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Production and characterization of self-colored dental zirconia blocks

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Abstract

The objective of this study is to produce and characterize self-colored dental zirconia blocks by using zirconia raw material having Fe_2O_3 content. Five different compositions with different amounts of Fe_2O_3 were prepared by using two different raw materials. The shaped samples were sintered at 1500 °C for 2 h. Color differences, phase formations, microhardness, fracture toughness, and microstructures of the specimens were investigated. Self-colored zirconia blocks and frameworks of desired physical and mechanical properties for dental restorations can be produced by using zirconia raw material having Fe_2O_3 content.

Keywords: Dental zirconia block; Self-colored zirconia framework; Production; Characterization

1. Introduction

Zirconia-based ceramics as restorative dental materials have generated considerable interests in the dental community due to their high mechanical properties. Zirconia is a fine-grained polycrystalline material, displaying a stress-induced tetragonal–monoclinic (t–m) phase transformation, possesses comparatively high strength and fracture resistance, and largely controlled by its manufacturing process [1]. Moreover, zirconia has an advantage over metal framework and alumina. Metal framework has a significant limitation for the esthetic appearance due to the absence of translucency, especially when a clear tooth color is to be reproduced. In fact, metal–ceramic restorations can only absorb or reflect light, while dental tissues show a high degree of translucency. Zirconia was introduced to solve the problem of brittleness of alumina and the consequent potential failure of implants. The mechanical properties of zirconia are the highest ever reported for any dental ceramic. This may allow the realization of posterior fixed partial dentures and permit a substantial reduction in core thickness [2–4].

The use of zirconium dioxide (ZrO_2) ceramics in dentistry as framework material is made by grinding zirconia blocks for the fabrication of posterior fixed partial dentures (FPDs). Manuel and CAD/CAM systems are used for fabrication of frameworks. The first idea for using CAD/CAM systems for production of tooth restorations originated with Duret in the 1970s. After 10 years, Mörmann developed CEREC-system which was transferred to practice by Siemens (now Sirona). There was a tendency to use CAD/CAM systems in order to achieve industrial quality standards, which are particularly important for ceramic materials and also because frameworks can be fabricated more efficiently by this way [5]. After that, there was significant increase in development of other CAD/CAM laboratory systems [5–7].

The white color of zirconia does not allow an optimal esthetic integration to be achieved per se; therefore a veneering material must be used. Liners and most recently staining solutions are common method to compensate for the possible effect of the white color of zirconia on the final color of the restoration [8]. The framework for crown and bridges can be stained into 1 of 7 shades by infiltration technique [9]. However, coloring by the staining solutions causes some disadvantages. First of all, each brand of the solutions contains different pigment types and ratios; hence they can give several different colors to the framework. In addition, each brand of dental zirconia block comes with varied porosity, which affects the color of the framework. Hence, coloring of zirconia frameworks is a

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very difficult and precision work. Furthermore, the staining solutions have a limited service life limiting their usage. Final color of zirconia framework can also differ due to change with time in concentration of the pigments in the staining solutions by evaporation or precipitation. Finally, the coloring with solutions means extra time and process.

This study aimed to produce self-colored dental zirconia blocks and characterize them for their properties such as microhardness, fracture toughness, color difference, microstructure and phase formation.

2. Materials and methods

2.1. Raw materials

In this work, two different ready to press zirconia raw materials, TZP and TZP-C, were used. TZP and TZP-C refer to 3 mol% Y_2O_3 stabilized tetragonal zirconia and 3 mol% Y_2O_3 stabilized tetragonal zirconia with Fe_2O_3 content of 0.2 wt% as coloring agent, respectively. The chemical characteristics and physical properties of the raw materials are given in Tables 1 and 2.

2.2. Preparation of the specimens

The standard dental zirconia block recipe (Z0), which is made of 100% TZP, was replaced by the TZP-C of 10% (Z1), 30% (Z2), 50% (Z3) and 70% (Z4). Chemical compositions of these newly prepared dental zirconia block recipes are presented in Table 3. Precisely weighed batches were dry-mixed in a zirconia jar for 3 h. The powders that have already had binder in their own composition were pre-shaped by using uni-axial press followed by final shaping using cold isostatic press at 300 MPa.

