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ORIGINAL PAPER

Nano-Scale Cordierite Glass-Ceramic from Natural Raw Materials with Different Fluoride Additions

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Abstract
Stable cordierite glass-ceramics were prepared from natural kaolin, silica sand and magnesite as raw materials. Furthermore the effect of fluorine additions was tested by addingAlF_3 or MgF_2tothe glass composition. Stable cordierite was crystallized in all glass-ceramic samples during thermal treatment at temperatures in the range from 900to 1200 °C. In the microstructure cordierite, crystals of sizes 15to 50 nm in parent sample and 500 nm to 1 μm in the sample prepared using AlF_3 as raw material were observed, while in the sample prepared from MgF_2as raw materials, the crystal sizes were > 1 μm. The coefficients of thermal expansion of the present cordierite glass-ceramic (CTE) were found to be, $1.14 \times 10^{-6}\ K^{-1}$ (100–300 °C) for the parent glass and $4.93 \times 10^{-6}\ K^{-1}$(100–500 °C) for the glass-ceramic containing high AlF_3sample.Also, the microhardness values were between 5. 20 and 6.34 GPa for glass-ceramic samples. The densities of cordierite glass-ceramics increased from 2.07 g/cc in the parent sample to 2.54 g/cc and 2.58 g/cc in AlF_3 and MgF_2 containing samples, respectively. The resultant material can resist the temperature up to 1200 °C.

Keywords Cordierite · Glass-ceramics · Nanoscale particles

1 Introduction

Fluorine additions play an important part during the melting and crystallization processes of glass. In nature, fluorine occurs as fluorite (CaF_2), sellaite (MgF_2), oskarssonite (AlF_3) and villiaumite (NaF). In glasses, the addition of fluorides usually enables to decrease the melting temperature and leads to increased nucleation rates and crystal growth velocities especially in aluminosilicate glasses [1–5].

According to the literature, the crystal phase cordierite was prepared by several different routes: crystallization of a melt during quenching, solid state reaction of appropriate oxides or wet chemical routes such as sol-gel processes. Cordierite is a favorable material because it combines outstanding properties such as low thermal expansion, refractoriness and chemical durability [1]. Using fluorite and magnesia, alumina and silica powders as raw materials enables the preparation of machinable cordierite/mica composite by using a sintering process [6]. Cordierite was also prepared at temperatures in the range from 900 to1400 °C through solid reaction with and without bismuth as flux [7].

Cordierite-anorthite phases were developed from glasses based on basalt, kaolin with little reducing agent, TiO_2 and LiF, MgF_2 and AlF_3 as nucleating catalysts. In the later work, MgF_2 was decreases the starting crystallization temperature and promote the crystallization of cordierite polymorphs with anorthite, while LiF enhances the crystallization of anorthite, β-quartz solid solutions (ss) with little spinel [8]. In other work, the heat-treatment of stoichiometric cordierite ($2Al_2O_3.2MgO.\ 5SiO_2$) glass gave surface crystallization. However, studies on the compact sample by high temperature x-ray diffraction (HT-XRD), scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) show that

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Table 1 Chemical composition of the starting local raw materials

Raw materials	Chemical composition									
	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	CaO	TiO_2	P_2O_5	IL
Kaoline	43.29	37.1	0.78	0.07	0.03	0.23	0.19	3.74	n.d.	14.1
Magnesite	4.25	0.25	0.09	41.83	0.06	0.11	5.76	<0.05	<0.05	47.73
Silica'sand	98.89	0.27	0. 14	n.d.	0.02	0.05	0.02	0.05	n.d.	0. 14

Kaoline: Az Zabirah; Magnesite: Zarghat; Silca'sand: Ad Dughm

Table 2 Chemical composition of the parent glass batch in oxide mass% in comparison with stoichiometric cordierite

Sample number	Chemical composition of the base glass batch							
	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	CaO	TiO_2
C0	50.05	33.5	0.75	11.79	0.05	0.23	0.18	3.40
Cordierite[a]	51.36	34.86	–	13.78	–	–	–	–

[a] Stoichiometric cordierite ($Mg_2Al_4Si_5O_{18}$)

