VICKERS MICROHARDNESS AND STRUCTURAL EVALUATION OF EXPERIMENTAL DENTAL PORCELAIN WITH ZIRCONIA ADDITION

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ABSTRACT. This work aimed to investigate the effect of ZrO_2 addition on the structural and mechanical properties of an experimental dental porcelain (DP) prepared from natural raw materials. ZrO_2 was added in different amounts (1, 3, and 5 wt.%) to the DP mass with the initial composition of 80 wt.% feldspar, 15 wt.% quartz, and 5 wt.% kaolin, obtained by sintering the mixture at 1200 ºC. The raw materials and raw materials mixture were analyzed by laser diffraction to obtain the typical particle size distribution (PSD). Subsequently, the obtained phases in the elaborated samples were investigated by X-ray powder diffraction (XRPD), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and microhardness tests. The structural analyses revealed that the obtained DP mainly comprised quartz and amorphous phases. In addition, certain peaks of weak corresponding to mullite and zirconia were detected. The measured Vickers microhardness (VMH) of DP sintered at 1200 °C was 794.07±106.56 kgf/mm², which is comparable with those reported for conventional porcelains. Moreover, ZrO_2 addition leads to an overall increase of

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the VMH, with the best value of 912.91±30.76 kgf/mm^2 obtained for the sample with 5 wt.% ZrO$_2$. In conclusion, the DP studied here exhibits good mechanical properties and could be potentially used in restorative dentistry.

Keywords: *dental porcelain, zirconia, structural analyses, Vickers microhardness*

INTRODUCTION

Besides many dental materials, porcelain continues to play a significant role in restorative dentistry. The most common applications include teeth full coverage as crowns, inlays and onlay porcelain bridges, veneering agents, castable ceramics, and porcelain fused to metal. Dental porcelain has very stable chemical properties and outstanding esthetics which are not influenced by their use over time. It has similar thermal conductivity and coefficient of thermal expansion to enamel and dentine and exhibits high compressive strength [1].

A classification of dental porcelains could be made based on their composition, fusion temperature, microstructure, translucency, fracture resistance, abrasiveness, and processing technique [2, 3]. The classification of dental porcelain based on composition includes feldspathic porcelains, leucite-reinforced feldspathic porcelain, leucite-reinforced glass ceramics, aluminous ceramics, glass infiltrated composites, alumina polycrystals, glass ceramics, lithium disilicate reinforced glass ceramics and zirconium oxide ceramics [4]. According to their fusion temperature, porcelains are classified into three categories namely high (1300-1400 °C), medium (1100-1300 °C), and low (850-1100 °C) fusing dental porcelains [4, 5]. The high-fusing dental porcelains are used for denture teeth, whereas the medium and low-fusing porcelain are used for crowns and bridges.

The composition of typical feldspathic dental porcelain (DP) by weight is feldspar (75 - 85%), quartz (12 - 22%), kaolin (3 - 5%) and metallic pigments which increase the opacity of dental porcelain (<1 %), including significant amount of feldspar (KAlSi$_3$O$_8$), quartz (SiO$_2$), and kaolin (Al$_2$O$_3$·2SiO$_2$·2H$_2$O). Feldspar, a greyish crystalline mineral found in rocks rich with iron and mica, is grounded, and after using strong magnets to remove iron compounds, it is milled to obtain the purest powder. Quartz, the matrix component is responsible for the translucency of the restoration, whereas kaolin is used in a limited amount as it has opaque properties, unlike the human teeth which are translucent. It is used in the composition of dental ceramics as it binds the loosely held ceramic particles together [6-9]. The main difference in composition between porcelain used in dentistry and that used in other products (*i.e.* dishes and china houseware) is in the proportions of the main raw materials [6]. The

exact compositions of dental porcelains differ between various products, but in general, there is a trend towards using less kaolin and more feldspar to improve translucency. This suggests that dental porcelain should be described more accurately as glasses. Compositions with low kaolin content require closely controlled firing times and temperatures to produce a satisfactory result due to the large glassy phases they develop [10].

