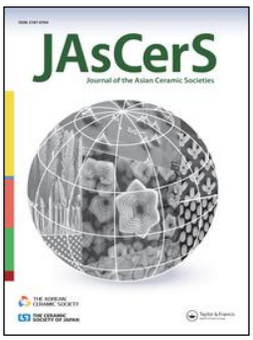

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FULL LENGTH ARTICLE



# Concurrent sinter-crystallization and microwave dielectric characterization of $CaO$-$MgO$-$TiO_2$-$SiO_2$ glass-ceramics

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**ABSTRACT**

The present work aims to clarify sinter-crystallization behavior and microwave dielectric features of $CaO$-$MgO$-$TiO_2$-$SiO_2$ glass-ceramics fabricated via one-step sintering procedure at 800–950°C for 4 h. In this regard, starting glasses were obtained from a conventional melt quenching technique, then subjected to the sinter-crystallization heat treatment. The crystallization behavior of sintered glass-ceramics was studied using X-ray diffraction (XRD) and electron backscatter diffraction (EBSD). On the basis of the obtained results, diopside ($CaMgSi_2O_6$) precipitated as the main crystalline phase in all sintered glass-ceramics; however titanite ($CaTiSiO_5$) was found as the secondary crystalline phase in glass-ceramics containing high $TiO_2$ content. The degrees of crystallization of the glass-ceramics prepared procedures were also characterized. Optimized glass-ceramics sintered at 800°C for 4 h showed the maximum relative density of 99%. Further increase of sintering temperature led to gradual decrease of density. The most promising microwave dielectric properties of the sintered glass-ceramics were as $\varepsilon_r$ = 6.8–9.4 and $Q \times f$ = 3,735–41,359 GHz.

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Glass-ceramic; sintering; crystallization; diopside; titanite; dielectric properties

## 1. Introduction

Development of mobile and satellite communication devices has greatly increased the demand for complex miniaturized circuits in microwave frequency range applications. In this regard, the technology of low temperature co-fired ceramics (LTCC) has played a crucial role to reduce the dimension of microwave circuits owing to its integration capability of different components such as substrates, resonators and electrodes materials. Low sintering temperature is the key parameter of this technology to keep the consistency of metallic electrodes with low melting temperature (such as silver, gold and copper) incorporated into the LTCC modules [1–4].

Glass-ceramics are well known as suitable candidates to be used as LTCC substrates in high-frequency applications owing to their favorable properties (including low dielectric constant, low dielectric loss, appropriate chemical durability and thermal expansion coefficient) as well as the advantage of comparatively easy mass production. In the case of glass-ceramics, it is also possible to control the kind of precipitated crystalline phases, degree of crystallization and microstructural features by tailoring the chemical composition of starting glasses and controlling of fabrication process [5–7].

Among various silicate-based glass-ceramics, the glass-ceramics of $CaO$-$MgO$-$SiO_2$ system are suitable candidates for LTCC technology owing to their low dielectric loss, excellent chemical durability as well as appropriate mechanical properties at low sintering temperature [7,8].

Complete densification and sufficient crystallinity are the main factors in the fabrication of desirable glass-ceramics used in LTCC substrates [9]. In this regard, many studies have been reported to elucidate the effect of nucleating agents and sintering aids on sinter-crystallization behavior of glass-ceramics and their correlation with microwave dielectric characteristics [10–14].

K.C. Feng *et al*. [14] investigated the effect of $ZrO_2$ as a nucleating agent on crystallization, microstructure and microwave dielectric properties of $CaO$-$MgO$-$SiO_2$ glass-ceramics at low sintering temperature. The best dielectric properties of modified $CaMgSi_2O_8$ glass-ceramics containing $ZrO_2$ sintered at 950°C were: $\varepsilon_r$ = 7.03, $Q \times f$ = 7318 GHz.

Diopside ceramics have a considerable temperature coefficient of resonant frequency ($\tau_f$) (−42 ppm/°C) [15]. In order to achieve glass-ceramics with nearly zero $\tau_f$, the presence of another crystalline phase having positive value of $\tau_f$ is necessary. Hence, diopside glass systems were modified by addition of $TiO_2$ (with $\tau_f$ value of +400 ppm/°C [16]) to the glass compositions.

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In the present work, the effect of simultaneous sintering and crystallization on microwave dielectric properties of CaO-MgO-($TiO_2$)-$SiO_2$ glass-ceramics has been explored alongside with the influence of $TiO_2$ on the crystallization trend, phase evolution and dielectric properties.

To this purpose, crystalline phase evolution and microstructural features were monitored to elucidate the relationship between crystallinity and microwave dielectric properties of the targeted glass-ceramics.

## 2. Experimental

Table 1 shows the chemical composition of starting glasses prepared through conventional melt quenching method. The glass batches were prepared from reagent chemicals of magnesium hydroxide (Merck-105870), calcium carbonate (Merck-102067), $TiO_2$ (GERMED, GDR, extra pure) and silica (SCHOTT AG). In all glass compositions, the weight ratios of $SiO_2$/CaO and $SiO_2$/MgO were kept constant, while different quantities of $TiO_2$ (5–20 wt %) were used. Glass batches were melted in a platinum/rhodium crucible at 1450°C, kept at this temperature for 1 h. Then, the molten glasses were casted on a brass mold and subsequently transferred to the annealing furnace preheated at 730°C. The furnace was switched off and annealed glasses were allowed to cool down to room temperature. The obtained glasses were milled and sieved to reach the average particle size of less than 40 µm using a planetary mill with zirconia cup and grinding balls.

The crystallization behavior of the obtained glass powders was investigated using a differential scanning calorimetry (DSC) (Linseis DSC Pt-1600) at the heating rate of 5°C/min. In addition, accurate determination of glass transition ($T_g$) and dilatometric softening point ($T_d$) temperatures were carried out by dilatometer (Netzsch, 402PC) at the heating rate of 5°C/min. Glass cylinders with dimension of 25 mm in length and 8 mm in diameter were used in dilatometry analysis.

