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High quality factor microwave dielectric diopside glass-ceramics for the low temperature co-fired ceramic (LTCC) applications

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ABSTRACT

In the present work, microwave dielectric properties of CaO-MgO-SiO_2 glass-ceramics based on the stoichiometric composition of diopside ($CaMgSi_2O_6$) were accurately investigated. The initial glass was prepared utilizing conventional melt quenching technique. Thermal properties of the milled glass particles were monitored by differential scanning calorimetry (DSC), dilatometry and hot stage microcopy (HSM). Glass-ceramic specimens were prepared through simultaneous one-step sinter-crystallization procedure. In order to achieve high quality factor (high-Q) microwave dielectric properties, glass-ceramics were also prepared through two-step sintering technique. The crystallization behavior of the heat treated specimens was examined by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM).

Based on the obtained results, diopside precipitated as the only crystalline phase in all sintered glass-ceramics. Diopside glass-ceramics sintered through one-step (at 925 °C for 4 h) and two-step (at 800 °C for 4 h, then followed by heating at 950 °C for 2 h) procedures exhibited high-Q microwave dielectric of 56,952 GHz and 64,524 GHz, respectively. The degrees of crystallization and crystallite sizes of the glass-ceramics prepared from both sintering procedures were also characterized.

1. Introduction

Owing to progressive development of wireless products and telecommunication in the past decade, microwave dielectric materials play a leading role within a wide range of applications, especially concerning microwave frequency devices. In this regard, low temperature co-fired ceramics (LTCC) technology has become crucial due to its capability to integrate different types of components, substrates and electrode materials.

The most important feature of the preparation of a LTCC module is a sintering temperature as low as 950 °C to enable concurrent sintering with low melting metallic electrode such as copper, silver, gold, and etc. [1–5].

Low dielectric constant (ε_r = 5–10) substrate materials are greatly applied to LTCCs because they enable high speed signal transmission. Glass-ceramic substrates have been known as indispensable constituent of the miniaturized LTCC modules due to their low sintering temperature and capability to precipitate crystalline phases with desired microwave dielectric properties [6,7]. Among various silicate glass-ceramics, diopside ($CaMgSi_2O_6$) glass-ceramics present low dielectric loss, excellent chemical durability as well as appropriate mechanical properties at low sintering temperature. These characteristics make them suitable candidates for LTCC applications [8,9]. Many efforts have been done to promote microwave dielectric properties of diopside glass-ceramics.

K. C. Feng and et al. examined the nucleating role of zirconia in crystallization behavior of diopside glass-ceramics and highlight the microwave dielectric properties of the relevant glass-ceramics [10,11]. E.S. Kim et al. reported the effect of various parameters including glass particle size, Cr_2O_3 content and sintering procedures (one and two step

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sintering) on the crystallization behavior of diopside glass-ceramics and their microwave dielectric properties [12–14]. It has been also that a glass with the same stoichiometry as crystalline diopside, nucleates solely at the surface, bulk crystallization does hence not occur. The nucleation is oriented and preferably crystals with their crystallographic a- and b-axis perpendicular to the surface are formed. During growth into the bulk, the orientation changes and the c-axis is oriented perpendicular to the surface [15,16].

In addition to the mentioned efforts, annealing treatment as one of the most common methods has been applied to increase the quality factor value (Q × f). According to reports in the literature, long time annealing treatment at high temperature may decrease lattice defects, dislocations and residual stresses in the crystalline structure [17,18]. By contrast if high quality factors are required, annealed ceramics are not cost-effective [19] and cannot be used in LTCC applications due to their high annealing temperatures.

The present work presents a study on the crystallization behavior, sinterability and microwave dielectric properties of diopside based glass-ceramics prepared from one and two step sintering procedures. For this purpose, thermal behavior, crystalline phase evolution, and microstructural features were monitored to evaluate sinter-crystallization behavior and to enable a correlation with microwave dielectric properties. Physical and structural properties including relative density, degree of crystallization and crystallite size were also examined and discussed in terms of microwave dielectric characterization.

1- Experimental procedure

The starting glass with the chemical composition of stoichiometric diopside ($CaMgSi_2O_6$) was prepared through conventional melt quenching method. The glass batch was prepared from reagent chemicals of magnesium hydroxide (Merck), calcium carbonate (Merck) and silica (SCHOTT AG).Then, 300 g homogenous mixture of glass batch was melted in a platinum/rhodium crucible at 1480 °C, kept at this temperature for 2 h. Afterward, the molten glass was casted on a brass mold and subsequently transferred to the annealing furnace preheated at 730 °C; the furnace was switched off and the glass was allowed to cool to room temperature. The obtained glass was milled and sieved to reach the particle size of < 40 μm using a planetary mill with zirconia cup and balls. Particle size distribution of the milled glass powder was characterized by the laser particle size analyzer (Fritsch analysete 22). The mean particle size was found to be about 10 μm.