Many attempts have been made to study the addition of different materials like metal oxides (MgO, ZnO, TiO_2 and ZrO_2) or $AgVO_3$ to DP powders to improve resistance to thermal shock, color, mechanical or antibacterial properties [1, 11-15]. Regarding the mechanical properties, one problem with the use of ceramics in tooth replacement is the fact that fracture occurs at a very low strain of ~ 0.1%, which means that the ceramic structure only exhibits a very low flexibility before fracture [16, 17]. Therefore, the mechanical behavior of dental porcelains still needs to be improved, and consequently, a lot of researchers are trying to develop the mechanical properties of ceramics. Some attempts have been made to overcome these shortcomings.

The research of Kaiyum et al. indicates that the MgO addition in a dental ceramic composition (70 wt.% feldspar, 20 wt.% quartz, and 10 wt.% kaolin) increases mechanical properties up to 1%, and indicates a fixed sintering temperature of 1100 °C. They conclude that MgO has great effects on grain growth, second-phase formation, and densification, which are the key factors that improve mechanical properties [18].

The effect of TiO_2 additions on the densification and mechanical properties of multifunction-resistant (MFR) porcelain prepared from economic raw materials was studied by Harabi et al. The chosen composition was 30 wt.% kaolins (20 wt.% kaolin halloysite type + 10 wt.% kaolin Tamazart), 45 wt.% k-feldspar and 25 wt.% quartz [19]. It has been found that the best three-point flexural strength (3PFS) and Vickers micro-hardness (VMH) values may recommend the use of multifunction-resistant porcelains for dental porcelains and abrasive materials. The best VMH value (12.30 GPa) achieved for the new MFR porcelain is nearly doubled when compared to that obtained by Santos et al. for porcelain-30% ZrO_2 composite (6.5 GPa) [20].

The influence of temperature and boric oxide (B_2O_3) addition on sintering and mechanical properties of dental porcelain prepared by using local Algerian raw materials was studied for the composition of 75 wt.% feldspar, 20 wt.% quartz and 5 wt.% kaolin [6]. It has been found that the sintering temperature was lowered by about 25 and 50 °C for 3 and 5 wt.% B_2O_3 additions, respectively. Moreover, the authors stated that B_2O_3 additions induce a glass matrix composition variation which hindered the leucite formation during sintering, knowing that the leucite is the most significant phase especially when mechanical properties of dental porcelain are concerned [6].

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Serragdj et al. have studied the effect of ZrO_2 additions on the densification and mechanical properties of modified resistant porcelains using economic raw materials [21]. The selected composition was 25 wt.% feldspar, 25 wt.% quartz, and 50 wt.% kaolin (25 wt.% kaolin Algerian nano-sized halloysite type + 25 wt.% kaolin Tamazart) and different amounts of ZrO_2 (5 and 8 wt.%). The authors found that the best VMH value of 13.08 GPa obtained for DP is higher than that found by other researchers for porcelain sample or porcelain containing 30 wt.% Al_2O_3 sintered at 1200 °C.

Briefly, many attempts have been made to increase the mechanical properties of dental ceramics by adding different metal oxide particles like MgO, TiO_2, B_2O_3 or ZnO. Apart from them, ZrO_2-reinforced glass-ceramic showed the improvement of the flexural strength and fracture toughness [20]. Although different dental porcelain compositions have been extensively studied, there are few investigations on the influence of zirconium oxide additive on the processing, structural and mechanical properties (*i.e.* microhardness). The novelty and major contribution of this study lies in its exploration of the synergistic properties of kaolin, quartz, feldspar and their tailored applications across various sectors, besides the biomedical domain occupy an important place. On the other hand, the novelty of this study arises from the newly developed composition considering two abundantly available and cheaper local raw materials, like quartz (Văleni, Romania) and feldspar (Muntele Rece, Romania). The chosen composition for DP in this work was 80 wt.% feldspar, 15 wt.% quartz, and 5 wt.% kaolin, using economic raw materials [10, 22]. Considering the important role played by zirconia particles in improvement of mechanical properties of dental porcelain this work aims to study the effect of ZrO_2 additions on the structural and mechanical properties of experimental feldspathic dental porcelain prepared from natural raw materials, as zirconia-reinforced porcelain represents a promising alternative to conventional feldspathic porcelains for the fabrication of prosthetic restorations.

