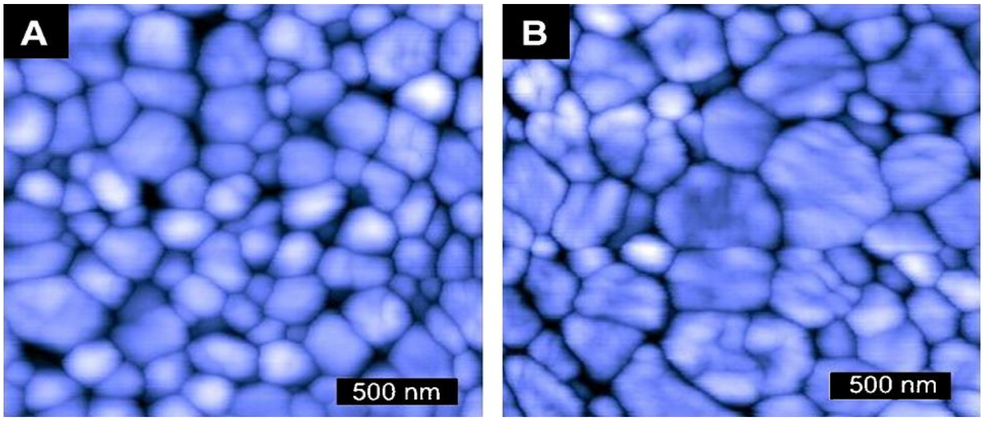


Figure I.5: Atomic force micrographs of 3Y-TZP sintered at 1300 °C and 1450 °C [15].

I.4.4.2. Glass-infiltrated zirconia-toughened alumina (ZTA)

Another approach to advantageously utilize the stress induced transformation capability of zirconia is to combine it with an alumina matrix, leading to a zirconia-toughened alumina (ZTA).

These materials have recently received interest as potential bio-ceramics. One commercially available dental product, In-Ceram® Zirconia® (VidentTM, Brea, CA), was developed by adding 33 vol % of 12 mol % ceria-stabilized zirconia (12Ce-TZP) to In-Ceram® Alumina® [15].

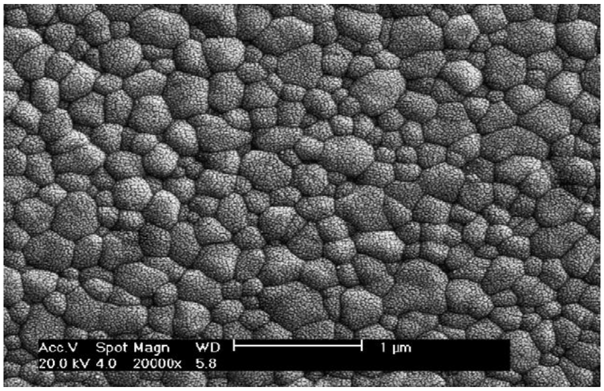


Figure I.6: Scanning electron micrograph of 3Y-TZP for dental applications sintered according to manufacturer's recommendations (Cercon®, Dentsply Ceramco) [15].

I.4.4.3. Partially stabilized zirconia (Mg-PSZ)

Although a considerable amount of research has been dedicated to magnesia partially stabilized zirconia (Mg-PSZ) for possible biomedical applications, this material has not been successful due mainly to the presence of porosity, associated with a large grain size (30 – 60 µm) that can induce wear. The microstructure consists of tetragonal precipitates within a cubic stabilized zirconia matrix. The amount of MgO in the composition of commercial materials usually ranges between 8 and 10-mol %. In addition to a high sintering temperature (between 1680 and 1800 °C), the cooling cycle has to be strictly controlled, particularly in the aging stage with a preferred temperature of 1100 ◦C. Precipitation of the transformable t-phase occurs during this stage, which volume fraction is a critical factor in controlling the fracture toughness of the material. Due to the difficulty of obtaining Mg-PSZ, precursors free of SiO_2, magnesium silicates can form that lower the Mg content in the grains and promote the t→m transformation. This can result in lower mechanical properties and a less stable material. Denzir-M® (Dentronic AB) is an example of Mg-PSZ ceramic currently available for hard machining of dental restorations [15].

I.4.5. Mechanical properties of zirconia

Zirconia has mechanical properties similar to those of stainless steel. Its resistance to traction can be as high as 900-1200 MPa and its compression resistance is about 2000 MPa. Cyclical stresses are also tolerated well by this material. Applying an intermittent force of 28 KN to zirconia substrates, Cales found that some 50 billion cycles were necessary to break the samples, but with a force in excess of 90 KN structural failure of the samples occurred after just 15 cycles. Surface treatments can modify the physical properties of zirconia. Exposure to wetness for an extended period can have a detrimental effect on its properties. This phenomenon is known as zirconia ageing. Moreover, also surface grinding can reduce toughness. Kosmac confirmed this observation and reported a lower mean strength and reliability of zirconium oxide after grinding [13].

I.4.6. Thermal properties

Zirconia, like all ceramics, is a weak thermal conductor. It thus makes it possible to isolate the pulp complex and thus to create prostheses on living teeth. The thermal conductivity of the zirconia is 2W / m.K. The presence of oxygen vacancies in its structure (integrated with yttrium ions) explains this low coefficient. Zirconia is therefore a very good thermal insulator and has no galvanic effect, an important difference with metal-ceramic systems.

The coefficient of thermal expansion of zircon is between 10.5 and 11 * 10^{-6} /K. Cosmetic ceramics must have the same coefficient in order to limit fractures. Indeed, if the difference between the two ceramics exceeds 1 * 10^{-6}, the ceramic is put in compression that causes a risk of fracture [14].

I.4.7. Degradation at low temperature

Zirconia undergoes a degradation phenomenon at low temperature (LTD: low temperature degradation) or aging. Indeed, the isothermal, spontaneous and progressive transformation of quadratic phase zirconia to a monoclinic phase reduces its mechanical properties. This slow t-m transformation occurs when the zirconia is in contact with water or steam causing surface damage. A non-aqueous solution may, however, destabilize the zirconia if it contains a pair of electrons opposed to a proton donor site. The reaction of water with Zr-O-Zr leads to training zirconium hydroxide (Zr-OH) which accelerates crack propagation from a structural defect and promotes t-m transformation.

- **The most important points of LTD:**

- t-m transformation starts at the surface Critical temperature between 200 and 300 °C.

- The effects of LTD are the decrease in strength, hardness and density of the material.

- It is accelerated by water or water vapor.

- It is caused by a t-m transformation accompanied by micro and macro cracks of the material.

- The transformation t-m start in the surface and progresses in the zirconia mass.

- The reduction of the grain size and / or the increase of the dopant level makes it possible to reduce the transformation speed t-m [14].

Chapter II:

Materials and experimental methods

II.1. Introduction

In this chapter, we describe the material used during the experiments. In addition, we describe all tests, equipment used, and the stages of preparation and implementation of the tests in detail.

II.2. Used materials

-Pieces obtained from the zirconium oxide disks.

-These pieces polished with different abrasive paper (120, 180, 220, and 320) and finish (1000, 1200).

-The zirconium oxide composition is as follows:

Table II.1 shows the chemical compositions of the samples used (percentage by mass).

Table II.1: Chemical compositions of zirconia.

composition	**Zr**	**O**	**C**	**Na**
wt. %	58.28	27.61	13.45	0.67

II.3. Experimental techniques used

II.3.1. X-ray diffraction

The X-ray diffraction technique allows detecting the phase composition of the sample. In fact, each phase presents specific diffractions peaks, based on the lattice structure and atom position. Moreover, this experimental method is employed to evaluate the structure of the crystalline materials and to measure the crystallite size.

In an analysis using this technique, an X-ray beam, emitted by a source, sent to the sample to analyze at an angle θ and a detector receives the X-ray beam diffracted by this sample and records the intensity as a function of the diffraction angle 2θ. The mesh parameters of the network can be calculated from the Bragg law. The cell parameters of the network can calculated starting from the law of Bragg (Equation II-1).

$$n\lambda = 2d_{hkl}\sin\theta \ldots \ldots \ldots \ldots \ldots \ldots \ldots \text{(Equation II-1).}$$

Where:

n: 1,2, ... order of the diffracted.

λ: the wavelength of the diffracted beam.

d_{hkl}: is the distance between the parallel crystalline planes.

θ: the angle of incidence of the X-ray beam.

The analysis of X-ray spectra provides information on:

- The crystalline phase (s) (position of the peaks);
- The size of the crystallites (width of the peaks at mid-height);
- Stacking defects (peak shape);
- The orientation of the crystallites (absence or presence of reflections) [16];

In this work, we used a Rigaku mini Flex 600 diffractometer (XRD) (Figure II. 1) of LPCMA laboratory in Mohamed Khider University of Biskra, with a Cu-Kα monochromatic radiation (λ = 1.541838 Å), a 40 kV voltage and a 15 mA current.

Figure II.1: The diffractometer used type Rigaku mini Flex 600.

II.3.2. Heat treatment

We used for sintering the samples a furnace of mark "Wisd FHPX-05" (Figure II. 2) of LPCMA laboratory in Mohamed Khider University of Biskra ,which has a maximum sintering temperature "1200 °C".

The cycles that we followed for sintering the samples are 3 cycles; they are almost as the cycles used at zirconia teeth manufacturers' laboratories, but with a variation in temperature and time.

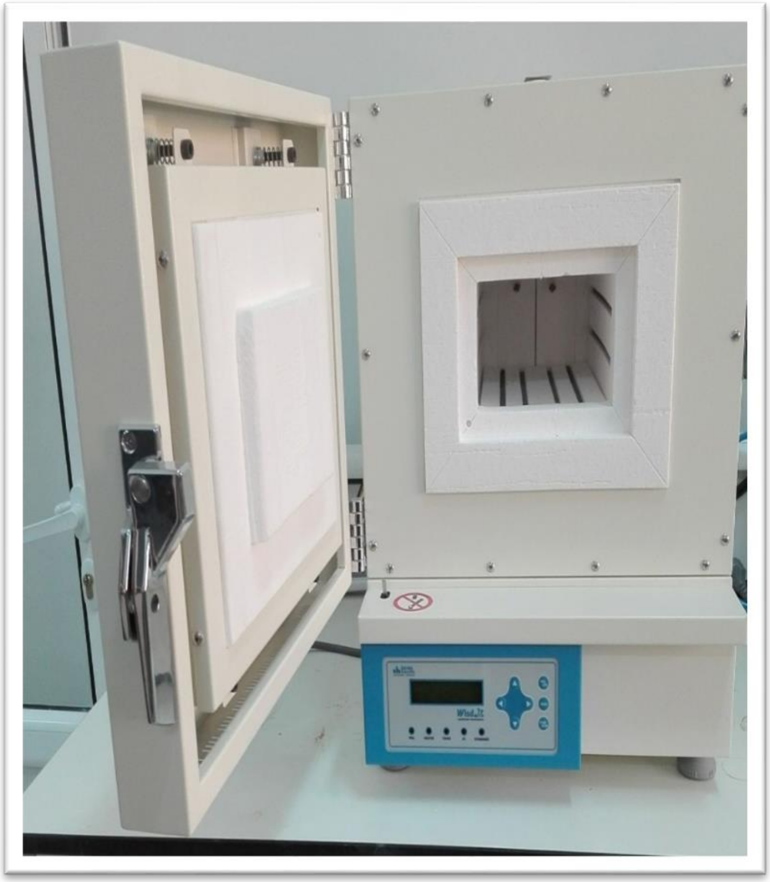


Figure II.2: The furnace used type Wisd FHPX-05.

In the sintering of the zirconia sample, which follow the third cycle where in this cycle the maximum sintering temperature is "1450 °C", we use the furnace of sintering (FigII.3) outside the laboratories of the university and is located in the laboratories of the manufacture of zirconia teeth.

Figure II.3: The furnace used type TABEO.