After shaping, the specimens were subjected to debinding, pre-sintering and full-sintering process. First, the samples were heated to 800 °C for 1.5 h at 1 °C/min for debinding. The samples were then heated to 1100 °C at a heating rate of 10 °C/min and sintered at that temperature for 2 h. The samples were then heated to 1500 °C at 10 °C/min and soaked for 2 h at that temperature for full sintering.

2.3. Characterization of the specimens

In order to determine the type of phase formations occurring due to incorporation of Fe_2O_3 into specimens, and to determine the effect of pre-sintering and full-sintering temperatures on this phenomenon, X-ray diffraction analysis was carried out using CuK_α radiation in a Rigaku Rint 2000 Series diffractometer at 40 kV and 30 mA.

For micro-structural studies, the samples were polished following standard preparation methods and then they were thermally etched at 1400 °C for 10 min dwelling time. Finally, the samples were coated with a thin film of gold–palladium and examined using a scanning electron microscope (Zeiss Supra 50 VP at 20 kV).

To determine the microhardness and fracture toughness, two types of indentations were performed with Emcotest M1C 010 on each sample at (i) 1 kg load for the pre-sintered samples, and (ii) 10 kg load for the fully sintered samples. Microhardness of the samples was determined using the following expression [10–15]:

$$Hv = \frac{1854 \times P}{d^2} \tag{1}$$

where Hv is the Vickers hardness, P is the applied load (kg), and d is the arithmetic mean of the two diagonal lengths (mm) in Fig. 1.

Fracture toughness of the samples was determined according to the following equation of Anstis et al. [11–12,15–19]:

$$K_{IC} = 0.0016\left(\frac{E}{H}\right)^{1/2}\left(\frac{P}{c^{3/2}}\right) \tag{2}$$

where K_{IC} is the fracture toughness (MPa m$^{1/2}$), E is the elastic modulus (MPa), H is the microhardness (MPa), P is the applied force (N), and c is the crack length (m) in Fig. 2.

The color differences (ΔE_{ab}) of the samples were assessed using CIELab*. In the CIELab* scientific system, the color differences in Minolta Spectrophotometer CM-3600d are calculated using the following formula:

$$\Delta E_{ab} = [(L_1-L_2)^2+(a_1-a_2)^2+(b_1-b_2)^2]^{1/2} \tag{3}$$

where L is the degree of lightness of an object, a is the degree of redness/greenness and b is the degree of yellowness/blueness.

Finally, the bulk density and porosity of the samples were determined by using Archimedes's principles.

Table 2
Physical characteristics of raw materials.

	Specific surface area (m^2/g)	Crystalline size (Å)
TZP	7*	340*
TZP-C	7*	350*

*The values received from the provider.

Table 1
Chemical characteristics of raw materials.

	ZrO_2+HfO_2 (wt%)	Y_2O_3 (wt%)	Al_2O_3 (wt%)	SiO_2 (wt%)	Fe_2O_3 (wt%)	Ignition loss (wt%)
TZP	91.19	5.21	0.27	0.02	0.01	3.30
TZP-C	90.88	5.15	0.25	0.02	0.20	3.50

Table 3
Chemical characteristics of the samples.

	ZrO_2+HfO_2 (wt%)	Y_2O_3 (wt%)	Al_2O_3 (wt%)	SiO_2 (wt%)	Fe_2O_3 (wt%)	Ignition loss (wt%)
Z0	91.190	5.210	0.270	0.02	0.010	3.30
Z1	91.159	5.204	0.268	0.02	0.029	3.32
Z2	91.097	5.192	0.264	0.02	0.067	3.36
Z3	91.035	5.180	0.260	0.02	0.105	3.40
Z4	90.973	5.168	0.256	0.02	0.143	3.44

