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# Sintered gahnite–cordierite glass-ceramic based on raw materials with different fluorine sources

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**Abstract.** **Glass-ceramic based on Zn-containing cordierite was prepared from kaolin, silica'sand and commercial ZnO. The addition of $AlF_3$, $MgF_2$ and $CaF_2$ was performed as nucleation catalysts. Dark brown glasses were obtained from the glass batches. The transformation and crystallization temperatures were in the range of 739–773 and 972–1007°C, respectively. Gahnite, cordierite and very little enstatite were the development crystalline phases through the heating and sintering process between 1000 and 1340°C. The microstructure of crystallized samples at 1340°C showed the appearance of dominant euhedral octahedral crystals of gahnite and hexagonal cordierite, in the low micro-scale, disseminated in the glassy matrix. The microanalysis of the crystallized samples indicated that Zn and Mg may replace each other in gahnite and cordierite structure. Densities of the crystallized samples were between 2.2517 and 2.5278 g $cm^{-3}$. The thermal expansion of the crystallized samples was ranging from 19.22 to 59.30 × $10^{-7}$°$C^{-1}$. However, the higher crystallization of both cordierite and gahnite accompany with the higher values of densities and the lower values of coefficient of thermal expansion.**

**Keywords.** **Sintered glass-ceramic; cordierite; gahnite.**

## 1. Introduction

Cordierite-containing glass-ceramic is well known from long time because it has been earlier used by Corning in the United States for space missile nose cones.[1] Cordierite-based glass-ceramic is strong, has excellent dielectric properties, good thermal stability, thermal shock resistance, has low coefficient of thermal expansion and thermal conductivity.[1] Cordierite ceramic or glass-ceramic is used for kiln furniture applications; it also finds use in other applications where rapid temperature changes take place. Cordierite was prepared from pure chemicals, raw materials,[2] some wastes,[3] and through composite[4] and sol–gel routes.[5] Beall and Pinckney[6] studied the $SiO_2$–$Al_2O_3$–ZnO–MgO system and they have obtained a transparent glass-ceramic of ultrafine microstructure. They added this to obtain the spinel phase and the sum of MgO and ZnO must be at least 13% and gahnite was developed in the glass-ceramic.

Little work was done on the Zn-containing cordierite glass-ceramic. The addition of Zn (6% ZnO) to the cordierite glass decreases the sintering temperature (by ∼20°C) and led to form gahnite ($ZnAl_2O_4$) in addition to cordierite.[7] In diesel particulate filters based on cordierite, the contamination by Zn gave zinc silicate, zinc aluminium with spinel structure, and a glassy phase above 1000°C.[8] Nucleation is studied in a magnesium aluminosilicate glass-containing ZnO and $TiO_2$ as nucleating agents; they found that zinc and titanium are major components in the first crystallized phases.[9]

In the MgO–$Al_2O_3$–$SiO_2$ system, replacement of $Al_2O_3$ by ZnO can lower the melting temperature of glass and crystallization temperature of the glass-ceramics and both cordierite and gahnite were successfully fabricated at relative low temperature (< 950°C).[10]

Gahnite or zinc spinel ($ZnAl_2O_4$) is a member of the spinel family and is being used as a catalyst and as an addition to glaze layers for floor tile and dental applications. In the crystallization of MgO–$Al_2O_3$–$SiO_2$ system, with the sequential addition of ZnO and with $B_2O_3$ and $ZrO_2$ additions, gahnite ($ZnO{\cdot}Al_2O_3$) and mullite were synthesized and the hardness increase with the increase in gahnite crystals.[11]

In this paper the results of the effect of partial substitution of MgO by ZnO in the cordierite parent glass, and also some additions of fluorine sources, i.e., $CaF_2$ , $MgF_2$ and $AlF_3$, on the crystallization process are reported. The thermal effect, microstructure and some properties were studied too.