II.3.3. Vickers microhardness

Vickers microhardness tests consist of studying the lengths of the diagonals of the impression left on the surface of the sample after applying a constant load of one straight pyramid-shaped penetrator with a square diamond base (Figure II.4). The charging time is 15 seconds, as is the load holding time.

The footprint is even larger than the material is soft. Vickers hardness given by the formula:

$$\mathbf{Hv}=1.8544\,\frac{F}{d^2}$$

With F: test load in kilogram force at ± 1%.

$$\mathbf{d=(d_1+d_2)/2\ (mm).}$$

During each test, with a low load, an average of five measurements taken.

The Vickers indenter used for hardness testing and microhardness testing. The hardness tests correspond to loads of between 5 and 100 kilograms force and the microhardness tests correspond to loads of less than 1000 g and relate the hardness on microscopic domains [17]. We used the load: 0.1kg.

The device used brand ZHVμ (Zwick / Roell) (Figure II.5), of LPCMA laboratory in Mohamed Khider University of Biskra, is equipped with an optical microscope to allow positioning the imprint on the desired face; it is allowing the automatic acquisition of microhardness values Hv.

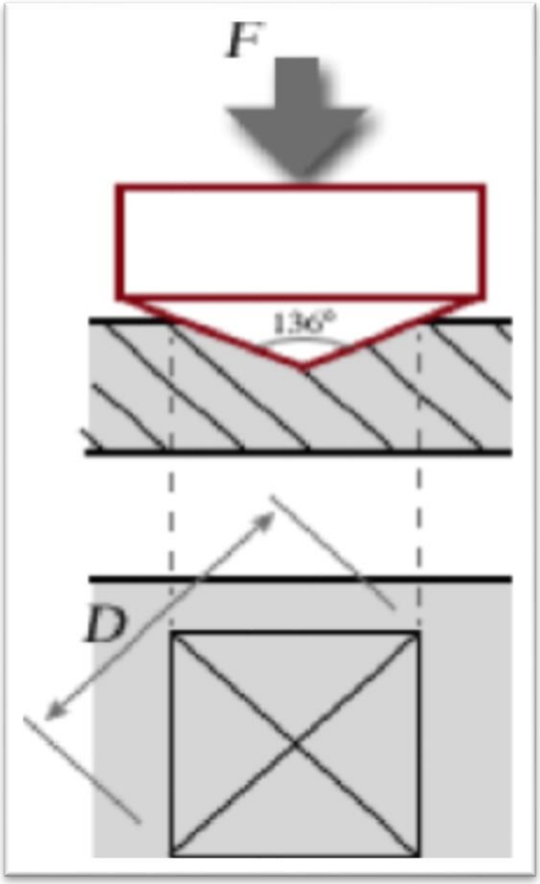


Figure II.4: Vickers hardness test [17].

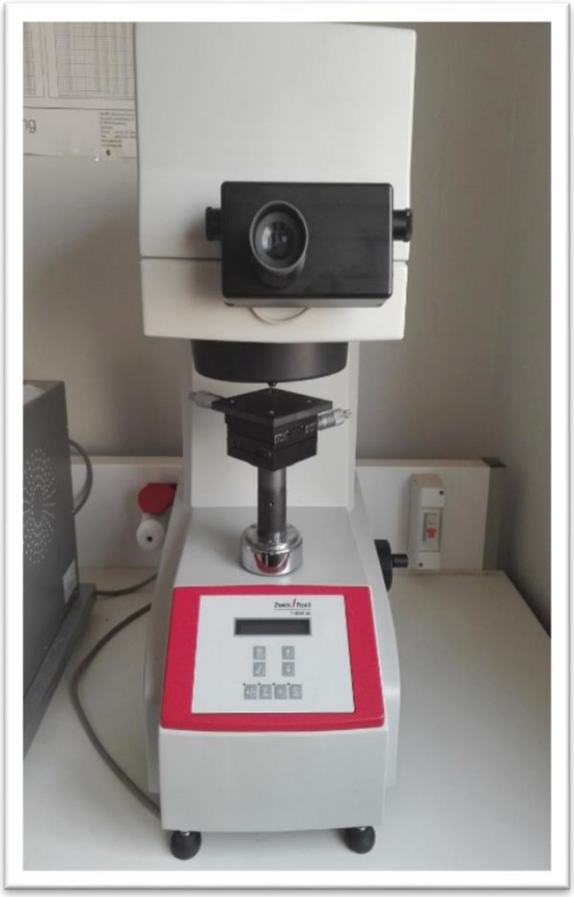


Figure II.5: Microdurometer type ZHVμ.

II.3.4. SEM

The Scanning Electron Microscopy (SEM) is a technique that allows a morphological characterization of powdered and massive samples. It uses the electrons for imaging, reaching higher magnifications and greater depth field than the light microscopy.

A schematic representation of an instrument reported in Figure II.5. From the electron emission source, a heated tungsten filament, the beam focused on the sample surfaces by a series of electromagnetic lenses. The incident electrons imply electrons emission from the sample surface; a suitable detector collects them during the scanning of a raster pattern, producing a topographical image of the analyzed surface [18].

The microstructure of the samples and their composites observed by using SEM type TESCAN VEGA3 (Figure II.6) of LPCMA laboratory in Mohamed Khider University of Biskra. Exploiting a gold sputtering pre-treatment of all samples in order to increase the sample conductivity.

Figure II.6: Schematic representation of a SEM instrument[18].

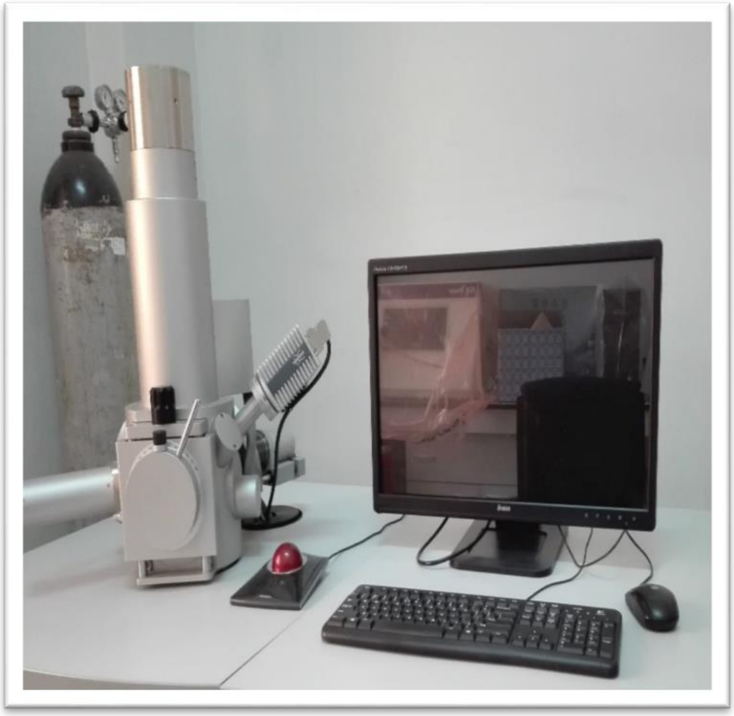


Figure II.7: SEM type TESCAN VEGA3.

Chapter III:

Experimental results and interpretations

III.1. Results of X-ray diffraction

III.1.1. X-ray diffraction of the ZrO_2 samples before sintering

The X-ray diffraction (XRD) analysis of the ZrO_2 samples before sintering is shown in FigIII.1. The main peak is associated with the plane (011), is located at approximately 29,96 ° gives access to the lattice parameter of the ZrO_2 of (a = 3.64 A°, b = 3.64 A°, c = 5.27 A°) and a tetragonal crystal system coherent with the ASTM file (98-000-9993). The peak (011) of the ZrO_2 phase has the greatest intensity, which could indicate the existence of a preferred orientation along this direction.

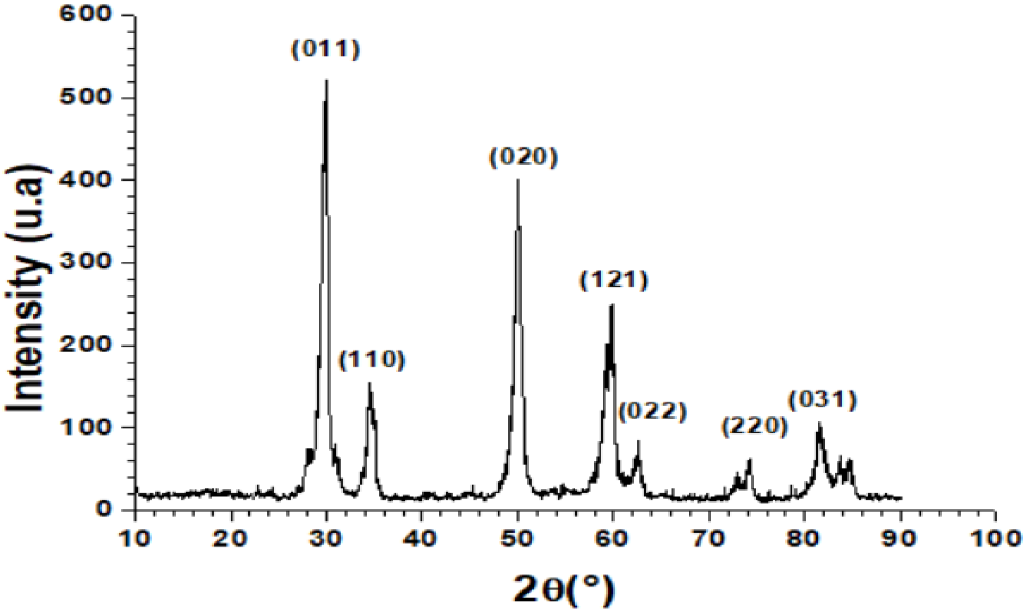


Fig.III.1: X-ray diffraction spectrum of ZrO_2sample before sintering.

III.1.2. X-ray diffraction spectroscopy of the zirconia samples after sintering

III.1.2.1. Sintering at 1000 °C

According to the sintering cycle shown in Fig.III.2, we got an X-ray diffraction (XRD) analysis shown in figure III.3. The stripping of the recorded spectrum assumes that the main crystalline phase is associated with the plane (011) and is located at approximately 30,14 °. It is interesting to note that the peak (011) of the ZrO_2 phase has the greatest intensity, which could indicate the existence of a preferred orientation in this direction. Moreover, presenting a schift to the big angles, which can be explained by the swell of the lattice.

This spectrum also shows a big difference between the intensities of the peak (011) and that of the others, which is the perfect orientation.

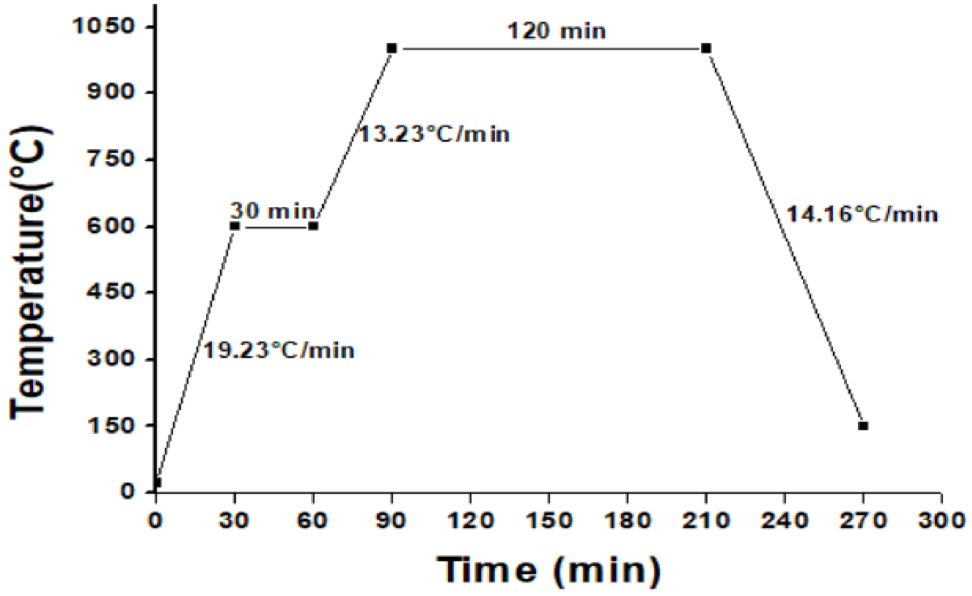


Fig.III.2: Sintering cycle at 1000 °C.