Crystallization behavior of the obtained glass powder was monitored by differential scanning calorimetry (DSC) (Linseis DSC Pt-1600) performed using the heating rate of 5 °C/min. Exact determination of glass transition (T_g) and dilatometric softening point (T_d) temperatures as well as of the thermal expansion coefficient was carried out by the dilatometry (Netzsch, 402PC) using the heating rate of 5 °C/min. Glass cylinders, 25 mm in length and 8 mm in diameter were used for dilatometry.

The sinterability of glass powder was explored by a side-view hot stage microscope (HSM). Cylindrical glass powder compacts were heated at the heating rate of 5 °C/min. The HSM software calculated variation of height, width and area of specimen with respect to its initial dimensions during heating.

The glass powders were shaped into discs with 16 mm in diameter and 8 mm in thickness by cold isostatic pressing under pressure of 80 MPa. Compacted glass powders were subjected to the one- and two-step sintering procedures, separately. One-step sintering was carried out at the temperature interval of 800–950 °C at the heating rate of 5 °C/min and soaking time of 4 h. In the two-step sintering route, glass compacts were heat treated at 800 °C for 4 h, then subjected to the subsequent heat treatment at 900 and 950 °C for 2 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 helium gas pycnometry (AccuPyc 1330).

The crystalline phases precipitated during sintering were identified by X-ray diffraction (XRD, Rigaku MiniFlex 300) with Cu-K_α radiation ($\lambda = 0.154$ nm) in the 2θ range of 10–80°. The degree of crystallization and the average crystallite size were determined according to the Rietveld analysis extracted from the XRD results and analyzed by Topas 4 software [20].

Microstructural features of the sintered glass-ceramics were characterized by the field emission scanning electron microscopy (FESEM, LEO Supra VP-55). Prior to the FESEM study, the glass-ceramics were polished and chemically etched by immersion in a 2.5-vol% HF solution. Finally, the glass-ceramics were coated by a thin layer of carbon.

Microwave dielectric properties of the sintered glass-ceramics were determined on the basis of the Hakki-Coleman method [21] where a cylindrical sample (diameter: thickness ratio ~2:1) was placed between two polished conducting plates. After that, the dielectric constant (ε_r), dielectric loss (tanδ) and resonance frequency (f) were measured by the network analyzer (Agilent E8362B PNA series) in the frequency range of 11–13 GHz. The quality factor (Q × f) was equal to 1/tanδ × f.

2. Results and discussions

Fig. 1 depicts the DSC, dilatometry and hot stage microscope (HSM) thermographs of the parent glass. Characteristic temperatures including glass transition (T_g), dilatometric softening point (T_d) and crystallization peak (T_c) temperatures were extracted from the DSC and dilatometry. The temperatures of the first (T_{FS}) and the maximum shrinkage (T_{MS}) were obtained from HSM micrographs. The obtained data of the parent glass are summarized in Table 1.

From both DSC and dilatometry, the glass transition and dilatometric softening point temperatures were found to be 730 and 776 °C, respectively. According to the DSC thermographs, a sharp crystallization peak is located at 899 °C with the onset temperature of 859 °C. Based on the Fig. 1c, the shrinkage of compacted glass powders starts at 780 °C (T_{FS}) and the maximum shrinkage occurs at 830 °C (T_{MS}).

The compacted glass powders were subjected to the one- and two-step sintering procedures, as described earlier. Fig. 2 shows the XRD patterns of the sintered specimens. From Fig. 2, it is obvious that the parent glass is completely amorphous without any crystallization effect. While increasing the temperature from 800 up to 950 °C, diopside precipitates as the only crystalline phase. The degree of crystallization and average crystallite size of the diopside glass-ceramics prepared via one- and two-step sintering (as described in section 2) were determined from XRD results on the basis of the Rietveld analysis method.