The glass powders were shaped into disc specimens (16 mm in diameter and 8 mm in thickness) by cold isostatic pressing at the pressure of 80 MPa. Compacted glass powders were then subjected to the one-step sinter-crystallization heat treatment at the temperature interval of 800–950°C using the heating rate of 5°C/min and soaking time of 4 h.

Sinterability of heat-treated specimens was evaluated by measuring the relative density (the ratio of bulk density/powder density). The bulk density was calculated on the basis of Archimedes method and the powder density of ground sintered specimens was measured by the helium gas pycnometry (AccuPyc 1330).

**Table 1.** Chemical composition of starting glasses (wt %).

| Glass code | $SiO_2$ | CaO | MgO | $TiO_2$ |
|---|---|---|---|---|
| DT5 | 52.73 | 24.60 | 17.67 | 5 |
| DT10 | 49.95 | 23.31 | 16.74 | 10 |
| DT15 | 47.18 | 22.01 | 15.81 | 15 |
| DT20 | 44.40 | 20.72 | 14.88 | 20 |

The crystalline phases precipitated during sintering were identified by X-ray diffraction (XRD, Rigaku MiniFlex 300) with Cu-$K_\alpha$ radiation ($\lambda$ = 0.154 nm) in a 2$\theta$ range from 10° to 80°. The degree of crystallinity and phase contents were determined according to the Rietveld analysis extracted from the XRD patterns analyzed by Topas 4 software [17].

Microstructural features of the sintered glass-ceramics were analyzed by scanning electron microscopy including electron backscatter diffraction (EBSD) using scanning electron microscope (Jeol JSM 7001 F) equipped with a TSL Digiview 3 EBSD-camera. Prior to EBSD measurements, the glass-ceramic specimens were polished using colloidal silica to increase their surface quality. Subsequently, the glass-ceramic were carbon coated at $10^{-4}$ Pa in order to avoid surface charging. Combined EDXS (energy dispersive X-ray spectroscopy) and EBSD-measurements were done at the acceleration voltage of 20 kV and working distance of 15 mm. This enabled the acquisition of chemical data and Kikuchi patterns for each data point in the map. Hence, a reliable phase indexing and phase attribution were achievable. The data sets were cleaned up by Confidence Index (CI) standardization. In phase maps and inverse pole figure (IPF) maps, a CI filter was applied (CI>0.1).

Microwave dielectric properties of glass-ceramics were evaluated by the Hakki–Coleman method [18], where a cylindrical sample (diameter: thickness ratio ~ 2:1) was placed between two polished conducting plates. Then, the dielectric constant and dielectric loss were measured using an Agilent E8362B PNA series network analyzer. Resonant peak frequencies (f) were in the 11–13 GHz range and the quality factor (Q × f) was equal to f/tanδ.

The temperature coefficient of resonant frequency ($\tau_f$) in the temperature range of 20–60°C was determined according to the following equation:

$$\tau_f = \frac{f_{60} - f_{20}}{f_{20}(60 - 20)} \times 10^{-6} (ppm/°C) \qquad (1)$$

where $f_{60}$ and $f_{20}$ are the resonant frequency at 60°C and 20°C, respectively [19].

## 3. Results and discussion

Figure 1 depicts the DSC theromographs and dilatometry profiles of the starting glasses. The extracted data including glass transition ($T_g$), dilatometric softening point ($T_d$) and crystallization peak ($T_c$) temperatures are summarized in Table 2. The glass transition temperatures of all glasses were found about 732 ± 1°C, being constant within the limits of error. The dilatometric

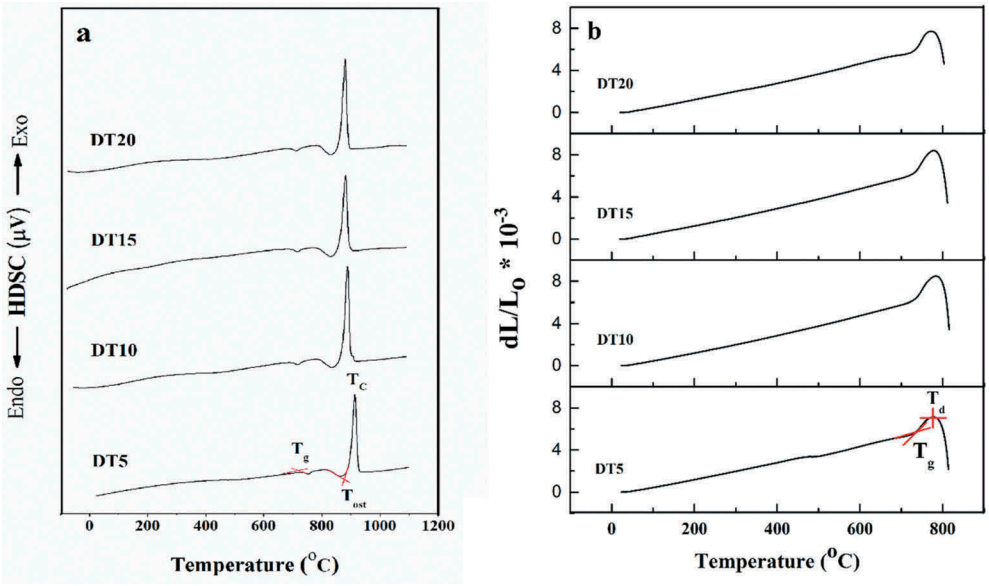


**Figure 1.** Thermal behavior of starting glasses: (a) DSC thermographs, (b) dilatometry at the heating rate of 5°C/min.

