

Crystallization, Sinterability and Microwave Dielectric Properties of CaO-SiO₂-Na₂O-MgO Glass Ceramics Containing Fe₂O₃ and ZnO

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CaO-SiO₂-Na₂O-MgO glass-ceramics containing Fe₂O₃ and ZnO were prepared using conventional melting of batch powders, quenching the molten glass in water and crystallization of sintered glass powder. FTIR spectroscopy exhibited main peaks at 930 cm⁻¹ and 950 cm⁻¹ are the characterizations of [SiO₄]⁻² and [SiO₄]⁻¹ bands of glassy network, respectively. XRD patterns introduce Wollastonite and Akermanite as two main crystallized phases of sintered glass-ceramics. Fe₂O₃ additive resulted in crystallization of Wollastonite more than ZnO additive. Also glass ceramics containing Fe₂O₃ exhibited sinterability better than ZnO glass ceramics. Consequently, dielectric properties of glass ceramics were measured via a network analyzer at 9 GHz. The bulks of Glass Ceramics showed low dielectric constant and dielectric loss, $\epsilon_r = 5.5 - 7.4$ and $\tan\delta = 0.001 - 0.009$ respectively. SEM micrograph of glass ceramic samples and glasses depicted morphology of Wollastonite and phase separation respectively.

Keywords: glass ceramic, wollastonite, akermanite, dielectric properties

1. INTRODUCTION

In recent years, Low Temperature Co-fired Ceramics (LTCCs) have been introduced as an attractive technology for electronic components and substrates. The most important parameter which is expected for a LTCC component is the low sintering temperature because of the use of low melting point metals in their wiring applications e.g. Cu, Ag, and Au.^[1,2] Initially, low dielectric constant ($\epsilon_r = 5 - 10$) materials were used for LTCCs due to their high speed transmission of signals. Thereafter, high dielectric constant materials ($\epsilon_r = 20 - 60$) were also developed to reduce the device size for low GHz frequency applications.^[3] Glass-ceramics shows favorable dielectric properties in microwave frequency and accordingly they have known as LTCC substrates. Compositional changes including crystallization of desirable phase and controllable growth of special microstructure are the most precious properties of glass-ceramics which could not be found for other ceramic materials.^[1,4] CaO-SiO₂-MgO based glass ceramic system is a suitable candidate for LTCC technology because of its favorable dielectric and mechanical properties.

In the present investigation, some glasses in CaO-SiO₂-Na₂O-MgO system containing Fe₂O₃ and ZnO are analyzed. The aim of this investigation is to introduce glass-ceramics with low dielectric constant and dielectric loss.

2. EXPERIMENTAL PROCEDURE

The compositions of glasses are listed in Table 1. Main composition of CaO-SiO₂-Na₂O-MgO glasses were reported based on weight ratio (wt. %). Then small amounts of ZnO and Fe₂O₃ (1 - 5 g in a 100 g batch) were added to each batches. Composition of glass was labeled as W (Wollastonite). Glasses were prepared by conventional melting process. All of raw materials were used in reagent grades with purities higher than 99 (wt. %) purchased from Merck Co. Germany. Glass frits were prepared by melting the raw materials at 1400°C for 1 h in zirconia crucible and quenched in cold water. Frits were dried and milled to particle size <63 μm . Thermal behavior of glass powders were determined by Differential Thermal Analysis (DTA-Linseis L181) at a heating rate of 10°C min⁻¹. Frits mixed with 5 wt. % polyvinyl alcohol solution and then pressed uniaxially 30 MPa into a pellet with 22 mm diameter and 4 mm thickness. The bulk densities of sintered glass ceramics was measured by Archimedes methods (ASTM C373-88). The powder density of glass ceramics was determined by pycnometry method (ASTM D2320-98). Crystalline phase precipitated during sintering were determined by x-ray diffraction (XRD) analysis (Siemens, model D-500). Fourier transform infrared (FT-IR) transmittance spectra of glasses were measured at room temperature using KBr-pellet technique on a FT-IR spectrophotometer (Tensor 27 Bruker Company) in the range of 400 - 1500 cm⁻¹. Microstructure of glass and glass ceramics were characterized by field emission scanning electron microscopy (FE-SEM-Mira Tescan). The

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Table 1. Chemical composition of glasses.

