SERAMİK
Journal of the Turkish Ceramics Society

Seramik - Journal of the Turkish Ceramics Society, 2 (1) 1-6 (2022)

Özgün Araştırma Makalesi / Original Research Article

Comparison of the Effect of TiO_2 and ZrO_2 Nucleating Agents on Mechanical & Physical Properties of $MgO-Al_2O_3-SiO_2-B_2O_3$ (MASB) System Glass-Ceramics

Melih Tümer, Bahadır Aydın, Zafer Yavuz Merkit, H. Özkan Toplan, Nil Toplan

Sakarya University, Engineering Faculty, Department of Metallurgical and Materials Engineering, 54187, Sakarya, Türkiye

Sorumlu Yazar / Corresponding Author
Melih Tümer
melihtumer9@gmail.com

Makale Bilgisi / Article Info
Sunulma / Received : 14/08/2021
Düzeltme / Revised : 06/11/2021
Kabul / Accepted : 18/11/2021

Destekleyen Kuruluş / Funding Agency
Sakarya University Scientific Research Projects Coordinatorship (BAP)
Project: 2021-7-24-7

Anahtar Kelimeler
MASB cam-seramik
Safirin
Sinterleme
Spinel

Keywords
MASB glass-ceramics
Sapphirine
Sintering
Spinel

ORCID
Melih Tümer
https://orcid.org/0000-0002-6918-0447
Bahadır Aydın
https://orcid.org/0000-0003-3414-4224
Zafer Yavuz Merkit
https://orcid.org/0000-0002-5549-5229
H. Özkan Toplan
https://orcid.org/0000- 0002-3928-2733
Nil Toplan
https://orcid.org/0000-0003-4130-0002

Abstract

In this study, the effect of TiO_2 and ZrO_2 nucleating agents on the mechanical and physical properties of $MgO-Al_2O_3-SiO_2-B_2O_3$ (MASB) system glass-ceramics were investigated. Three different glass compositions were prepared by using different nucleating additives according to the phase region determined from the MAS ternary diagram. MASB glasses were obtained via melting at 1500°C with a heating rate of 5°C/min. Differential thermal analysis (DTA) was applied to determine the heat treatment procedure, glass transition temperature (T_g) and crystallization peak temperature (T_p). The crystallization process was carried out by heating the samples from room temperature to 900°C, 1000°C and 1100°C for 1 hour at a heating rate of 5°C/min, based on the results of DTA. The phase analysis of glasses and glass-ceramics were performed by X-ray diffraction analysis (XRD) and microstructures were examined with scanning electron microscope (SEM). Vickers hardness test and Archimedes density measurements were also conducted to determine their physical and mechanical properties. The results show that sapphirine is the major phase in glass-ceramics where only TiO2 is used as nucleating agent, while the spinel phase is the main phase in glass-ceramic samples in which ZrO_2 as the nucleating agent.

TiO_2 ve ZrO_2 çekirdeklendirici ajanların $MgO-Al_2O_3-SiO_2-B_2O_3$ (MASB) sistemi cam-seramiklerin mekanik ve fiziksel özelliklerine etkisinin karşılaştırılması

Özet

Bu çalışmada, TiO_2 ve ZrO_2 çekirdeklendiricilerinin $MgO-Al_2O_3-SiO_2-B_2O_3$ (MASB) esaslı cam-seramiklerin mekanik ve fiziksel özellikleri üzerine olan etkisi araştırılmıştır. Bu amaç doğrultusunda üç farklı cam kompozisyonu MAS üçlü denge diyagramında belirlenen faz bölgesine göre farklı çekirdeklendirici katkılar eklenerek hazırlanmıştır. MASB camları 5°C/dak ısıtma hızında 1500°C sıcaklığa çıkılarak ergitme yöntemiyle üretilmiştir. Isıl işlem parametreleri ile birlikte camsı geçiş sıcaklığı (T_g) ve kristalizasyon pik sıcaklıklarının (T_p) belirlenebilmesi için üretilen camlara Diferansiyel Termal Analiz (DTA) uygulanmıştır. Kristalizasyon işlemleri DTA analizlerinden elde edilen veriler ışığında 5°C/dak ısıtma hızında oda sıcaklığından 900°C, 1000°C ve 1100°C sıcaklıklara çıkılarak 1 saat süreyle gerçekleştirilmiştir. Üretilen cam ve cam-seramik numunelerin faz tayinleri X-ışını kırınım analizi (XRD) ile gerçekleştirilirken, taramalı elektron mikroskobu (SEM) mikroyapıların incelenmesinde kullanılmıştır. Vickers sertlik testi ve Arşimet yoğunluk ölçümleri numunelerin fiziksel özelliklerinin anlaşılabilmesi için gerçekleştirilmiştir. Elde edilen sonuçlar sadece TiO_2'nin çekirdeklendirici olarak kullanıldığı kompozisyonlarda yapıdaki baskın fazın safirin olduğunu ortaya koyarken, çekirdeklendirici olarak sadece ZrO_2'nin kullanıldığı durumda ise spinel fazının cam-seramik bünyelerde baskın faz olarak çökeldiğini göstermektedir.