**Table 2.** Characteristic temperatures of the starting glasses.

| Glass | $T_g$ (°C) | $T_d$ (°C) | $T_{C,\ onset}$ (°C) | $T_{C,\ peak}$ (°C) |
|---|---|---|---|---|
| DT5 | 733 | 778 | 877 | 914 |
| DT10 | 734 | 784 | 866 | 912 |
| DT15 | 732 | 779 | 864 | 907 |
| DT20 | 733 | 772 | 864 | 905 |

softening point temperatures of the glasses were slightly increased from 778°C to 784°C by increase in $TiO_2$ content from 5 to 10 wt %. Further increase of $TiO_2$ content up to 20 wt % led to the decrease of $T_d$ (772°C) in sample DT20. The slight decrease in the crystallization peak ($T_c$) temperatures from 914°C to 905°C was observed with the gradual increase of $TiO_2$ content. This trend could be attributed to the role of $TiO_2$ as the nucleating agent. It is worth mentioning that titanium oxide is a well-known nucleating agent for many system glasses and promotes their crystallization tendency [20–22].

XRD patterns of the compacted glass powders heat-treated at 800–950°C for 4 h are presented in Figure 2. It is obvious that the specimens sintered at 800°C have a very low degree of crystallinity. However, increasing sintering temperature from 825 up to 950°C results in the extensive precipitation of crystalline phases and sharp diffraction peaks. Diopside ($CaMgSi_2O_6$, ICSD no. 30,522) was identified as the main crystalline phase in all samples. Nevertheless, the XRD patterns of the glass-ceramics with higher content of $TiO_2$ showed further diffraction lines.

In order to highlight the role of $TiO_2$ content and sintering temperatures on the crystallization behavior, the XRD patterns of sintered specimens (at 950°C for 4 h) and DT20 glass-ceramics sintered at various temperatures for 4 h in the 2θ range of 15–40° were considered (see Figures 3(a) and 4(a)). Moreover, titanite, Diopside and amorphous phase contents were calculated using Rietveld analysis extracted from XRD patterns of Figures 3(a) and 4(a) (see Figures 3(b), 4(b), Tables 3 and 4). In the case of specimens having more than 10 wt % of $TiO_2$ (see Figure 3(a)) and DT20 glass-ceramics sintered at temperatures higher than 850°C (see Figure 4(a)), two peak lines are detectable at 2θ ≈ 17.87° and 2θ ≈ 34.40°, which cannot be assigned to diopside. These peaks can, respectively, be attributed to the 011-peak and 220-peak of the monoclinic titanite ($CaTiSiO_5$, ICSD no. 50283). Also, as can be observed in Figures 3(a), 4(b), Tables 3 and 4 titanite contents increased gradually up to 18% with increase of $TiO_2$ concentration and sintering temperatures. Furthermore, the ratio of diopside to titanite declined from 51.76 to 4.56 and 40.68 to 4.56 with addition of $TiO_2$ concentration and increase of sintering temperature, respectively (see in Tables 3 and 4). The amorphous phase refers to residual glass phase in sintered glass-ceramics that will be discussed in more detail in Figure 6.

It is well known that the XRD patterns of titanium oxide and titanite overlap with the XRD peak lines of diopside. Therefore, electron backscatter diffraction (EBSD) was carried out on the glass-ceramic DT20 to identify the precipitated crystalline phases, accurately. Figure 5 shows the Image Quality (IQ) map, elemental distribution maps (collected by energy dispersive X-ray spectroscopy) as well as the phase map of glass-ceramic DT20 sintered at 950°C for 4 h. It can be realized from elemental distribution maps that Ti and Mg are clearly enriched and depleted, respectively, in some regions. According to the phase + IQ map, the major crystalline phase is diopside (shown in green) and titanite (shown in yellow) as the second phase is detectable. According to the elemental distribution maps, titanite regions are enriched in Ti and depleted in Mg. Titanite phase is mostly distributed at