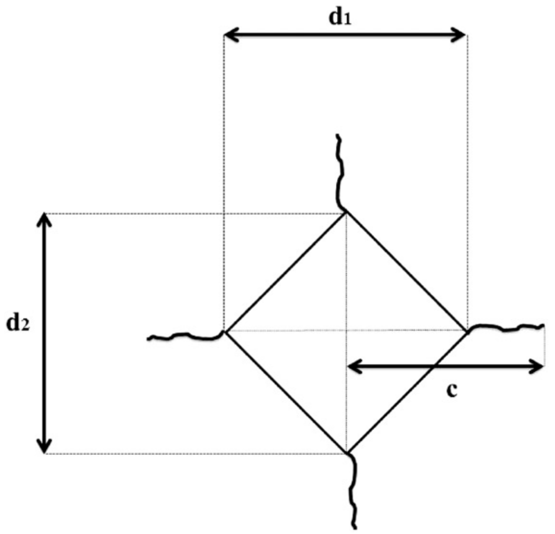

Fig. 1. Schematic drawing of Vickers indentation, diagonal lengths and crack lengths.

All tests were performed on the ten samples belonging to each recipe.

3. Results and discussions

The XRD patterns of the specimens are shown in Fig. 3. The monoclinic phase can be well distinguished by its most intense peaks at $2\theta=28^\circ$ $(1\bar{1}1)$ and 31° (111), whereas the tetragonal or cubic phases present the same peak at 30° (111). Nevertheless, the tetragonal structure can be distinguished from cubic structure by the presence of a characteristic splitting of the diffraction peaks [20]. Although, tetragonal phase is the main crystal structure, there are traces of monoclinic phase in almost all the pre-sintered and fully-sintered zirconia samples. It is well known that tetragonal crystal form has the highest fracture strength among all the crystal forms of zirconia. X-ray diffraction patterns of fully-sintered Z0 and Z4 indicate that specimens have nearly the same crystal structure (Fig. 4). Therefore, it could be clearly said that there is no negative effect of Fe_2O_3 content, which imparts color to the zirconia samples, on the tetragonal crystal phase formation. Nascente and de Souza [21] concluded that addition of iron oxide to ceria-stabilized zirconia helped the stabilization of the tetragonal phase. In addition, Ning et al. [9] declared that XRD spectra obtained from Fe_2O_3 and Bi_2O_3 pigmented dental zirconia ceramic showed only tetragonal phase. These studies also confirm the formation of the tetragonal phase in this study.

Density results of the pre-sintered specimens are given in Table 4. The density and porosity of Z0 is around 3.119 g/cm^3 and 47.7%, respectively. With transition from Z0 to Z4, the density values increased slightly and the porosity decreased and eventually reached values of 3.178 g/cm^3 and 46.4%, respectively. Nascente and Souza [21] also observed that the presence of iron promoted the densification of ceria-stabilised zirconia.

The microhardness data of pre-sintered samples are shown in Table 5. Expectedly, the microhardness of the samples increased from Z0 (*Hv*1: 47.9 MPa) to Z4 (*Hv*1: 71.9 MPa). Microhardness results also confirmed the increase in density of the samples. When it is considered that specific surface area, crystallite size and chemical compositions of the TZP and TZP-C raw materials are almost same, the increase in density and microhardness of pre-sintered zirconia samples can be attributed to the increase of the Fe_2O_3 content. Microhardness of the commercial zirconia blocks is an important parameter for milling. If hardness of the blocks rises, wearing of the milling tools increases consequently, milling performance of the blocks deteriorates. Therefore, controlling microhardness of the self-colored zirconia blocks by changing the pre-sintering temperature is important.

The microhardness and fracture toughness of the fully sintered specimens are shown in Tables 6 and 7, respectively. The tables indicate that fully sintered microhardness value of 1250 MPa and fracture toughness value of 4.5 MPa m$^{1/2}$ are not significantly changed by variation of F_2O_3 content. The results confirm that Fe_2O_3 from TZP-C coded zirconia raw material did not have negative effect on the mechanical properties of the dental zirconia frameworks in contrast to adding Fe_2O_3 as metal oxide to the batches or presence of Fe_2O_3 in staining solutions as a coloring agent.