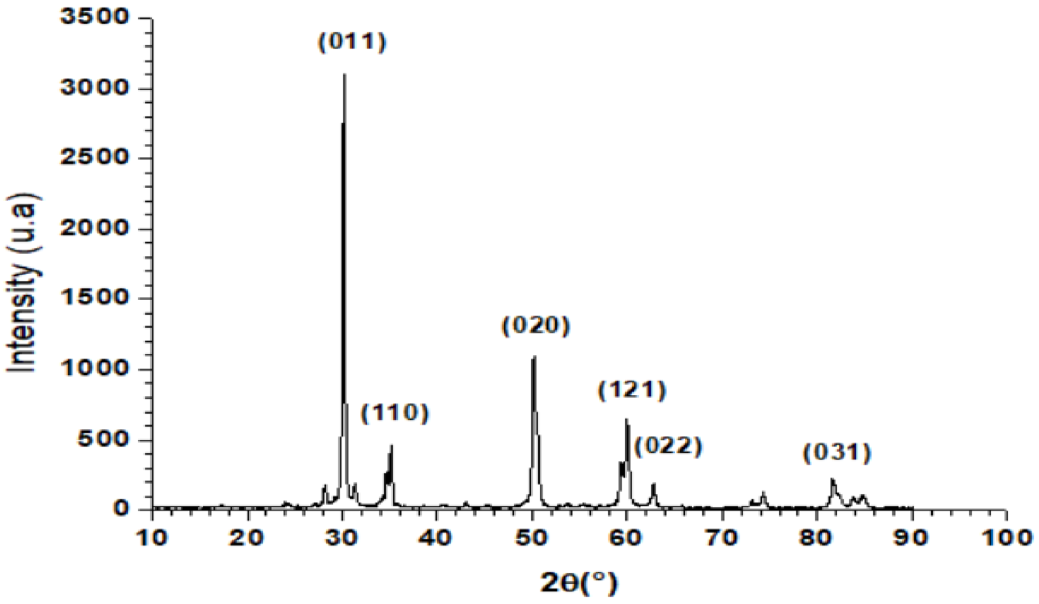


Fig.III.3: X-ray diffraction spectrum of the ZrO_2 sample after sintering cycle at 1000 °C.

III.1.2.2. Sintering at 1200 °C

According to the sintering cycle shown in Fig.III.4, we got an X-ray diffraction spectroscopy as it shown in figure III.5. The X-ray spectrum of the ZrO_2 sample after sintering shows as well that the main phase that crystallizes in this sample is associated with the plane (011) and is located at approximately 30,22°. The peak (011) of the ZrO_2 phase has the greatest intensity, which could indicate the existence of a preferred orientation along this direction. In addition, presenting a schift to the big angles, which can be explained by the swell of the lattice. In addition, this spectrum shows a big difference between the intensities of the peak (011) and that of the others, which is the preferred orientation.

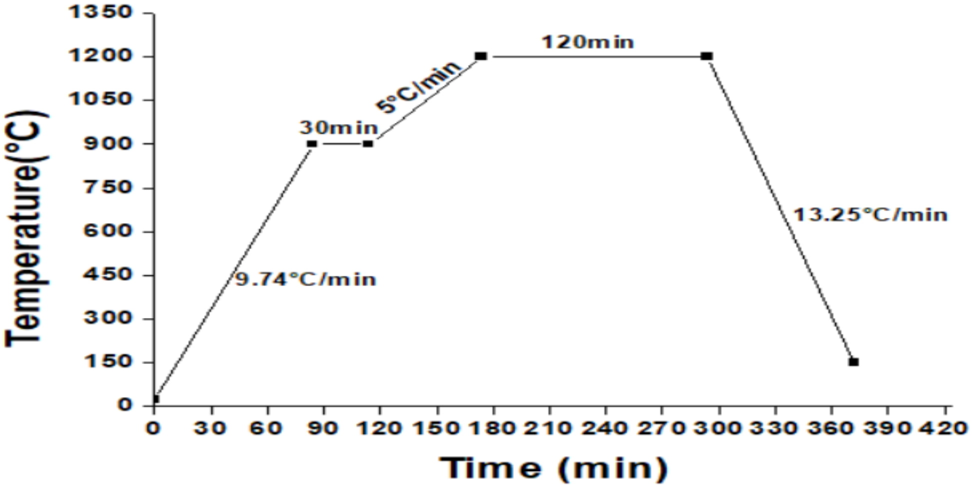


Fig.III.4: Sintering cycle at 1200 °C.

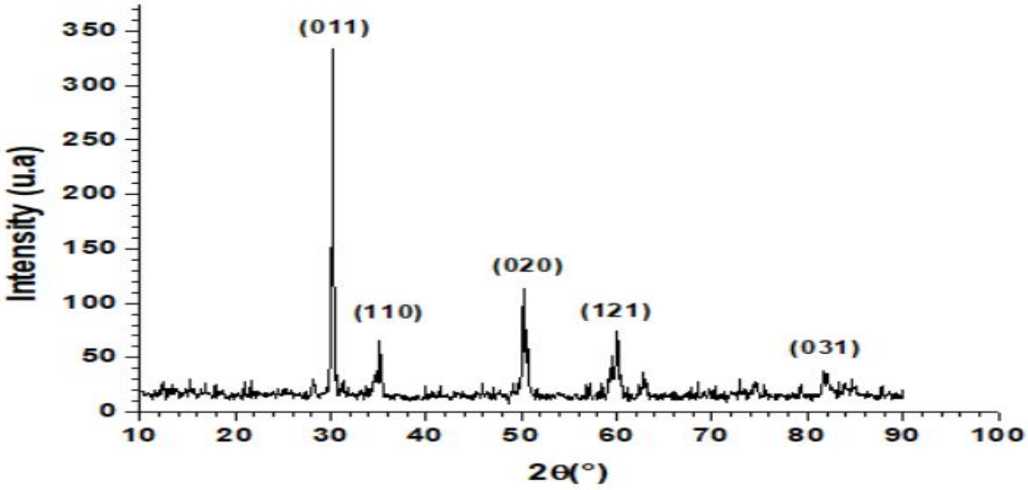


Fig.III.5: X-ray diffraction spectrum of the ZrO_2 sample after sintering cycle at 1200 °C.

III.1.2.3. Sintering at 1450 °C

According to the sintering cycle shown in Fig.III.6, we have this X - ray diffraction spectroscopy, which is shown in figure III.7. The X-ray diffractogram of the sample shows a crystal structure with the orientations (011) (020). The main peak is associated with the plane (011) and is located at approximately 30,3 °.

The spectrum shows a big difference between the intensities of the peak (011) and that of the others, which means that this is the preferred orientation.

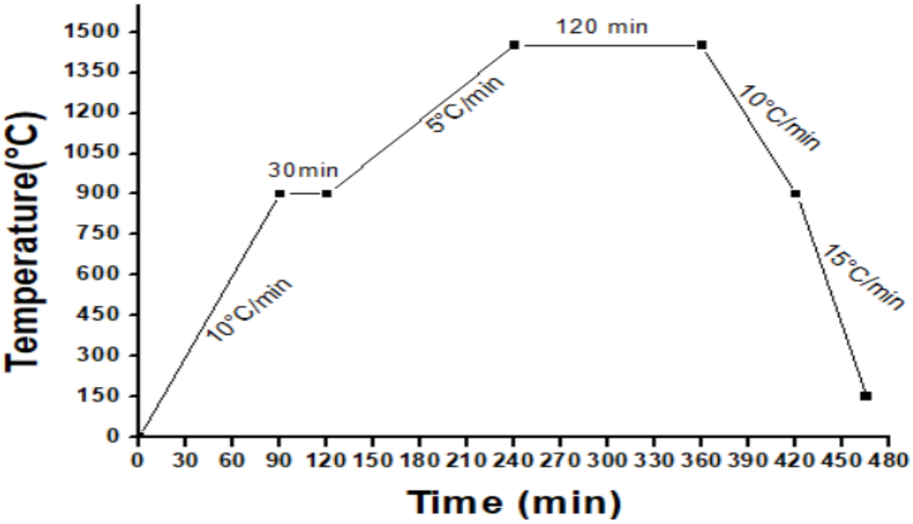


Fig.III.6: sintering cycle at 1450 °C.

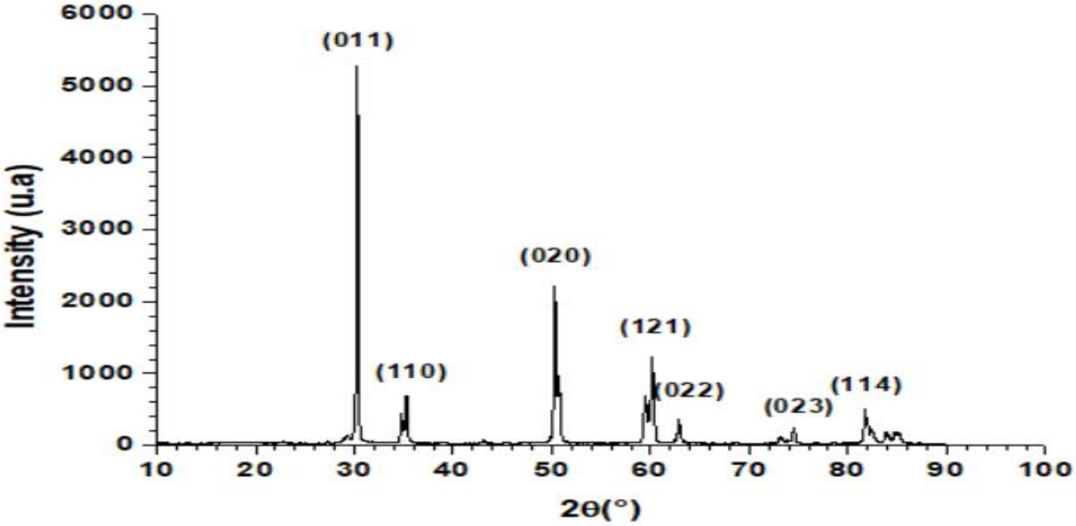


Fig.III.7: X-ray diffraction spectrum of the ZrO_2 sample after sintering cycle at 1450 °C.