RESULTS AND DISCUSSION

The PSD of the granules is of particular interest, fine particles will react completely while large particles will only partially react, and only a part of them will end up participating in the reaction. It is well known that particle size distribution (PSD) of powders affects the sintering behavior, physical and mechanical properties of ceramic materials. Therefore, the results of the granulometric analyses are presented below. Both the raw materials and raw materials mixture after wet homogenization were analyzed using laser diffraction with the results presented in **Table 1** and **Figure 1.** The results of PSD analyses are summarized in **Table 1**, where the modal and median diameters, defined for the cumulative distribution, are also shown.

Table 1. The results of PSD analyses performed on raw materials and
raw materials mixture.

Sample	Modal D (µm)	Median D (µm)	Mean V (µm)	50.0% D (µm)	Standard Deviation (SD)
Feldspar	0.224	0.222	0.305	0.222	0.305
Kaolin	0.178	0.171	0.209	0.171	0.171
Quartz	0.708	1.227	1.545	1.227	2.589
Raw materials mixture	0.708	1.169	1.399	1.169	0.395

The results presented in **Figure 1a** showed that kaolin and feldspar show a bimodal distribution presenting two maximum points, which are centered at around 0.15 - 0.2 µm, respectively 0.8 µm, whereas the quartz shows a wide distribution with fractions ranged from 0.1 to 50 µm. The raw materials mixture has a wide and monomodal PSD, with an average particle value of 1.399 µm with particle sizes of the powder falling in a wide size range between 0.3 and 10 µm (**Figure 1b**). This specifies that width of the PSD offers good mixing and uniform distribution between the particles.
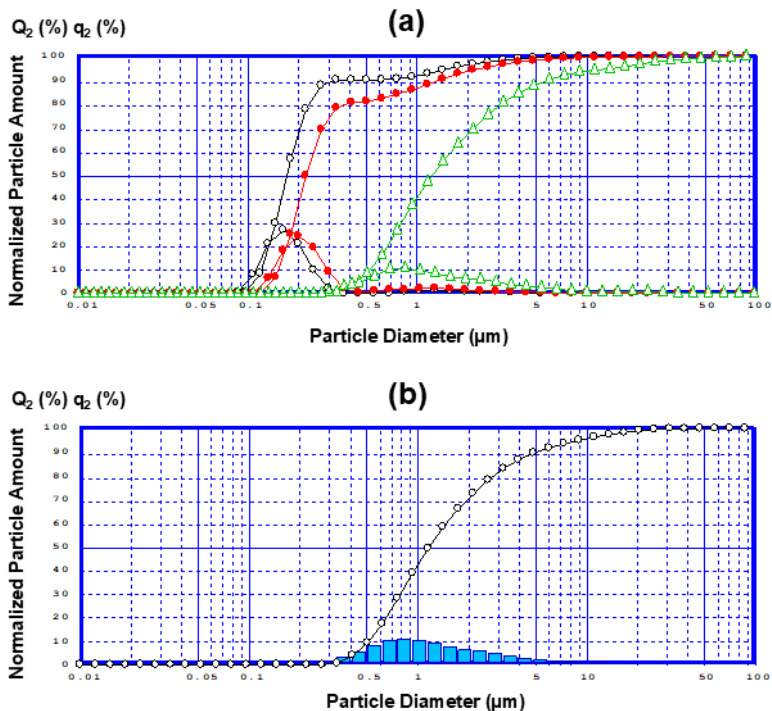

Figure 1. PSD (cumulative and differential curves) for (a) kaolin (black), feldspar (red), quartz (green), and (b) raw materials mixture.

All the prepared samples were analyzed using XRPD. The corresponding diffractograms of the samples DP0 and those with 1%, 3%, and 5% ZrO_2 additions are presented comparatively in **Figure 2.** The presence of quartz (Q) is observed as the main phase in all the analyzed spectra (PDF # 96-901-0145). The evidenced diffraction peaks belong to its β form resulted after the high temperature sintering.
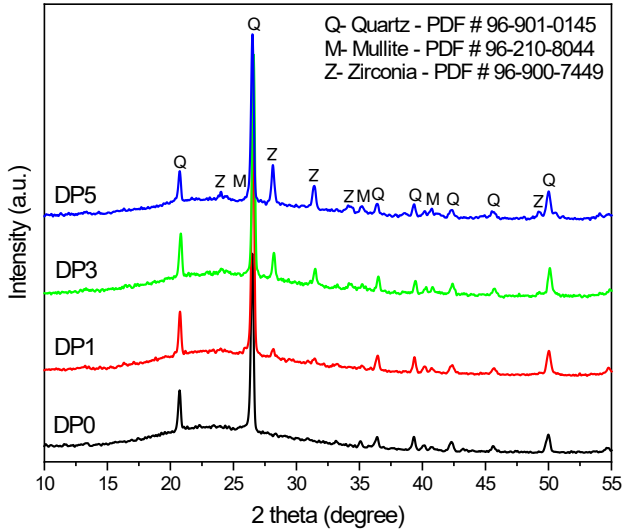

Figure 2. XRPD patterns of DP samples sintered at 1200 °C.