The color differences of the fully sintered specimens and their pictures are given in Table 8 and Fig. 3, respectively. According to the coloring parameters, while lightness (*L* value) decreased, yellowness (*b* value) and ΔE_{ab} values increased. As expected, the color of samples changed from white (Z0) to yellowish-brown (Z4) by increasing the level of Fe_2O_3 content in the batches. As a result, color scope obtained from this study is suitable for dental color matching. By mixing different concentration of Fe_2O_3,

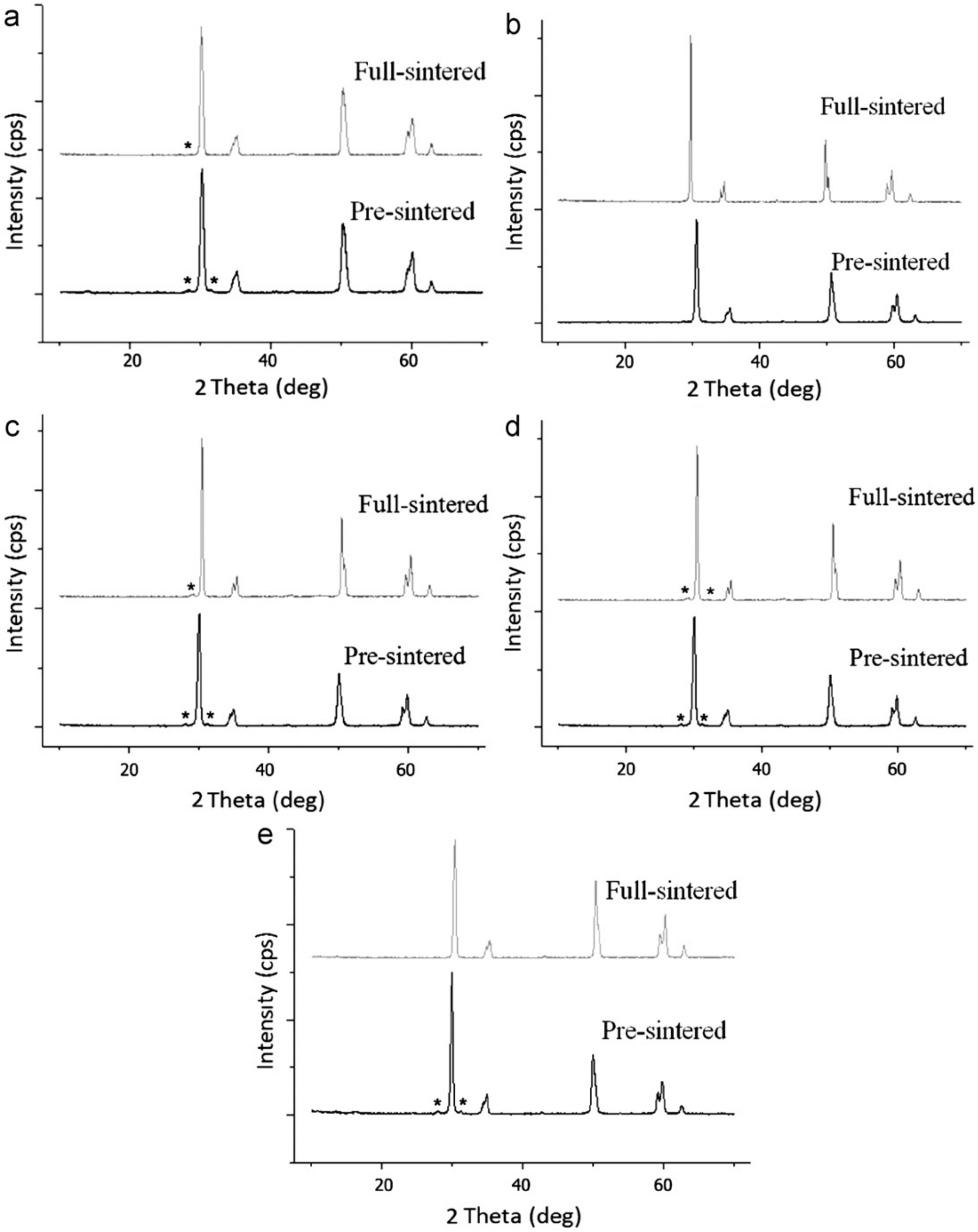

Fig. 2. XRD pattern of the specimens (a) Z0, (b) Z1, (c) Z2, (d) Z3, and (e) Z4 (*: monoclinic zirconia, other peaks belong to tetragonal zirconia).