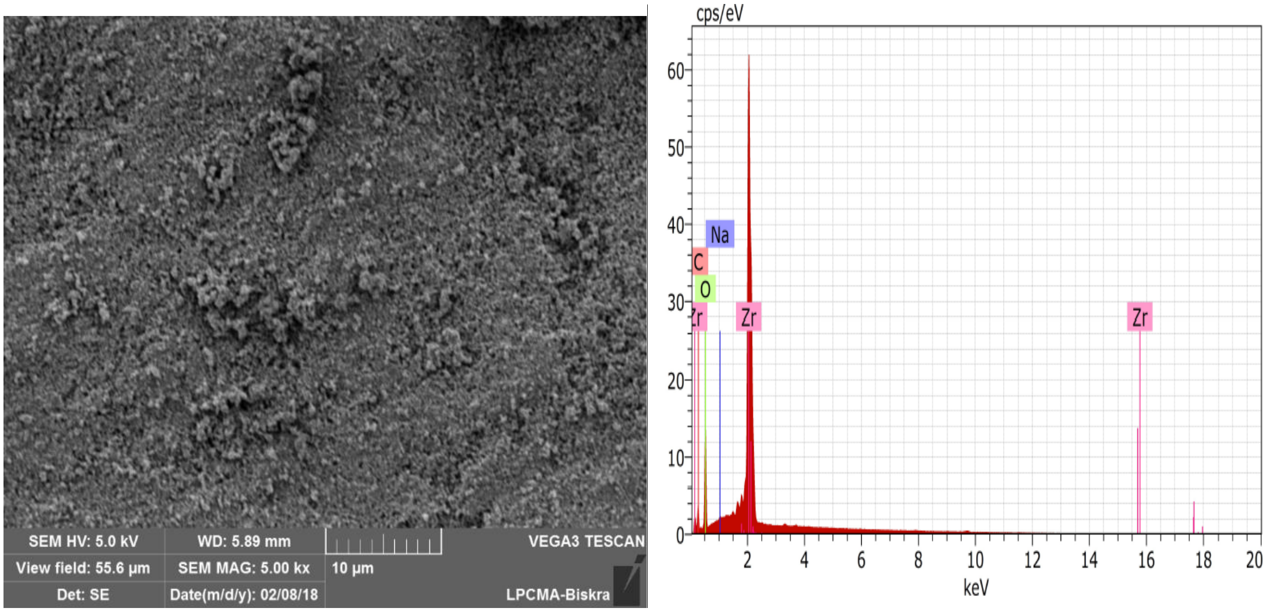
It noted that after the sintering heat treatment of the ZrO_2 samples, the relative intensity of the peaks is increased compared to that of the peaks of the sample before sintered. We can explain this result by the due to a decrease in grain size of the particles of the dominant phase during the sintering.

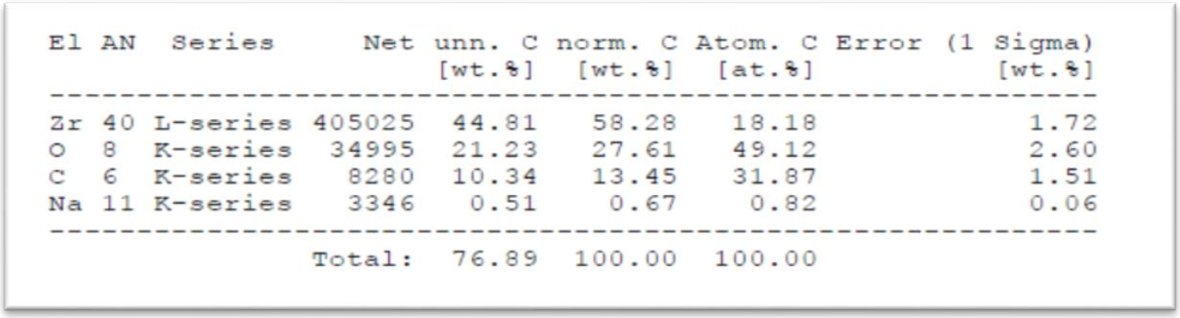
III.2. Results of SEM (The Scanning Electron Microscopy) analyses

III.2.1. Before sintering

Figure III.8 shows the structure observed at low magnification and high magnification zirconia studied before heat treatment.

The surface characterized by spherical granules less than one µm in size. It is homogeneous, compact and has no defects.





```
El AN  Series      Net unn. C norm. C Atom. C Error (1 Sigma)
                       [wt.%]   [wt.%]   [at.%]          [wt.%]
-------------------------------------------------------------
Zr 40 L-series 405025   44.81    58.28    18.18            1.72
O   8 K-series  34995   21.23    27.61    49.12            2.60
C   6 K-series   8280   10.34    13.45    31.87            1.51
Na 11 K-series   3346    0.51     0.67     0.82            0.06
-------------------------------------------------------------
               Total:   76.89   100.00   100.00
```

Fig.III.8: Image obtained by the scanning electron microscope of ZrO_2 samples with their own EDS: (Before sintering).

III.2.1. Influence of heat treatment (After sintering)

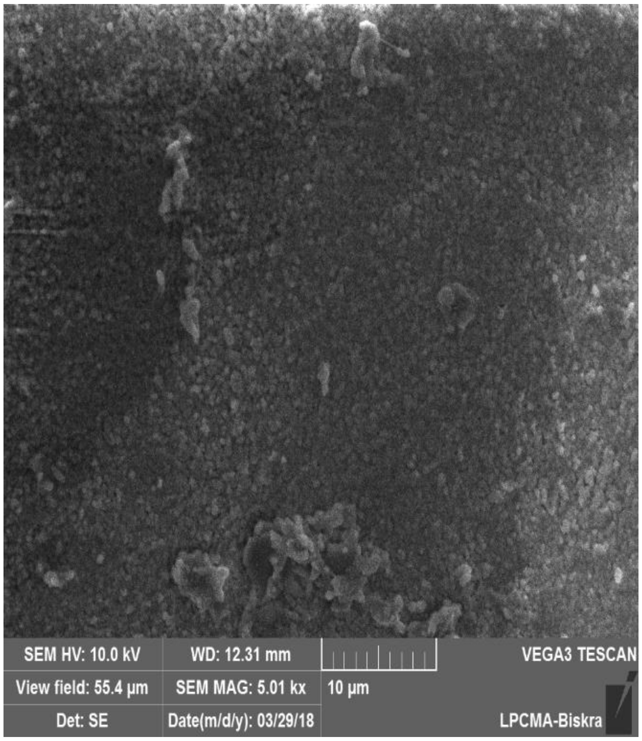
The SEM images, EDS precision analysis of polished surfaces and results presented in Figure III.9, Fig III.10 and Fig III.11. This type of test (EDS) allows microscopic chemical analysis.

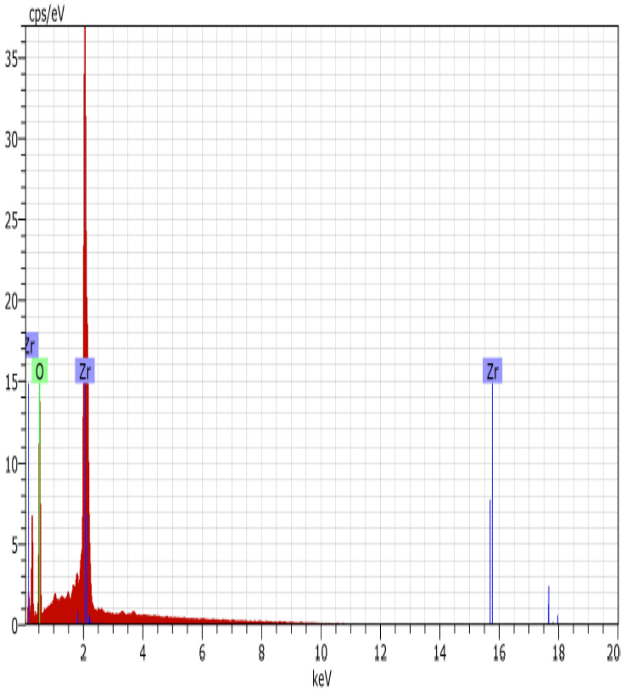
The results show that the grain size decrease for samples of sintering at 1000 °C and 1200 °C comparing with the reference sample (sample not sintered) but the surface stay croaks.

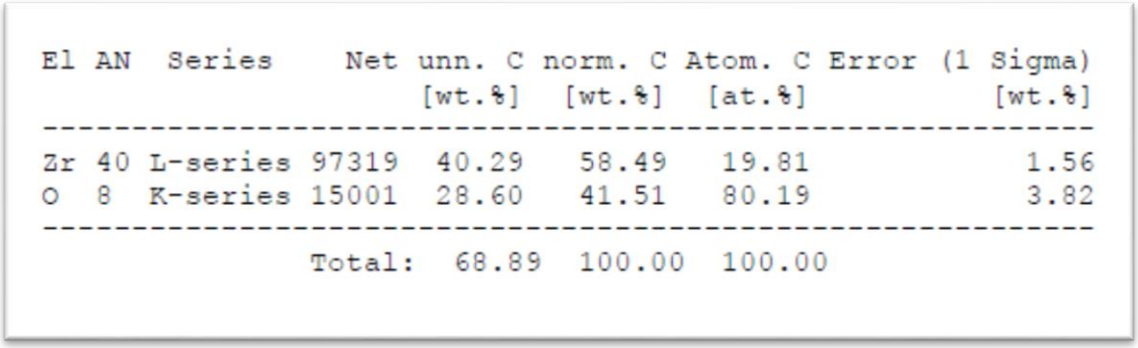
We clearly see a significant decrease in grain size of the granules until their total disappearance for sample sintered at 1450 °C; the surface becomes dense and has a smooth appearance with disappearing pores (Fig. III.8).

The EDS results shows that sintering causes the disappearance of the peaks relative to the elements C and Na. The structure becomes a pure zirconia, only peaks of Zr and O_2 detected.

The results showed that the structure is homogeneous, compact and becomes more compact by increasing the sintering temperature that affects the size of the zirconium granules, which, through EDX, shows that its ratio in the structure is the highest. Depending on the observed homogeneity size, we can conclude that the structure becomes unruffled and look as a natural tooth.

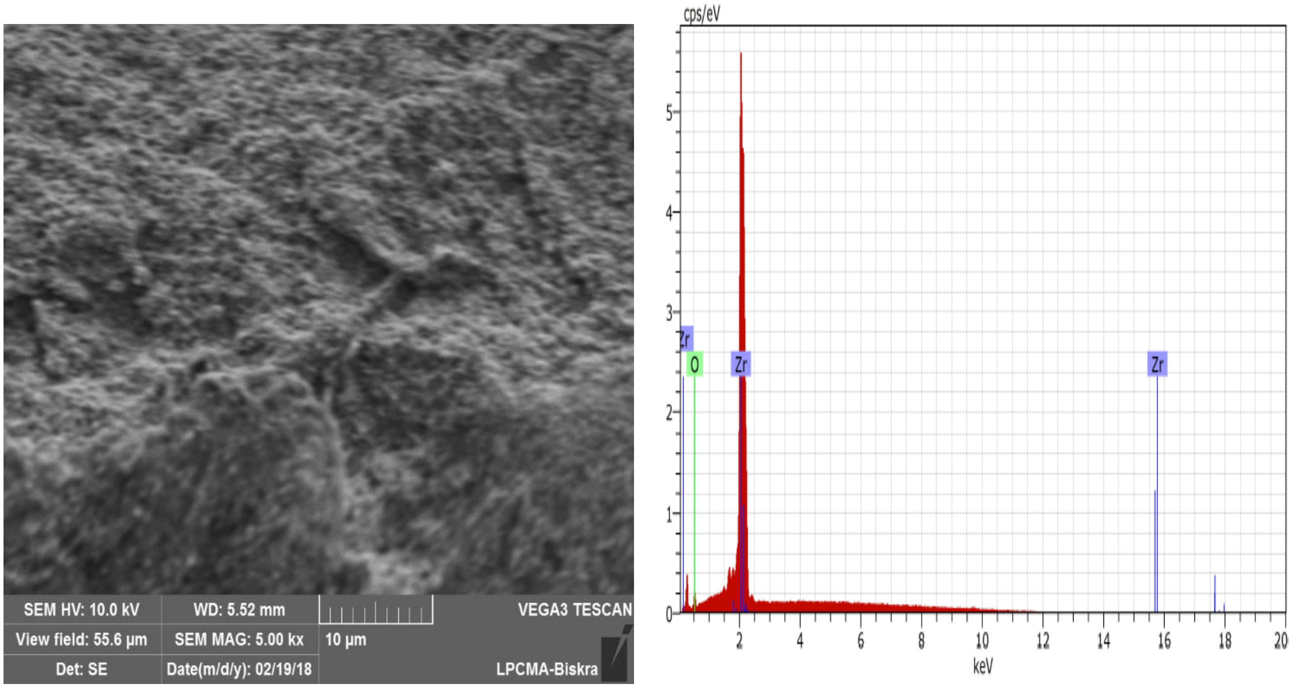


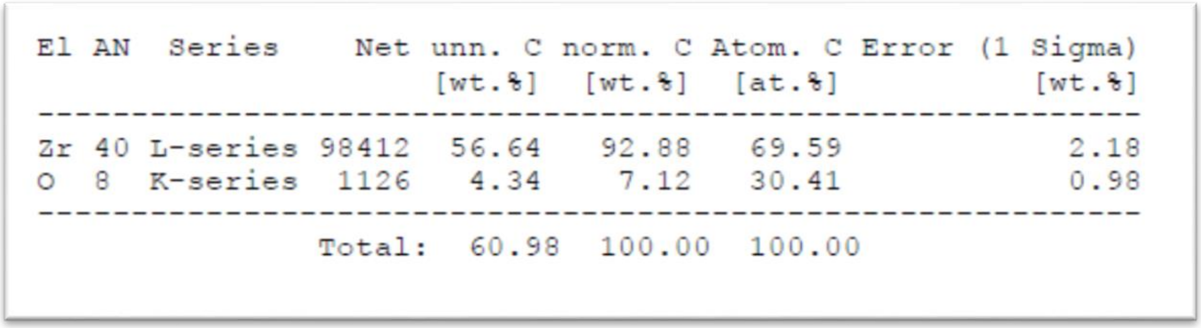




```
El AN  Series     Net unn. C norm. C Atom. C Error (1 Sigma)
                      [wt.%]   [wt.%]   [at.%]            [wt.%]
-------------------------------------------------------------
Zr 40 L-series 97319  40.29    58.49    19.81             1.56
O   8  K-series 15001  28.60    41.51    80.19             3.82
-------------------------------------------------------------
                Total:  68.89   100.00   100.00
```

