

CMAS BASED CERAMICS PRODUCTION USING DOLOMITE, KAOLIN AND ZIRCONIA

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Abstract: CMAS (CaO-MgO-Al₂O₃-SiO₂) based ceramics were fabricated by using dolomite, kaoline and zirconia as raw materials. Natural calcia and magnesia containing material (dolomite) and silica and alümina containing kaolin were used to develop a new ceramic of CMAS system. The calculated amounts of oxides for the indicated compositions were ball milled for 3 h using distilled water as the milling media. After drying, the powders pressed in cylindrical mould under the pressure of 300 MPa. The samples were fired in an electric furnace with a heating rate of 10°C.minute⁻¹ at 900°C to 1200°C for periods of 1, 3, and 5 hours. Then, the fired samples were cooled to room temperature in the furnace. Microstructure of produced CMAS ceramics were investigated and their phases analysis was determined. The effects of ZrO₂ oxide on microstructure and phase structure of CMAS ceramics were also investigated.

Keywords: CMAS ceramics, anorthite, diopside, dolomite, kaoline

Introduction

Glass-ceramic materials, prepared by the controlled crystallization of glasses, have a variety of established uses that depend on their uniform reproducible fine-grained microstructures, absence of porosity and other wide-range of properties, which can be tailored by an adjustment of composition and the heat treatment procedure applied. Recently, glass-ceramics based on chain silicate structures have been developed (Khater, 2010). The glass-ceramics based on CMAS quaternary system, which are mainly produced from inexpensive natural or synthetic materials, such as fly ash, blast furnace slag, basalt, oil shale, granite and tuff, lithium porcelain clay tailings have received increasing attention during the past few decades. Blast furnace (BF) slag is one of the most abundant solid by-products in steel plants. Currently most of BF slag in China has been used for cement manufacturing and civil engineering, and the remaining amount is deposited in landfill. BF slag, which is mainly composed of CaO, SiO₂, Al₂O₃ and MgO, is the excellent raw material for the production of glass-ceramics. Recycling these slags is necessarily beneficial not only for economy, but also for environmental friendly steel plants (Yang et al, 2015). CMAS ceramic is one of the most promising glass-ceramic systems, and has excellent mechanical properties, high abrasive resistance and good chemical resistance due to the precipitation of crystals like diopside [CaMgSi₂O₆], anorthite [CaAl₂Si₂O₈] and cordierite [Mg₂Al₄Si₅O₁₈]. CMAS ceramics have become good candidates for functional applications such as sealant for solid oxide fuel cells, architectural applications such as building materials for interior and exterior walls, and heavy industrial applications such as protective materials for bunker, funnel and chute. As well known, the crystallization of CMAS glass-ceramics is very difficult, and also hard to control, which largely restricts the preparation and application of CMAS glass-ceramics. Sintering process and body crystallization process are two main preparation methods of CMAS glass-ceramics. Sintering process is derived from the sintering of fine ceramics, consisting of glass melting, water quenching, particle molding and high-temperature sintering, while body crystallization process is similar to the production procedures of plate glass, including glass melting, molding, annealing, nucleation and crystallization. In comparison with body crystallization process, it is relatively easy to control the crystallization of CMAS glass, but it is too difficult to obtain the fully dense glass-ceramics, for sintering process. Recently improving the crystallization of CMAS glass by adding nucleation agent has received considerable attentions. However, the present researches mainly focus on the crystallization of CMAS glass-ceramics prepared by sintering process (Yang et al,2014)

Controlled bulk crystallization is the method most frequently used for producing glass-ceramics through controlled crystallization. The study of the CMAS system was also important for understanding the reactions taking place in rocks, blast furnace slags and MgO refractories. In most cases, published phase diagrams are related to equilibrium conditions that are not usually encountered in glass-ceramic preparations. Therefore, it is necessary to determine

the relationship between the compositions of glass-ceramics and the crystal phases developed under conditions in which such polycrystalline materials were actually produced. In a previous paper Khater (2006) managed to obtain a glass-ceramic material based on by-pass silica sand and magnesite. From cement kiln dust which made up about 57 wt.% of the batch constituents depending on the composition. Cement kiln dust is generated in the cement kiln and associated equipment. Dust from the raw mix and the surroundings of the plant is normally suppressed with closed systems and through water sprays. During the burning process, the gas flows entrain a substantial quantity of dust that forms part of the kiln exit gasses. The production of cement kiln dust strongly depends upon the chemistry of raw materials, type of process and the design of gas velocities in the kiln. Other factors such as kiln performance and dust collection systems also play vital roles in kiln dust generation. The production of alkaline-earth aluminosilicate glasses in the system CMAS has been broadly investigated in the past decade. Crystalline phases such as cordierite, diopside, wollastonite, mullite, etc., have been precipitated from glasses under controlled conditions resulting in glass-ceramics with attractive dielectric properties and high mechanical and chemical resistance (Khater, 2010).