Fe ₂ O ₃	ZnO	Na ₂ O (wt. %)	MgO (wt. %)	CaO (wt. %)	SiO ₂ (wt. %)	Glass
-	1	5.50	2.75	44.29	47.45	WZ1
-	3	5.50	2.75	44.29	47.45	WZ3
-	5	5.50	2.75	44.29	47.45	WZ5
1	-	5.50	2.75	44.29	47.45	WF1
3	-	5.50	2.75	44.29	47.45	WF3
5	-	5.50	2.75	44.29	47.45	WF5

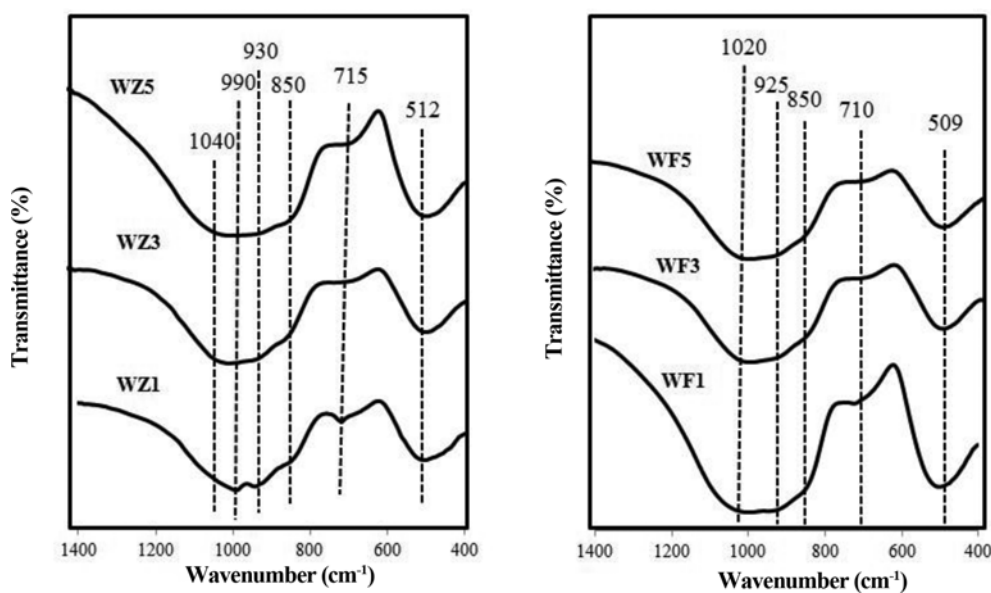
glass ceramics were polished and etched in 0.5 wt. % HF solution and then were coated by a thin film of gold for 30 seconds. Dielectric properties of glass ceramic samples were measured by waveguide transmission method with network analyzer (HP 8757D) with the frequency of 9 GHz. It's shown that Crystallization of wollastonite area in CaO-SiO₂-MgO ternary diagram phase is narrow. Therefore, we used stoichiometry composition of wollastonite as a base composition.

3. RESULTS AND DISCUSSION

3.1 Structure of glasses

Figure 1 depicts the FT-IR spectra of glasses in the presence of variable amounts of ZnO and Fe₂O₃ additives. Each chemical band in molecule vibrates at a frequency which is characteristic of that band. Because of the stretching and bending motions of a group of atoms in molecule, multiple modes of oscillation may occur in molecule. If a change happens in dipole by an oscillation then it will absorb a photon which has the same frequency. The vibration frequencies of most molecules correspond to the frequencies of infrared light. The bands in the range of 850 - 1040 cm⁻¹