The intensities of the diffraction peaks of quartz did not change in the DP samples with ZrO_2, but a new phase was identified as zirconium oxide (Z; PDF # 96-900-7449). The intensity of the peaks corresponding to ZrO_2 increases with the increase of the percentage of ZrO_2. ZrO_2 leads to an increase in the intensity of the maxima presented at 2θ ~ 24, 28.2, and 31.5, which belongs to baddeleyite. Certain peaks of weak intensity were identified as corresponding to mullite (M, $Al_6Si_2O_{13}$; PDF# 96-210-8044). It is known that mullite is responsible for the DP microstructure and mechanical properties. Therefore, the formation of mullite mainly depends on the type and proportion of kaolin used [23]. There is a competition effect between the formation of mullite and the crystallization of the amorphous silica present in the matrix during sintering. Besides, the fraction and nature of the quartz used in the porcelain composition batch influences the amount of unreacted residual quartz during sintering. Quartz has a higher coefficient of thermal expansion as compared to that of the surrounding glassy phase. Therefore, it gives rise to thermal stresses

which affect the porcelain strength [24, 25]. In addition, at this sintering temperature the feldspar melted and its diffractogram presented a large band related to the amorphous phase, as revealed in the XRPD patterns [14].

The FTIR spectra obtained for all samples appear to be almost similar (**Figure 3**). In the spectra of DP0, the broad absorption peak with a maximum of around 3449 cm^{-1} is assigned to the stretching modes of O–H bond vibrations, which is related to surface absorbed water, whereas the broad absorption band around 1624 cm^{-1} is assigned to H−O−H bending vibrations related to the surface chemically adsorbed water [26, 27]. In the spectra of DP1, DP3, and DP5 this vibration is located at 1630 and respectively at 1626 cm^{-1}.
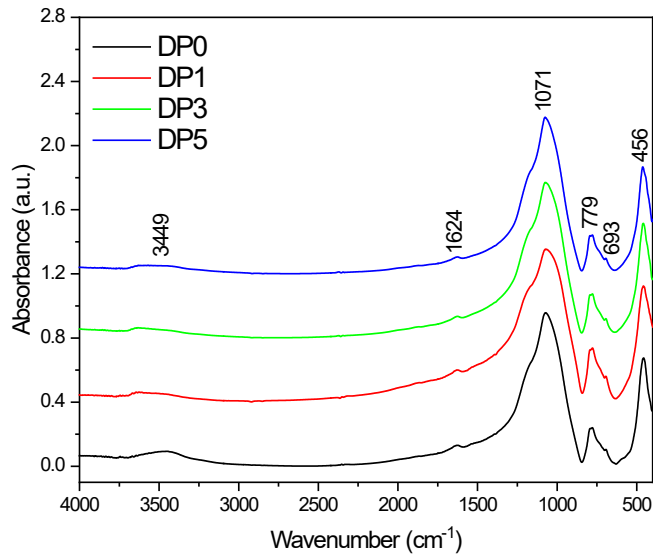

Figure 3. FTIR spectra of DP samples.

In function of the composition of the samples, the region of great interest is in the spectral range between 1400-845 cm^{-1}, which is the specific region for the bands corresponding to the vibration of the bonds in SiO_2. The maximum of the dominant bands identified in the FTIR spectra of DP is situated around 1624, 1071, 779, 693, and 456 cm^{-1}. The band located around 1071 cm^{-1} could be attributed to asymmetric stretching vibrations of Si-O-Si bridges in amorphous SiO_2 while the absorption peak around 779 cm^{-1} is ascribed to symmetric stretching vibrations of the same bonds [27-29]. These vibrations are also found in the spectra obtained for the three samples, DP1, DP3, and DP5, but with small shifts. Our results agree with the results previously reported, which identified absorption bands ranging from 400 to 1400 cm^{-1}

associated with the quartz bending band [6, 30]. In the spectral range 1400-845 cm^{-1} there are changes in FWHM, which compared to the value obtained for sample DP, increases in DP1, but decreases in DP3 and DP5.