## 2. Materials and methods

In the present work, the parent glass based on the cordierite formula $MgZnAl_4Si_5O_{18}$ with ZnO/MgO partial replacement was used. Other three glasses were prepared with the addition of different fluorine sources. The starting materials were kaolin as a source of $Al_2O_3$ and $SiO_2$, magnesite as a source of MgO, and silica'sand as a source of $SiO_2$ and commercial ZnO. Fluorine was incorporated in the form of commercial

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**Table 1.** Chemical composition of the base glass in wt% and the additives.

| | Oxides from raw materials in wt% | | | | | | | | Commercial additions | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Oxides | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $Na_2O$ | $K_2O$ | $TiO_2$ | ZnO | $AlF_3$[a] | $MgF_2$[a] | $CaF_2$[a] |
| SC[b] | 51.36 | 34.86 | — | — | 13.78 | — | — | — | — | — | — | — |
| SCZ[c] | 48.07 | 32.63 | — | — | 6.44 | — | — | — | 13.02 | — | — | — |
| CZ-0 | 45.32 | 21.12 | 1.02 | 1.20 | 19.12 | 0.25 | — | 1.92 | 9.47 | — | — | — |
| CZ-Al | 45.32 | 21.12 | 1.02 | 1.20 | 19.12 | 0.25 | — | 1.92 | 9.47 | 2.5 | — | — |
| CZ-Mg | 45.32 | 21.12 | 1.02 | 1.20 | 19.12 | 0.25 | — | 1.92 | 9.47 | — | 2.5 | — |
| CZ-Ca | 45.32 | 21.12 | 1.02 | 1.20 | 19.12 | 0.25 | — | 1.92 | 9.47 | — | — | 2.5 |

SC: stoichiometric composition, SCZ: stoichiometric composition containing Zn replaces Mg.
[a]Added in grams over 100 wt% oxide.
[b]Zn-free stoichiometric cordierite in oxide wt%.
[c]Zn-containing stoichiometric cordierite in oxide wt%.

$MgF_2$, $CaF_2$ and $AlF_3$. The chemical composition of the present samples in oxide weight% with the addition of different fluorine sources is shown in table 1.

The glass batch was subjected to mixing by ball milling to ensure homogenization and then melted in sintered alumina crucible. The glass melt was poured in air and then annealed in a muffle furnace at 550°C. The resulting glass was crushed and sieved to give powder of <0.038 mm in size. The glass powders with binder (7% polyvinyl alcohol (PVA)) were pressed (uniaxial pressures—20 kN) in pellets. Sintering process was carried out in a muffle furnace at 10°C heating rate between 700 and 1340°C temperature ranges.

To detect the thermal behaviour of the glasses, differential thermal analysis (DTA-Mislo-SDTQ-600, USA) was used with a 10°C heating rate. X-ray diffraction (XRD: Model Brukur D8, Germany, with Ni-filtered CuK$\alpha$ radiation) analysis was used to identify the crystalline phases that developed after heat-treatment process. Scanning electron microscopy (SEM: SEM model FEJ quanta 250 Fei-Holland) was used to show the microcrystalline structure of the sintered glass-ceramic samples.

The densities of the sintered glass-ceramic samples were measured using Quantachrome instrument (Upyc 1200e v5, 03; USA) using helium gas. The coefficient of thermal expansion (CTE-$\alpha$) of the sintered glass-ceramic samples were measured by using Netzsch Dilatometer (DIL 402 PC-Germany) up to 550°C with a heating rate of 10°C $min^{-1}$.

## 3. Results and discussion

### 3.1 *DTA*

Dark brown glasses were produced after melting process between 1450 and 1500°C. The DTA curves of the glass samples are shown in figure 1. The glass softening temperature $T_s$ (°C) was between 739 and 773°C. The parent glass has relatively the highest $T_s$ (°C) value (773°C) whereas $T_s$ (°C) of other samples was in order: sample ($AlF_3$) > ($MgF_2$) > ($CaF_2$) (figure 1). All the exothermic peaks were clear; however, relatively sharpening takes place in case of $AlF_3$-containing CZ-Al sample. The exothermic peak temperatures were between 1007°C ($CaF_2$-containing sample, CZ-Ca) and 972°C