might be attributed to the asymmetric stretch vibrations of SiO₄ tetrahedral with different non-bridging oxygens (NBOs). A broadband with main peaks at 925 - 930 cm⁻¹, 990 cm⁻¹ and 1020 - 1040 cm⁻¹ are related to presence of asymmetric stretch vibrations of Si-O⁻ bonds in Q¹ tetrahedral units, Q² tetrahedral units and coexistence of various asymmetric stretch vibrations of Si-O⁻ bonds in Q² and Q³ tetrahedral units, respectively (Qⁿ = [SiO₄]-tetrahedral with (n-1) non bridging oxygen). These peaks are formed resulting in network-modification by cations of additives. Shoulder at 850 cm⁻¹ shows the Q⁰ unit. Two bands at low frequency i.e. 509 and 710 cm⁻¹, indicate rocking motions and bending vibrations of Si-O-Si bridges, respectively. It is well known that Q¹ tetrahedral units (i.e. [Si₂O₇]⁶⁻ dimer) and Q² tetrahedral units (i.e. single chain silicate, [SiO₃]²⁻) constitute soro-silicates and ino-silicates in the structure of silicate glasses.^[4] Also after sintering these glasses, it will be indicated that main crystalline phase are wollastonite and akermanite. These crystalline phases are attributed to ino-silicate and soro-silicate structures, respectively. With increasing the amount of modifier and according to high field strength of cations in the glass structure, disordering and bandwidth of Q-species is enhanced.^[5]

**Fig. 1.** FT-IR spectra of the investigated glasses.

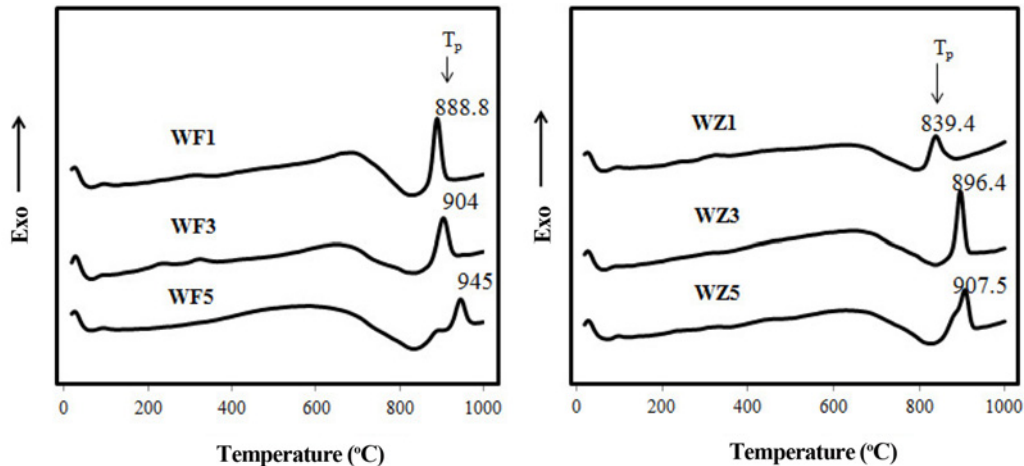


Fig. 2. DTA curves of glasses with a heating rate of 10°C/min.

3.2 Thermal behavior

Figure 2 represents DTA curves of specimens containing ZnO and Fe₂O₃ additives. With increasing of ZnO and Fe₂O₃ contents, peak crystallization temperature (T_p) increases as shown in Fig. 2. This increase can be attributed to high field strength of Zn⁺² (0.53) and Fe⁺³ (0.88) ions.^[6] These ions make strong bonds with oxygen anions and gradually increase the viscosity of glasses. Therefore, crystallization energy increases. Besides, as the ZnO and Fe₂O₃ content of specimens increases, crystallization ability of akermanite goes up as well. According to ternary phase diagram of the CaO-SiO₂-MgO system, crystallization of akermanite happens in higher temperatures than wollastonite.^[7] Compositions in

which Fe₂O₃ plays the role of modifier, display a higher T_p than those containing ZnO. It is probably due to the higher field strength of Fe⁺³ than Mg⁺², Ca⁺², and Na⁺, and its stronger bonds composed with oxygen anions in the glassy structure.^[6]