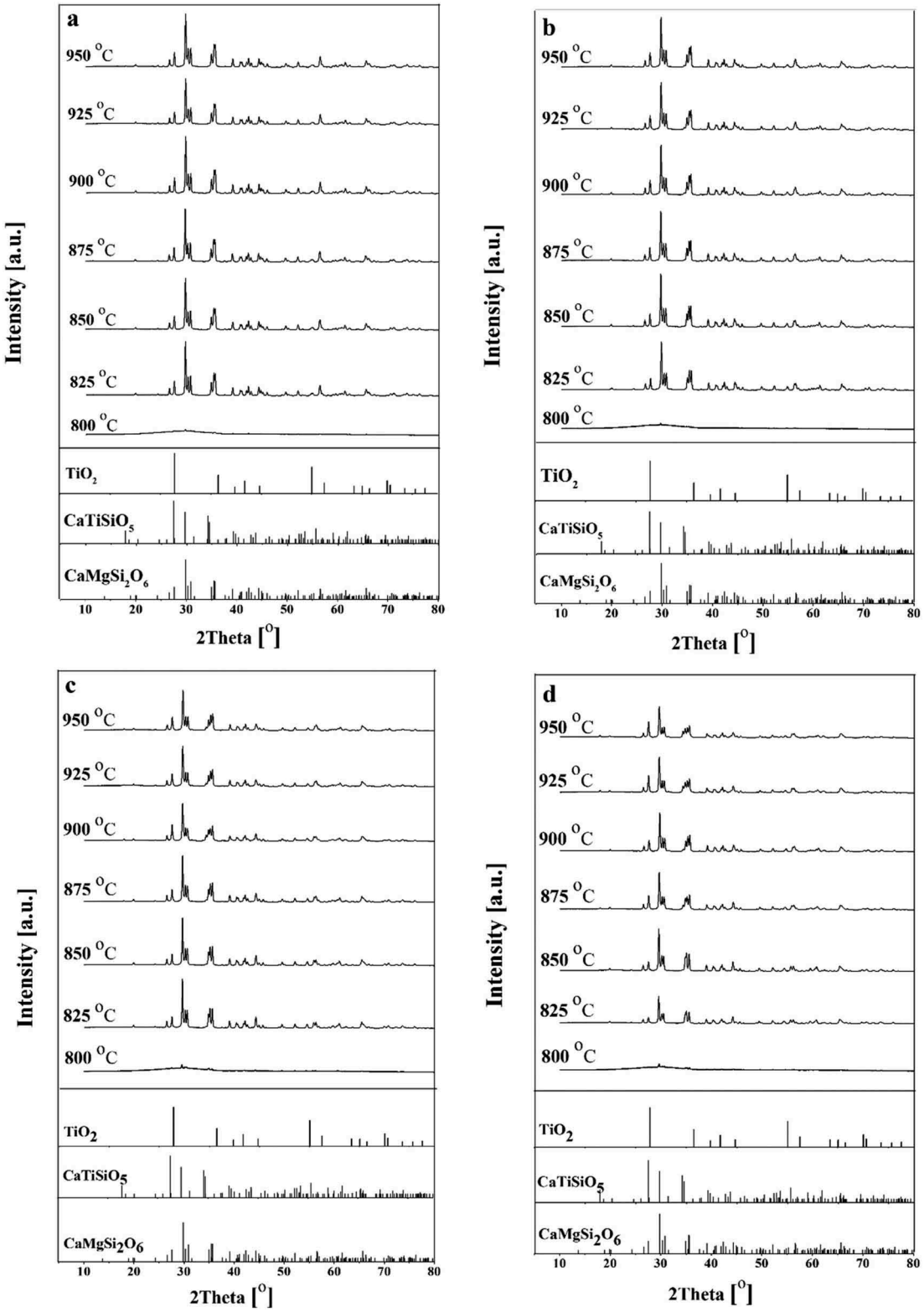


**Figure 2.** XRD patterns of the glass compacts sintered at 800–950°C for 4 h: (a) DT5, (b) DT10, (c) DT15 and (d) DT20.

positions between Diopside phases. Some black areas are also observed in the phase + IQ map, most of them occur at or near the phase boundaries.

These black areas might originate from porosity or glassy phase (do not produce Kikuchi bands) or from two neighboring crystals with different composition or different orientations which have overlapped Kikuchi lines. From Figure 5, there is no evidence for the presence of titanium oxide.

Figure 6 illustrates the degree of crystallization (crystallinity) for glass-ceramics sintered at various temperatures for 4 h. It is implied that crystallinity sharply increases with the increase of sintering temperature from 800°C to 825°C. However, further increase of

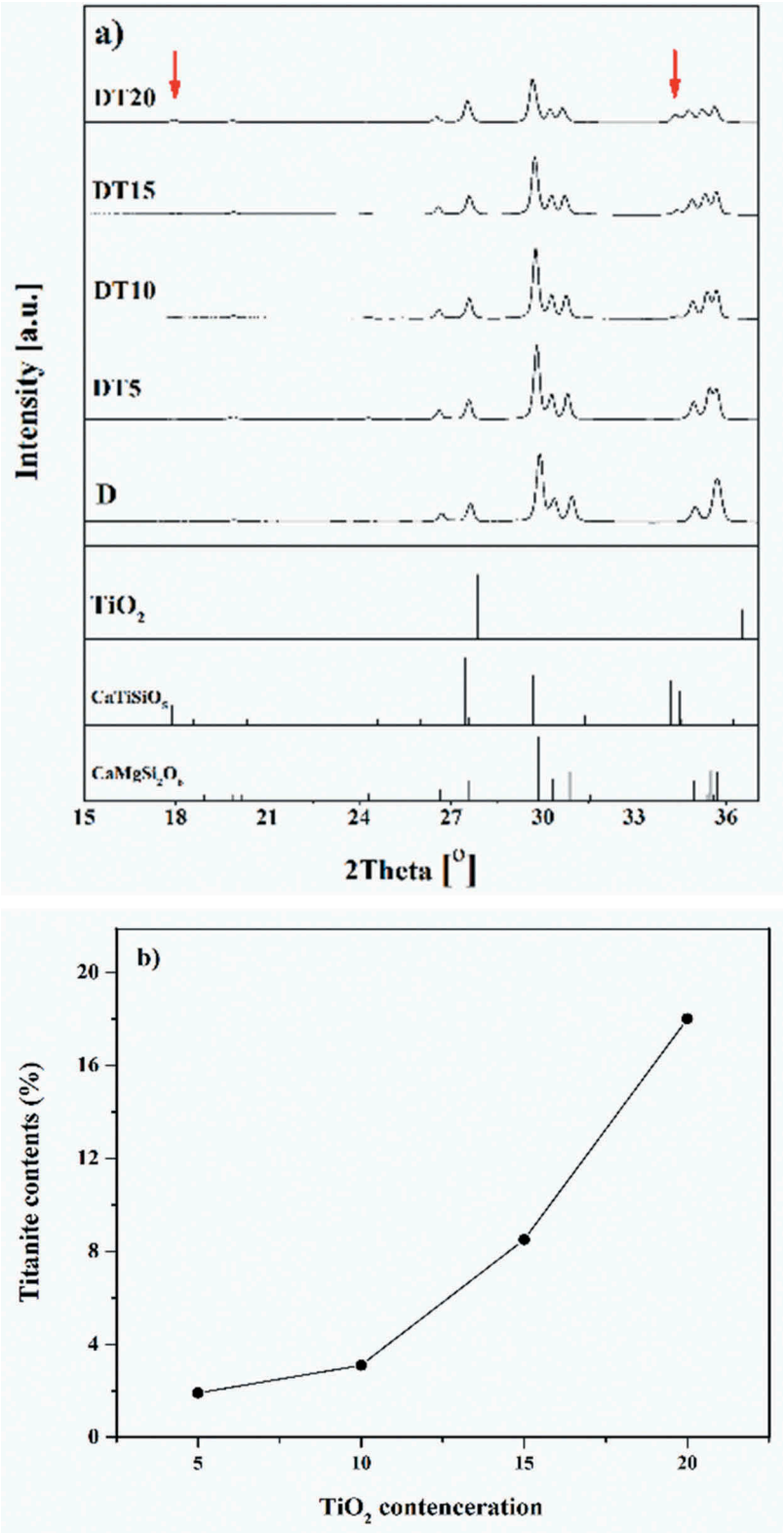


**Figure 3.** (a) XRD pattern of glass-ceramics sintered at 950°C for 4 h in the 2θ range of 29–30.5°. (Peak lines of $TiO_2$, $CaTiSiO_5$ and $CaMgSi_2O_6$ based on the ICSD files are also shown.), and (b) titanite contents of glass-ceramics containing various $TiO_2$ concentrations sintered at 950°C for 4 h.

sintering temperature up to 950°C, slightly changes the crystallinity. Considering the onset of crystallization temperatures (864–877°C) (see Figure 1 and Table 1), low sintering temperature is apparently responsible for low crystallinity (37%) of the glass-ceramics sintered below 825°C.