1. INTRODUCTION

Glass-ceramic materials are advanced materials in which many phases can be precipitated in their glassy structures in accordance with the composition in which they are synthesized from, and their properties also differ according to these precipitated phases[1,2]. $MgO-Al_2O_3-SiO_2$ (MAS) system glass-ceramics find wide industrial application areas due to possess superior mechanical properties, chemical resistance, low dielectric constant and thermal shock resistance[3]. These abovementioned properties of MAS glass-ceramics depend on crystalline phases such as sapphirine, cordierite, mullite, spinel and cristobalite, which can be precipitated during the heat treatment process by adjustments in the compositions[3-5]. Various oxides such as Cr_2O_3, TiO_2, Fe_2O_3, CaF_2, V_2O_5 and ZrO_2 can be used in this glass system as nucleating agents to promote nucleation and crystallization process[6].

Although many methods can be used in the fabrication of glass-ceramics today; melting, sintering and sol-gel methods stand out as the basic methods[7].

In this study MAS-based glass-ceramics with boroxide content as fluxing agent were successfully synthesized by melting and subsequent crystallization process. The effect of TiO_2, ZrO_2 nucleating agents along with their combined (TiO_2+ZrO_2) effect on crystallization ability, mechanical, microstructural, physical properties and phase distribution of MAS glass-ceramics were investigated.

2. METHODS

$MgO-Al_2O_3-SiO_2-B_2O_3$ (MASB) glasses were prepared using reagent grade $MgCO_3$, Al_2O_3, SiO_2, H_3BO_3, Sb_2O_3, TiO_2 and ZrO_2 raw materials according to the chemical composition given in Table 1.

Table 1. The chemical composition of the MASB glasses with different nucleating additives.

	Glass compositions (mol%)		
	MASB-T	MASB-Z	MASB-TZ
MgO	37.72	37.72	37.72
Al_2O_3	20.45	20.45	20.45
SiO_2	24.35	24.35	24.35
B_2O_3	12.8	12.8	12.8
TiO_2	4.46	-	2.23
ZrO_2	-	4.46	2.23
Sb_2O_3	0.22	0.22	0.22

In this experiment, boroxide derived from boric acid were introduced as fluxing agent, TiO_2 and ZrO_2 served as nucleating agent and Sb_2O_3 was used as fining agent. Starting materials were precisely weighed and homogenized by ball milling for 24 h in dry conditions. Homogenized powder mixtures were first heated at 900°C for 1 h to make carbonates decompose and then melted at 1500°C in alumina crucibles for 2 h. Melts were poured into graphite mould and to eliminate residual stress annealing process was conducted at an electric furnace at 600°C for 1h. Considering the differential thermal analysis (DTA) results, two-stage heat treatment process (nucleation and crystallization) were employed to convert MASB glasses to glass-ceramics. DTA measurements (DTA, Netzsch STA 449, Germany) were performed to determine the specific glass transition (Tg) and crystallization (Tc) temperatures of MASB glass samples. For this purpose, powdered glass samples (< 45µm) were prepared, and tests were carried out from room temperature to 1200°C with a heating rate 5°C min^{-1} using α-alumina as a reference material under air atmosphere.