Bi_2O_3 and their combinations with 3Y-TZP powders Wen et al. [9] reported that the hue of the sintered materials shift from yellow–green to yellow–red with increasing concentration of the Fe_2O_3 and Bi_2O_3. The results also showed that the types of coloring oxide, their concentrations and preparing route of the pigmented batches had very big effects on the final color of the product. It is thought that using zirconia raw materials having Fe_2O_3 instead of adding Fe_2O_3 to the batches as coloring pigment gives more suitable colors for dental restorations.

The photographs of self-colored zirconia framework (Z2) and all-ceramic fixed dental prosthesis, which were prepared by using the Naritake brand CZR model body (A2B), enamel (E2), translucent (T0) and self-colored zirconia framework milled from Z2 coded zirconia block by Yena brand D 40 (5 AXIS) model CAD/CAM system are presented in Fig. 4a and b. It is obvious that all the ceramic dental prosthesis produced by self-colored zirconia framework has required color, esthetic appearance and high translucency indicating that they are more suitable to produce all-ceramic dental prosthesis (Fig. 4).

The SEM micrographs of the fully sintered specimens are given in Fig. 5. It is clear that all the samples were sintered fully without any remaining porosity. The fully sintered samples exhibited ultra-translucency which is believed to be due to their small grain size (100–400 nm).

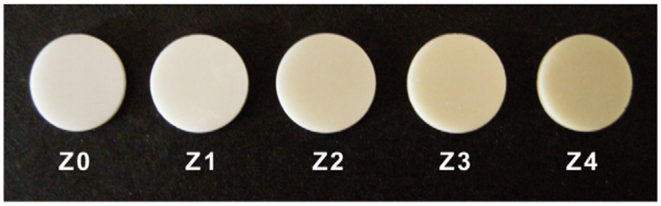

Fig. 3. Photograph of fully sintered samples. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