The CMAS ceramic system has attracted much attention due to its low densification temperature, low thermal expansion coefficient ($TCE < 5.10^6 /1C$), low dielectric constant ($\epsilon_r < 10$) and better chemical durability. To facilitate CMAS glass crystallization different nucleating agents, such as TiO_2 , CaF_2 , and ZrO_2 have been used. It is well known that the flexural strength and fracture toughness can be improved by precipitating nano-size tetragonal ZrO_2 particles into the bulk glass. However, the pure glass easily bloats or softens during firing, leading to distortion of the components and requires the addition of ceramic fillers (such as alumina, cordierite, and rutile etc.) to eliminate softening at 800–900°C (Wang et al, 2014). Hanning et al (2006) explained that the glass compositions, the kind and content of nucleating agent and the schedule of heat-treatment, all greatly affect the microstructure and properties of glass–ceramics. In this work, sintering behaviors and microstructural properties of CMAS ceramics in the presence of the ZrO_2 nucleation agent was investigated.

Experimental procedures

Kaolin, dolomite, and zirconia were used as starting materials for preparations of CMAS based ceramics. ZrO_2 was added as a nucleation agent after the heat treatment schedule was determined, in attempt to promote the crystallization and improve performance of ceramics. The method of preparation of CMAS ceramics in present study is illustrated in Fig. 1. As shown in Figure the calculated amounts of the starting oxides for the indicated compositions were ball milled for 3 h using distilled water as the milling media and dried than sintering different temperature and times. Table 1 presents the chemical analyses of the raw materials, and Table 2 presents the chemical composition of the two CMAS ceramics. ZrO_2 was added into the CMAS-D ceramics composition for preparations of CMAS-DZ coded ceramics.

Scanning electron microscopy (SEM, Jeol 6060LV) and energy-dispersive X-ray spectroscopy (EDS) were used to characterization of produced CMAS ceramics microstructure. X-ray diffraction (XRD) analysis was performed with RIGAKU D/Max/2200/PC to determine the crystalline phases occurred in the produced CMAS ceramics. The volume density was measured by Archimedes method. The Vickers hardness (H_V) of the samples were measured using a microhardness tester (LEICA VMHT MOT) with a 100 g load, its load time was 15 s along the whole cross-section. Chemical durability of CMAS ceramic specimens was analyzed by measuring weight loss after chemical attacked at 2h later in 10% NaOH solutions at 100°C.