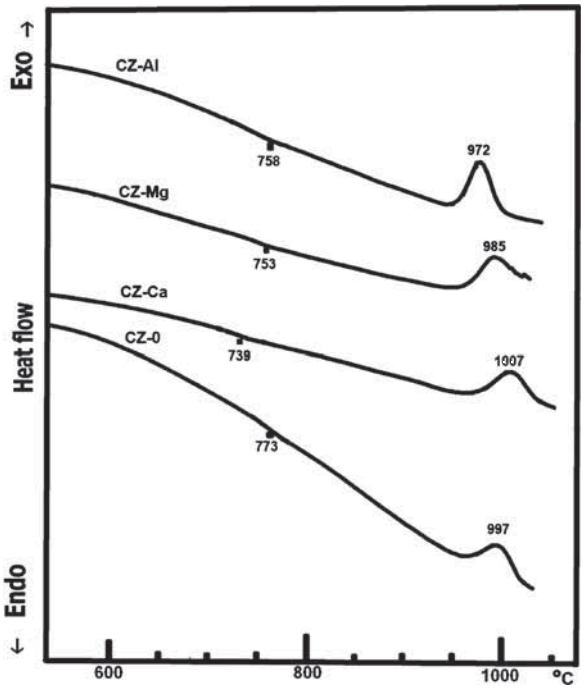


**Figure 1.** DTA thermograms of the present glass samples.

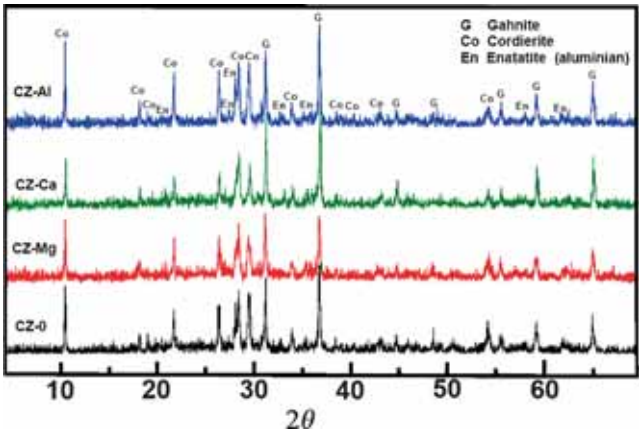


**Figure 2.** X-ray diffraction analysis of the present glass samples treated at 1250°C/2 h.

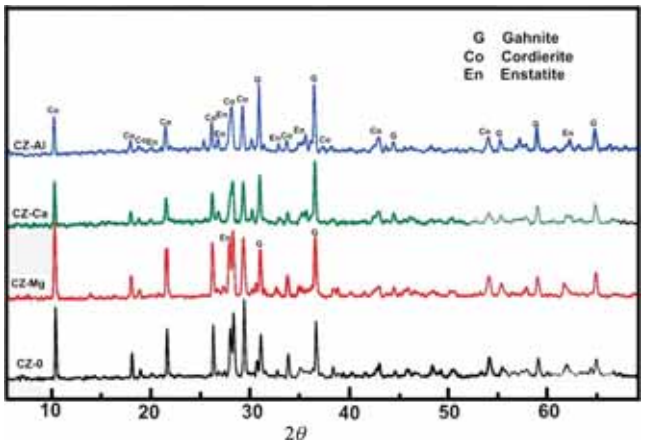


**Figure 3.** X-ray diffraction analysis of the present glass samples treated at 1340°C/2 h.

($AlF_3$-containing sample, CZ-Al). It is clear that the CZ-Ca sample has the highest crystallization temperature value of 1007°C (melting point, m.p., of $CaF_2$ = 1418°C) whereas CZ-Mg (m.p. of $MgF_2$, 1263°C) and CZ-Al samples (m.p. of $AlF_3$ 1291°C) have lower values (figure 1).