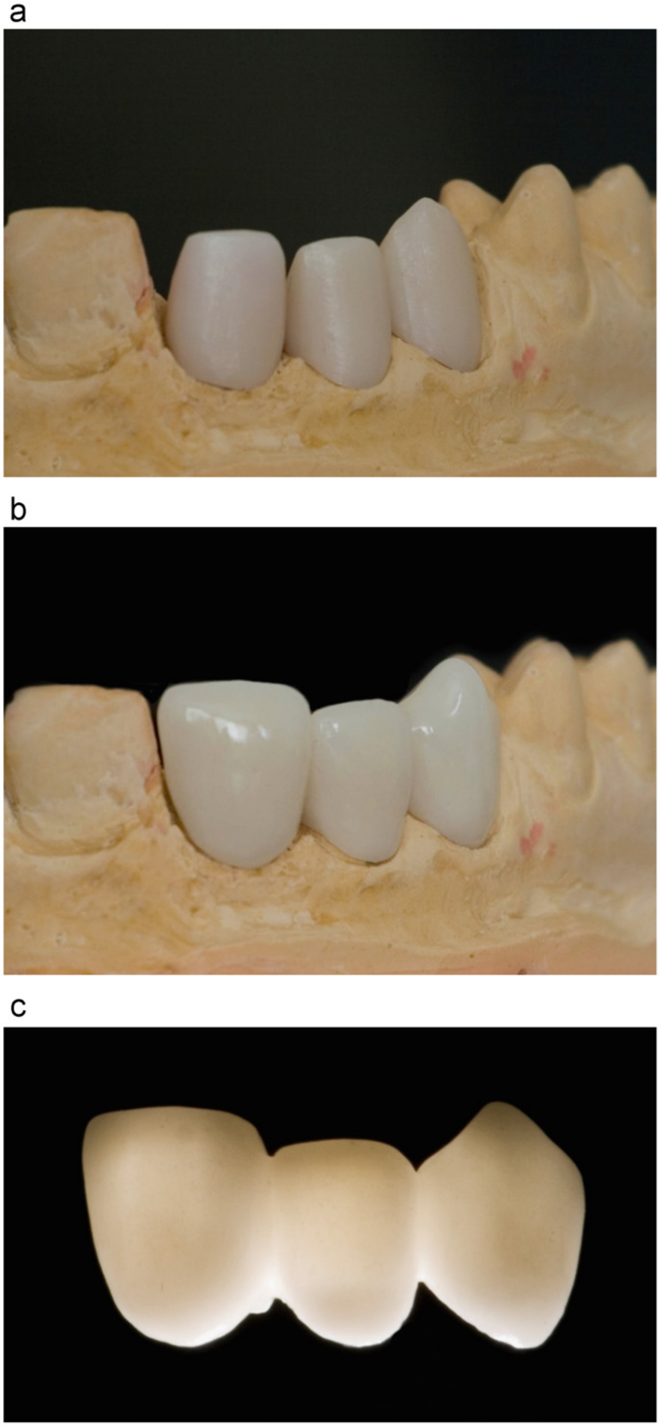

Fig. 4. Photographs of (a) self-colored zirconia framework, (b) all-ceramic prosthesis, and (c) translucency of the prosthesis.

Table 4
Density values of the pre-sintered samples.

Sample code	Z0	Z1	Z2	Z3	Z4
Density (g/cm^3)	3.119	3.128	3.147	3.171	3.178

Table 5
The microhardness values of pre-sintered samples.

Sample code	Hardness (*Hv*/1)	Standart deviation
Z0	47.9	0.09
Z1	49.9	0.07
Z2	62.9	0.07
Z3	68.8	0.08
Z4	71.9	0.09

Table 6
The microhardness values of fully sintered samples.

Sample code	Hardness (*Hv*/10)	Standart deviation
Z0	1250	7.3
Z1	1255	8.1
Z2	1256	5.4
Z3	1253	7.2
Z4	1258	6.7

Table 7
The fracture toughness values of fully sintered samples.

Sample code	Fracture toughness (MPa m$^{1/2}$)	Standart deviation
Z0	4.53	0.08
Z1	4.54	0.09
Z2	4.53	0.08
Z3	4.52	0.08
Z4	4.55	0.09

Table 8
Measured color differences of the specimens.

	Z0	Z1	Z2	Z3	Z4
a	1.56	4.84	−2.62	−1.16	0.58
b	−0.09	−2.70	12.13	17.78	19.86
L	80.60	83.60	81.34	78.0	75.99
ΔE_{ab}	–	7.16	12.94	18.26	20.49

Chaim et al. [22] reported that Y_2O_3, CeO_2 and ThO_2 are equally effective in inhibiting grain growth during sintering of zirconia; however, La_2O_3 has smaller effect on this phenomenon. Chaim et al. [22] also observed the presence of very large grains in ZrO_2–Bi_2O_3 alloys, which confirmed the presence of a liquid phase and a dissolution–reprecipitation mechanism in the system. In the present study, the micrographs (Fig. 5) indicate that small amount of Fe_2O_3 (0.029–0.143 wt%) did not have a significant effect on the microstructure and grain growth, which can cause decrease in fracture strength of the materials.