Figs. 3 and 4 illustrate the variation of crystallinity and average crystallite size versus sintering temperature in the one-step procedures. Fig. 5 also shows the variation of the relative density of the mentioned glass-ceramics with the supplied temperature. The relevant measurements for both sintering procedures have been compared in Table 2. It is implied that in the case of one-step sintered glass-ceramics, crystallinity and average crystallite size are continuously increased with increasing sintering temperature to values in the range from 48 to 85% and 48–74 nm, respectively. It is noticeable that the main increase of crystallinity occurs at temperatures higher than 800 °C. Considering the onset temperature of crystallization (859 °C), it seems that the comparatively low sintering temperature is responsible for the low degree of crystallinity (48%) of the glass-ceramic sintered at 800 °C. It is evident from Table 2 that both the crystallinity and the average crystallite size are higher in the two-step sintering procedure. By increasing the

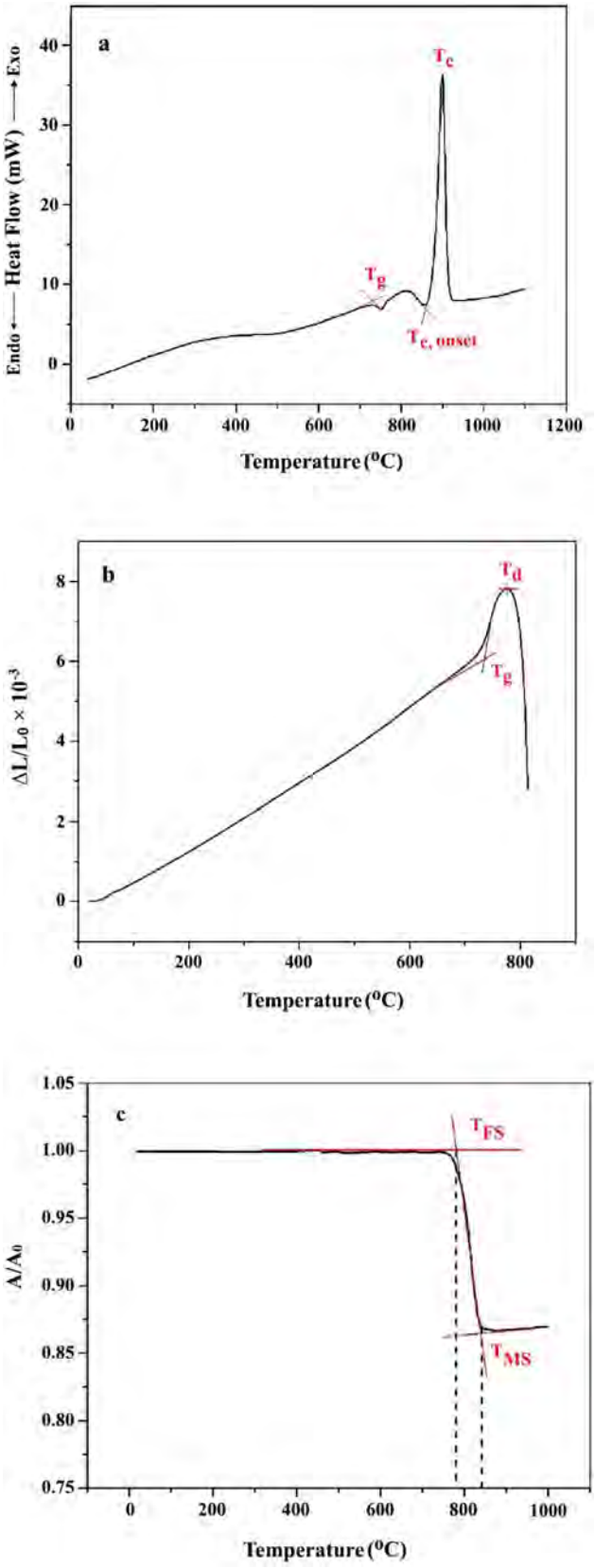

Fig. 1. Thermal behavior of the parent glass: (a) DSC; (b) dilatometry, (c) HSM thermographs.

temperature up to 950 °C in the second sintering step the highest crystallinity of 90% was obtained.

From Fig. 5 and Table 2, the maximum relative density (near 98%) was obtained for the glass-ceramic sintered at 800 °C for 4 h. According to the HSM images, this temperature falls in the main densification temperature interval (778–830 °C) and below the onset of crystallization (859 °C). It is well known during concurrent sinter-crystallization of glass powders, that viscos flow and crystallization take place at the same time to decrease the system's free energy. If crystallization surpassed densification, sintering would be interrupted by crystallization. In this state, increased viscosity of the residual glass phase inhibits appropriate densification. But, if the crystallization could satisfactorily be controlled and takes place at low rates, densification

Table 1
Characteristic temperatures of the parent glass.