Figure 7 indicates variations of the relative density of the glass-ceramics sintered at different temperatures for 4 h. The glass-ceramics sintered at 800°C for reached the maximum relative density of about 98%. Further increase of sintering temperature up to 950°C, resulted in continuously decrease of relative density.

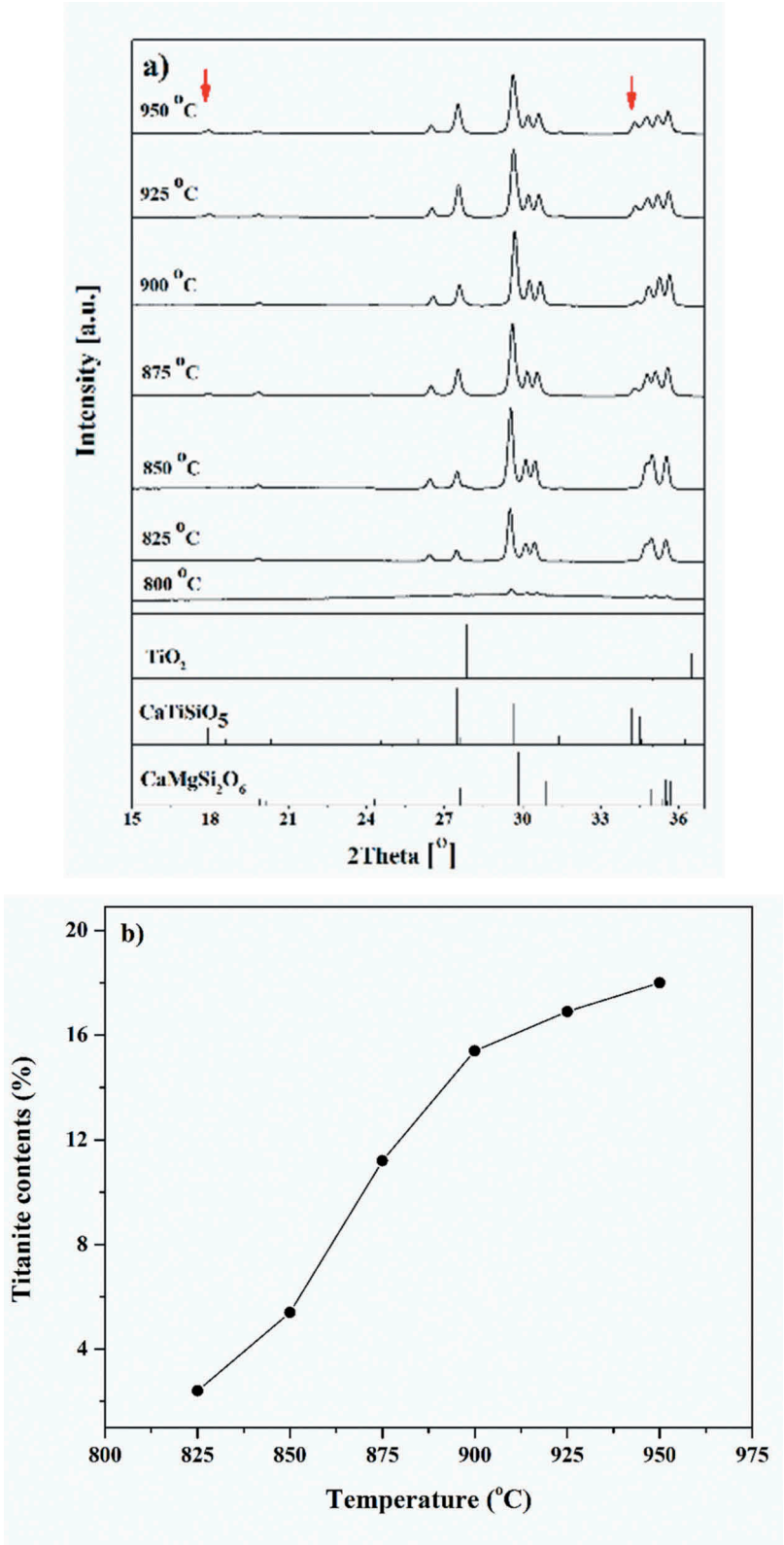


**Figure 4.** (a) XRD pattern of DT20 glass-ceramics sintered at 800–950°C for 4 h in the 2θ range of 29–30.5°. (Peak lines of $TiO_2$, $CaTiSiO_5$ and $CaMgSi_2O_6$ based on the ICSD files are also shown.), and (b) titanite contents of DT20 glass-ceramics sintered at 800–950°C for 4 h.

After sintering at 950°C, relative densities of 88–91% were obtained depending on the glass composition.

It is well known that during heat treatment of a glass powder compact, densification through viscos flow competes with crystallization at the same temperature interval to decrease the overall free enthalpy. If the crystallization tendency is comparatively small, densification can be completed before development of notable quantities of crystalline phases. In most cases, sintering of glass powder is interrupted by its crystallization. It should be noted that the increased viscosity of the residual glass phase after crystallization inhibits

**Table 3.** Amorphous and crystalline phases contents of sintered glass-ceramics at 950°C extracted from Figures 3(b) and 6.

| Glass-ceramics | Am | T | D | D/T |
|---|---|---|---|---|
| DT5 | 14 | 1.63 | 84.37 | 51.76 |
| DT10 | 14.9 | 2.64 | 82.46 | 31.23 |
| DT15 | 20.3 | 6.77 | 64.96 | 9.59 |
| DT20 | 12.1 | 15.82 | 72.08 | 4.56 |

Am: Amorphous phase, T: Titanite, D: Diopside.