3.3 Crystallization, sinterability and dielectric properties

Figure 3 illustrates XRD patterns of all specimens after heat treatment at their crystallization peak temperatures for 1 h. According to Fig. 3(a), the main phase in WZ1 was wollastonite (CaSiO₃) and other phases were akermanite (Ca₂MgSi₂O₇), sodium calcium silicate (Na₂Ca₂Si₃O₉) and pseudo-wollastonite (Ca₃Si₃O₉), respectively. As the amounts

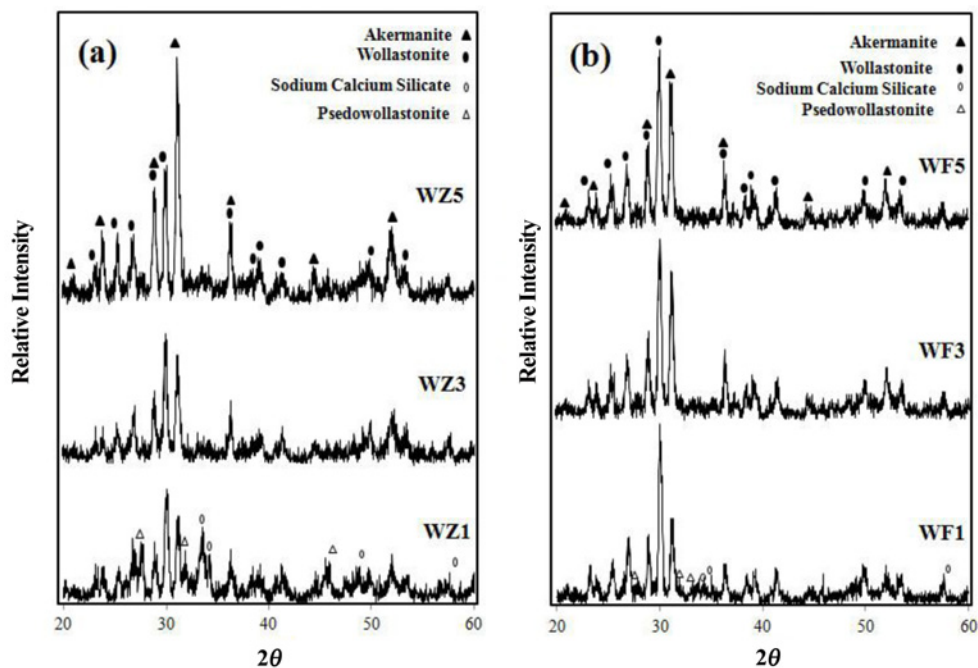


Fig. 3. XRD patterns of glass ceramics heat treated at their DTA peak crystallization temperature for 1 h.

of ZnO increased, sodium calcium silicate and pseudo-wollastonite, phases decreased while wollastonite and akermanite. Improvement of akermanite was predominant upon the other phase. Similar to WZ1, the main phase of WZ3 was wollastonite while akermanite was increased greatly and akermanite was as the main phase in WZ5. Wollastonite was the main phase in all the samples containing Fe₂O₃ as shown in Fig. 3(b). Wollastonite and akermanite increased with increasing of Fe₂O₃ contents. In sample WF1, sodium calcium silicate and pseudo-wollastonite were minor phases. Again by increasing the Fe₂O₃ content, especially in WF5, more crystallized akermanite was detected. The reason may be due to the high field strength of Zn⁺² and Fe⁺³ ions resulting in phase separation of glasses and the reduction of activation energy of crystallization.^[8] Crystallization of akermanite in glass ceramics containing ZnO was more than those containing Fe₂O₃. It's probably due to the same field strength and coordination number of Zn⁺² and Mg⁺² ions.

Table 2 shows dielectric properties and relative density of glass ceramics heat treated at peak crystallization temperature for 1 h.