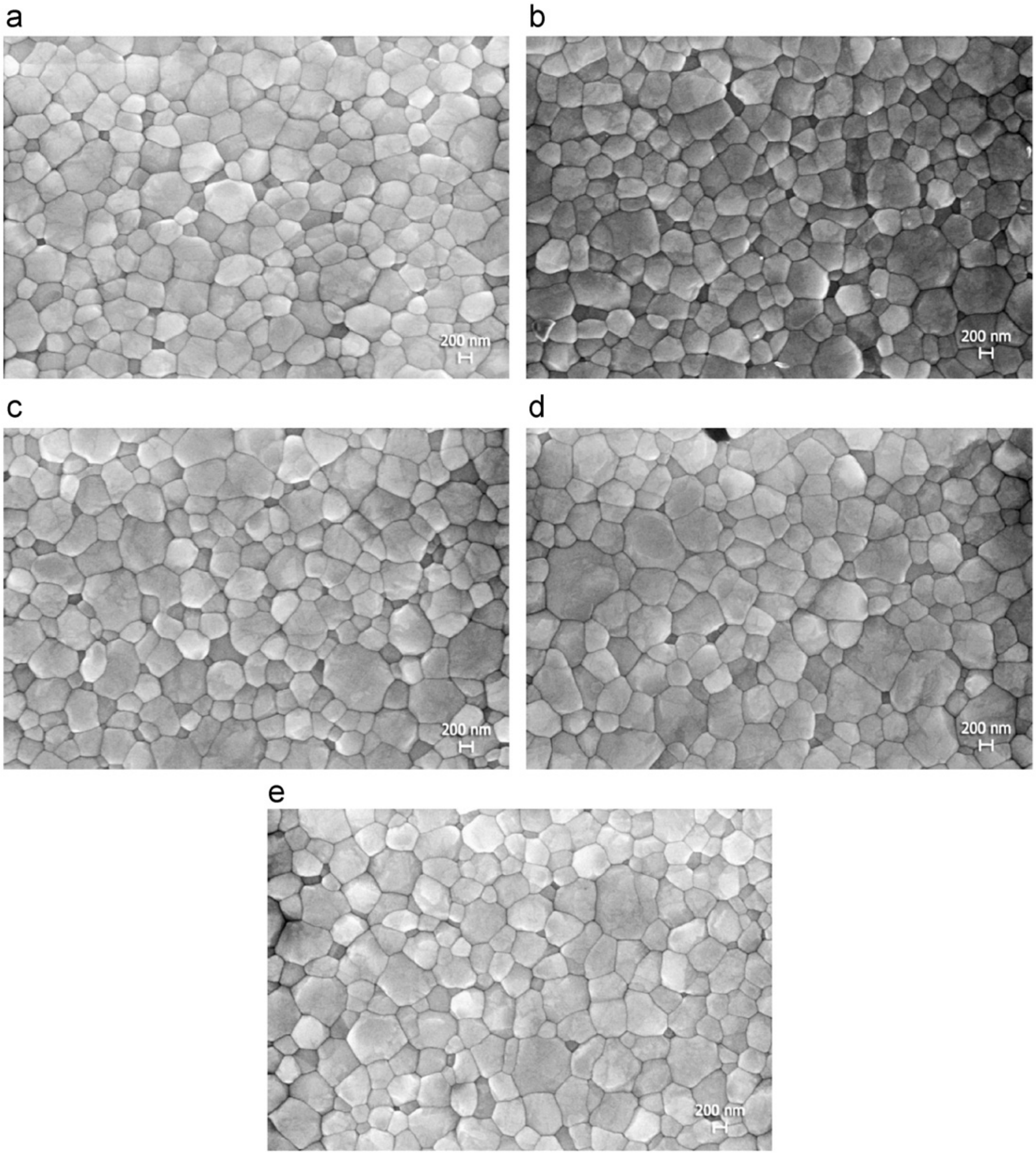

Fig. 5. SEM micrographs of fully sintered specimens (a) Z0, (b) Z1, (c) Z2, (d) Z3 and (e) Z4.

4. Conclusion

The results of this study indicated that self-colored dental zirconia blocks can be produced by using zirconia raw material having Fe_2O_3 content between 0.029 and 0.143 wt%. All the disadvantages of using staining solutions for coloring of zirconia frameworks can be eliminated by this approach. There was no negative effect of Fe_2O_3 content on the tetragonal zirconia phase formation. Although increasing the Fe_2O_3 content raised the density and the microhardness of the pre-sintered samples, these values of the fully sintered samples were not significantly changed. The color of samples was changed from white to yellowish-brown due to the increasing Fe_2O_3 content. Using zirconia raw materials having small amount of Fe_2O_3 instead of adding Fe_2O_3 to the batches as coloring agent gives more suitable colors for dental restorations and suitable for all-ceramic dental prosthesis. All samples were fully sintered without any remaining porosity and exaggerated grain growth. Fe_2O_3 did not have considerable effect on the microstructure and grain growth of the samples.

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