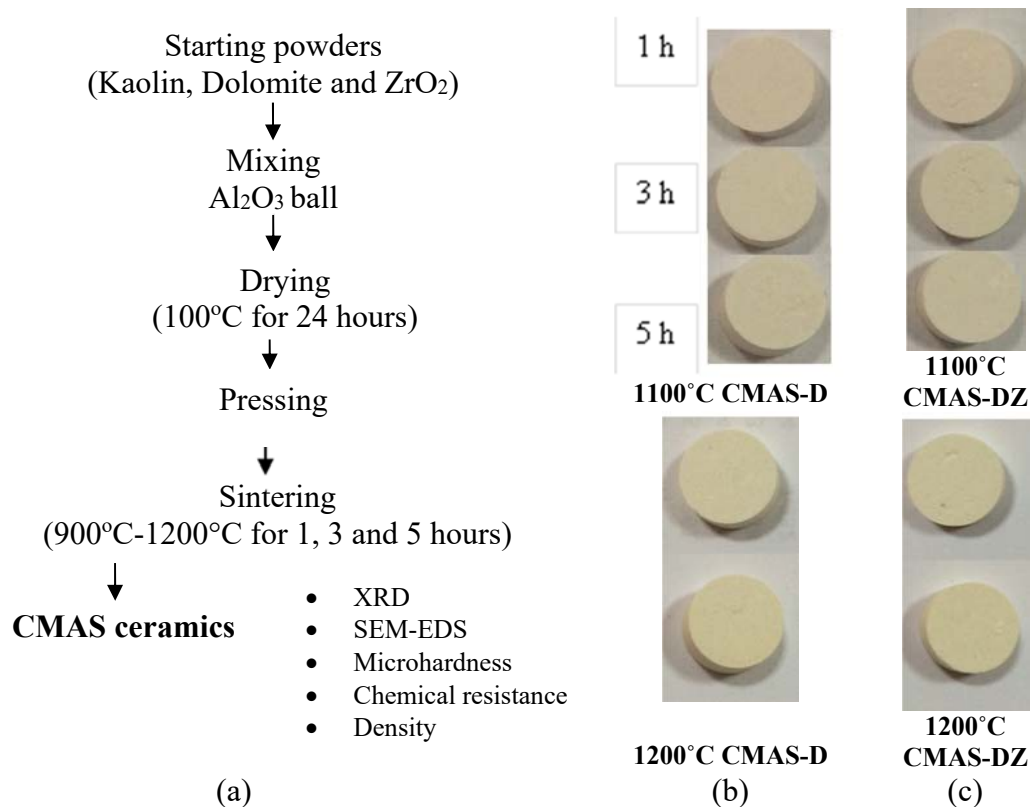


Figure 1. (a) Flow chart for the CMAS ceramics production, (b) and (c) macro structure of CMAS-D and CMAS-DZ coded ceramics

Table 1. Chemical analysis of the used raw materials (wt.%)

Raw Materials	CaO	MgO	Al ₂ O ₃	SiO ₂	H ₂ O	ZrO ₂
Dolomite	50	50	-	-	-	-
Kaolin	-	-	39.5	46.54	13.96	-
Zirconia	-	-	-	-	-	100

Table 2. Chemical composition of the investigated CMAS ceramics (wt.%)

Composition (wt. %)	SiO ₂	Al ₂ O ₃	CaO and MgO		ZrO ₂
	Kaolin		Dolomite		
CMAS-D	64		36		-
CMAS-DZ	64		36		5

Results and discussion

Fig. 2 shows the SEM micrographs of two coded ceramic samples crystallized at 1100 °C to 1200° C for 1 and 3 hours. It can be seen that the complex nucleation agents have an important role on the shape of crystals. With the addition of ZrO₂ (CMAS-DZ sample), the crystals irregularly arrange with sheet shape and low crystallinity (Khater, 2010). According to the SEM image of CMAS, a large number of granular crystals and a small quantity of lamellar shape crystal were distributed in the glass matrix after treated at 1100°C. S. Banijamali et al. (2009) explained that sintered CMAS ceramics reveals a coarser microstructure in which the needle-like crystals have been extended from the surface toward the center of glass particles. This behavior has led to the crack-like defects in the middle of particles.

In Fig. 3, the columnar and small granular crystalline phases were distributed in CMAS specimen after crystallization at 1100 °C. It is well known diopside is a columnar crystal in ceramics. Furthermore, the EDS microanalyses were carried out on different areas of CMAS specimens. The magnesium content of 1 coded area is higher than other areas. The aluminium and oxygen content of 4 and 5 areas is apparently higher than 1, 2 and 3 coded areas, which showed that the columnar crystalline phases were diopside. The addition of zirconia which can enhance the heterogeneous nucleation of phases, and limit the growth of long anisotropic anorthite grains which will result in new voids where equiaxed grains are originally located.