As it was mentioned in section (2), dielectric properties i.e. dielectric constant and dielectric loss, were measured by network analyzer through waveguide transmission line rout in 9 GHz. Complex permittivity (ϵ_r) were calculated by measurement of S parameters (i.e. S₁₁ : reflected signal and S₂₁ : transmitted signal). In this case, the real part is dielectric constant and the proportion of imaginary part to real part is dielectric loss.^[9] Dielectric constant and dielectric loss depend mainly on the precipitated crystalline phase, density and porosity of glass ceramics.^[10,11] Dielectric Constant of materials can be assessed according to the following equation when the crystalline grains are aligned randomly,

$$\log \epsilon = \sum v_i \log \epsilon_i \quad (1)$$

Where, v_i and ϵ_i are the volume fraction and the dielectric constant of phase i , respectively.^[2]

The total dielectric loss is the sum of intrinsic and extrinsic losses. Intrinsic dielectric losses are related to perfect crystals which depend mainly on the crystal structure. Extrinsic losses are associated with imperfections in the crystal lattice such as impurities, microstructural defects, porosity, micro-cracks, random crystallite orientations, vacancies, dopant atoms and so on.^[12] Four different dielectric loss mechanisms

are known in glassy materials:

- (1) Conduction loss through electric conductivity,
- (2) Dipole relaxation loss from relaxation necessitated when the alkali ions, OH⁻ ions and some others reciprocate between the adjacent positions due to the electric fields,
- (3) Distortion loss when the network structure of glass distorts due to the electric field, and dipole orientation occurs momentarily and,
- (4) Ion vibration loss taking place when there is a resonance at the proper oscillation frequency initiating by the mass of structural ions and the chemical bonding strength of the surroundings.^[13]

Dielectric constant of glass ceramics increases by enhancement of ZnO and Fe₂O₃, as shown in Table 2. It is shown in Fig. 3 that more ZnO and Fe₂O₃ content resulted in more akermanite phase. Hence it will be quoted that akermanite has a higher dielectric constant than the other crystallized phases in this system. CaSiO₃ ceramics possess excellent dielectric properties: $\epsilon_r = 5$, $\text{tg} \delta = (1.0-3.0) \times 10^{-4}$.^[14] Therefore, dielectric properties of wollastonite are better than akermanite. WZ1 and WF1 demonstrate lower dielectric constant than other specimens. It's probably due to the predominance wollastonite phase in WZ1 and WF1.

Sintering behavior of WZ1 and WF1 glasses were carried out at temperatures ranging from 790°C to 910°C for 1 h at heating rate of 10°C/min. Figure 4 shows the variation of

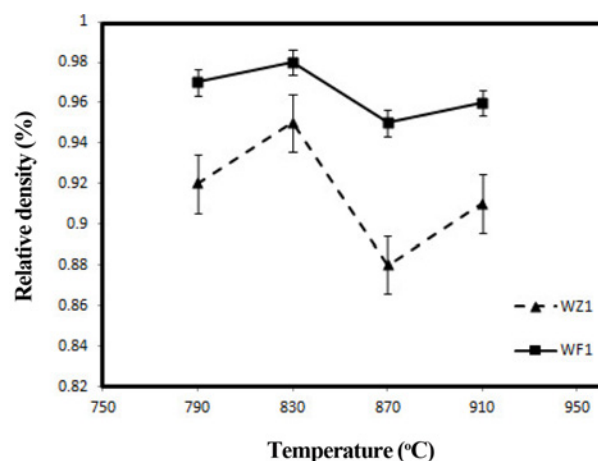


Fig. 4. Relative densities of WZ1 and WF1 heat treated at various sintering temperatures.

Table 2. Dielectric properties of samples 9 GHz.

WF5	WF3	WF1	WZ5	WZ3	WZ1	Samples
$\epsilon = 6.93 - 0.022j$	$\epsilon = 7.06 - 0.070j$	$\epsilon = 6.42 - 0.012j$	$\epsilon = 7.51 - 0.035j$	$\epsilon = 6.96 - 0.010j$	$\epsilon = 6.28 - 0.015j$	$\epsilon = \epsilon' + \epsilon'' * j$
6.93	7.06	6.42	7.51	6.96	6.28	Dielectric constant (ϵ')
0.0031	0.0090	0.0018	0.0046	0.0014	0.0040	Dielectric loss ($\text{tg} \delta = \epsilon'' / \epsilon'$)
0.97	0.98	0.98	0.96	0.97	0.90	Relative density

relative density of glass ceramics WZ1 and WF1 with sintering temperature.