### 3.2 *XRD analysis*

The XRD analysis of the present samples heat treated at 1250°C is shown in figure 2. The main crystalline phase was gahnite ($ZnAl_2O_4$, ICDD 74-1136)[12] and a considerable cordierite ($Mg_2Al_4Si_5O_{18}$, ICDD 89-1458) with very little enstatite aluminian ($Mg_{0.961}Al_{0.027}SiO_3$, ICDD 76-2428). These phases were developed in all the samples heat treated within 1000–1300°C temperature range, however, in the sintering at 1340°C cordierite lines become more intense in the CZ-0 and CZ-Mg than gahnite lines (figure 3 compares the XRD lines).

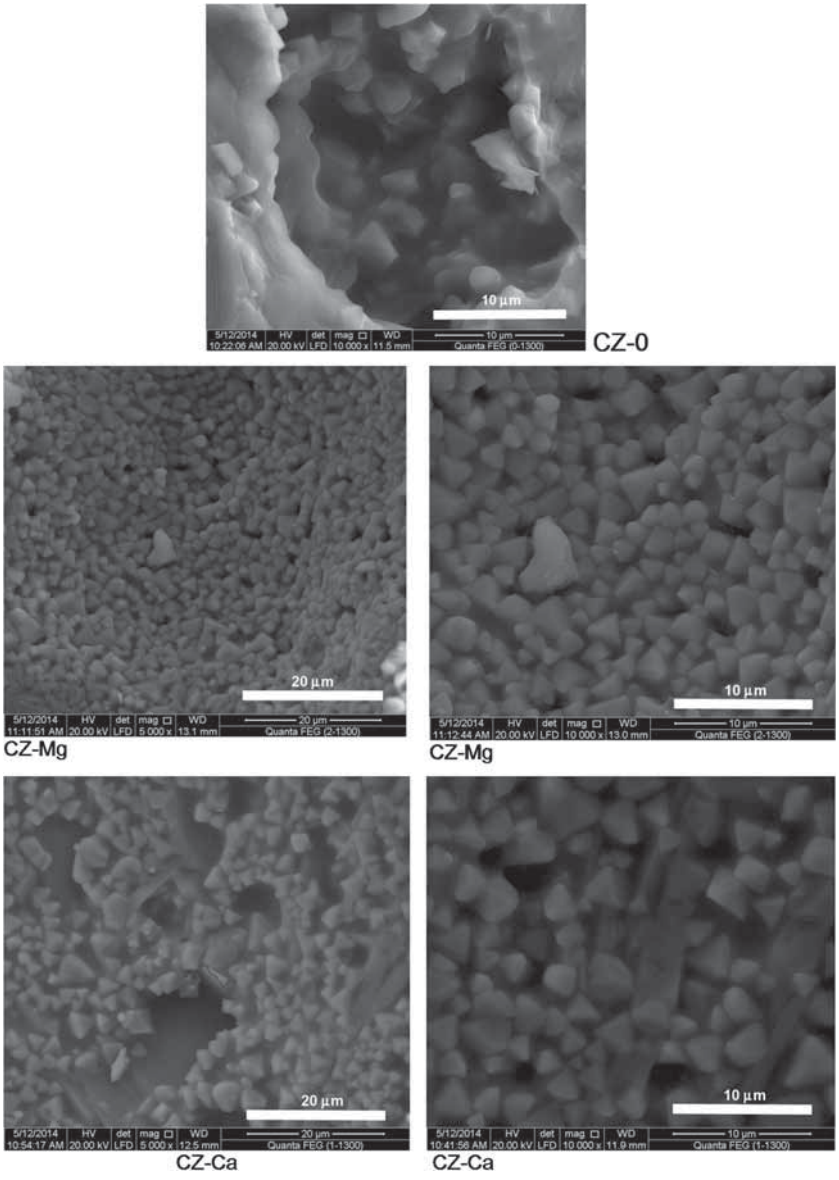


**Figure 4.** SEM micrograph of CZ-0 , CZ-Ca and CZ-Mg samples treated at 1300°C.

Crystallization of gahnite as the major phase, in all the crystallized samples, may be related to the field strength (charge/radius ratio), for this concept, the high field strength of $Zn^{2+}$ [0.467 $(Å)^{-2}$] ions compared with $Mg^{2+}$ [0.444 $(Å)^{-2}$] ions causes withdrawal of mainly Al ions to form the spinel ($ZnAl_2O_4$). For both phases, the reported data on the heat of formation revealed that cordierite ($500 \pm 40$ kJ $mol^{-1}$)[13] needs more energy than gahnite (314 kJ $mol^{-1}$).[14] Also, it must be added that, the effect of fluorine in the samples other than base glass, helps greatly in the crystallization of higher systems (gahnite, spinel group-cubic) other than the lower system ($\alpha$-cordierite, ring or cyclosilicate group-hexagonal).

### 3.3 *Microcrystalline structure and microanalysis*

The microcrystalline structure of the sintered samples at 1340°C showed clear euhedral crystals of the developed

**Table 2.** EDS microanalysis of the octahedral and hexagon crystals in CZ-Al sample.

| | Sample CZ-Al, the microanalysis and the nominal composition | | | |
|---|---|---|---|---|
| Oxides | Cubic–octahedral gahnite | Nominal gahnite | Hexagonal cordierite | Nominal cordierite |
| $SiO_2$ | 10.91 | | 48.39 | 51.36 |
| $Al_2O_3$ | 53.51 | 55.61 | 27.48 | 34.86 |
| $Fe_2O_3$ | 2.14 | | 0.87 | |
| $TiO_2$ | 0.81 | | 0.97 | |
| MgO | 11.94 | | 12.81 | 13.78 |
| CaO | 0.24 | | 0.50 | |
| ZnO | 19.28 | 44.39 | 7.81 | |
| $Na_2O$ | 1.03 | | 1.18 | |