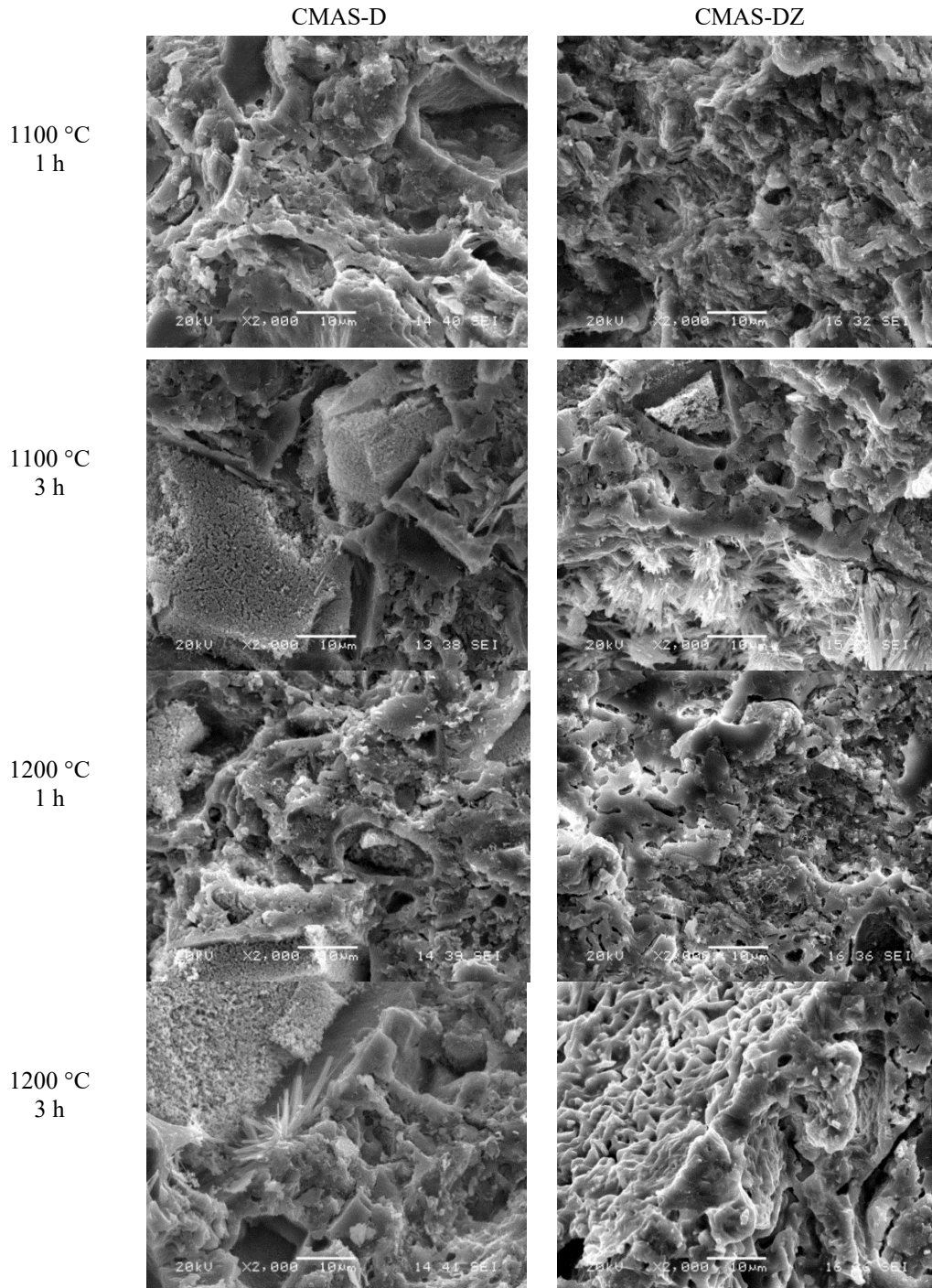
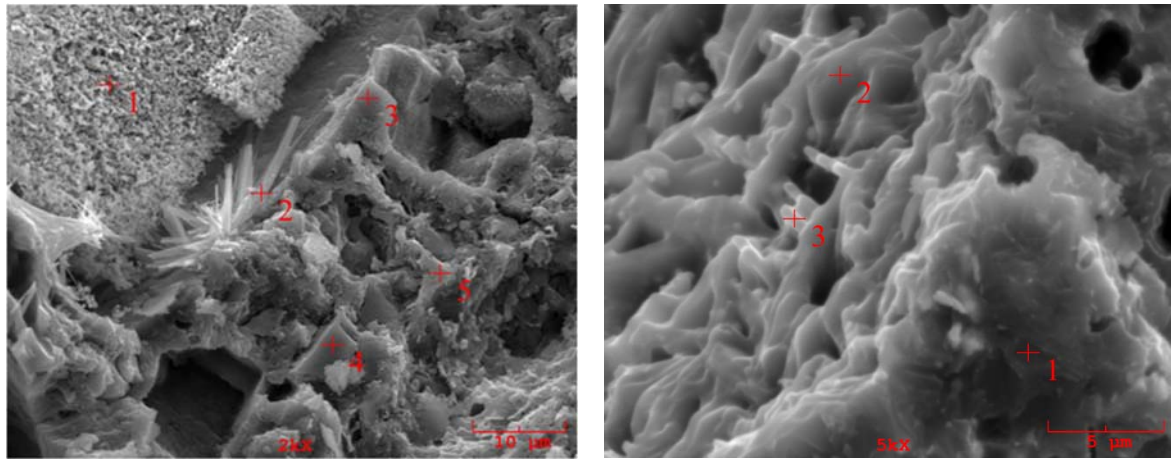