Glass ceramics containing ZnO were demonstrated lower relative density than those containing Fe₂O₃ and this can be attributed to the further crystallization of akermanite in WZ1 and increasing the viscosity of amorphous phase which in turn leads to unfavorable sinterability. It is clear that the optimum sintering temperature of both WZ1 and WF1 are 830°C. As the sintering temperature goes up, relative density decreases at 870°C. It's probably because of the progress of crystallization before enough densification.

XRD pattern of WZ1 and WF1 heat treated at various sintering temperatures are shown in Fig. 5.

It can be seen that wollastonite has been precipitated more

in glass ceramics containing 1 wt. % Fe₂O₃ compare with the glass ceramics containing 1 wt. % ZnO. At lower temperatures sodium calcium silicate (Na₂Ca₂Si₃O₉) (only in WZ1 glass ceramics), pseudo-wollastonite (Ca₃Si₃O₉), wollastonite and akermanite had been precipitated in glass ceramics. Upper sintering temperatures reduced sodium calcium silicate the same as pseudo-wollastonite, and raised akermanite similar to wollastonite.

Dielectric properties of WZ1 and WF1 glass ceramics at various sintering temperatures have been shown in Fig. 6. As it was discussed earlier, dielectric constant of glass ceramics depend mainly on the relative density and crystalline phase. It can be seen that dielectric constant and dielectric loss decreased as sintering temperatures increased. According to

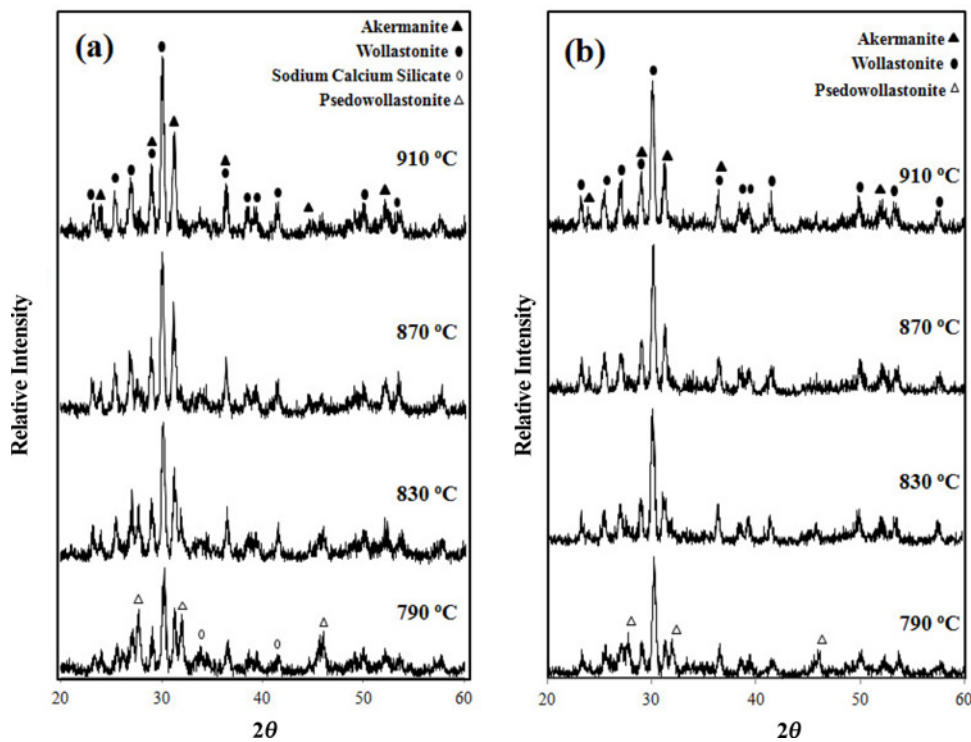


Fig. 5. XRD patterns of glass ceramics heat treated at various temperatures for 1 h, (a) WZ1 glass ceramics and (b) WF1 glass ceramics.