**Table 4.** Amorphous and crystalline phases contents of DT20 glass-ceramics sintered at various temperatures extracted from Figures 4(b) and 6.

| Sintering temperatures (°C) | Am | T | D | D/T |
|---|---|---|---|---|
| 825 | 15.8 | 2.02 | 82.28 | 40.68 |
| 850 | 13.6 | 4.67 | 81.73 | 17.50 |
| 875 | 13.9 | 9.64 | 76.46 | 7.93 |
| 900 | 12.2 | 13.52 | 74.28 | 5.49 |
| 925 | 17.6 | 13.93 | 68.47 | 4.91 |
| 950 | 12.1 | 15.82 | 72.08 | 4.56 |

Am: Amorphous phase, T: Titanite, D: Diopside.

appropriate densification [23–25]. Hence, it can be concluded that lower degree of crystallization (37%) is responsible for the improved densification of glass compacts sintered at 800°C. By increasing sintering temperature, the crystallinities drastically increased and the relative density continuously declined to ~88%. Therefore, the increase of sintering temperature interrupts densification through enhancement of crystallinity and effective increase of the residual glass phase viscosity [26].

Figure 8 shows the microwave dielectric properties of glasses with different $TiO_2$ content and glass-ceramics sintered at various temperatures for 4 h [27,28].

As shown in Figure 8(a), $\varepsilon_r$ values continuously increase with increase of $TiO_2$ content from 5 to 20 wt %. Because $TiO_2$ has a high dielectric constant of about 100 [16], this increase can be attributed to the precipitation of $TiO_2$ in glasses containing high concentration of $TiO_2$. However, the glass-ceramic specimens show a different variation trend of $\varepsilon_r$ against sintering temperature (see Figure 8(b)). The maximum dielectric constant was obtained for all studied glass-ceramics sintered at 800°C. It was observed that the increasing of sintering temperature to 825°C, led to a significant decrease in dielectric constant. The dielectric constants of the glass-ceramics DT5 and DT10 were not more affected by further increase of sintering temperature up to 950°C. On the contrary, dielectric

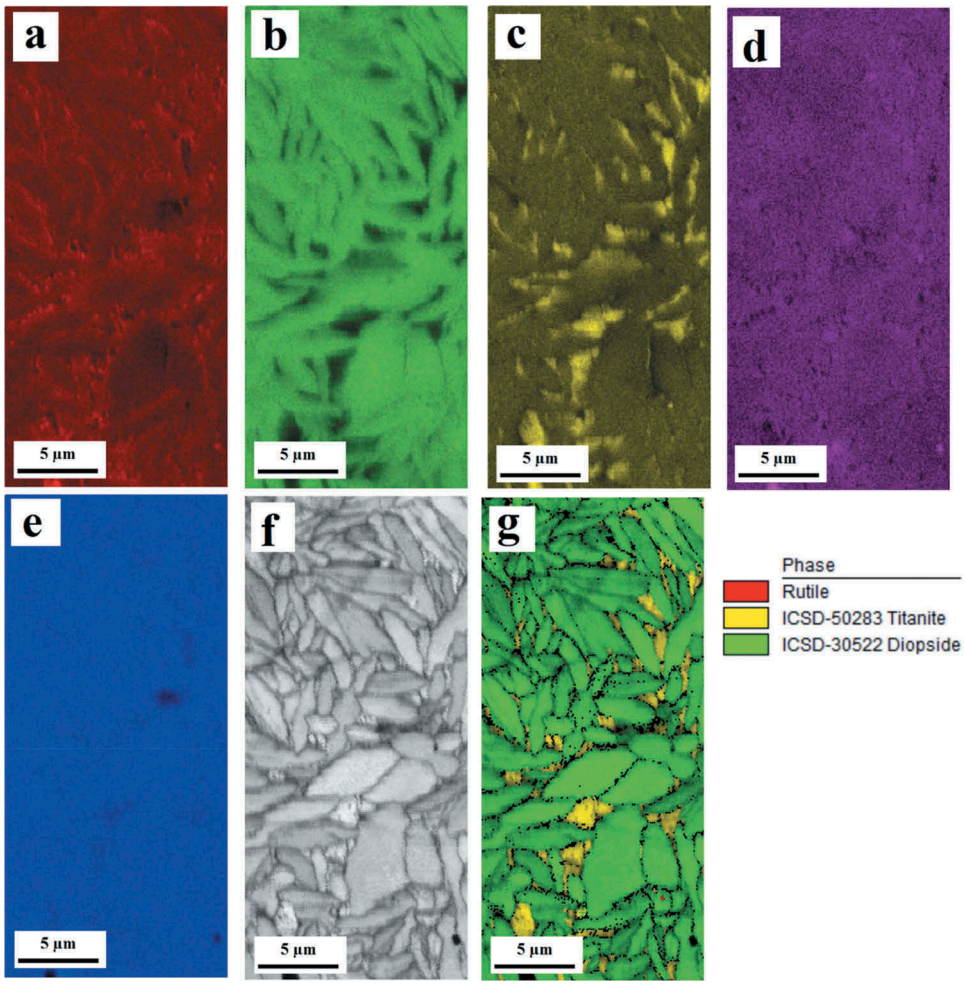


**Figure 5.** The elemental distribution maps of (a) Si, (b) Mg, (c) Ti, (d) Ca, (e) O, (f) IQ-map and (g) the phase + IQ-map of glass-ceramic DT20 sintered at 950°C for 4 h.