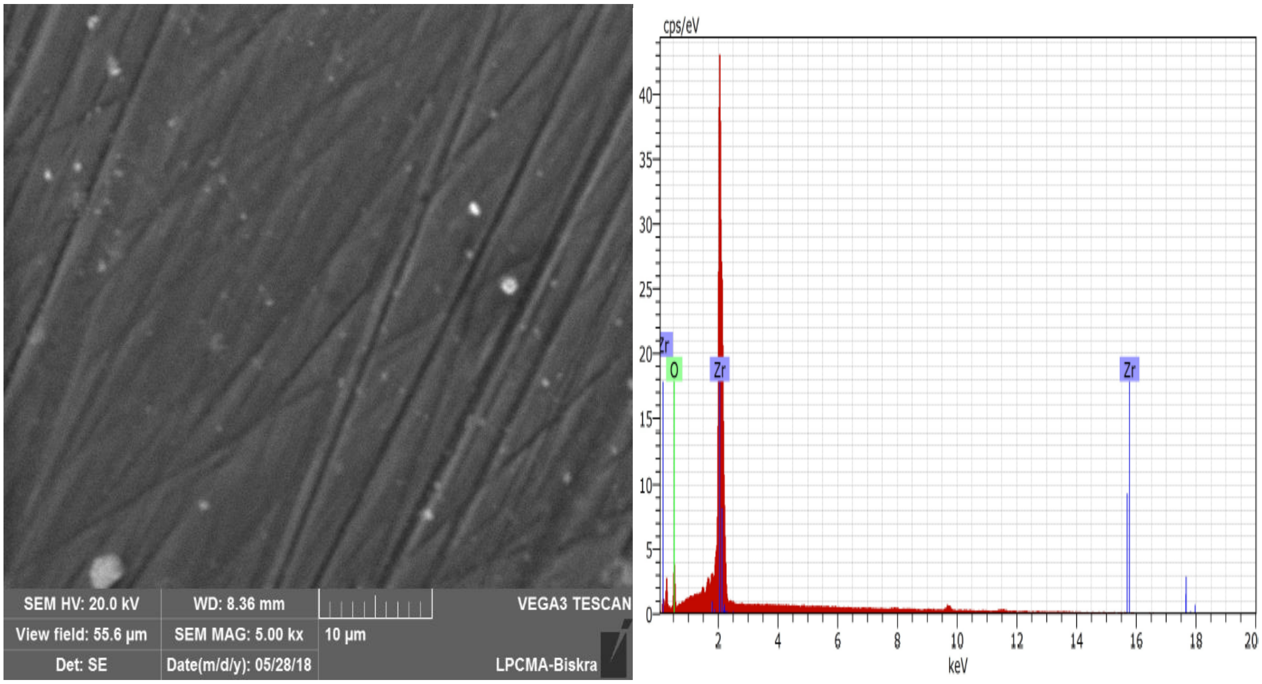
Fig.III.9: Image obtained by the scanning electron microscopy of ZrO_2 sample sintered at (1000 °C) with its own EDS.

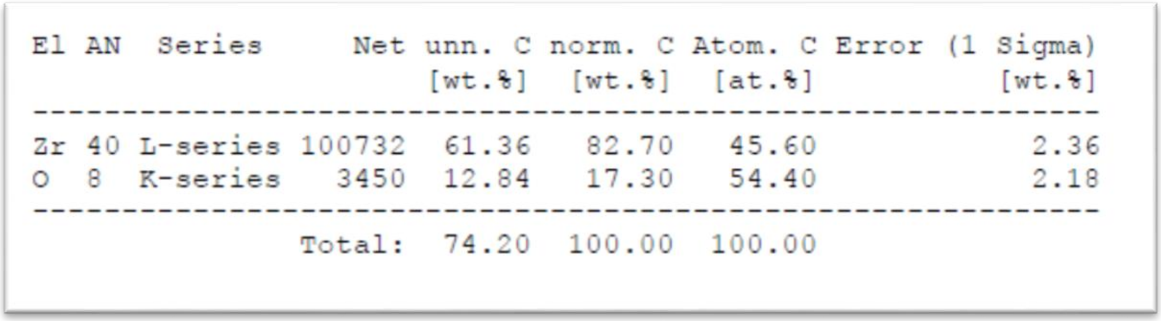




```
El AN  Series     Net unn. C norm. C Atom. C Error (1 Sigma)
                      [wt.%]   [wt.%]   [at.%]            [wt.%]
-------------------------------------------------------------
Zr 40 L-series 98412  56.64    92.88    69.59             2.18
O   8  K-series  1126   4.34     7.12    30.41             0.98
-------------------------------------------------------------
                Total:  60.98   100.00   100.00
```

Fig.III.10: Image obtained by the scanning electron microscopy of ZrO_2 sample sinter at (1200 °C) with its own EDS.





```
El AN  Series      Net unn. C norm. C Atom. C Error (1 Sigma)
                       [wt.%]   [wt.%]   [at.%]          [wt.%]
-------------------------------------------------------------
Zr 40 L-series 100732  61.36   82.70   45.60             2.36
O   8 K-series   3450  12.84   17.30   54.40             2.18
-------------------------------------------------------------
               Total:  74.20  100.00  100.00
```

Fig.III.11: Image obtained by the scanning electron microscope of ZrO_2 sample sintered at (1450 °C) with its own EDS.

III.3. Microhardness measurement results

III.3.1. Microhardness measurement of the reference

Measurements of the microhardness of the studied sample before sintering is shown in table III.1.

Table III.1: The microhardness of the reference sample.

Samples	Hv					Average Hv
Reference	37	38	38	40	42	39

The average value of the sample before sintering is about 39 Hv. We Note that zirconia microhardness values are very low before heat treatment (25 °C), because the surface is less dense and weak.

III.3.2. Influence of sintering on the microhardness

The measurements of the microhardness of the thermally treated samples are summarized in the following table. (Table III.2)

Table III.2: The microhardness of the samples after sintering.

The sintering temperature	Average Hv
1200 °C	460
1450 °C	877.2

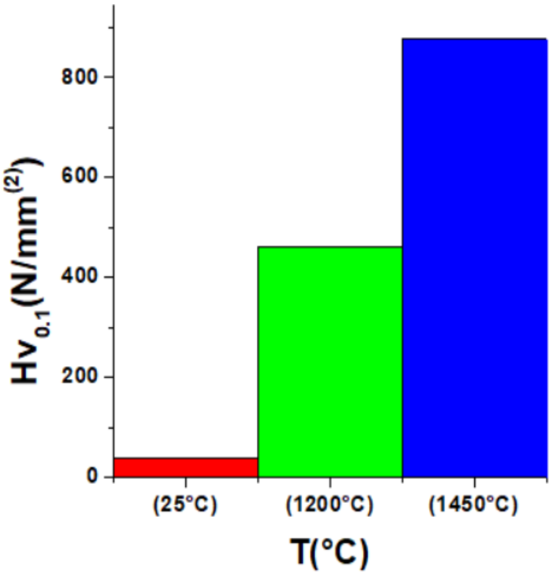
During the microhardness tests, we tried to measure the microhardness of the samples that had sintered at 1000 °C but we were unable to do so because the imprint did not appear so we could not measure. We can conclude that sintering at 1000 °C is not suffisant to give a compact and homogenous structure, the sample become weak.

The microhardness values increased after heat treatment at 1200 °C and reached to an average value of 460 Hv, due to the increase of material's density. However, we observed a variation of the microhardness values on the same surface when we took the measurement; we can explain it by the heterogeneity of the material. The applied temperature (1200 °C) is not sufficient to obtain a compact zirconia material.

At heat treatment with 1450 °C, we observe a significant increase in microhardness values, which indicates a great homogeneity and density. When we took the hardness measurements, we observe that the values obtained at 1450 ° C were very close. This shows that it has become denser, more homogeneous, more compact and more hardened; we can say that we got a zirconia teeth.

The exact measurements of the studied samples show that the value of the hardness increases as the temperature of the sintering increases. This is because the grains size decreases due to the sintering and thus the structure becomes more compact and the density increases.

Fig.III.12 shows the variation of microhardness versus the sintering temperature.



FigIII.12: Variation in the microhardness of the ZrO_2 samples versus the sintering temperature.

III.4.Thermal shock results

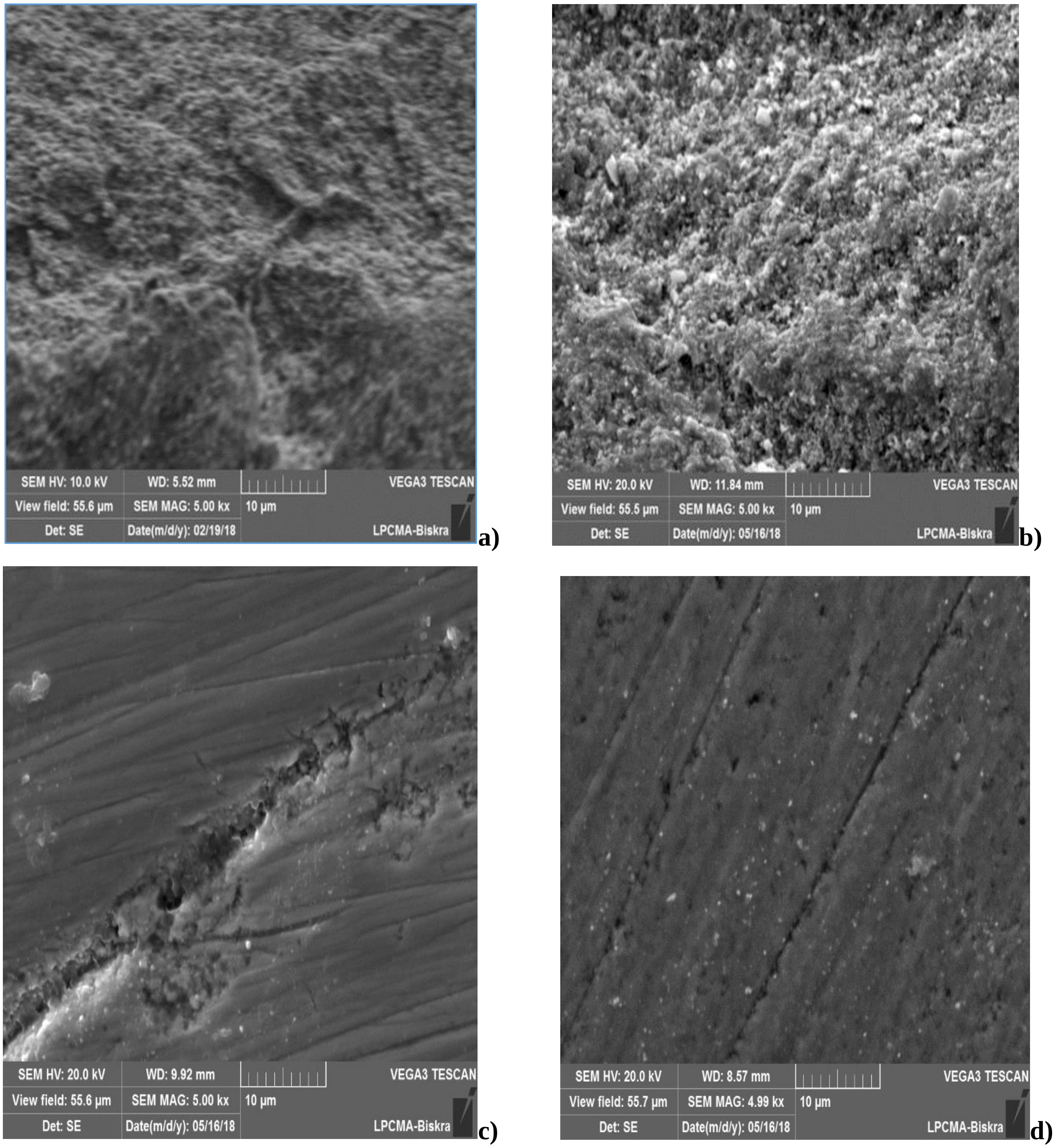
III.4.1. For samples, which had sintered at heat treatment of 1200 °C