T_g (°C)	T_d (°C)	T_{FS} (°C)	T_{MS} (°C)	$T_{C,\ onset}$ (°C)	T_C (°C)
730	776	778	830	859	899

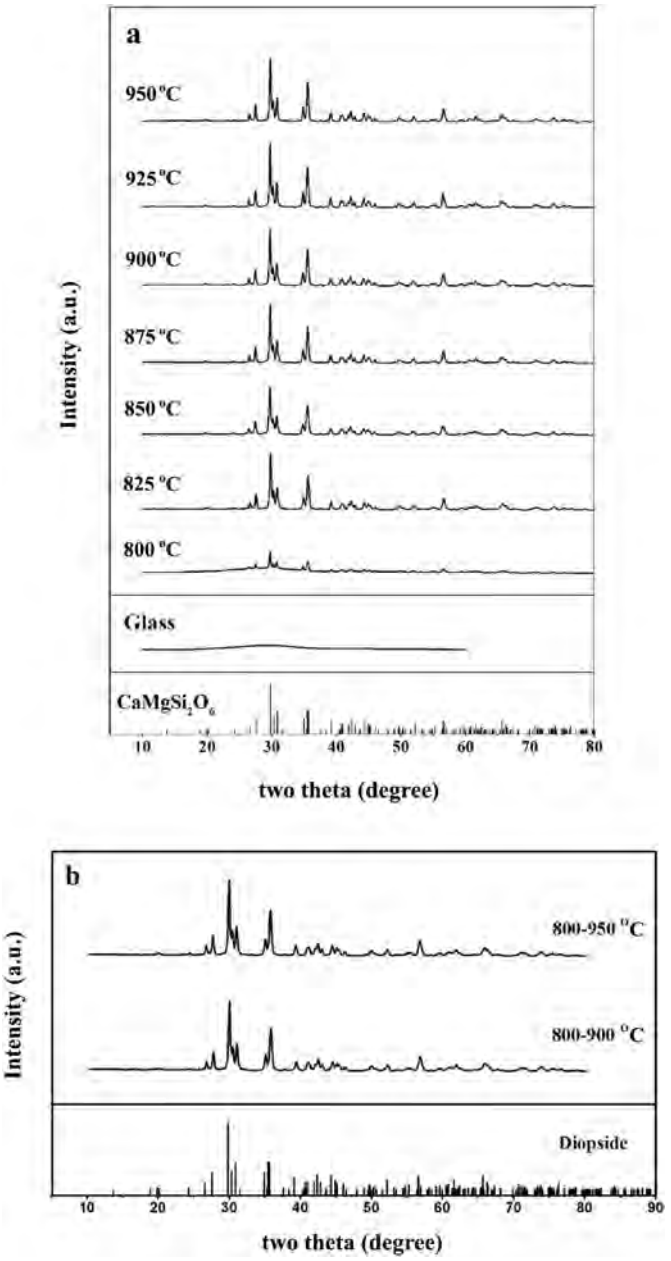

Fig. 2. XRD patterns of the glass compacts sintered at (a) 800–950 °C for 4 h, (b) 800 °C for 4 h, consequently sintered at 900 and 950 °C for 2 h.

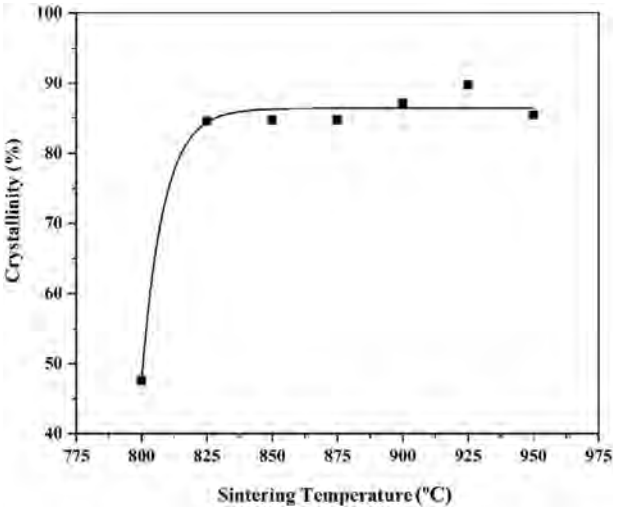

Fig. 3. Variation of crystallinity of the one-step sintered glass-ceramics versus sintering temperature.