Table 3 Additive of both AlF_3 and MgF_2 to the parent glass batch

Additive	Sample number Addition in grams to100 g parent oxide glass						
	C0	C4A	C7.5A	C10A	C4M	C7.5M	C10M
AlF_3	00	4	7.5	10	00	00	00
MgF_2	00	00	00	00	4	7.5	10

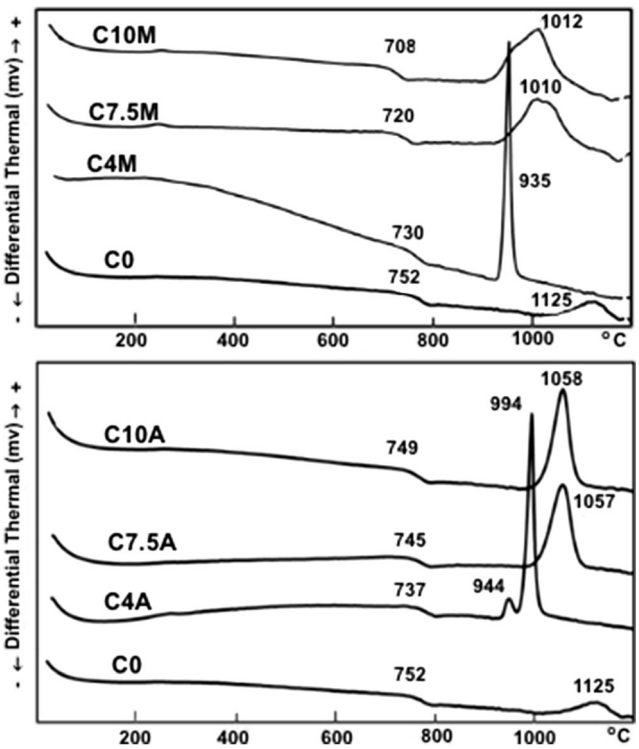

Fig. 1 DTA-profiles of the parent glassC0 and glasses containing, AlF_3 (C4A, C7.5A and C10A) or MgF_2 (C4M, C7.5M and C10M)

the formation of an oriented layer at the immediate surface is not observed, therefore, this is in disagreement with previous reports in the literature [9]. Crystallization of cordierite from stoichiometric glass is observed in situ in the scanning electron microscope, using a heating stage, operated at 1000 and 1100 °C. The early state of surface crystallization was recorded in which the crystals were still well separated. In surprise, at the late stage of crystallization, the formation of cracks as well as a squeezing out of a low viscous phase took place under the conditions inside an SEM [10].

In recent work, cordierite – gahnite glass-ceramic was prepared from kaolin, magnesite, silica and ZnO with the addition of AlF_3, MgF_2 and CaF_2 as nucleation catalysts. The latter glass-ceramics have comparatively low thermal

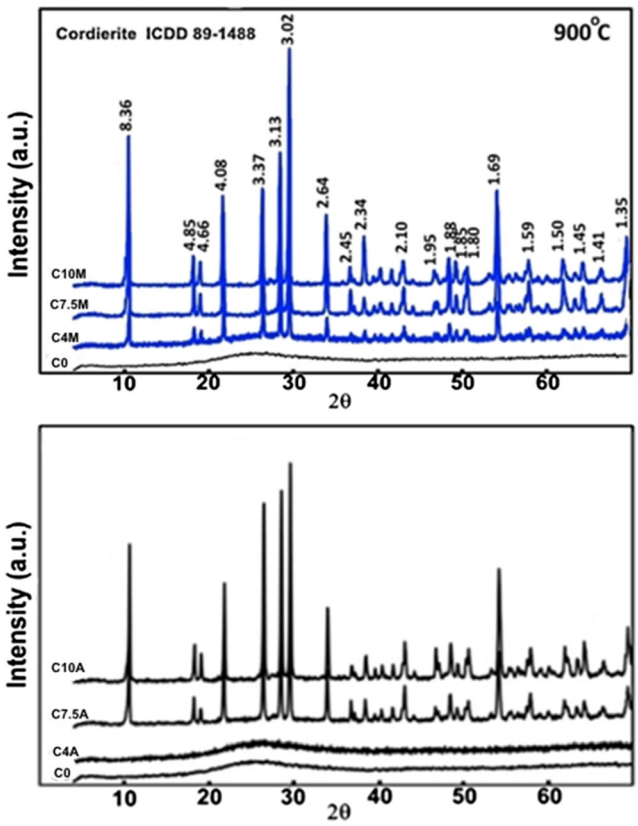

Fig. 2 X-ray diffraction patterns of the parent glass C0 and glasses containing AlF_3 (C4A, C7.5A and C10A) or MgF_2 (C4M, C7.5M and C10M), heat-treated at 900 °C for 2 h