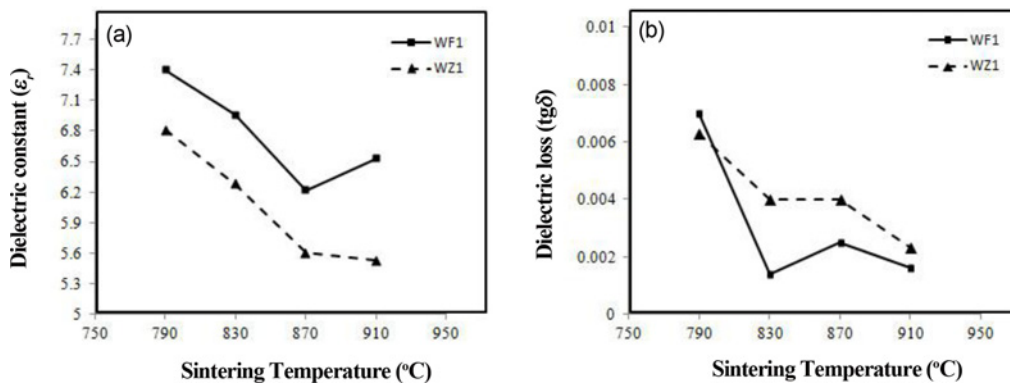


Fig. 6. Dielectric properties of WZ1 and WF1 heat treated at various temperatures for 1 h, (a) Dielectric constant and (b) Dielectric loss.

equation (1), relative density curve and XRD patterns of WZ1 and WF1, it is probably due to promotion of crystallinity and variation of relative density. Dielectric constant of porosity is nearly 1, dielectric constant will go down with

relative density decrease. By increasing temperature from 790°C to 830°C, relative density was increased but dielectric constant decreased and this may be due to crystallization of more wollastonite. The minimum dielectric loss was for the

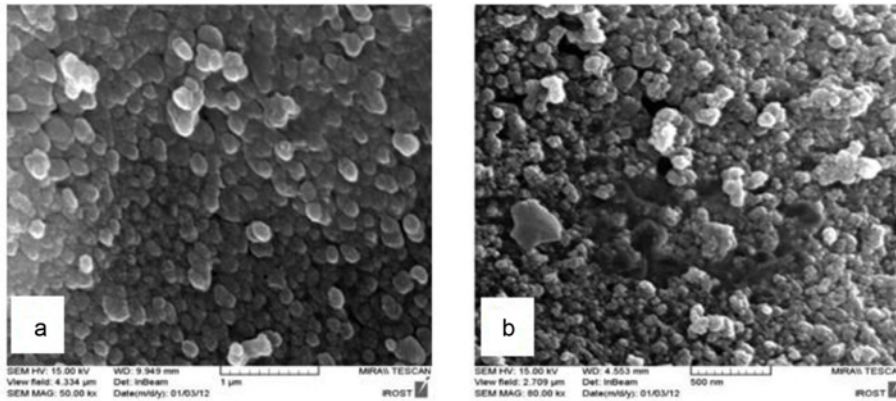


Fig. 7. SEM micrograph of WF1 glass, (a) 40000× and (b) 80000×.

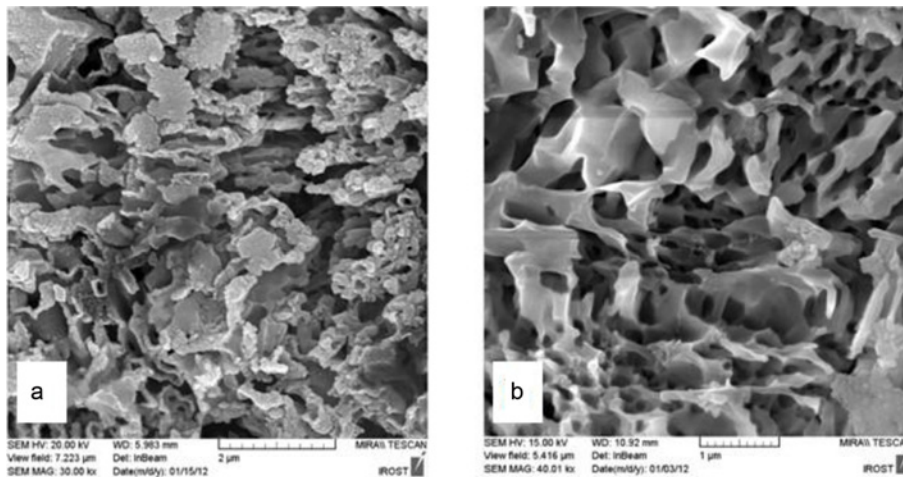


Fig. 8. SEM microstructure of WZ1 glass ceramic, (a) 30000× and (b) 40000×.