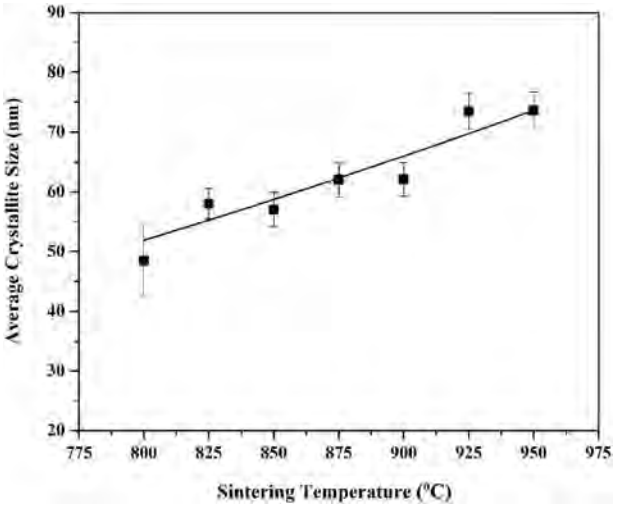

Fig. 4. Variation of average crystallite size of the one-step sintered glass-ceramics versus sintering temperature.

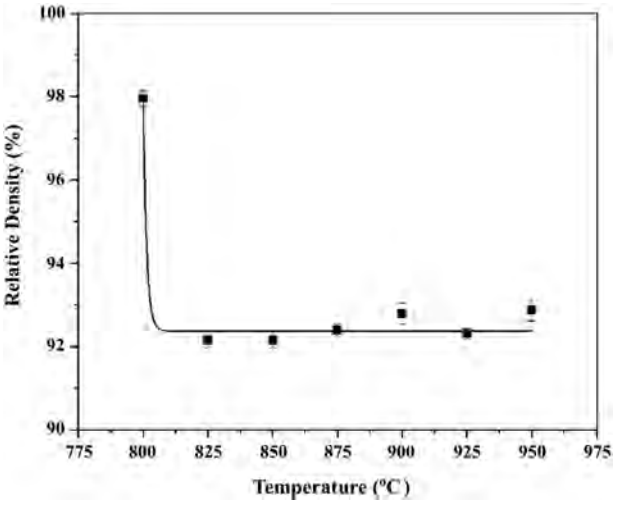

Fig. 5. Variation of relative density of the one-step sintered glass-ceramics versus sintering temperature.

Table 2
Relative density, degree of crystallization and average crystallite size of diopside glass-ceramics prepared via one- and two-step sintering procedures.

Sintering temperatures and condition	Degree of crystallization (%)	Average crystallite size (nm)	Refinement parameters		Relative density (%)
			R_p	R_{wp}	
800 °C/4 h	48	48 ± 5	10.69	12.98	98 ± 0.3
825 °C/4 h	84	58 ± 2.5	3.79	5.33	92 ± 0.4
850 °C/4 h	85	57 ± 3	4.16	5.76	92 ± 0.4
875 °C/4 h	85	62 ± 3	4.37	6.13	92 ± 0.6
900 °C/4 h	87	62 ± 3	4.22	5.92	93 ± 0.3
925 °C/4 h	90	73 ± 3.5	4.12	5.89	92 ± 0.5
950 °C/4 h	86	74 ± 3.5	4.26	6.04	93 ± 0.2
800 °C/4 h – 900 °C/2 h	89	83 ± 5	3.95	5.40	92 ± 0.2
800 °C/4 h – 950 °C/2 h	90	100 ± 7	4.04	5.53	91 ± 0.3

Rp and R_{wp} are respectively referred to the profile factor and the weighted profile factor.

Table 3
Microwave dielectric properties of the glass and two-step sintered glass-ceramics.

Heat treatment procedure	Dielectric constant	Q × f (GHz)
Without heat treatment (parent glass)	8.59	4125
800 °C/4 h-900 °C/2 h	6.99	57,350
800 °C/4 h-950 °C/2 h	6.96	64,524

would be completed before crystalline phases are precipitated [22,23]. Hence, a lower degree of crystallization (48%) is responsible for the improved densification of the glass compact sintered at 800 °C for 4 h.

By increasing the sintering temperature up to 950 °C, the glass compacts were heated for a long time to temperatures > 859 °C and hence out of the effective densification temperature interval. As a result, the crystallinities drastically increased and the relative density sharply dropped to ~ 92%. Hence, the increase of the sintering temperature results in an increase of crystallization and thus interrupts the densification through an increase of the effective viscosity.