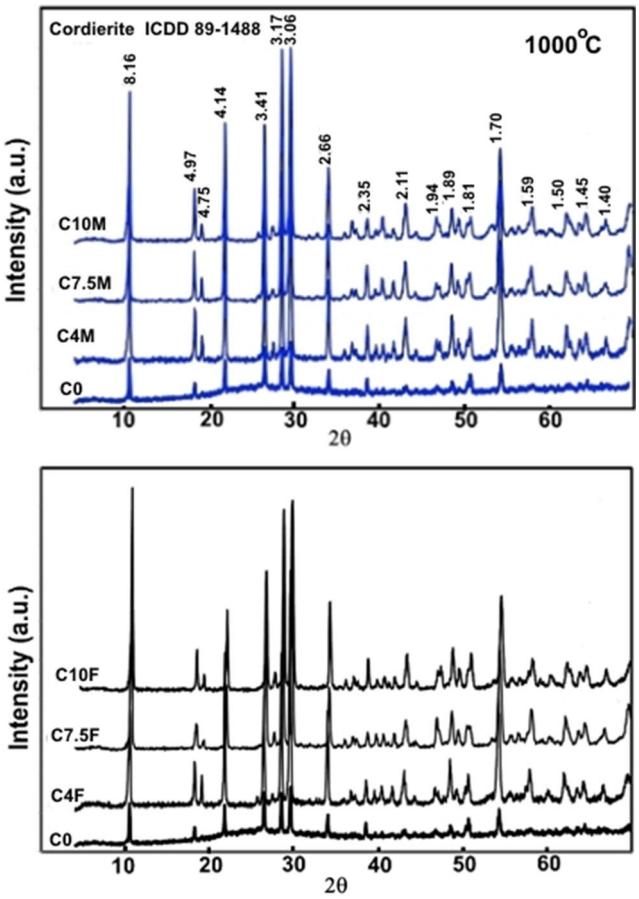

Fig. 3 X-ray diffraction patterns of the parent glass C0 and glasses containing AlF_3 (C4A, C7.5A and C10A) or MgF_2 (C4M, C7.5M and C10M), heat-treated at 1000 °C for 2 h

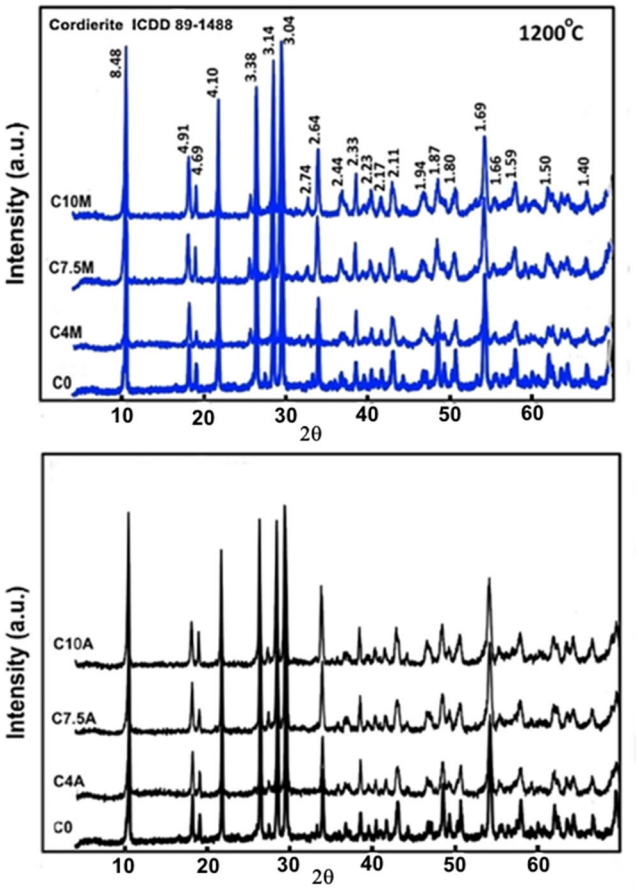

Fig. 4 X-ray diffraction patterns of the parent glass C0 and glasses containing AlF_3 (C4A, C7.5A and C10A) or MgF_2 (C4M, C7.5M and C10M), heat-treated at 1200 °C for 2 h