DSC was used to investigate the thermal stability and behavior of the prepared DP. The results of the DSC analyses for the investigated samples are presented in **Figure 4.**
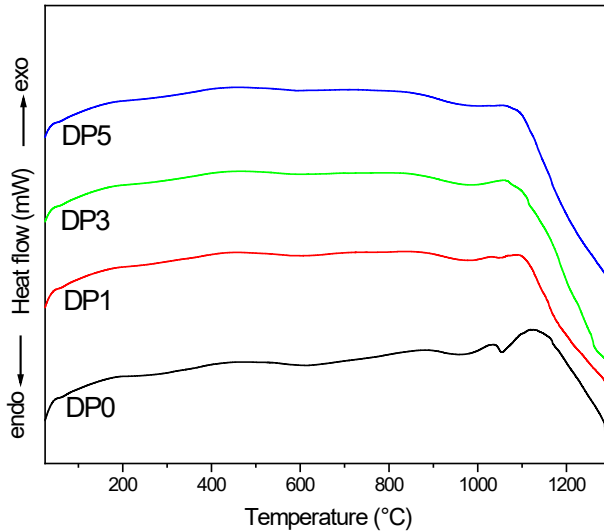

Figure 4. The DSC thermograms of DP samples.

It was observed that the addition of ZrO_2 caused broadening of exothermic peaks between 1000 and 1100 ºC, which may be due to overlapping of peaks. The exothermic peaks shifted into a single broad peak with further ZrO_2 addition to the DP. No sharp exothermic effect was observed for DP1, DP2, and DP3 samples in the DSC curves, it means that the number of crystalline phases developed during the DSC run was small, in agreement with XRPD analysis revealed in **Figure 2**. It is evident from DSC results that the addition of ZrO_2 caused a progressive inhibition of the second thermal event confirmed by a reduction in intensity of the exothermic peaks [31, 32].

The surface microhardness of a material refers to its resistance to permanent indentation. It is an important property for restorative materials as it reflects their mechanical strength [33], resistance to wear, and abrasiveness to opposing dental tissues and restorative materials [34]. A change in the surface microhardness indicates structural degradation or solubility, which is associated with a reduction in the material's strength and mechanical performance. Microhardness is generally dependent on the mechanical

strength of the microstructure. When there are weak points such as defects or micro-cracks, the hardness will be lower due to the presence of these cracks. The determined Vickers microhardness (VMH) values of DP samples containing 0, 1, 3, and 5 wt.% ZrO_2 are revealed in **Table 2**.

Table 2. VMH values (mean and standard deviation-SD) obtained for
the prepared DP compositions.

Sample ID	DP0	DP1	DP3	DP5
Mean VMH	794.07 ± 106.56	868.83 ± 18.97	846.49 ± 38.85	912.91 ± 30.76

As observed from **Table 2**, an overall increase of VMH in all samples with ZrO_2 addition if compared to DP was observed. The VMH value obtained for DP was slightly influenced by ZrO_2 additions. The higher VMH value of 912.91 ± 30.76 (8.953 GPa) was measured for sample DP5, containing 5 wt.% ZrO_2. The presence of ZrO_2 increased the microhardness of porcelain. A comparison between mechanical properties values of the prepared materials in this study and for those reported in the literature are reported in **Table 3**.

Table 3. Comparative values of the VMH of the dental porcelain obtained from this
study and those reported in the literature.