A comparison of the relative densities obtained from the one- and two-step sintering procedure (Tables 2 and 3) confirms the lower relative density of the two-step sintered glass-ceramics. Based on the crystallite size measurements (Fig. 4) and microstructural observation (Fig. 6), this behavior can be attributed to the grain growth during two-step sintering of the mentioned glass-ceramics which leads to a concentration of the trapped gases in the microstructural pores and the subsequent pore coalescence and growth.

Fig. 6 shows FESEM micrographs of the glass-ceramics sintered via one- and two-step procedures. As is observed, the glass-ceramic sintered at 800 °C for 4 h (Fig. 6a and b) contains a small volume of diopside crystals dispersed in the glass matrix. This result is in conformity with the crystallinity measurements (Fig. 3 and Table 2). By the increase of sintering temperature, the microstructural coarsening is clearly detectable (Fig. 6c, d, e and f and f). Furthermore, the glass-ceramics prepared by two-step sintering contain a higher volume of pores and the maximum size of crystallites (Fig. 6g and h). Apparently, decreased amount of relative density is responsible for the presence of pores in these glass-ceramics.

Variation of microwave dielectric properties (dielectric constant and quality factor) of the one-step sintered glass-ceramics are illustrated in Fig. 7. Moreover, microwave dielectric features of the parent glass as well as of the two-step sintered glass-ceramics have been compared in Table 3.

Fig. 7a shows the variation of dielectric properties versus sintering temperature in the one-step procedure. It is obvious that the dielectric constant reaches a maximum value (8.29) at 800 °C. Further increase of sintering temperature declines the dielectric constant, significantly. As