expansion [11]. From pure chemicals with the addition of 0.5 to 12.0 mol% fluoride, sintered glass-ceramics containing hexagonal cordierite with very small enstatite, anorthite and high sandine concentrations were prepared [12]. The latter glass ceramics possess very good dielectric as well as good mechanical properties.

However, cordierite glass-ceramic based on raw materials other than its inexpensive, it may have outstanding physical properties such as resistance for temperature > 1000 °C, low coefficient of thermal expansion and good hardness [8, 11, 13].

The present work deals with the preparation of cordierite glass ceramic totally from kaolin, magnesite and silica 'sand. The effect of different ratio of each MgF_2 and AlF_3 on the parent glass were tested. Characterization of glasses and its glass-ceramics were by differential thermal analysis DTA, x-ray diffraction analysis XRD and scanning electron microscopy SEM attached with energy dispersive x-ray microanalysis EDX were performed. Some properties like density, microhardness and coefficient of thermal expansion were carried out too.

2 Methods and Procedures

The starting materials were kaolin, magnesite and silica sand from Saudi Arabia. The chemical analysis of the raw materials was done using advanced x-ray fluorescence in ALS Chemex Lab (Canada) (Table 1). The batch was prepared by mixing 70.37 wt.% of kaolin with21.89 wt.% of magnesite and 7.74 wt.% of silica sand which is near the composition of stoichiometric cordierite ($Mg_2Al_4Si_5O_{18}$) (Table 2). Commercial MgF_2 and AlF_3 were added to see their influence on the developed phases and some properties (Table 3). The starting materials were mixed by ball milling for 2 h and dried at 110 °C overnight. The melting process took place in a sintered alumina crucible in the 1450 to 1500 °C temperature range. The glass samples were annealed at 650 °C.

Differential thermal analysis (DTA, A Shimadzu DTG-60H) was used to detect the glass transition Tg °C and exothermic crystallization Tc °C temperatures in the glass sample using the grain size fraction 25–50 μm. The glass samples were heat-treated in single stage at temperatures in the range from 900 to 1200 °C for 2 h. In order to identify the developed phases, the heat-treated samples were studied by X-ray

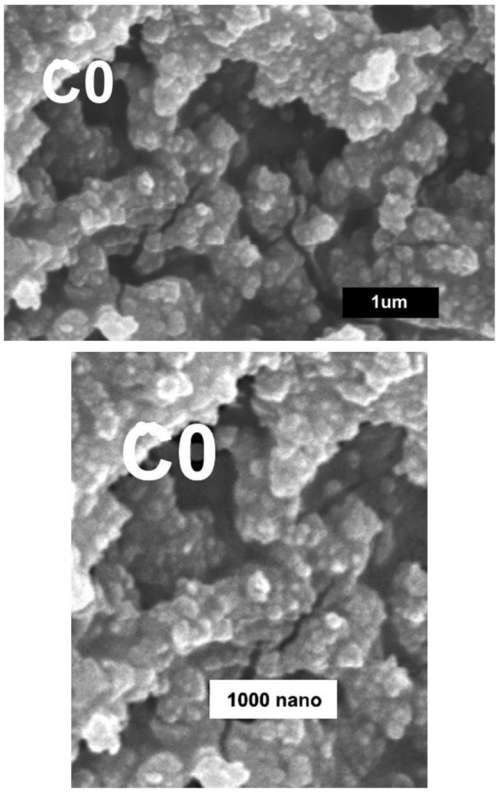

Fig. 5 SEM micrographs of the C0 base glass heat-treated at 1000 °C for 2 h

diffraction (XRD, Mini Flex of Rigaku (Japan), adopting Ni filtered Cu-radiation). The microstructures of the crystallized glasses were investigated by scanning electron microscopy, SEM (Jeol-JSM-5800, Japan). For clear microstructure, the crystallized samples were etched by 1%HF +1%HNO_3 for half minute, well rinsed by distilled water then dried for examination.