X-ray diffraction analysis (XRD, Rigaku D/Max/2200/PC, Radiation=Cu Kα radiation, 2θ= 10-80°, Step size=2°/min.) was performed to determine the phase evolution of synthesized MASB glass-ceramics. In order to examine glass-ceramic microstructure and determine possible crystals, scanning electron microscope (SEM, Jeol 6060LV) analyses were performed. SEM analyses were performed on the polished surfaces of the samples, so the sample surfaces were prepared properly and etched with 5% HF for 90 s and then coated with a thin gold layer. Hardness of the MASB glass-ceramics were measured with a Vickers indenter (Leica) with a load of 50 g and 10 s loading time. To ensure the accuracy of the results, 5 indentation tests were performed on each sample and average values were taken into account. The bulk densities of MASB glass-ceramic samples were calculated by Archimedes method using the distilled water as the medium.

3. RESULTS AND DISCUSSION

3.1. DTA Results

Fig. 1 shows the DTA curves of the MASB glasses obtained at a heating rate of 5°C min^{-1}. DTA curves of the MASB glasses exhibit an endothermic peak corresponding to the glass transition temperature (Tg) between 685-713°C and an exothermic peak refers to crystallization peak temperature (Tp) between 800-826°C. Different from the MASB-T and MASB-Z compositions, another small exothermic peak was detected at 920°C in the DTA graph of the MASB-TZ composition at a heating rate of 5°C min^{-1}.

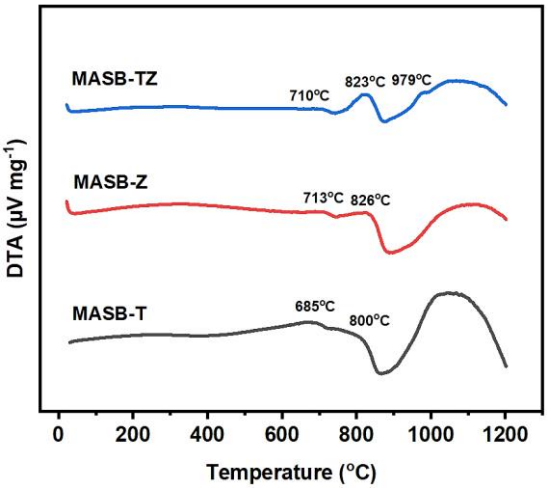

Figure 1. DTA result of MASB glass powders at a heating rate of 5°C min^{-1}.

3.2. XRD Results

The XRD analyses of the MASB glass-ceramics that obtained via heat

treatment at 900-1100ºC for 1 hour were given in Fig. 2-4. Fig. 2 shows the XRD pattern of MASB-T glass-ceramics which comprise TiO_2 as nucleating agent and at 900 ºC crystallization temperature only consist of boromullite ($Al_9BSi_2O_{19}$) crystalline phase. However, it was observed that with the increase the temperature to 1000 and 1100ºC, quartz, spinel ($MgAl_2O_4$), rutile (TiO_2) and sapphirine ($(Mg,Al)_4(Al,Si)_2O_{20}$) phases were also precipitated besides boromullite crystals.

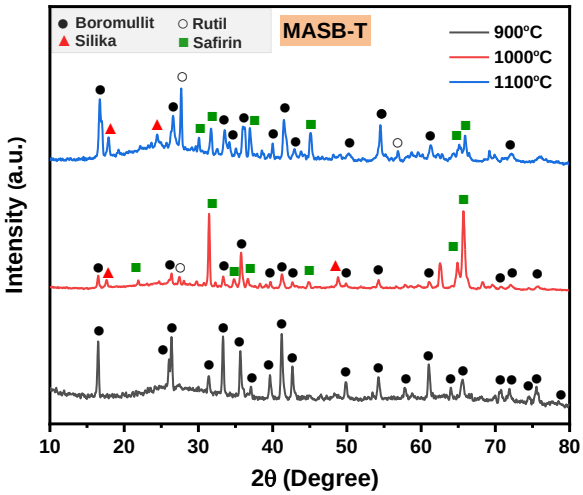

Figure 2. XRD results of MASB-T glass-ceramics.