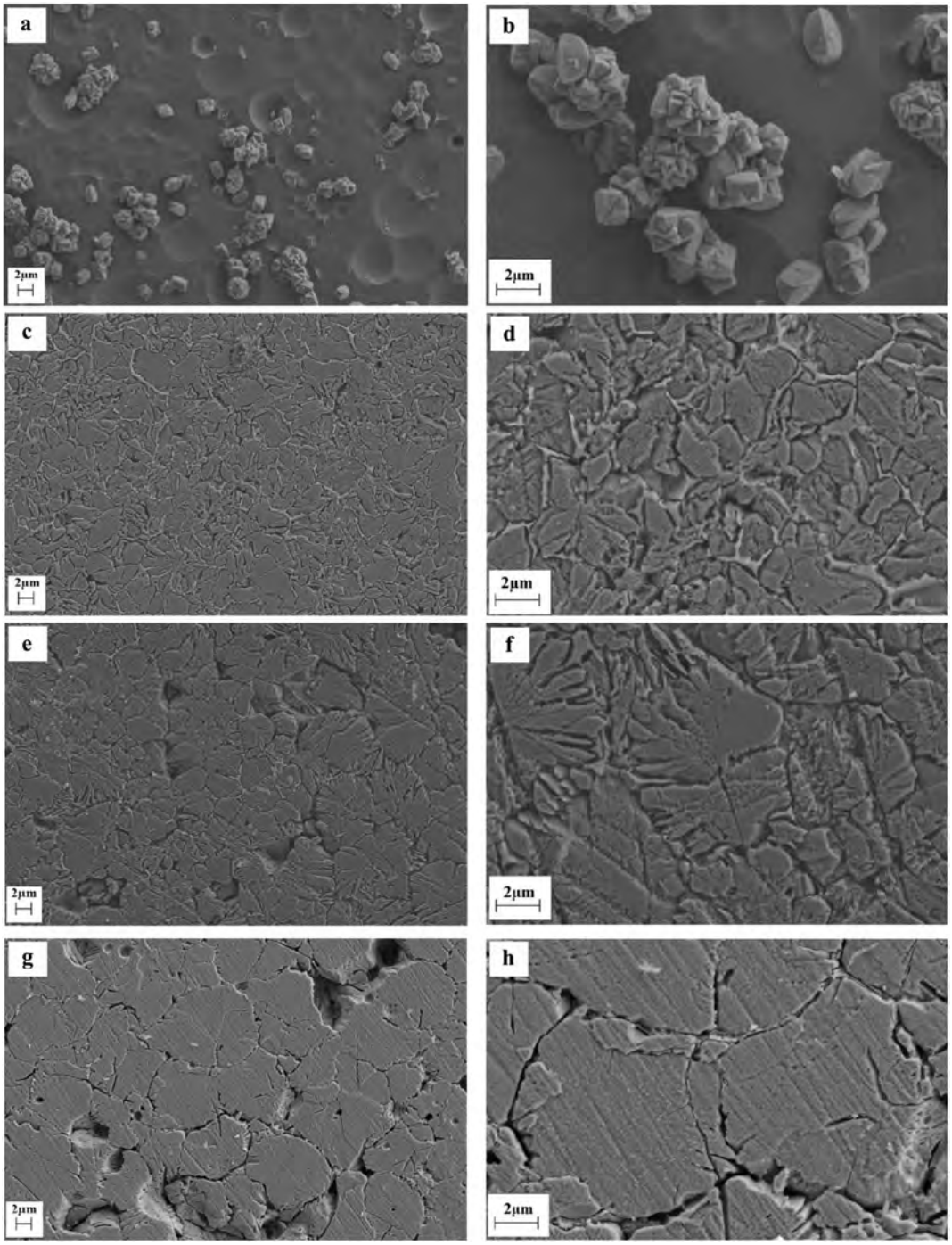

Fig. 6. FESEM micrographs of the glass-ceramics sintered at different temperatures and conditions: (a) 800 °C/4 h, (b) 800 °C/4 h (higher magnification), (c) 875 °C/4 h, (d) 875 °C/4 h (higher magnification), (e) 925 °C/4 h, (f) 925 °C/4 h (higher magnification), (g) 800 °C/4 h and 950 °C/2 h, (h) 800 °C/4 h and 950 °C/2 h (higher magnification).

well known, the dielectric constant is affected by various parameters including molecular volume, ionic polarizability, porosity and secondary phases [24,25]. Concerning the relative density measurements (Fig. 5 and Table 2), it is evident that the trends of dielectric constant variation is as the same of the relative density. By the increase of the relative density, the pore volume would be decreased and more dielectric dipoles would be present in the volume. Therefore, the whole specimen can be more easily polarized which leads to increasing ε_r values [26,27].

In the case of multi phase specimens, the dielectric constant is affected by volume fraction and dielectric constant of each constituent [3]. Hence, the dielectric constant of the fabricated glass-ceramics is influenced by dielectric constant of both diopside crystalline phase and glass matrix. As shown in Table 3, the dielectric constant of the parent glass is 8.59. According to the literature, the dielectric constant of the diopside ceramic sintered at 1300 °C is in the range from 6.9 to 7 [28].

On the basis of the obtained results, the glass-ceramic sintered at 800 °C with the highest relative density and the lowest crystallinity has the dielectric constant near to that of the parent glass. However, by sintering at higher temperatures, the dielectric constant drops to about 7 due to decrease of relative density and the high amount of crystalline diopside.

By contrast, the quality factor of the glass-ceramic sintered at 800 °C shows a minimum value of 4821 GHz owing to the smallest

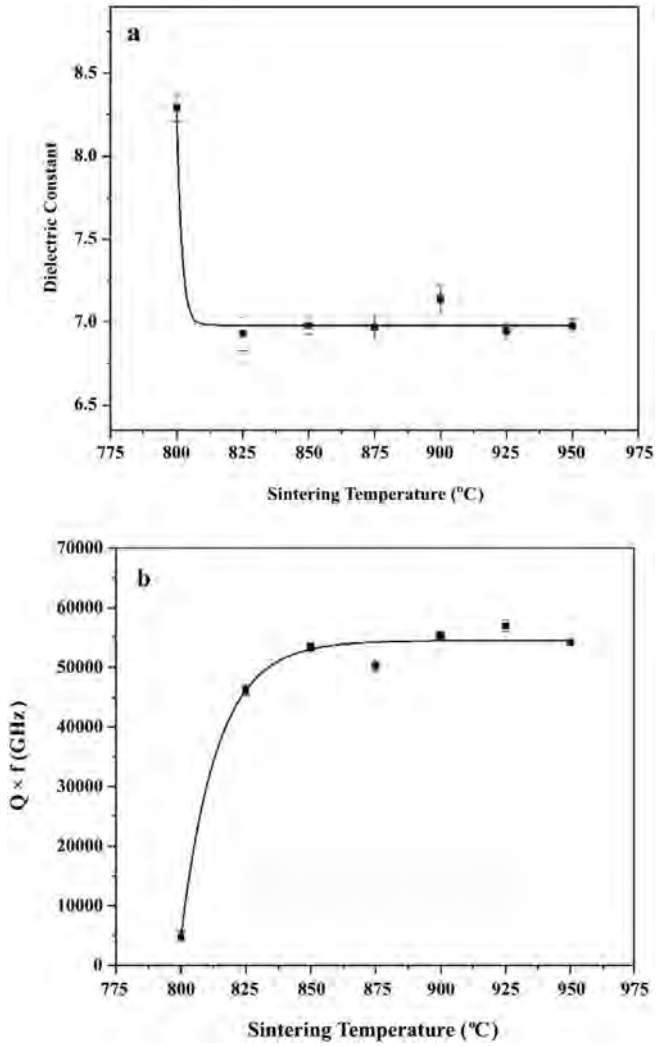

Fig. 7. Microwave dielectric properties of the glass-ceramics sintered at different temperatures:
(a) dielectric constant, (b) quality factor (Q × f).