In addition, some properties such as the coefficient of thermal expansion, the microhardness and density were determined. The coefficient of thermal expansion CTE of the crystallized samples, was determined using a dilatometer (Netzsch-Dil 402 PC, Germany) with the heating rate 5 °C/min. A Vickers microhardness tester (Shimadzu HMV 2000-Japan) was used to measure the microhardness values for the heat-treated glasses. The densities of glass-ceramic samples were determined with a Quantachrome pycnometer (Upyc 1200e v5, 03; USA) using helium gas.

3 Results and Discussion

Results of differential thermal analyses are shown in Fig. 1. After the melting process, carried out at temperatures in the range of 1450 to1500 °C, dark brown glasses were obtained. The coloration is supposedly due to minor Fe_2O_3 and TiO_2 impurities in the raw materials (ilmenite coloration). The sequential additions of AlF_3(melting point 1290 °C) and MgF_2(melting point 1263 °C) leads to a decrease in viscosity and enables to decrease the melting temperature from 1500 to 1450 °C. As mentioned before, while addingAlF_3, the effect of fluoride on the viscosity is probably compensated by the counteraction of Al^{3+}, which increase the melt viscosity [14].

The DTA profiles show that additions of 4, 7.5 and 10 g MgF_2 to 100 g of the parent glass composition lead to a continuous decrease in the glass transition temperatures Tg °C from 752 to 730, 720 and finally to 708 °C. The addition of 4 g AlF_3leads to a decrease of T_g from 752 to 737 °C while further increasing AlF_3 concentrations lead to a re-increase to 746 and 749 °C (Fig. 1).

The DTA-profile of the base glass shows a broadexothermic peak in the range from 1030 to 1175 °C. In MgF_2-containing

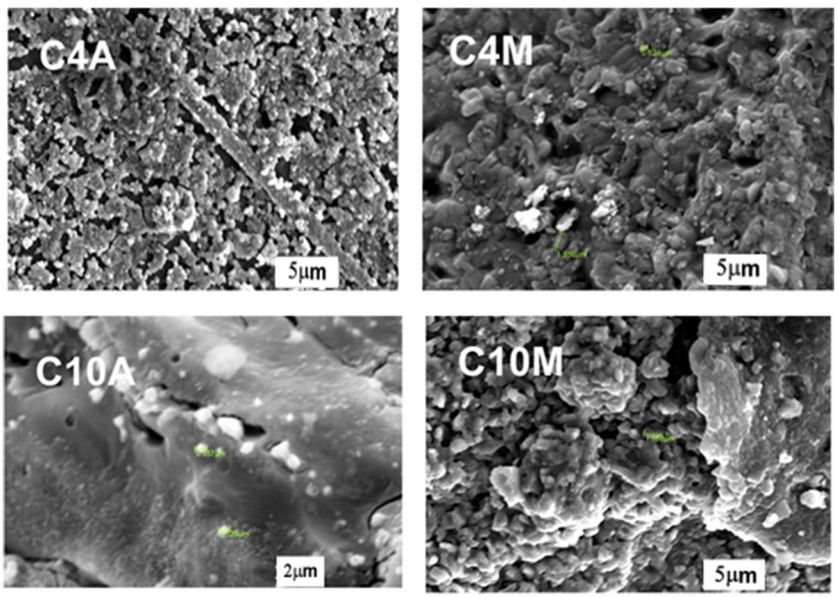

Fig. 6 SEM micrographs of the glasses C4A, C4M, C10A and C10M, heat-treated at 1000 °C for 2 h