When the XRD result of the sample with a crystallization temperature of 1100°C was examined, no different phase was observed in the structure from the sample crystallized at 1000°C. Noticeable changes for peak intensity related for sapphirine. The crystal structure of the sapphirine crystal formed in the aluminium rich and poor in the silicon zone that consists of an anion network formed by oxygen atoms with Al+Si and Al Mg tetrahedral and octahedral spaces[8]. Shao et al. applied crystallization to the glass in the $MgO-Al_2O_3-SiO_2-TiO_2$ system with a waiting time of 2 hours. They observed that as a result of this crystallization process, α-quartz and sapphirine were formed in addition to β-quartz at 950°C and β-quartz at 1000°C, respectively[9]. The results are in agreement with the work of Shao et al. The crystallization phases peak of MASB-Z that heat treated at 900-1100ºC was shown at Fig3. As a result, it is seen that there is an amorphous structure in the sample at 900°C due to non-crystallized. When the crystallization temperature is rise up 1000°C, boromullite phase and spinel phase are seen in the structure. In addition to these, silica and zircon precipitation are observed. When the XRD analysis at the crystallization temperature was 1100°C, it was observed that the phases in the structure were not different from the phases of the sample crystallized at 1000°C. Seidel et al. investigated the effect of CeO_2 additive on $MgO-Al_2O_3-SiO_2-ZrO_2$ glasses. When they crystallize these glasses at 1060°C for 1 hour, they reported that quartz, spinel and zirconia phases were present in the microstructure[10].

When the XRD results of MASB-TZ for 900-1100ºC (Figure 4) is examined, the amorphous structure is dominant in the sample with a crystallization temperature of 900°C, but the boromullite peaks have started to be seen as very small. When the crystallization temperature is 1000°C, boromullite, sapphirine and spinel phases are observed in the structure. In addition to these, rutile, zirconia and silica were deposited in the structure. When the phases with a crystallization temperature of 1100°C are examined, it is seen that they are the same as the phases at 1000°C. Carl et al. investigated the crystallization behavior of $MgO-Al_2O_3-SiO_2-TiO_2-ZrO_2$ glasses. They reported that as a result of crystallization at 1050°C for 3 hours, zirconium titanate, spinel, sapphirine and cristobalite were observed in addition to the quartz solid solution in the structure[11].

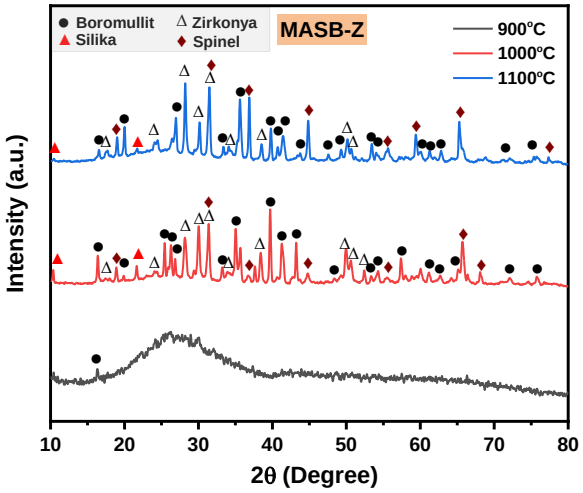

Figure 3. XRD results of MASB-Z glass-ceramics.

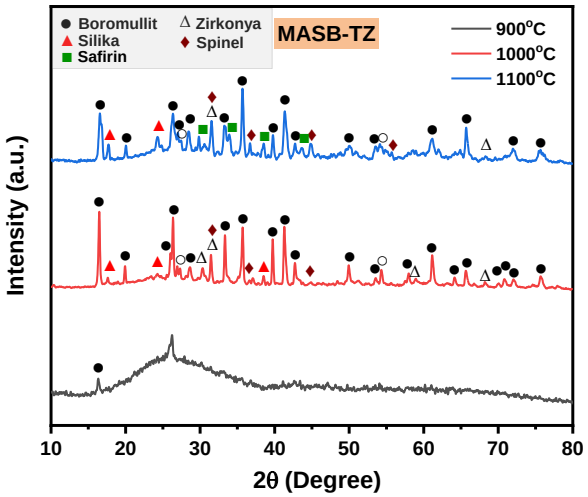

Figure 4. XRD results of MASB-TZ glass-ceramics.

3.3. Vickers Hardness Tests Results

Vickers Hardness values were determined by applying a load under 50 gram-force (gf) for 10 seconds on the crystallized samples surfaces. The measurements were made from at least five different points and the average values of these measurements were taken. Fig. 5. shows the hardness values of MASB-T, MASB-Z and MASB-TZ glass-ceramics samples that sintered at different temperatures for 1 h.