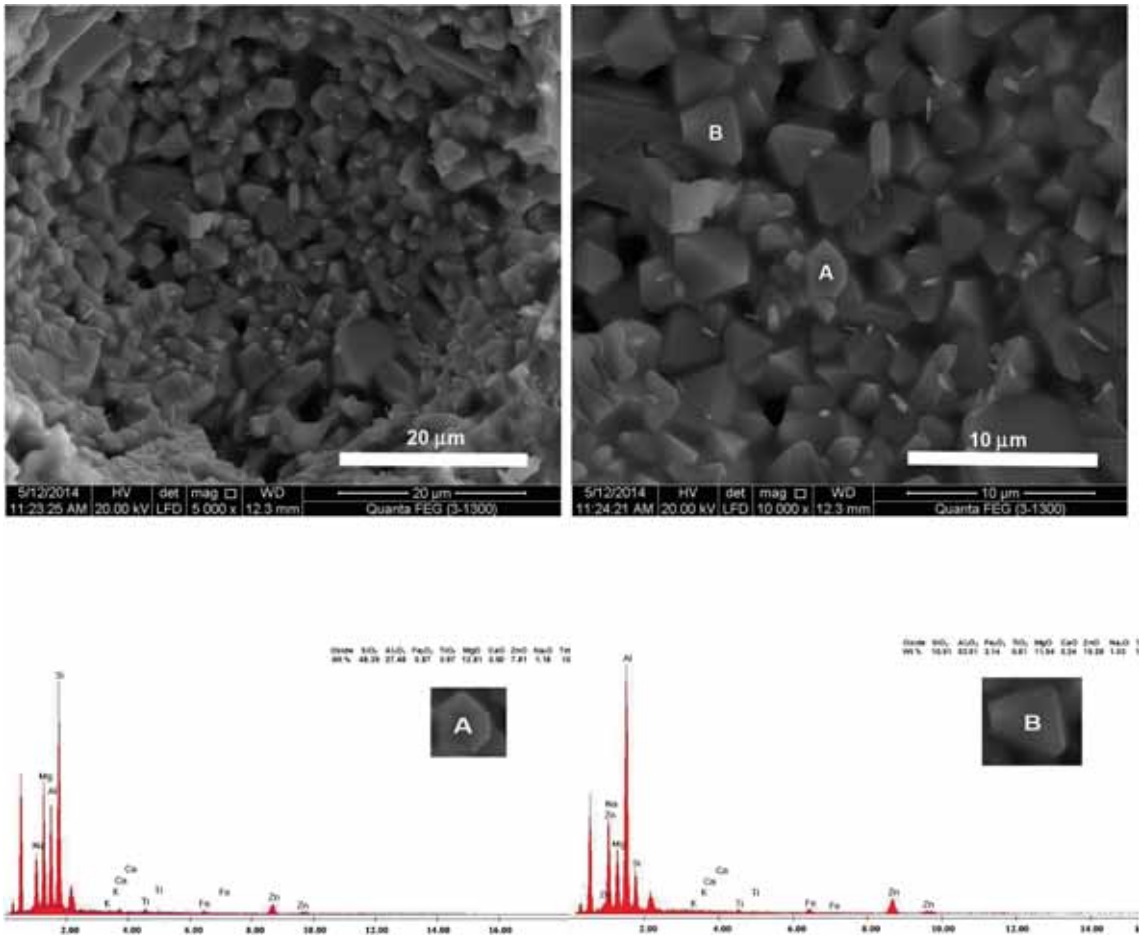


**Figure 5.** SEM micrograph and EDS analysis of the CZ-Al sample treated at 1300°C.

crystalline phases. Octahedral (cubic system) and hexagonal crystals were developed in the glassy matrix, which represent gahnite and cordierite phases, respectively. Owing to that Mg (in $MgF_2$) and Al (in $AlF_3$) were in the structure of the development phases, their samples, i.e., CZ-Mg and CZ-Al, were highly crystalline than that containing $CaF_2$ (CZ-Ca) (comparisons of SEM of CZ-Mg and CZ-Al with CZ-Ca are shown in figures 4 and 5).

Typical octahedral (within cubic system) crystals of the dominant gahnite were spread in glassy matrix and the EDS microanalysis showed that the major constituents were: $Al_2O_3$ (53.51%), ZnO (19.28%), MgO (11.94%), $SiO_2$ (10.91%) with little, $Fe_2O_3$ (2.14%), $Na_2O$ (1.03%), $TiO_2$ (0.81%) and CaO (0.24%) (table 2, figure 5). Actually the presence of $SiO_2$ and little $Na_2O$ may be contributed from the surrounding amorphous glassy matrix. Also the hexagonal crystals of cordierite phase were developed in the glassy ground mass and the EDS microanalysis depicts that the main constitutes were: $SiO_2$ (48.39%), $Al_2O_3$ (27.48%), MgO (12.81%), ZnO (7.81%) with low $Fe_2O_3$ (0.87%), $TiO_2$ (0.97%), CaO (0.50%) and $Na_2O$ (1.18%) contents (table 2).

### 3.4 *Densities and coefficient of thermal expansion*

As recorded in recent literature, the general formula of spinel is (Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn) (Al, Ga, In, Ti, V, Cr, Mn, Fe, Co, Ni)$_2$ ( O, S, Se,...)$_4$. The latter formulae mean that the incorporation of some elements in the gahnite structure (Zn, Mg, Fe) (Al, Fe, Ti)$_2O_4$ is possible. On the other hand, some authors reported some substitution of alkali (Li, Rb, Na and K),[15] iron ($Fe^{2+}$ and $Fe^{3+}$)[16] and zinc ($Zn^{2+}$)[17] in cordierite structure, however, the authors do not give a general formula of cordierite. Therefore, the present cordierite may be accept Zn, Na and Fe in their structure.