Table 4 The EDX microanalyses of the glass samples wt.%

Elements	Microanalyses and nominal composition of cordierite			
	C10M	C10A	C0	Nominal cordierite $Mg_2Al_4Si_5O_{18}$
O	46.52	47.63	45.80	49.23
Si	12.34	18.86	16. 8	24.01
Al	10.55	19.11	17.6	18.45
Mg	25.76	9.74	13. 8	8.31
Ca	0.54	0.43	0.65	–
Ti	4.28	4.58	1.44	–

samples, little addition of fluoride (4 g MgF_2/100 g parent oxide glass) resulted in a sharp exothermic peak at 953 °C, while higher MgF_2 concentrations led to broad exothermic peaks at 1010 to 1012 °C. In both the C7.5M and C10M compositions, a partial splitting of the exothermic peak was observed. In the AlF_3- containing samples the exothermic peaks were sharp and the sample with the smallest AlF_3 concentration (in C4A) leads to a splitting of the peak and to a shift in the peak temperatures to 944 and 994 °C. At higher AlF_3 concentrations (C7.5A and C10A), the exothermic peaks occur at 1057 and 1058 °C.

Generally, in comparison with the parent glass, the incorporation of fluoride leads to lower transition temperatures Tg °C down to 708 °C and, in analogy, also to a decrease in the crystallization temperature down to 944 °C.

The sintering process at 900, 1000, 1100 and 1200 C° show the crystallization cordierite alone ($Mg_2Al_4Si_5O_{18}$, ICDD, 89–1488). Figures 2, 3 and 4 show XRD-patterns of samples thermally treated at 900, 1000 and 1200 °C, respectively. After sintering, in all samples, i.e. in the parent glass and samples prepared from MgF_2- or AlF_3–containing samples, cordierite was formed as the only crystalline phase during the heat-treatment process. In the C0 parent glass, heat-treatment at 900 °C led to an amorphous hump. In analogy, also the sample C4A shows only an amorphous hump (see in Fig. 2). With increasing fluorine concentration, the XRD-patterns of the samples C7.5A and C10A show sharp lines of increasing intensity attributable to cordierite. In all samples prepared from MgF_2, sharp lines attributed to cordierite are observed. The increase of the fluoride concentrations in these samples, results in an increase in the intensity of the XRD-lines (see Figs. 2 and 3).

Figure 4 shows XRD-patterns of all studied samples, thermally treated at 1200 °C for 2 h. In all the patterns, sharp lines attributed to cordierite are observed. The intensities of the XRD-lines do not notably depend on the sample composition, i.e. of the type and concentrations of additives (MgF_2 or AlF_3) after thermal treatment at a temperature of 1200 °C.

In summary, the intensity of XRD-patterns increases with increasing fluoride concentration during thermal treatment at