When the hardness values of MASB-T are examined, it is seen that the hardness values increase as the crystallization temperature increases. The hardness value increased significantly when the crystallization temperature increased from 900°C to 1000°C. This is thought to be due

to the formation of the sapphirine phase at 1000°C, unlike 900°C. In addition, when the hardness values at 1000°C and 1100°C are examined, it is seen that the values are very close to each other. Because there is no different phase between 1000°C and 1100°C. When the hardness values of MASB-Z glass-ceramics were examined, the hardness values increased significantly with the increase in crystallization temperature. This increase in hardness values is thought to be due to the formation of the boromullite phase from the amorphous structure, and then the formation of the spinel phase.

When the hardness values of the samples with the same crystallization temperatures of MASB-T and MASB-Z are compared, the hardness of MASB-T is higher at 900°C. Because there is boromullite phase in MASB-T at 900°C but amorphous structure is seen in MASB-Z. In other words, while MASB-T is glass-ceramic at 900°C, MASB-Z is still in amorphous form. The hardness of glass-ceramics is generally higher than glass. When the crystallization temperature is 1000°C, the hardness of MASB-T is higher than MASB-Z. Because, as a result of crystallization at 1000°C, in addition to boromullite, sapphirine, a hard phase, is also seen in the structure of MASB-T. In the case where the crystallization temperature is 1100°C, the hardness value of MASB-Z is higher than MASB-T. Because at 1100°C, spinel phase was prominently formed in the structure of MASB-Z. Consequently, when the hardness values of MASB-TZ were examined, the hardness value increased as the crystallization temperature increased, just as in MASB-Z.

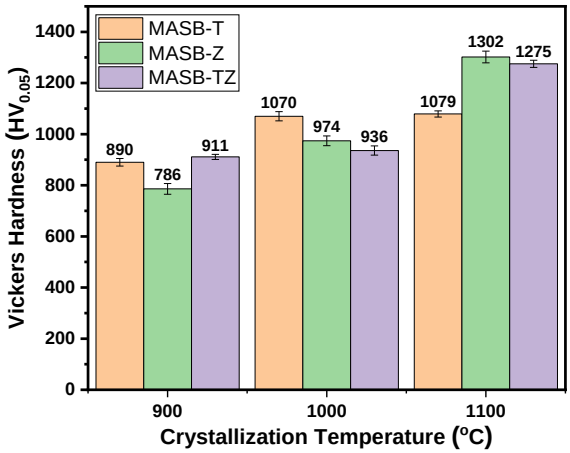

Figure 5. Vickers hardness values of MASB glass-ceramics.

3.4. Archimedes Density Test Results

The results of the Archimedean density tests of MASB-T, MASB-Z and MASB-TZ glass-ceramics crystallized at 900, 1000 and 1100°C for 1 hour are given graphically in Figure 6.

When the results in Figure 6 are examined, the density value of MASB-T glass-ceramic was the same at 900°C and 1000°C, while the density decreased at 1100°C. Unlike 900°C, MASB-T has sapphirine, precipitated silica and rutile in its structure at 1000°C. From this point of view, if the crystallization temperature rises from 900°C to 1000°C, the density is expected to increase. However, the density value at 1000°C was the same as the density value at 900°C due to the voids formed in the material due to the precipitated phases. In the case where the crystallization temperature was 1100°C, the density decreased slightly. From this point of view, it can be concluded that the crystallization temperature should be as low as possible in order to obtain a dense structure in TiO_2 added MASB glass-ceramics.

In MASB-Z glass-ceramics, the density increased significantly as a result of increasing the crystallization temperature from 900°C to 1000°C. This can be explained by the transformation of the amorphous structure at 900°C into a crystalline structure at 1000°C. The density value at the crystallization temperature of 1100°C decreased insignificantly compared to the value at 1000°C.

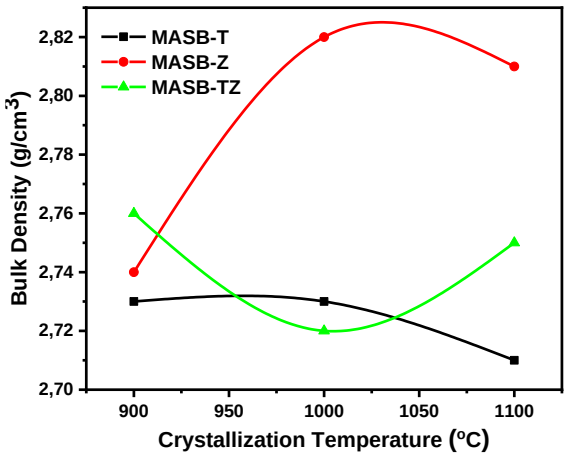

Figure 6. Archimedes density values of MASB glass-ceramics.