Figure 2. SEM images of the CMAS-D and DZ coded samples in the sintering of 1100 °C to 1200 °C for 1 and 3 hours



(a) (b)

Elementler	Miktar (%)				
	1	2	3	4	5
O	36.893	48.117	40.688	42.623	44.007
Mg	60.474	6.927	4.660	1.041	1.194
Al	0.704	12.893	14.711	25.653	21.825
Si	1.493	10.829	17.436	29.334	32.024
Ca	0.436	21.234	22.505	1.349	0.950

(c)

Elementler	Miktar(%)		
	1	2	3
O	28.393	30.556	43.716
Mg	0.728	1.729	3.251
Al	23.232	12.992	15.095
Si	27.582	20.047	19.157
Ca	17.194	32.147	14.937
Zr	2.871	2.530	3.844

(d)

Figure 3. SEM-EDS analysis of (a), (c) CMAS-D and (b), (d) CMAS-DZ samples sintered at 1200°C for 3h

Fig. 4 shows XRD patterns of the CMAS-D and CMAS-DZ coded samples crystallized at 900°C, 1000°C, 1100°C and 1200°C for 3 h. It can be seen that the CMAS-D, and CMAS-DZ samples have the same main crystalline phases, such as diopside and anorthite, their frequency depending largely on the base composition and crystallization parameters. It can be noticed that, with increasing the ZrO₂ content, the intensity of diopside becomes stronger gradually. In the Khater's (2014) X-ray diffraction showed that monoclinic or triclinic wollastonite (CaSiO₃), diopside (CaMgSi₂O₆) and anorthite (CaAl₂Si₂O₈) were the main crystalline phases developed in the CMAS ceramics.

CMAS-DZ ceramics exhibited slightly higher relative density and less porosity than CMAS-D ceramics, which is consistent with the results of Table 3. The corrosion resistance of CMAS ceramics is evaluated from the weight losses after leaching in alkali solution. The results are given in Table 3. Samples weight loss values for CMAS-D ceramics change between the ranges of 2.12 % to 3.73 % and for CMAS-DZ ceramics change between the ranges of 2.02% to 2.98%. It can be seen that, in general, the durability of CMAS ceramic is increased depend on crystallization temperature and adding ZrO₂ nucleating agent.