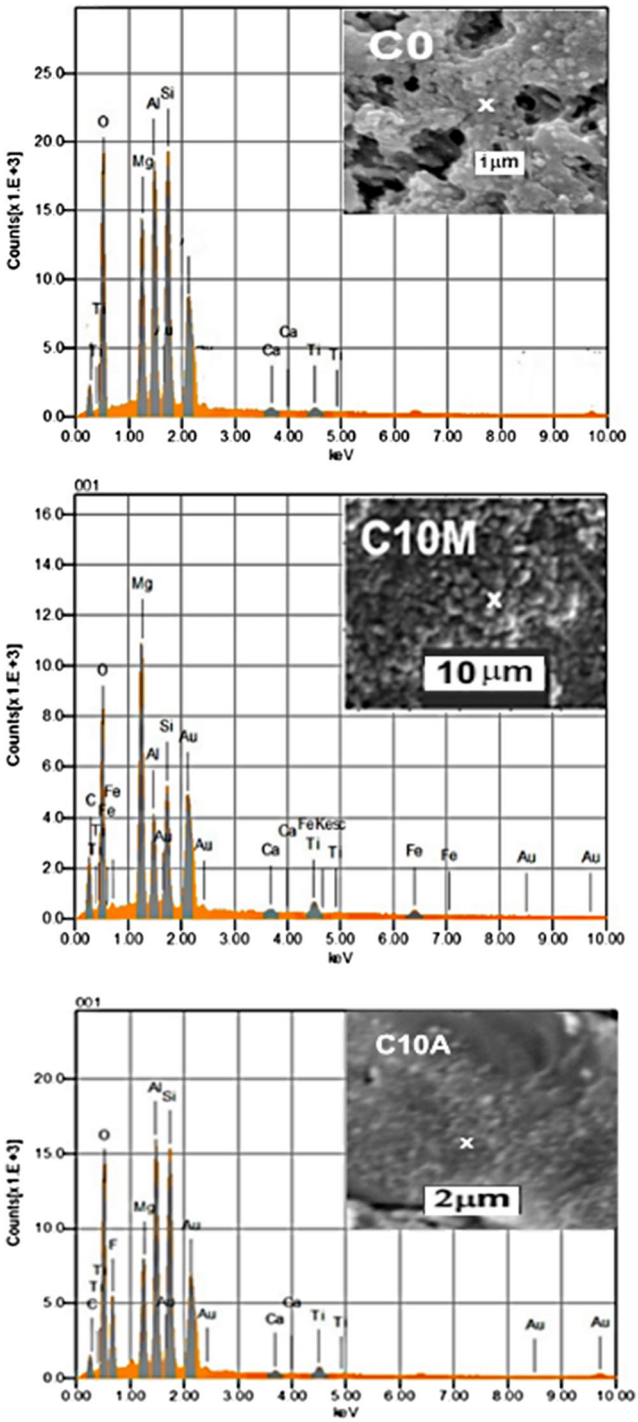

Fig. 7 EDX microanalyses of the glasses C0, C10M and C10A, heat-treated at 1000 °C for 2 h

900 °C and with increasing the crystallization temperature (compare at 900 to 1200 °C).

The SEM micrographs of the glass samples crystallized at 1000 °C for 2 h show ultrafine microstructures. In the parent sample C0, cluster of rounded crystals, with sizes of 15 to 50 nm were spread in glassy matrix (see Fig. 5). In the samples prepared by adding AlF_3, accumulated round grains with sizes

Table 5 CTE, densities and micro hardness of C0, C10A and C10M glasses heat-treated at 1000 °C for 2 h

Sample No	CTE $\alpha \times 10^{-6}$ K^{-1}		Density	Microhardness
	100–300 °C	100–500 °C	g/cc	GPa
C0	1.161	4.931	2.07	5. 16
C10A	1.984	4.328	2.53	5.92
C10M	1.141	3.559	2.58	6.34

in the range from 700 nm and 1 μm are observed in sample CA4, while the crystals in sample CA10 had sizes between 100 and 500 nm spread in the glassy matrix (Fig. 6). Also in samples CM4 and CM10, prepared by adding MgF_2, small cordierite crystals were embedded in the glass matrix. The microstructure of glass-ceramics prepared from AlF_3 are finer than those prepared from MgF_2 (Fig. 6).

The EDX microanalyses of the rounded grains show the incorporation of Ca and Ti into the cordierite structure (see Table 4 and Fig. 7). It has already been described in the literature that Ti^{4+} (ionic radius = 0.65 Å) may occupy Mg^{2+} (ionic radius = 0.72 Å) or Al^{+3}sites (ionic radius = 0.53 Å) in the $Mg_2Al_4Si_5O_{18}$ structure. The charges are balanced by vacancies in cationic sites [15–17]. According to EDX microanalyses, calcium is nearly exclusively incorporated in the glassy matrix.

The coefficient thermal expansion (CTE) was measured for some selected samples crystallized at 1000 °C for 2 h (Table 5 and Fig. 8). In the literature, CTEs in the range from 0.9 to 6 × $10^{-6}K^{-1}$ have been reported for cordierite glass-ceramics [11, 18, 19]. In the present glass-ceramic samples the CTE value were between 4.931 (100–500 °C) for base glass and 1.141 × $10^{-6}K^{-1}$ (100–300 °C) for C10M (see Table 4). The values of CTE were 4.931, 4.328 and 3.559 × $10^{-6}K^{-1}$(100–500 °C) for the samples C0, C10A and C10M, respectively. The densities of the previous glass ceramic were 2.07, 2.53 and 2.57 g/cc for C0, C10A and C10M samples. Also, the microhardness values were 5. 16,5.92 and 6.34 GPa for C0, C10A and C10M respectively. The later microhardness values and previous densities of glass-ceramic samples are in agreement with the previous work [11, 19] (Table 5).