Figure III.13.b present sintered samples at 1200 °C, cooled to 25 °C then tempered in ice water for 3 minutes. We observe a surface damage, which becomes with big granules and without fissures, neither pores compared with Fig III.13.a. The damage happens when the zirconia is in contact with water at low temperature that causes a surface damage.

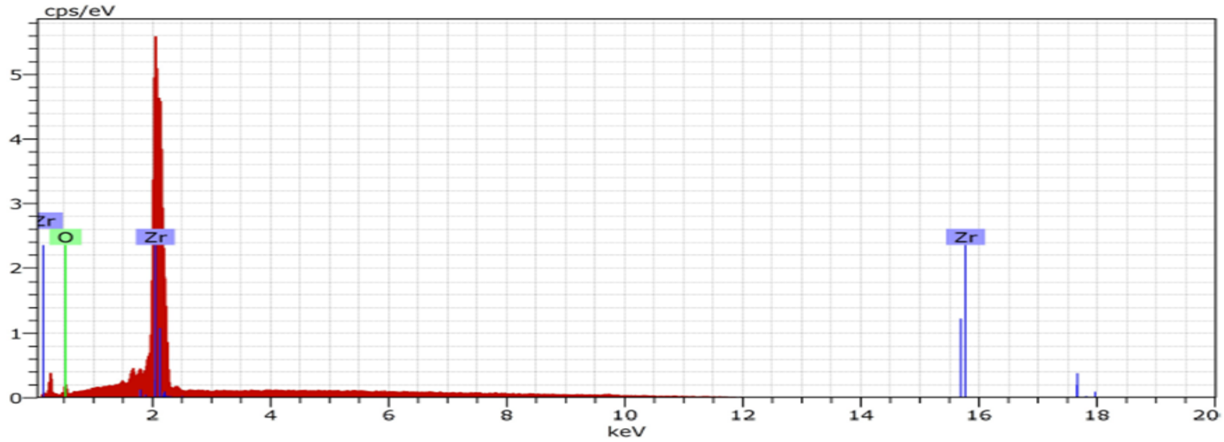
In the second treatment as it show in Figure III.13.c, the samples sintered at 1200 °C, cooled to 25 °C, after that it heated for 3 minutes at T = 50 °C to homogenize it’s temperature. Then it instantly tempered in ice water (at 0 °C) for 3 minutes. We can easily detect the fissures on the surface, which it means that the sample of ZrO_2 is fragile against thermal shocks. The reaction of water with Zr-O-Zr leads to training zirconium hydroxide (Zr-OH) which accelerates crack propagation.

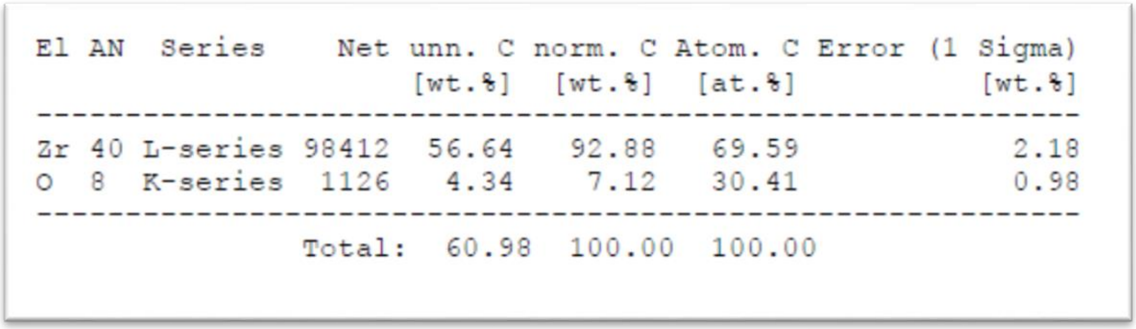
Figure III.13.d present the third treatment, that the samples sintered at 1200 °C, cooled to 25 °C, after that it heated for 3 minutes at T = 75 °C to homogenize it’s temperature. Then it instantly tempered in ice water (at 0 °C) for 3 minutes. We can remark the presence of fissures and pores on the surface, the fissures start in the surface and progresses in the zirconia mass because of the reaction of water, which accelerates crack propagation. Therefore, this treatment is not good.

EDS results in Figure III.14 shows that only peaks of Zr and O_2 detected (pure zirconia) and there is no changing in the structure's elements although applied a thermal shock, which means that the thermal shock does not affect at the structure's elements of the samples.



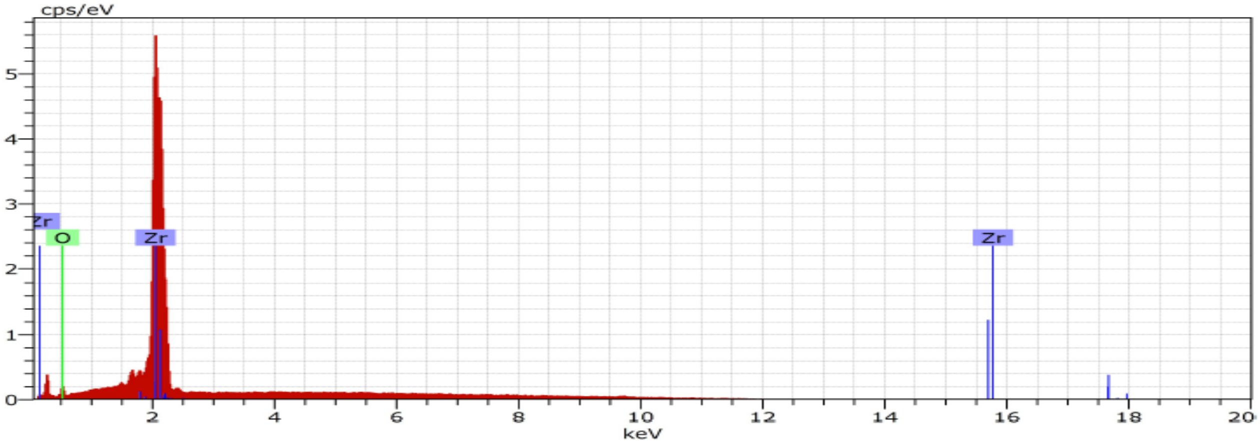
FigIII.13: Images obtained by scanning electron microscopy of ZrO_2 samples that had a thermal shock: a) reference sample, b) 25 °C, c) 50 °C, d) 75 °C.

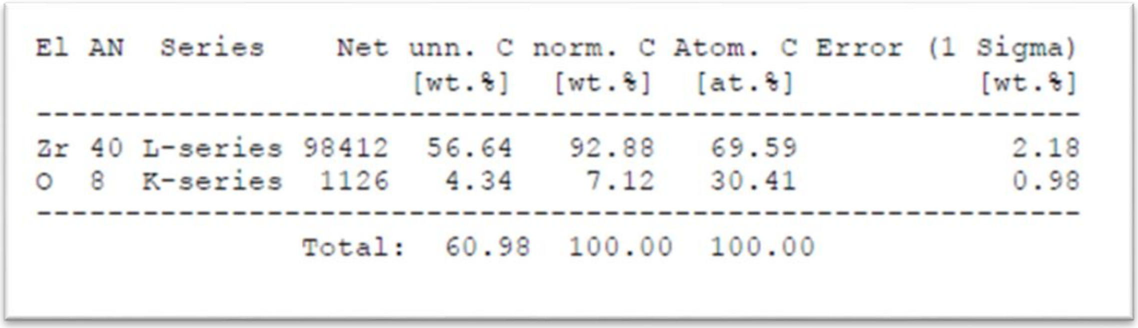




```
El AN  Series    Net unn. C norm. C Atom. C Error (1 Sigma)
                     [wt.%]   [wt.%]   [at.%]          [wt.%]
-------------------------------------------------------------
Zr 40 L-series 98412  56.64    92.88    69.59            2.18
O  8  K-series  1126   4.34     7.12    30.41            0.98
-------------------------------------------------------------
               Total:  60.98   100.00   100.00
```

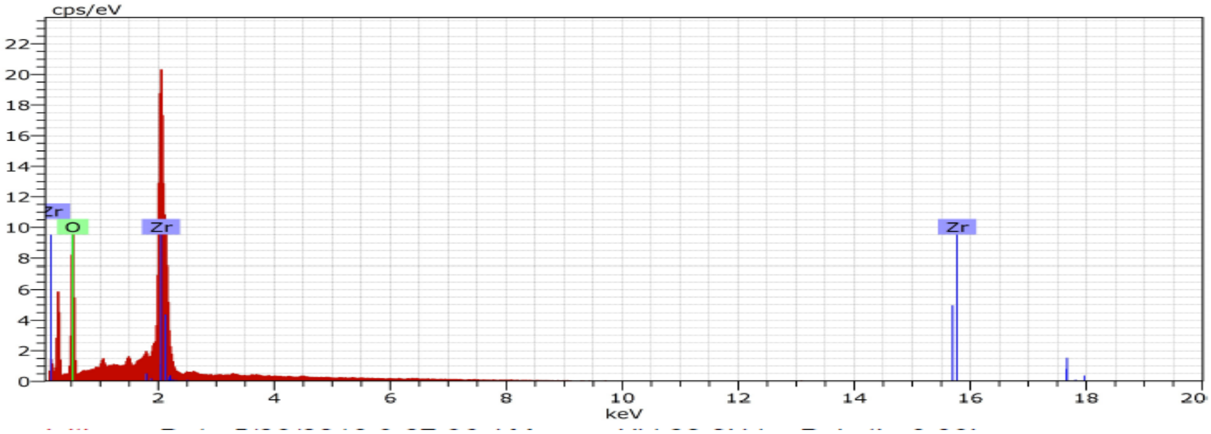
a)