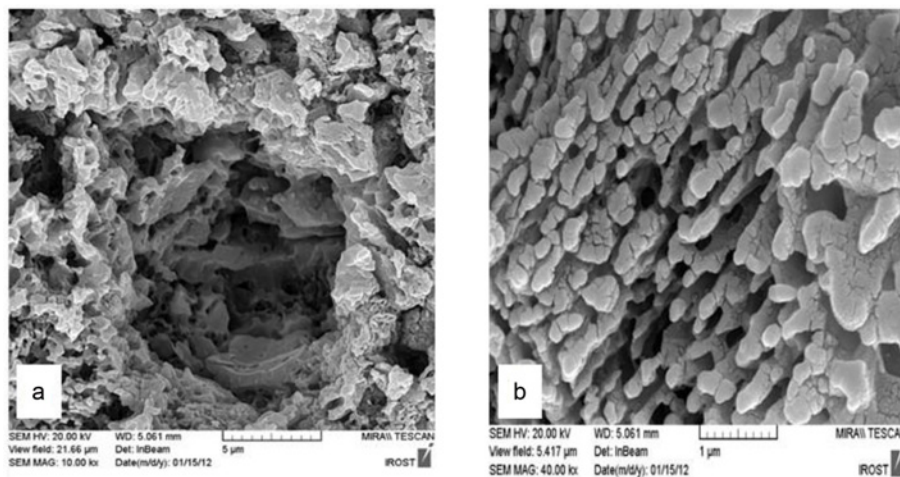


Fig. 9. SEM microstructure of WF1 glass ceramic, (a) 10000× and (b) 40000×.

sample sintered at 830°C. It is probably due to highest relative density or the minimum porosity. WZ1 glass ceramics have a lower dielectric constant and a higher dielectric loss than WF1 glass ceramics. Moreover, WZ1 glass ceramics have a lower relative density than WF1 samples.

3.4 SEM micrograph

Figure 7 depicts SEM micrograph of WF1 glass. An obvious phase separation can be detectable in the figure and it can be attributed to crystallization of akermanite.

Microstructures of WZ1 and WF1 heat treated at 830°C for 1 h are shown in Figs. 8 and 9, respectively. The high porosity was detectable in the microstructure of WZ1 glass ceramic. Small acicular crystals in microstructure of WZ1 and WF1 glass ceramics may be attributed to wollastonite phase.

4. CONCLUSIONS

This study examined the crystallization, sintering and dielectric behavior of CaO-SiO₂-Na₂O-MgO glass-ceramics containing ZnO and Fe₂O₃ additives. Following conclusions were determined from this study.

- Glass frits were prepared via rapid quenching in water with melted glasses at 1400°C for 1 h. The main constituents of glass network were Q¹, Q² and Q³ units. Obvious phase separation was detected in glass microstructures.
- After heat treatment at crystallization peak temperature, all specimens showed wollastonite and akermanite as their main phases. Crystallization of akermanite increased by increasing ZnO and Fe₂O₃ contents of samples. ZnO addition facilitate akermanite to be crystallized more than Fe₂O₃ in this system.
- Wollastonite was crystallized more in WZ1 and WF1 glass ceramics.
- Dielectric constant was increased by crystallization of akermanite. Dielectric constant and dielectric loss of all

glass ceramics were in range of 5.5-7.4 and 0.001-0.009, respectively.

- Optimum sintering temperature for WZ1 and WF1 glass ceramics was 830°C and their relative densities were 0.95 and 0.98, respectively.

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