crystallinity. According to Fig. 7b, by the increase of the sintering temperature from 825 to 950 °C, the quality factor sharply rises from 45,000 up to 57,000 GHz. It is worth mentioning that the dielectric loss (tanδ) of ceramic materials originates from both categories, intrinsic and extrinsic losses. Intrinsic loss happens in perfect crystals as a result of phonon damping; whilst extrinsic loss is associated with heterogeneities such as impurities, extended dislocations, grain boundaries, secondary phases, microstructural defects and random crystallite orientations [2,29]. Dielectric loss of sintered ceramic materials usually falls in the second category. In the case of glass materials, dielectric loss is always higher than in corresponding single crystals with the same chemical composition due to profound microwave absorption by the glass network at high frequencies [30].

It can be concluded that the increase of the quality factor of the glass-ceramics sintered at higher temperatures is attributed to the gradual increase of crystallinity with increasing temperatures. Furthermore, by increase the sintering temperature, the enhancement of crystallite size (shown in Table 2) and microstructural coarsening (shown in Fig. 6) is evident. As a result, the interphase boundaries will be decreased which are an important source of dielectric loss [31–34]. As observed in Table 3, applying the two-step sintering process improves quality factor due to an increased crystallinity and fewer interphase boundaries.

Table 4 shows a comparison between physical properties and microwave dielectric features of the fabricated glass-ceramic and those were obtained in previous research [12–14]. Based on this comparison, diopside glass-ceramics fabricated in the present work offer appropriate densification behavior, higher amount of crystallinity as well as considerable improvement of quality factor.

3. Conclusions

Diopside glass-ceramics were successfully prepared throughout one- and two-step sinter-crystallization procedures. In one-step sintering procedure, the highest relative density (98%) and diectric constant (8.29) was obtained after sintering at 800° C for 4 h. However, the highest quality factor (56,952 GHz) was obtained for the glass-ceramics sintered at 925 °C for 4 h due to its improved crystallinity (90%) and larger crystallite size (73 nm).

In the two-step sintering procedure, the relative density was considerably declined compared to that of the one-step sintered glass-ceramics due to the noticeable increase of crystallinity. Two-step sintered glass-ceramics showed higher values of quality factor thanks to the simultaneous enhancement of crystallinity and crystallite size.

The most promising diopside glass-ceramic was fabricated through two-step sintering (800 °C/4 h and 950 °C/2 h) with the highest crystallinity (90%), largest mean crystallite size (100 nm), and highest quality factor (64,524 GHz).

Table 4
A comparison between microwave dielectric properties of the diopside glass-ceramics.

Research	Sintering condition		Relative density (%)	Crystallinity (%)	Crystallite size (nm)	ε_r	Q × f (GHz)
Proposed by Choi et al. [12] (glass particle size of 6.88 μm)	1 step: 900 °C-1 h		~ 91	85.1	–	7.03	43,197
Proposed by Choi et al. [13]	1 step: 950 °C-1 h		92.34	87.4	31.42	~ 6.97	46,780
	2 step: 763 °C-3 h 950 °C-1 h		91.48	89.2	28.09	7.03	53,197
Proposed by Choi et al. [14]	1 step: 900 °C-1 h		92.45	84.1	~ 35	~ 7.05	~ 46,000
(0.5 wt% Cr_2O_3)	2 step:	1 h	91.73	85.2	~ 32.1	~ 7	~ 46,000
	763 °C-1-10 h	3 h	90.52	88.1	~ 32	~ 6.98	50,460
	950 °C-1 h	5 h	90.32	87.4	~ 30	~ 6.96	~ 48,000
		10 h	89.79	87.2	~ 29.5	~ 6.93	~ 42,000
Present work	1 step: 925 °C-4 h		92 ± 0.5	90	73 ± 3.5	6.95	56,952
	2 step: 800 °C-4 h 950 °C-2 h		91 ± 0.3	90	100 ± 7	6.96	64,524

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