When the density values of MASB-T and MASB-Z glass-ceramics at the same crystallization temperature are compared with each other, it is observed that the density values of MASB-Z are significantly higher than MASB-T at all crystallization temperatures. The main reason for this situation is related to the higher molecular weight of ZrO_2, which is used as nucleating agent, compared to TiO_2. In MASB-TZ glass-ceramics, the density decreases significantly when the crystallization temperature is 1000°C. However, the density value slightly increased when the crystallization temperature was 1100°C. While boromullite peaks were formed at 900°C in MASB-TZ glass-ceramic, spinel and sapphirine phases tried to form together in addition to boromullite at 1000°C. Both TiO_2 and ZrO_2 were used as nucleators in MASB-TZ glass-ceramics. This is why spinel and sapphirine are formed together at 1000°C. Because while TiO_2 additive promotes the formation of sapphirine, ZrO_2 additive promotes spinel formation. If the crystallization temperature rises from 1000°C to 1100°C, no new phase is formed in the structure. From this point of view, it can be thought that the reason for the increase in density from 1000°C to 1100°C is the decrease in porosity with the effect of high temperature. The density value of MASB-TZ containing both TiO_2 and ZrO_2 at 1100°C is between the density value of MASB-T containing only TiO_2 and MASB-Z containing only ZrO_2. This proves that ZrO_2 added to MASB glass-ceramics forms a denser material than TiO_2. Liu et al. have done structure, characterization and property analysis by adding Cr_2O_3 to the MASB system. The density values they found in their study ranged from 2.652 g/cm^3 to 2.761 g/cm^3 according to the change in the amount of nucleating additives[12].

3.5. SEM Results

Fig. 7 shows the polished surface SEM micrographs at 1000X magnification of MASB-T, MASB-Z and MASB-TZ glass-ceramics, which were crystallized for 1 hour at 900, 1000 and 1100°C. Dendritic structures are prominent in the sample containing the addition of TiO_2 nucleator after heat treatment at 900ºC. Although no crystal phase can be detected in the image of glass-ceramic containing only ZrO_2, there is an amorphous appearance as indicated in the XRD analysis. In the MAS-TZ sample, where TiO_2 and ZrO_2 are used together, there are light coloured crystals precipitated in the glass phase. By increasing the temperature to 1000ºC, the formation of dark-coloured dendritic crystals becomes evident, while light-coloured dendritic crystals are present with ZrO_2. However, the addition of TiO_2 encouraged the formation of rod-like structures. At 1100ºC, an increase in the size of light-coloured rod-like structures was observed in all three compositions. The resulting structures exhibit three-dimensional growth behaviour.

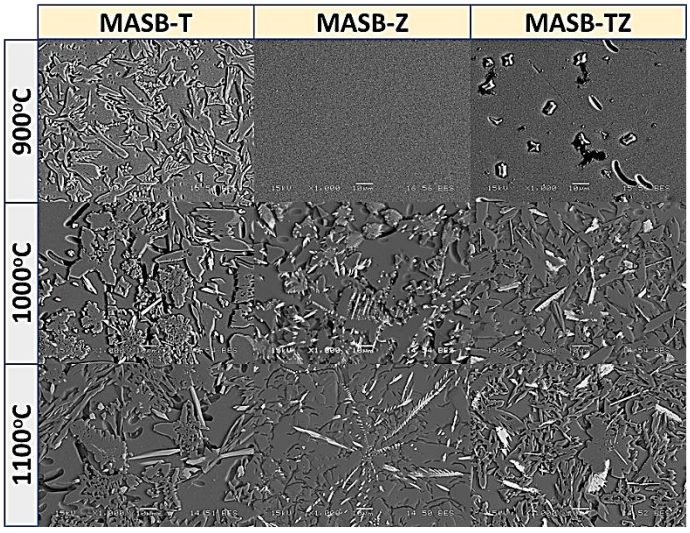

Figure 7. SEM images of MASB glass-ceramics.

In order to identify the crystals in the microstructure of MASB glass ceramics with various nucleating additives, the results of the EDS analysis at temperatures between 900-1100°C are given in Figure 8.