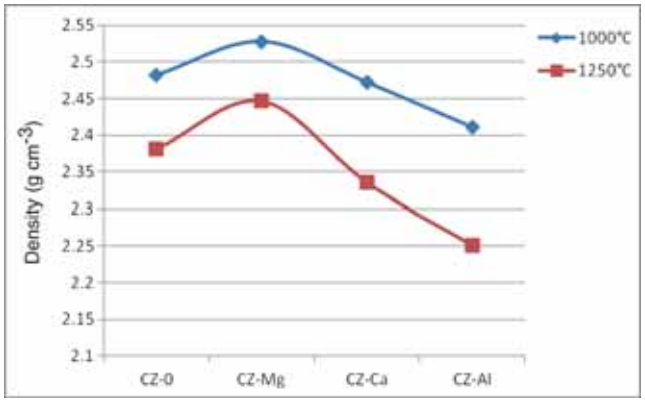


**Figure 6.** Density curves of treated samples at 1000°C/2 h and 1250°C/2 h.

The recorded densities of gahnite, cordierite and the enstatite were between 3.6 and 4.6, 2.6 and 2.66, and 3.2 and 3.99 g cm$^{-3}$, respectively (data from the Internet). The densities of the present crystallized samples were between 2.4113 and 2.578 (at 1000°C) and 2.2517 and 2.4465 g cm$^{-3}$ (at 1250°C) g cm$^{-3}$ (figure 6). Variation of densities, in our crystallized samples was the function of the ratio between the content of cordierite, gahnite, enstatite and the glassy portion. However, the relative decrease in densities at higher temperature (at 1250°C) was due to the relative increase in the glass contents caused by little partial melting. Increase in the density in the Mg-containing CZ-Mg sample appoint to the higher crystallization of both cordierite and gahnite (table 3).

The reported coefficient of thermal expansion value of sintered cordierite glass-ceramics was ranging from 9 to $39 \times 10^{-7}$ K$^{-1}$.[18] The only recorded CTE value of gahnite glass-ceramic, within ZnO–$Al_2O_3$–$SiO_2$ system, with a beta quartz solid solution was $-5.00$ to $+3.10 \times 10^{-6}$ K$^{-1}$ (20–500°C).[1] The present results of the sintered glass samples at 1340°C, within 20–300 and 20–500°C ranges, were ranging from 19.22 to $59.30 \times 10^{-7}$°C$^{-1}$ (table 3). The present results showed that the higher crystallization of cordierite and gahnite means decrease in the CTE value.

The aforementioned results show that, in the crystallized samples, the higher crystallization of cordierite and gahnite leads to increase in the density values whereas in contrary decrease in the CTE values was concomitant with the increase in the later phase (table 3).

## 4. Conclusion

Based on the nominal cordierite, with partial substitution of Mg by Zn, brown glasses were prepared from kaolin, talc and commercial zinc oxide. Gahnite, cordierite and little enstatite were crystallized after sintering process. The EDX

**Table 3.** Densities and CTE of the sintered samples.

| | Density (g cm$^{-3}$) | | | | |
|---|---|---|---|---|---|
| | Sample treated at | Sample treated at | CTE ($\alpha$) sample sintered at 1340°C/2 h | | |
| Sample | 1000°C/2 h | 1250°C/2 h | 20–300°C | 20–500°C | Developed phases |
| CZ-0 | 2.4817 | 2.3806 | 23.60 | 19.22 | Cordiertie–gahnite–enatatite (l) |
| CZ-Mg | 2.5278 | 2.4465 | 42.84 | 35.28 | Cordiertie–gahnite–enatatite (l) |
| CZ-Ca | 2.4722 | 2.3353 | 59.30 | 48.89 | Gahnite–cordierite–enatatite (l) |
| CZ-Al | 2.4113 | 2.2517 | 55.25 | 38.26 | Gahnite–cordierite–enatatite (l) |

I: little.

microanalysis of the sintered samples shows possible partial substitution of Zn for Mg in cordierite and Mg for Zn in gahnite, however, other low percentage elements as Fe, Na, Ti and Ca may be included in the structure too. The densities of the crystallized sample, between 2.3806 and 2.5278 g $cm^{-3}$, were of high value in case of the higher crystallization of cordierite and gahnite. The coefficient of thermal expansion of the sintered samples was between 19.22 and $59.30 \times 10^{-7\circ}C^{-1}$ and was of low value in case of higher crystallization of cordierite and gahnite.

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