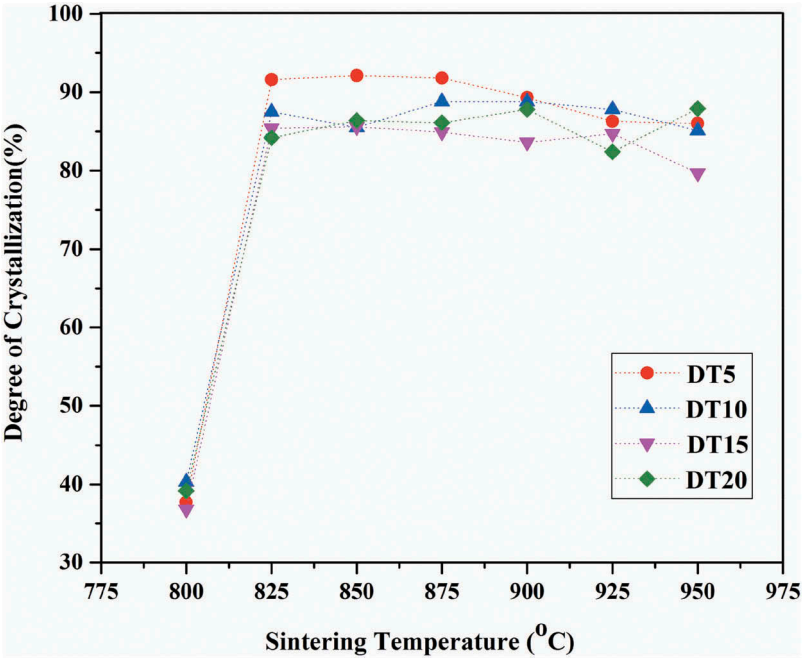


**Figure 6.** Variations of crystallinity of the studied glass-ceramics versus sintering temperature. The line between dots is a guide to the eye.

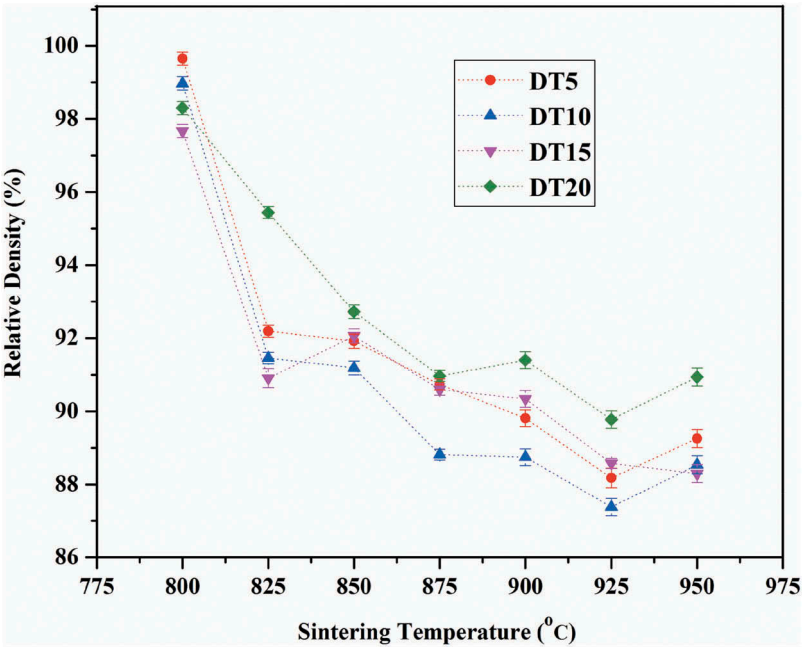


**Figure 7.** Variations of relative density of the studied glass-ceramics versus sintering temperature. The line between dots is a guide to the eye.

constant for the glass-ceramics DT15 and DT20 increased by further increase in the sintering temperature from 850°C to 950°C.

It is well known that dielectric constant is affected by various parameters including molecular volume, ionic polarizability, porosity and the existence of secondary phases [24,25]. In general, the dielectric constant of a multiphase material is affected by volume fraction and dielectric constant of each phase [2]. In the prepared glass-ceramics, four phases are present including residual glass, diopside, titanite and pores. Therefore, the decrease of $\varepsilon_r$ with increase of sintering temperature is mainly due to the formation of higher porosity volume as shown in Figure 7. When density is high enough, more dielectric dipoles occur per unit volume and the glass-ceramics can be more easily polarized leading to an increase in the $\varepsilon_r$ value [29,30]. Therefore, the glass-ceramics sintered at 800°C with the highest relative density and the lowest crystallinity possess dielectric constants close to that of their corresponding glasses. By increasing the sintering temperature, dielectric constant drops to lower