Generally the thermal expansion coefficient decreased with increasing AlF_3 and MgF_2 concentrations. The decrease in the CTE while incorporating fluorine may be ascribed to the role

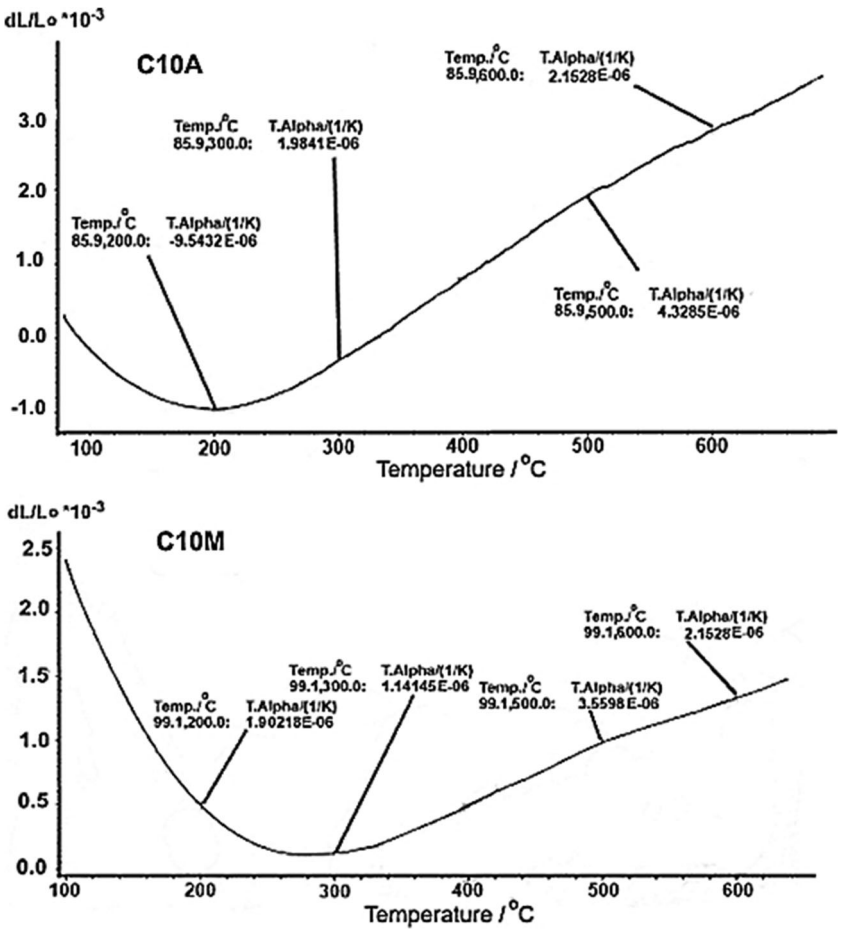

Fig. 8 Coefficient of thermal expansion curves of C10M and C10A samples heat-treated at 1000 °C for 2 h

of fluorine in weakening of [SiO_4] − tetrahedral bonds into [SiO_3F] – bonds [20], However, this weakening effect of fluorine in the glass structure results in easier atomic rearrangements upon reheating the glass and consequently nucleation is promoted [21] and crystallization can be achieved.

4 Conclusion

Glasses based on cordierite constituents (MgO-Al_2O_3-SiO_2) were prepared from raw materials with different concentrations of AlF_3 and MgF_2. During single stage heat-treatment at temperatures in the range from 900 to 1200 °C, solely cordierite was crystallized. The microcrystalline structure of the samples heat treated at 1000 °C for 2 h show nanometer and low micrometer sized rounded cordierite crystals embedded in a glassy matrix. The coefficient of thermal expansion of cordierite glass-ceramic was between 4.27 and 5.0×10^{-6} $C^{-1}$for the temperature range from150 to 680 °C. Densities were increased with the addition of fluorine containing compounds from 2.07 g/$cm^3$for the sample without fluoride additions to 2.58 g/cm^3 in the sample MgF_2addition. In the same later consequence, the microhardness values change from 5. 16 GPa in base sample to 6.34 GPa in MgF_2-containing samples. The production of cordierite glass-ceramics from natural raw materials offers a new low cost route to this interesting material that can resist temperature up to 1200 °C.

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