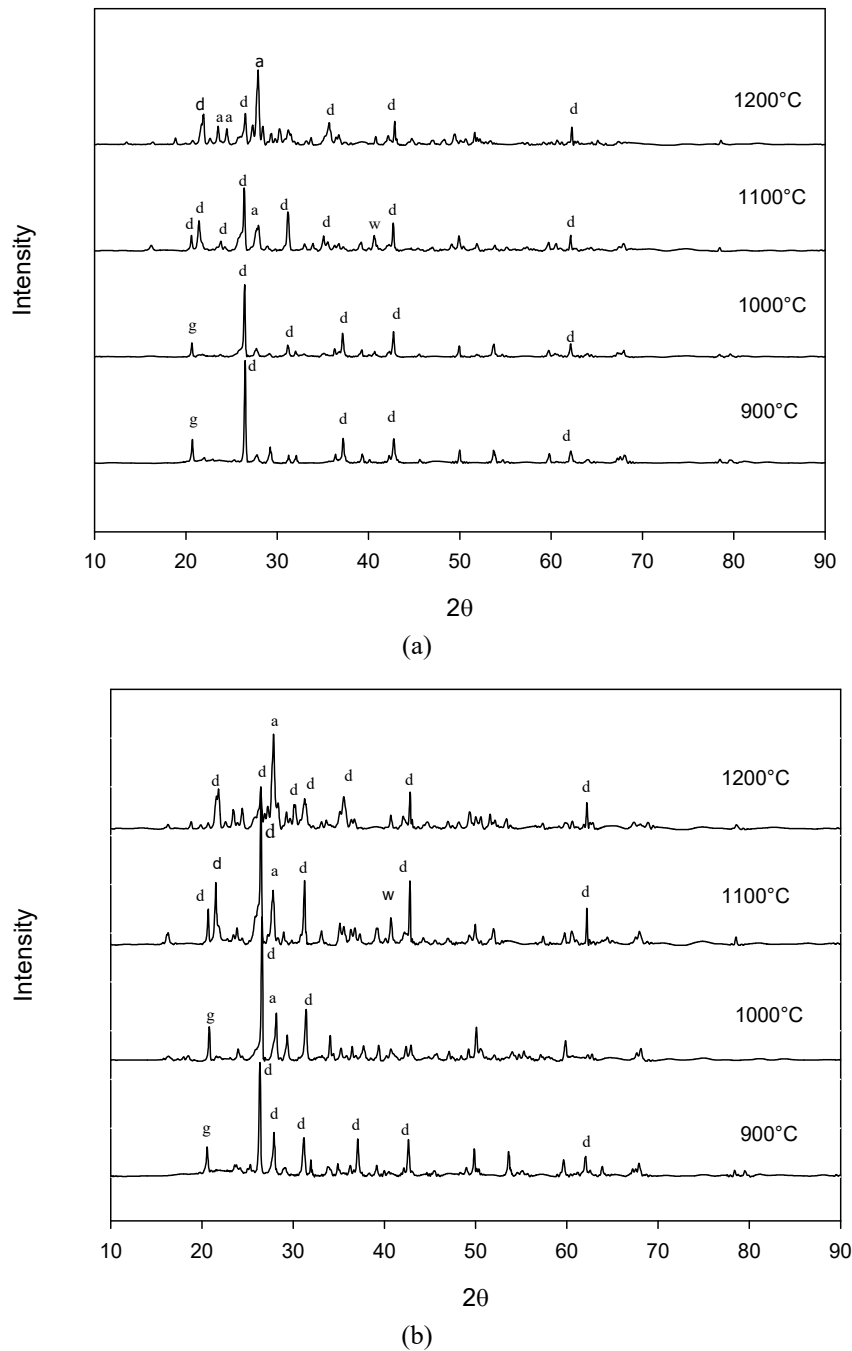


Figure 4. (a) XRD patterns of the CMAS-D and (b) CMAS-DZ samples crystallized at 900°C, 1000°C, 1100°C and 1200°C for 3 h (a:anorthite, d: diopside, w: wollastonite, g:gehlenite)

Indentation microhardness measured for the obtained CMAS ceramic materials (Table 3) was found to lie in the range 522–844 HV, indicating high abrasion resistance of these materials and making them suitable for many applications under aggressive mechanical conditions. Samples hardness values for CMAS-D ceramics change between 522 HV to 787 HV and for CMAS-DZ ceramics change between 612 HV to 844 HV. The hardness of the samples drops from a value of about HV=844 for CMAS-DZ to about HV=522 for CMAS-D. Vickers hardness of CMAS ceramics were observed to increase with addition of ZrO₂. Average value of HV for the desert sand glass was found to be 6.37 GPa. This value of Vickers microhardness for desert sand glass falls is smaller than in this study results (Choi et al., 2015).

S. Banijamali et al. (2009) chose raw materials from commercial grade calcium carbonate, corundum, silicon oxide, titanium oxide, zirconium oxide and calcium fluoride. The homogenized mixture of raw materials was transferred to a zircon crucible and melted at 1450 °C for 1 h in an electric furnace. The melts were water quenched and the obtained frits were dried and milled to the required particle sizes (<75µm). According to the obtained results, in spite of less crystallization in SZ6 (ZrO₂ containing specimens), this sample shows the highest Vickers hardness and improved chemical resistance rather than fluorine containing specimens.

Table 3. Various properties of the CMAS-D and CMAS-DZ ceramics

Sample name	Sintering temperature (°C)	Time (h)	Density (g/cm ³)	Hardness (HV)	Mass loss in NaOH (wt.%)
CMAS-D	1000	1	1.70	522	3.73
		3	-	532	-
		5	1.72	568	-
	1100	1	1.72	570	2.65
		3	1.73	582	-
		5	1.77	612	2.35
	1200	1	1.84	747	2.31
		3	1.92	787	2.12
	CMAS-DZ	1000	1	-	612
3			1.805	634	-
5			1.825	673	-
1100		1	1.845	705	2.5
		3	1.88	736	-
		5	1.95	765	2.33
1200		1	1.97	827	2.27
		3	1.99	844	2.02

Marques et al. (2010) reported that, the glass-ceramics based on diopside, with excellent mechanical properties, high abrasive resistance and good chemical resistance, were good candidates for decorative materials in construction field.

Conclusions

In the present work, the reported results show that dolomite, kaoline and zirconia can be used to develop a new ceramic of CMAS system. For sintering temperature lower than 1100°C, the CMAS specimen were digested. Diopside and anorthite were found as major crystalline phases. With the raise of sintering temperature, the crystal shape changed from spherical to needle and the crystal size became much larger. Vickers hardness of CMAS ceramics were observed to increase with the addition of ZrO₂.

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