Material	Temperature (ºC)	Vickers microhardness (GPa)	Reference
P (porcelain)	1200 ºC	7.6 ± 2.0	Serragdj et al.
P	1200 ºC	9.3 ± 0.2	Kitouni et al.
P + 30 wt.% alumina and 5 wt.%TiO_2	1200 ºC	7.3	Kimura et al.
P + 5 wt.% ZrO_2	1200 ºC	12.8 ± 2.0	Serragdj et al.
P + 8 wt.% ZrO_2	1200 ºC	13.1 ± 1.0	Serragdj et al.
Dental porcelain (DP)	1200 ºC	7.787	present work
DP + 1 wt.% ZrO_2	1200 ºC	8.521	present work
DP + 3 wt.% ZrO_2	1200 ºC	8.302	present work
DP + 5 wt.% ZrO_2	1200 ºC	8.953	present work

The best VMH value achieved for the DP5 sample is higher compared to that obtained by Santos et al. (6.5 GPa) for porcelain of 30 wt.% ZrO_2 composite, even though their mixtures were hot pressed in vacuum at 970 °C for 2 min [20]. Moreover, this VMH value is comparable to that reached by both Kitouni

and Harabi (9.3 GPa) for porcelain samples and greater compared to the works carried out by Kimura et al. (7.3 GPa) for porcelain containing 30 wt.% Al_2O_3 sintered at 1200 °C [35, 36]. Therefore, replacing the more expensive starting materials like Al_2O_3, whose price is much higher, by other low-cost raw materials, is significantly important.

Most ceramics have comparatively higher hardness values than human enamel and metal alloys [37, 38]. It is known that dental hard tissue comprises a combination of enamel and dentin, both of which have different compositions and structures.

Enamel, which has a glossy surface and varies in color from light yellow to grayish white, is mainly made of the mineral hydroxyapatite, which is crystalline calcium phosphate. It is the hardest tissue in the human body because it contains almost no water. Structurally, enamel covers the entire anatomic crown of the tooth above thegum and protects the dentin. Dentin consists of the mineral hydroxyapatite (70%), organic material (20%), and water (10%). Dentin is harder than bone but softer than enamel, and it is mostly made of phosphoric apatite crystallites Following the results of Chun et al., the measured hardness value of enamel specimens (HV = 274.8 ± 18.1) was around 4.2 times higher than that of dentin specimens (HV = 65.6 ± 3.9) [39]. The Vickers microhardness of the DP prepared in this study is superior to that of dentin and enamel.

Further, the microhardness values of the DP prepared in this study were compared with three commercial CAD/CAM ceramics: IPS e.max CAD (lithium disilicate), VITA ENAMIC (polymer-infiltrated ceramic), and Celtra Duo CAD (zirconia-reinforced lithium silicate). The reported mean microhardness values are 853.82 (±16.89) for IPS e.max CAD, 342.79 (±25.69) for VITA ENAMIC, and 853.68 (±19.46) for Celtra Duo CAD [40]. It was observed that all the new formulations from the present work showed a significant increase in microhardness if compared with VITA ENAMIC. Concerning both IPS e.max CAD and Celtra Duo CAD, a slight increase of 1.7% was observed even at low percentages of material added (1 wt.% ZrO_2), but an increase of microhardness values with 7% at high percentages of material added (5 wt.% ZrO_2). In conclusion, the microhardness values of the experimental dental porcelain developed in this research demonstrated a greater level of microhardness compared to several commercially available dental porcelains. This enhanced microhardness is likely due to the incorporation of the ZrO_2 crystalline phase, which may contribute to the material's performance in dental applications.

CONCLUSIONS

In this study, a newly developed dental porcelain (DP) using economic raw materials was proposed. The selected composition was 80 wt.% feldspar, 15 wt.% quartz, and 5 wt.% kaolin. Additionally, the effect of zirconium oxide (ZrO_2) addition on the structural and mechanical properties of DP was studied. Structural analyses reveal that quartz, mullite and amorphous phases are present on the obtained DP. In the samples with ZrO_2 addition, some peaks of zirconia were identified. The measured Vickers microhardness (VMH) of DP sintered at 1200 °C was 794.07 ± 106.56 kgf/mm^2, a value comparable with those reported for conventional porcelains. Moreover, the addition of ZrO_2 improved the overall microhardness with the best value of 912.91 ± 30.76 kgf/mm^2 obtained for the sample with 5 wt.% ZrO_2. Finally, these VMH values may recommend the use of the DP material for dental applications, as feldspathic porcelains are the most used ceramic materials in dentistry for the manufacture of indirect restorations and as a veneering material for bilayer prostheses over metallic or ceramic infrastructures. Further studies are required to completely elucidate the effect of ZrO_2 as a candidate for potentially improving the mechanical properties of the prepared ceramic dental material.