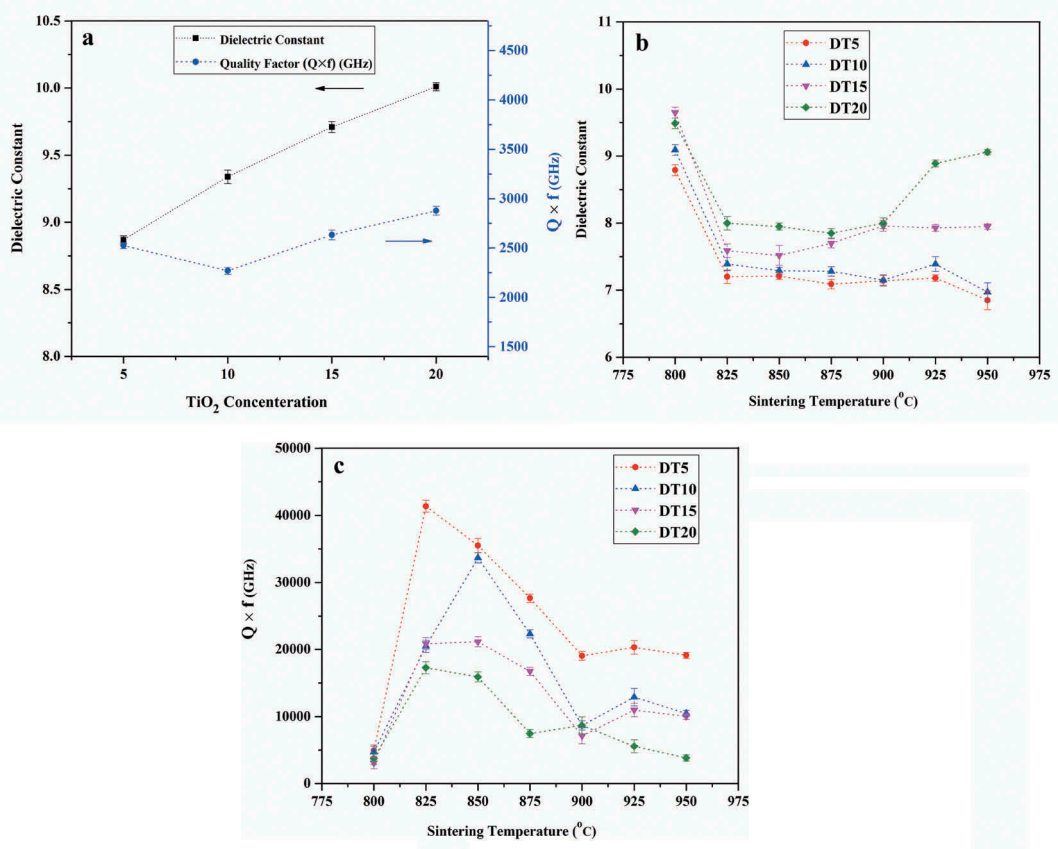


**Figure 8.** Microwave dielectric properties of the (a) studied glasses containing different $TiO_2$ content, and: (b) dielectric constant of glass-ceramics at different sintering temperatures and (c) quality factor of glass-ceramics at different temperatures (Q × f). The line between dots is a guide to the eye.

values due to the decrease of relative density and the considerable amount of diopside crystalline phase. In the case of glass-ceramics DT15 and DT20, the increase of dielectric constant after sintering at temperatures higher than 850°C can be attributed to the formation of notable quantities of titanite as the secondary phase which possesses a high dielectric constant of about 45 at a frequency of 1 MHz [31,32].

The variation of the quality factor of the studied glass-ceramics is shown in Figure 8(c). The glass-ceramics sintered at 800°C shows minimum values of Q × f about 4000 GHz which is attributed to the lowest crystallinity. Glassy materials always have higher dielectric loss rather than their corresponding single crystals due to the profound absorption of microwave power by glass network at high frequencies [33]. The Q × f values of sintered glass-ceramics firstly increased and then decreases with the increase in sintering temperature. The significant jump of Q × f values for the glass-ceramics sintered at the temperature range of 825–850°C may be attributed to the increase of their crystallinity by temperature. The gradual decrease of Q × f at the higher sintering temperature range from 850°C to 950°C is due to the enhanced formation of the secondary phase (titanite) with a larger dielectric loss [31,32].

**Table 5.** Temperature coefficient of resonant frequency $\tau_f$ (ppm/°C) of studied glasses containing different $TiO_2$ content and glass-ceramics sintered at 950°C for 4 h.

| | Glasses | | | | Glass-ceramics | | | |
|---|---|---|---|---|---|---|---|---|
| | DT5 | DT10 | DT15 | DT20 | DT5 | DT10 | DT15 | DT20 |
| $\tau_f$ (ppm/°C) | −80 | −107 | −53 | −96 | −60 | −63 | −56 | −92 |

The $\tau_f$ values of studied glasses containing different $TiO_2$ content and glass-ceramics sintered at 950°C for 4 h are summarized in Table 5. The $\tau_f$ values for sintered glass-ceramics changes from −60 to −92 ppm/°C with increasing $TiO_2$ concentration except DT15 glass-ceramic shows $\tau_f$ value of −56 ppm/°C. Also, studied glasses containing various $TiO_2$ concentrations have negative $\tau_f$ in range of −53 to −107 ppm/°C.

The theoretical value of $\tau_f$ is defined as follows:

$$\tau_f = X_1\tau_{f1} + X_2\tau_{f2} + X_3\tau_{f3} \quad (2)$$

where X1, X2 and X3 are the volume fractions of diopside, titanite and residual glass, and $\tau_{f1}$, $\tau_{f2}$ and $\tau_{f3}$ are $\tau_f$ values of diopside, titanite and residual glass, respectively. The $\tau_f$ value of diopside ceramic was reported as −42 ppm/°C [15]. Also, Titanite is known as a dielectric ceramic with negative value of $\tau_f$ [31]. According to $\tau_f$ values of studied glasses and sintered glass-ceramics, it can be predicted that residual glasses have negative

values of $\tau_f$. Therefore, $\tau_f$ values of glass-ceramics were negative because of negative values of all three components of glass-ceramics.

## 4. Conclusions

In this work, diopside glass-ceramics containing various content of $TiO_2$ were prepared by a sinter-crystallization technique. Diopside was precipitated as the main crystalline phase in all studied glass-ceramics. However, the presence of titanite as the secondary phase was confirmed by EBSD technique in the glass-ceramics containing higher content of $TiO_2$.

The highest relative density (about 99%) and dielectric constant ($\varepsilon_r$ = 8.8–9.5) were obtained for the glass-ceramics sintered at 800°C for 4 h due to minimized crystallinity. By increase of sintering temperature, the dielectric constant of the glass-ceramics decreased. However, the dielectric constants of the glass-ceramics DT15 and DT20 sintered at temperatures higher than 850°C increase due to the more volume fraction of titanite. The glass-ceramics sintered at 825–850°C showed the most quality factor owing to their enhanced crystallinity (85–92%).

## Compliance with ethical standard

The authors declare that they have no conflict of interest.

## Disclosure statement

No potential conflict of interest was reported by the authors.

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