According to these results, it is seen that the sample, in which TiO_2 was added at 900ºC, is rich in the amount of “Al” and “Si” elements in regions 1 and 3. Since element “B” could not be detected in the EDS analysis, it can be said that this region corresponds to the boromullite phase detected in the XRD analysis. Region 2 contains “Mg, O, Si, Al” elements and forms the glass phase region. For the MASB-Z coded composition containing ZrO_2 at 1100ºC; “Mg, Si, O, and Al” elements were detected at points 2 and 3, along with the glass region number 1. These rod-like structures form the sapphirine phase. In addition, ZrO_2 added as nuclei promoted the formation of this phase. Area 2 and 3 for the composition of MASB-TZ at 1000°C corresponds to the structure of boromullite because it contains “Al, O and Si” elements. The light-coloured dot 1 shows the presence of ZrO_2 added as nuclei.

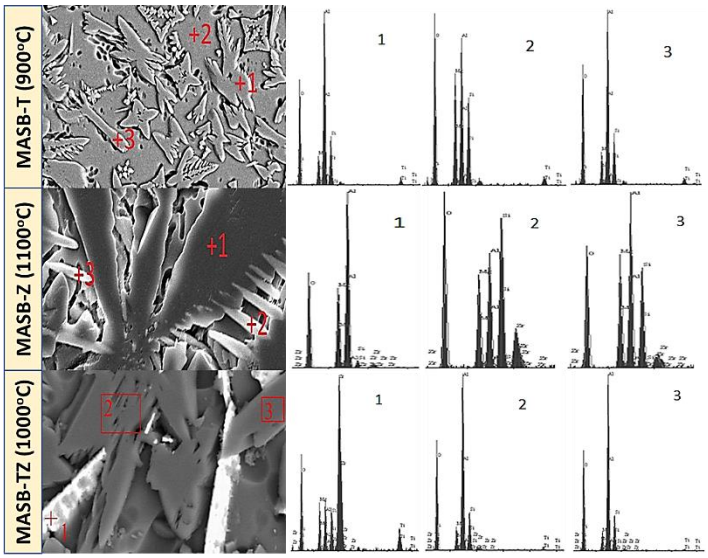

Figure 8. EDS Results of MASB glass-ceramic crystallized at different temperatures.

4. CONCLUSIONS

In the present study, the effect of TiO_2 and ZrO_2 added to MASB glass-ceramics as nucleators was investigated. Looking at the results of the study, it is seen that the dominant phase is the sapphirine phase only in the TiO_2 added sample. However, the spinel phase is the dominant phase only in the ZrO_2 doped sample. In addition, in samples where TiO_2 and ZrO_2 are used together, the dominant phases are sapphirine and spinel phases. From this point of view, it can be concluded that TiO_2, which is added to MASB glass-ceramics as a nucleator, promotes the sapphirine phase and ZrO_2 promotes the spinel phase. In addition, when the XRD results of the samples crystallized at 900°C are examined, the sample containing TiO_2 has a boromullite phase, while the sample containing ZrO_2 has an amorphous structure. However, peaks of boromullite phase started to occur at very low intensity in the sample where TiO_2 and ZrO_2 were added together. From this point of view, it can be concluded that the addition of TiO_2 to MASB glass-ceramics promotes the crystallization ability more than ZrO_2 at low temperatures.

When crystallized at high temperature, the hardest sample is the sample containing ZrO_2. The sample with the lowest hardness is the sample containing TiO_2. The hardness of the sample containing TiO_2 and ZrO_2 additives is intermediate. From this point of view, it can be concluded that the ZrO_2 additive added to the MASB glass increases the hardness more than the TiO_2 additive in case the crystallization temperature is high. However, since the material has better crystallization ability at low temperature with TiO_2 additive, the samples containing TiO_2 in the low temperature crystallization process are the samples with the highest hardness according to the sample MASB-Z.

Considering the density values after crystallization at high temperature, the density value of the ZrO_2 added samples is the highest. However, the density of the sample containing TiO_2 is at the lowest value. The density of the sample, which contains TiO_2 and ZrO_2 additives together, is in the intermediate value. From this point of view, when the MASB

glass is crystallized at high temperature, the densest sample can be obtained with the addition of ZrO_2.