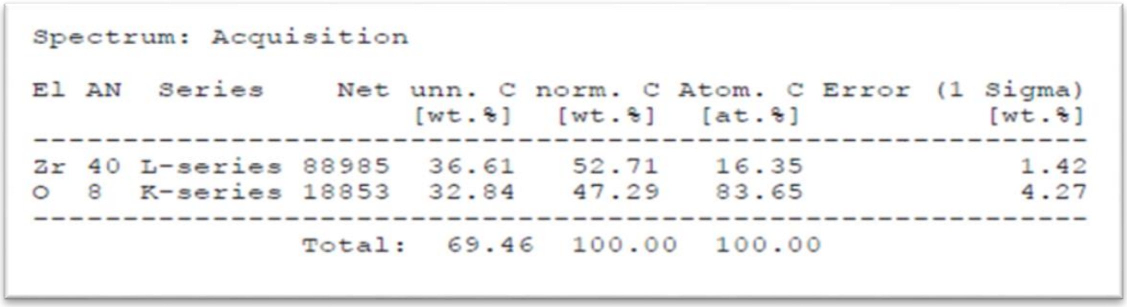




```
El AN  Series    Net unn. C norm. C Atom. C Error (1 Sigma)
                     [wt.%]   [wt.%]   [at.%]          [wt.%]
-------------------------------------------------------------
Zr 40 L-series 98412  56.64    92.88    69.59            2.18
O  8  K-series  1126   4.34     7.12    30.41            0.98
-------------------------------------------------------------
               Total:  60.98   100.00   100.00
```

b)

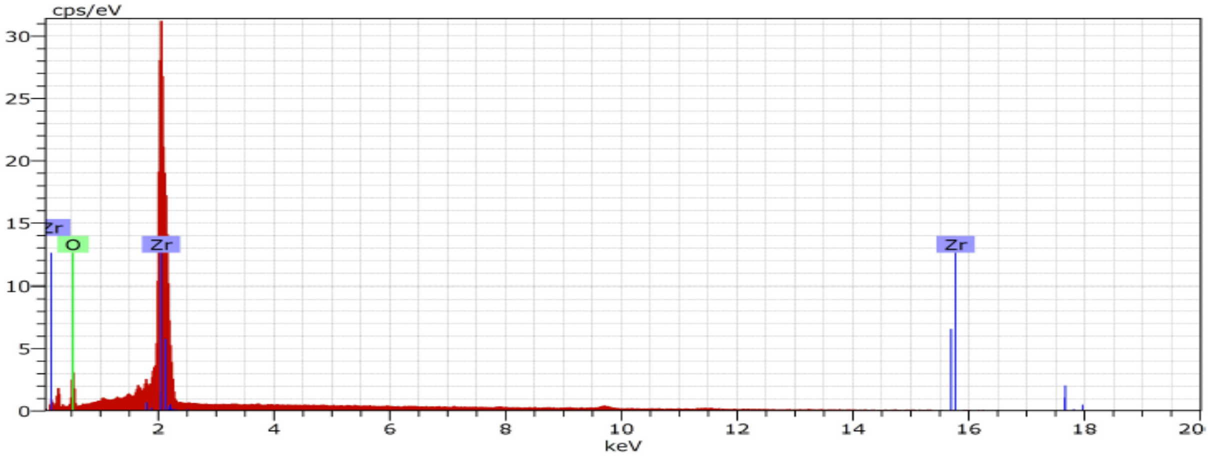


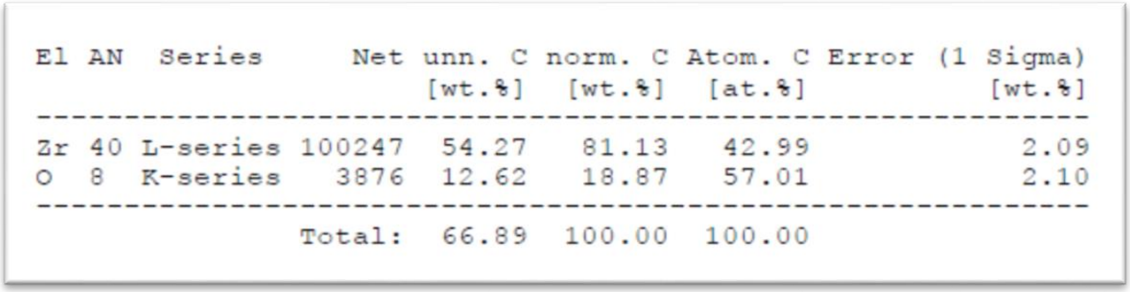


```
Spectrum: Acquisition

El AN  Series     Net  unn. C norm. C Atom. C Error (1 Sigma)
                       [wt.%]  [wt.%]  [at.%]            [wt.%]
-------------------------------------------------------------
Zr 40 L-series 88985  36.61   52.71   16.35              1.42
O   8 K-series 18853  32.84   47.29   83.65              4.27
-------------------------------------------------------------
                Total:  69.46  100.00  100.00
```

c)





```
El AN  Series     Net  unn. C norm. C Atom. C Error (1 Sigma)
                       [wt.%]  [wt.%]  [at.%]            [wt.%]
-------------------------------------------------------------
Zr 40 L-series 100247  54.27   81.13   42.99              2.09
O   8 K-series   3876  12.62   18.87   57.01              2.10
-------------------------------------------------------------
                Total:  66.89  100.00  100.00
```

d)

FigIII.14: Specter’s EDS of ZrO_2 samples that had a thermal shock: a) reference sample b) 25 °C, c) 50 °C, d) 75 °C.

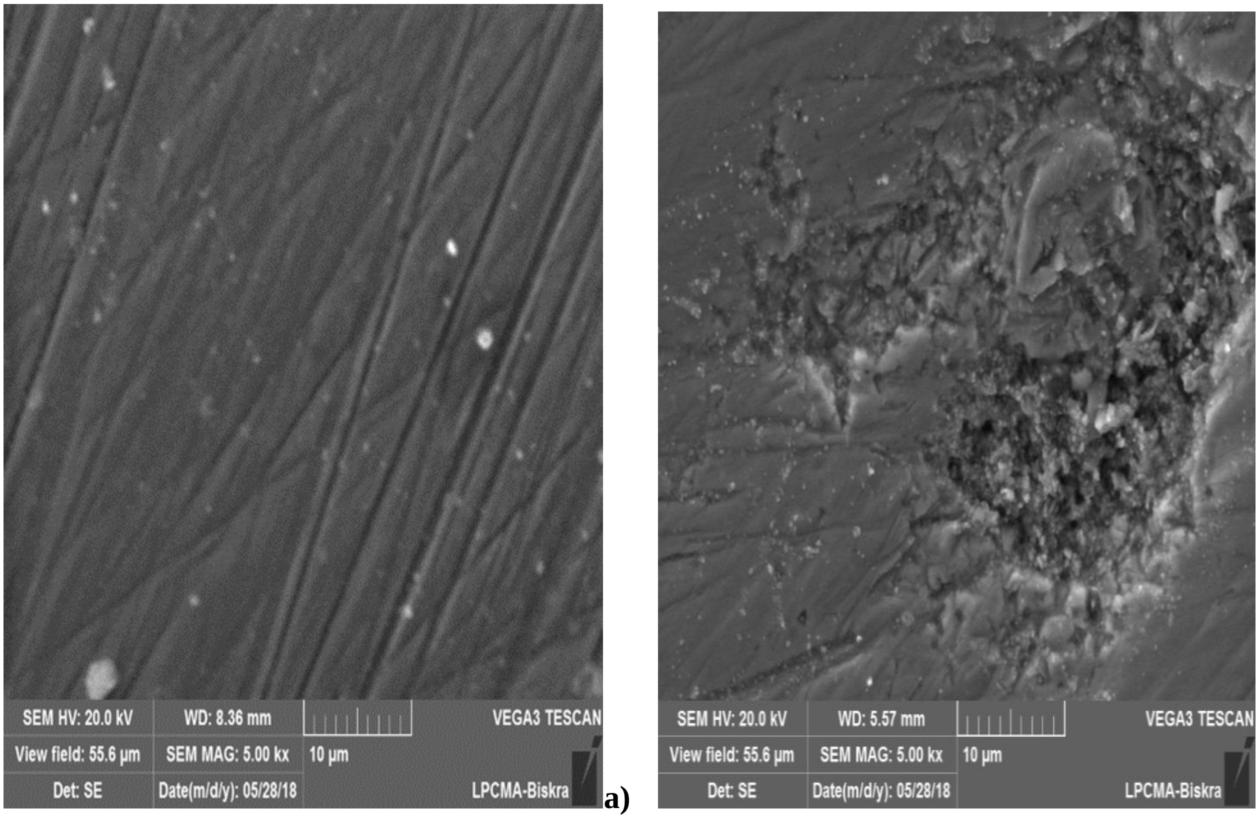
III.4.2. For samples that had sintered at heat treatment of 1450 °C

Figure III.15.b present a sintered sample at 1450 °C, cooled to 25 °C then tempered in ice water for 3 minutes. We observe a surface damage compared with FigIII.15.a. That is happen when the zirconia is in contact with water at low temperature, which causes a surface damage.

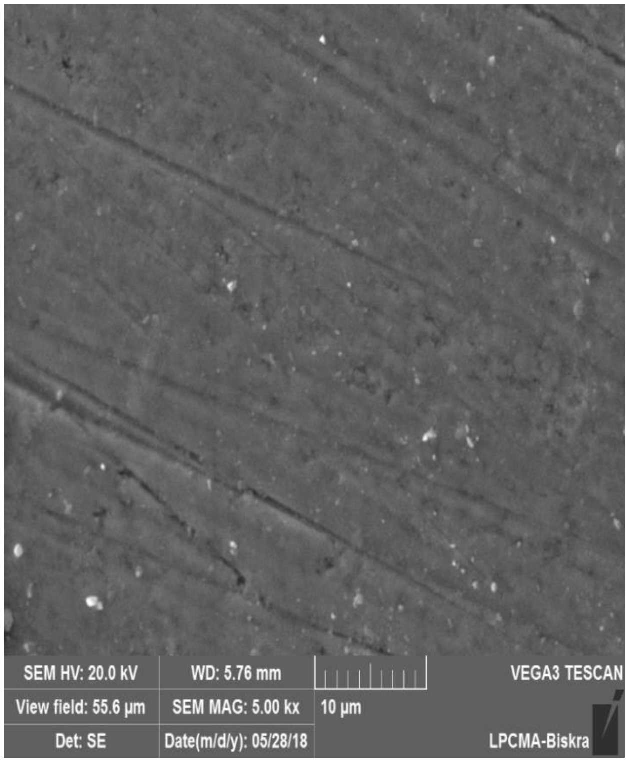
In the second treatment as it show in Figure III.15.c, the sample sintered at 1450 °C, cooled to 25 °C, after that it heated for 3 minutes at T = 50 °C to homogenize it’s temperature. Then it instantly tempered in ice water (at 0 °C) for 3 minutes. We can easily see that no fissures neither pores are on the surface.

EDS results in Figure III.16 affirm that the thermal shock does not affect on the structure’s elements of the samples.

We conclude that samples sintered at 1450 °C had a good and perfect treatment compared with that at 1200 °C.