EXPERIMENTAL SECTION

Raw materials

The raw materials used to prepare DP are kaolin (Zettlitz, Czech Republic), quartz (Văleni, Romania), and feldspar (Muntele Rece, Romania) with the chemical composition presented in **Table 4**. All the raw materials were used as received without any further purification and serve for different functional attributes: feldspar provides natural translucency and forms the main structure of the porcelain, quartz prevents shrinkage during firing, provides stability, and increases durability, whereas kaolin, present in only 1-5% of the powder, is heat-resistant, provides elasticity to the porcelain paste, and helps bind other materials together.

The reinforcing material used in this study was high-purity zirconium oxide (ZrO_2, Riedel-de Haën AG, Seelze, Germany, 99%) which played a crucial role as improving agent.

Table 4. Chemical compositions of raw materials (wt.%).

Raw materials	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	LOI*
Kaolin	47.27	35.62	0.66	0.38	0.75	0.20	0.20	0.87	14.2
Feldspar	76.41	12.61	0.31	-	0.42	0.4	0.4	8.5	0.95
Quartz	97.08	0.24	0.02	-	0.96	0.06	0.03	0.03	1.17

*Loss on ignition

Dental porcelain preparation

The composition of the experimented dental porcelain was 80 wt.% feldspar, 15 wt.% quartz, and 5 wt.% kaolin, following the procedure previously reported [14]. The selected raw materials were wet milled and homogenized in a planetary ball mill (Pulverisette 6, Fritsch, Germany) for 30 min at 250 rpm to obtain the typical size distribution. Afterward, the obtained slurry was dried at 105 °C for 1 day using a Memmert incubator. Different ZrO_2 amounts, 1, 3, and 5 wt.%, have been added to the raw materials mixture to improve the mechanical properties of the sintered DP samples. The specimens in the form of discs of 2 g and about 10 mm in diameter were obtained by uniaxially cold press using a metallic dye and a pressure of about 0.5 tons, by a Carver Inc., hydraulic press (Carver Inc., Wabash, IN, USA). The obtained pellets were subsequently sintered at 1200 °C for 12h using a Nabertherm LHT 04/16 (Lilienthal, Germany) furnace, with a constant heating and cooling rate of 5 °C/min. The obtained samples, in the form of powder or pellets, were further used for different analyses. Depending on the amount of ZrO_2 used, 0, 1, 3, and 5 wt.%, the samples have been named as follows: DP0 (without ZrO_2 addition), DP1, DP3, and DP5, respectively.

Characterization methods

Particle size analysis by laser diffraction was performed with a nanoparticle size analyzer SALD-7101 (Shimadzu, Japan). The samples were dispersed in a water medium to form a suspension and drawn into the size analyzer. The particle aggregation was reduced using treatment with ultrasounds.

XRPD analysis was performed to investigate the structure of the samples using a Shimadzu XRD-6000 diffractometer operating at 40 kV, 30 mA, with Ni- filter and graphite monochromator for CuKα (λ=1.54060 Å). The diffraction patterns were recorded in the 2θ range of 10-80° at a scan speed of 2 °/min. The phase identifications and crystallographic information files corresponding to the quartz (Q, PDF # 96-901-0145), zirconium oxide (Z;

PDF # 96-900-7449) and mullite (M, PDF# 96-210-8044) phases were selected from the Crystallography Open Database (COD) using version 3.13 (Build 220) of Match! software.

The FTIR measurements were carried out using a Jasco FTIR 6200 spectrometer. The spectra were recorded from KBr pellets, with a spectral resolution of 4 cm^{-1}.

The TA Instruments SDT Q600 Thermogravimetric Analyzer (TGA) & Differential Scanning Calorimeter (DSC) was used to investigate the thermal properties of the samples. The analyses were performed from room temperature to 1300 °C with a ramp of 10 °C/min, using alumina pans.

Vickers microhardness (VMH) values were measured with a Micro Hardness Tester (FALCON 600G2FAO2). Indentations were conducted in the air with loads of 3 kgf. The indentation time was 15 s. For all experiments only well-defined indents, without chipping or cracks, were considered. The samples were thoroughly inspected with a magnifying lens to exclude specimens with any surface defect. The Vickers microhardness (VMH) value of each indent was automatically calculated. Each sample was subjected to 5 indentations and the mean VMH value was calculated in kgf/mm^2.

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