- Effect of different nucleating agents on physical and mechanical properties of MASB glass-ceramics was investigated. It has been clarified that the crystalline phase of sapphirine can only be obtained in MASB composition where TiO_2 is used as nucleating agent.
- As a result, TiO_2 can promote sapphirine formation on MASB glass ceramics. As the crystallization temperature increases, the intensity and density of the precipitated crystalline phases increase. Moreover, the hardness and density values of MASB glass ceramics show improvement depending on this crystallinity.
- The highest hardness value was obtained with 1302 $HV_{0.05}$ at 1100°C crystallization temperature in the MASB composition in which ZrO_2 was used as nucleating agent.

References

[1] P. Kumari, R.K. Gangwar, P.M. Sarun, D. Kumar, "Effect of $BaTiO_3$ addition on the microwave dielectric properties of MgO–Al_2O_3–SiO_2–TiO_2 glass-ceramic", *Materials Chemistry and Physics*, **275**, 125276 (2022).

[2] B. Mirhadi, B. Mehdikhani, N. Askari, "Effect of zinc oxide on microhardness and sintering behavior of MgO–Al_2O_3–SiO_2 glass–ceramic system", *Solid State Sciences*, **14** (4) 430-434 (2012).

[3] X. Xu, X. Lao, "Effect of MgO/SiO_2 ratio and Al_2O_3 content on crystallization behavior and properties of cordierite-based glass–ceramics", *Journal of the European Ceramic Society*, **41** (2) 1593-1602 (2021).

[4] C. Gao, X. Zhao, B. Li, "Influence of Y_2O_3 on microstructure, crystallization, and properties of MgO-Al_2O_3-SiO_2 glass-ceramics", *Journal of Non-Crystalline Solids*, **560**, 120728 (2021).

[5] T. Liu, C. Li, Q. Huang, C. Liu, C. Lin, Q. Zhang, Z. Luo, L. Zhu, A. Lu, "Characterization of structure and properties of MgO-Al_2O_3-SiO_2-B_2O_3-Cr_2O_3 glass-ceramics", *Journal of Non-Crystalline Solids*, **543**, 120154 (2020).

[6] S. Zhang, Y. Zhang, Z. Qu, "Effects of soluble Cr_2O_3 doping on the glass structure, microstructure, crystallization behavior, and properties of MgO–Al_2O_3–SiO_2 sapphirine glass ceramics", *Materials Chemistry and Physics*, **252**, 123115 (2020).

[7] L. Deng, Z. Fu, Z. Mingxing, H. Li, B. Yao, J. He, H. Chen, Y. Ma, "Crystallization, structure, and properties of TiO_2-ZrO_2 co-doped MgO-B_2O_3-Al_2O_3-SiO_2 glass-ceramics", *Journal of Non-Crystalline Solids*, **575**, 121217 (2022).

[8] H. Li, Z. Yin, L. Deng, S. Wang, Z. Fu, Z & Y. Ma, "Effect of SiO_2/Al_2O_3 ratio on the structure and electrical properties of MgO–Al_2O_3–SiO_2 glass-ceramics doped with TiO_2", *Materials Chemistry and Physics*, **256**, 123653 (2020).

[9] H. Shao, K. Liang, F. Zhou, G. Wang, A. Hu, "Microstructure and mechanical properties of MgO–Al_2O_3–SiO_2–TiO_2 glass–ceramics", *Materials Research Bulletin*, **40** (3) 499-506 (2005).

[10] S. Seidel, C. Patzig, M. Krause, T. Höche, A. Gawronski, Y. Hu, C. Rüssel, "The effect of CeO_2 on the crystallization of MgO-Al_2O_3-SiO_2-ZrO_2 glass", *Materials Chemistry and Physics*, **212** 60-68 (2018).

[11] G. Carl, T. Höche, "Crystallisation behaviour of a MgO–Al_2O_3–SiO_2–TiO_2–ZrO_2 glass", *Physics and Chemistry of Glasses*, **43** (1) 256-258 (2002).

[12] T. Liu, C. Li, Q. Huang, C. Liu, C. Lin, Q. Zhang, Z. Luo, L. Zhu, A. Lu, "Characterization of structure and properties of MgO-Al_2O_3-SiO_2-B_2O_3-Cr_2O_3 glass-ceramics", *Journal of Non-Crystalline Solids*, **543**, 120154 (2020).