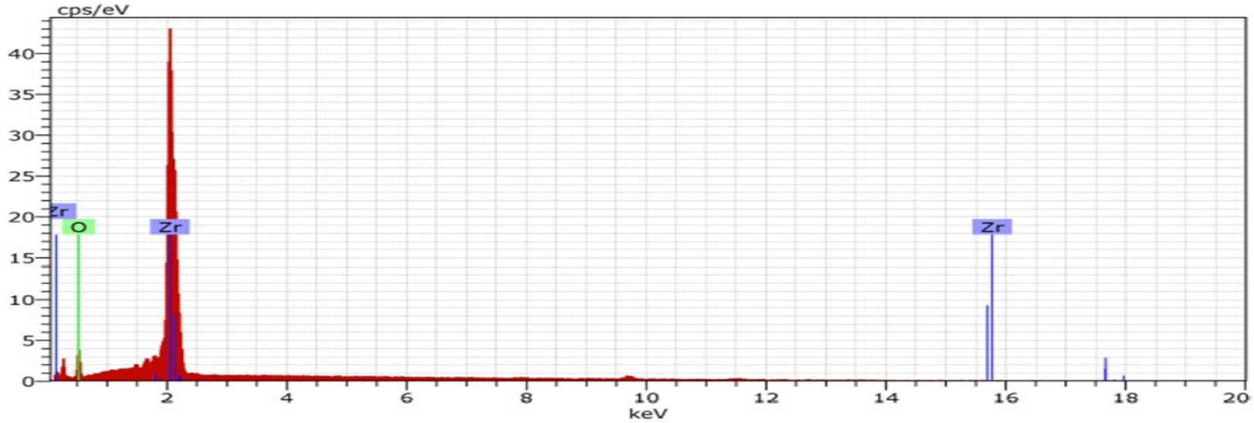


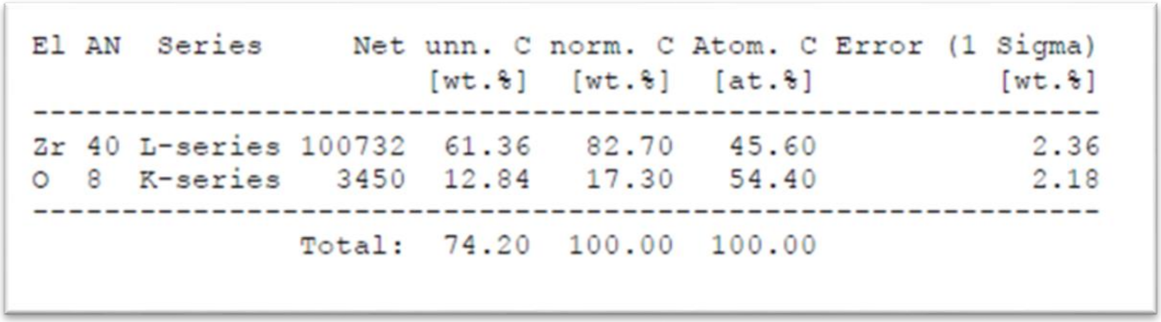
a) **b)**



c)

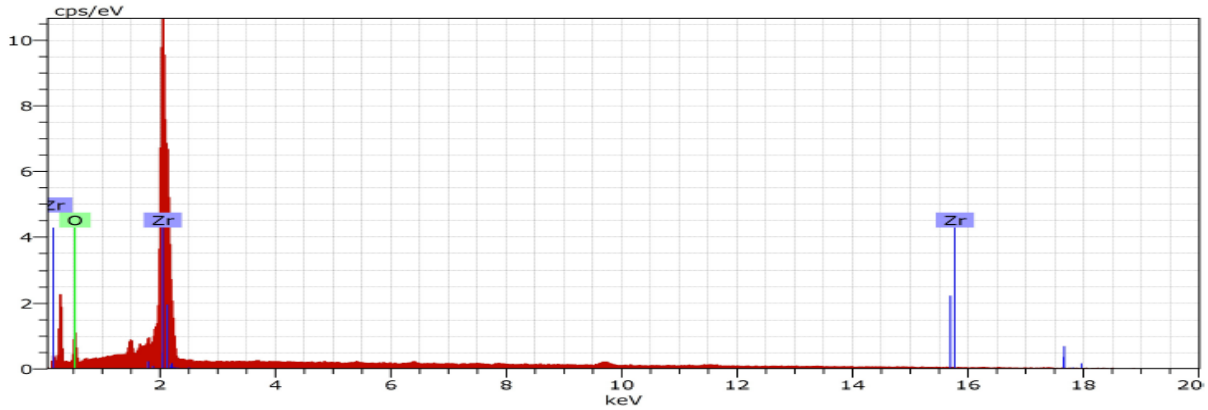
FigIII.15: Images obtained by scanning electron microscopy of ZrO_2 samples that had a thermal shock: a) reference sample, b) 25 °C, c) 50 °C.

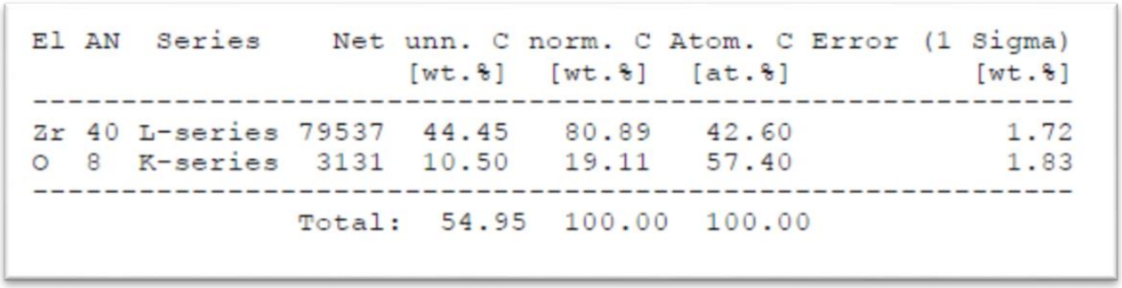




```
El AN  Series      Net unn. C norm. C Atom. C Error (1 Sigma)
                        [wt.%]  [wt.%]  [at.%]           [wt.%]
---------------------------------------------------------------
Zr 40 L-series 100732  61.36   82.70   45.60             2.36
O  8  K-series   3450  12.84   17.30   54.40             2.18
---------------------------------------------------------------
               Total:  74.20  100.00  100.00
```

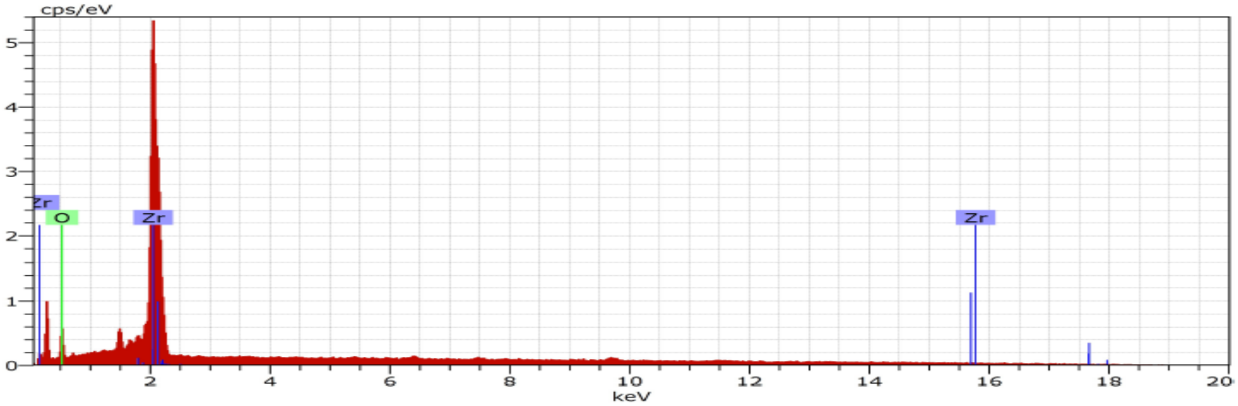
a)

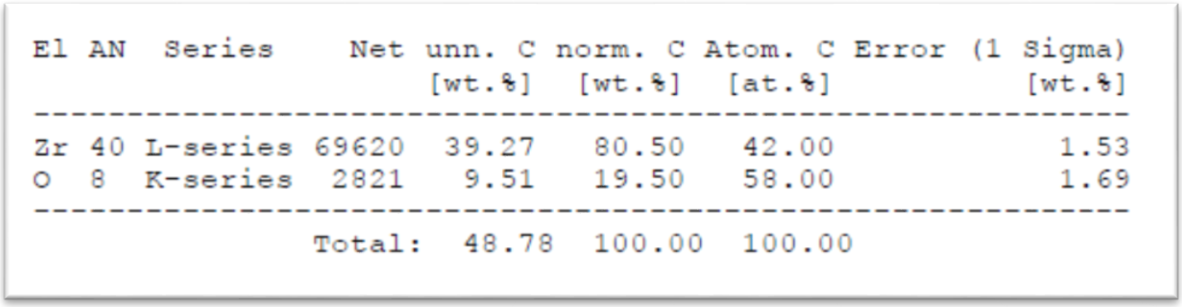




```
El AN   Series     Net  unn. C  norm. C  Atom. C  Error  (1 Sigma)
                         [wt.%]   [wt.%]   [at.%]              [wt.%]
---------------------------------------------------------------------
Zr 40  L-series  79537   44.45    80.89    42.60               1.72
O   8  K-series   3131   10.50    19.11    57.40               1.83
---------------------------------------------------------------------
                 Total:   54.95   100.00   100.00
```

b)





```
El AN   Series     Net  unn. C  norm. C  Atom. C  Error  (1 Sigma)
                         [wt.%]   [wt.%]   [at.%]              [wt.%]
---------------------------------------------------------------------
Zr 40  L-series  69620   39.27    80.50    42.00               1.53
O   8  K-series   2821    9.51    19.50    58.00               1.69
---------------------------------------------------------------------
                 Total:   48.78   100.00   100.00
```

c)

FigIII.16: Specter's EDS of ZrO_2 samples that had a thermal shock: a) reference sample, b) 25 °C, c) 50 °C.

General conclusion

GENERAL CONCLUSION

The work we have done in the context of this Dissertation had the main objective, which is the study of sintering effects on the mechanical and structural properties of zirconium oxide ZrO_2 used for tooth restoration.

To achieve this goal, we used the following techniques: X-ray diffraction (XRD), scanning electron microscopy (SEM), microanalysis EDS and microhardness.

The synthesis of the results obtained during this study made it possible to draw the following conclusions:

- Scanning electron microscopy (SEM) + EDS analysis of the microstructure showed a change in the microstructure of the zirconia when we varied the sintering temperature: 1000 °C, 1200 °C and 1450 °C compared with an un-sintered sample.
- X-ray diffraction analysis confirmed the presence of the main crystalline phase of ZrO_2 and revealed a small shift of the peaks towards the big angles sign of a swelling on the lattice or the existence of the stress.
- The microhardness of zirconia increased with increasing temperature and at 1450 °C, we obtain a mechanically homogeneous dental zirconia material.
- The results of heat shock showed that the sintering at 1450 °C was the best for arriving at the properties of the natural tooth.

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ملخص

كان الهدف من هذا العمل هو دراسة تأثير المعالجة الحرارية (التلبيد) على الخصائص الميكانيكية والبنيوية لمادة أكسيد الزركونيوم المستعملة في استبدال وترميم الاسنان، بالإضافة الى تأثير الصدمة الحرارية على هذه المادة من حيث البنية المجهرية والصلادة. لهذا، استخدمنا عدة طرق تجريبية ممثلة في حيود الأشعة السينية، المجهر الإلكتروني الماسح، الصلادة.

يمكننا القول إن هذه المادة يمكن استخدامها لتحل محل الأسنان الطبيعية من حيث الخصائص الميكانيكية ولهذا فإننا نقترح ان تتم دراستها مستقبلا من حيث الخصائص الضوئية.

كلمات مفتاحية: أكسيد الزركونيوم، معالجة حرارية، بنية مجهرية، الصلادة.

Résumé

Le but de ce travail était d'étudier l'éffet du traitement thermique (frittage) sur les propriétés mécaniques et structurales de l'oxyde de zirconium utilisé dans le remplacement et la restauration dentaire, en plus de l'effet du choc thermique sur ce matériau en termes de microstructure et de dureté. Pour cela, nous avons utilisé plusieurs méthodes expérimentales à savoir : la diffraction des rayons X, la microscopie électronique à balayage et la microdureté.

Nous pouvons dire que ce matériau peut être utilisé pour remplacer les dents naturelles en termes des propriétés mécaniques, et comme perspective, nous proposons d’étudier ses propriétés optiques.

Les mots clés : Oxyde de zirconium, traitement thermique, microstructure, microdureté

Abstract

The aim of this work is to study the effect of heat treatment (sintering) on the mechanical and structural properties of zirconium oxide used in tooth replacement and restoration, in addition to the effect of thermal shock in terms of microstructure and microhardness of this material. For this, we used several experimental methods represented in X-ray diffraction, scanning electron microscopy and microhardness.

We can say that this material can be used to replace natural teeth in terms of mechanical properties and therefore we suggest to study its optical properties.

Key words: Zirconium oxide, heat treatment, microstructure, microhardness