

Comparison of the Effect of TiO₂ and ZrO₂ Nucleating Agents on Mechanical & Physical Properties of MgO-Al₂O₃-SiO₂-B₂O₃ (MASB) System Glass-Ceramics

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Abstract

In this study, the effect of TiO₂ and ZrO₂ nucleating agents on the mechanical and physical properties of MgO-Al₂O₃-SiO₂-B₂O₃ (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 ZrO₂ as the nucleating agent.

TiO₂ ve ZrO₂ çekirdeklendirici ajanların MgO-Al₂O₃-SiO₂-B₂O₃ (MASB) sistemi cam-seramiklerin mekanik ve fiziksel özelliklerine etkisinin karşılaştırılması

Özet

Bu çalışmada, TiO₂ ve ZrO₂ çekirdeklendiricilerinin MgO-Al₂O₃-SiO₂-B₂O₃ (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 katkıları eklenerek hazırlanmıştır. MASB camları 5°C/dak ısıtma hızında 1500°C sıcaklığa çıkılarak ergitme yöntemiyle üretilmiştir. Isıl işlem parametreleri ile birlikte camın 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 TiO₂'nin çekirdeklendirici olarak kullanıldığı kompozisyonlarda yapıdaki baskın fazın safirin olduğunu ortaya koyarken, çekirdeklendirici olarak sadece ZrO₂'nin kullanıldığı durumda ise spinel fazının cam-seramik bünyelerde baskın faz olarak çökelediğini 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-Al₂O₃-SiO₂ (MAS) system glass-ceramics find wide industrial application areas due to possess superior mechanical properties, chemical resistance, low dielectric constant and thermal shock resistance³. 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 compositions³⁻⁵. Various oxides such as Cr₂O₃, TiO₂, Fe₂O₃, CaF₂, V₂O₅ and ZrO₂ can be used in this glass system as nucleating agents to promote nucleation and crystallization process⁶.

Although many methods can be used in the fabrication of glass-ceramics today; melting, sintering and sol-gel methods stand out as the basic methods⁷.

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 TiO₂, ZrO₂ nucleating agents along with their combined (TiO₂+ZrO₂) effect on crystallization ability, mechanical, microstructural, physical properties and phase distribution of MAS glass-ceramics were investigated.

2. METHODS

MgO-Al₂O₃-SiO₂-B₂O₃ (MASB) glasses were prepared using reagent grade MgCO₃, Al₂O₃, SiO₂, H₃BO₃, Sb₂O₃, TiO₂ and ZrO₂ 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 ₂ O ₃	20.45	20.45	20.45
SiO ₂	24.35	24.35	24.35
B ₂ O ₃	12.8	12.8	12.8
TiO ₂	4.46	-	2.23
ZrO ₂	-	4.46	2.23
Sb ₂ O ₃	0.22	0.22	0.22

In this experiment, boroxide derived from boric acid were introduced as fluxing agent, TiO₂ and ZrO₂ served as nucleating agent and Sb₂O₃ 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 (T_g) and crystallization (T_c) 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 (T_g) between 685-713°C and an exothermic peak refers to crystallization peak temperature (T_p) 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.

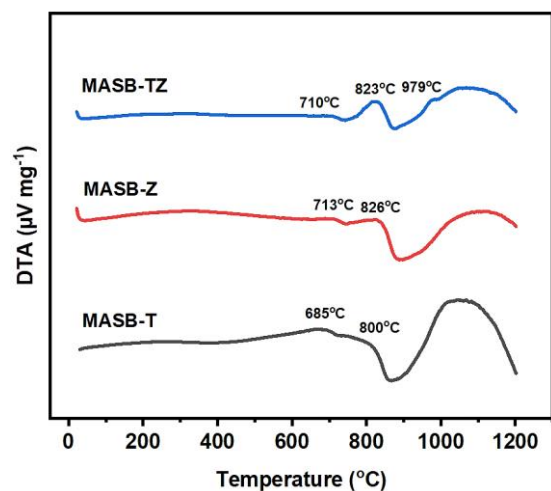


Figure 1. DTA result of MASB glass powders at a heating rate of 5°C min⁻¹.

3.2. XRD Results

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

treatment at 900-1100°C for 1 hour were given in Fig. 2-4. Fig. 2 shows the XRD pattern of MASB-T glass-ceramics which comprise TiO₂ as nucleating agent and at 900 °C crystallization temperature only consist of boromullite (Al₉BSi₂O₁₉) crystalline phase. However, it was observed that with the increase the temperature to 1000 and 1100°C, quartz, spinel (MgAl₂O₄), rutile (TiO₂) and sapphirine ((Mg,Al)₄(Al,Si)₂O₂₀) phases were also precipitated besides boromullite crystals.

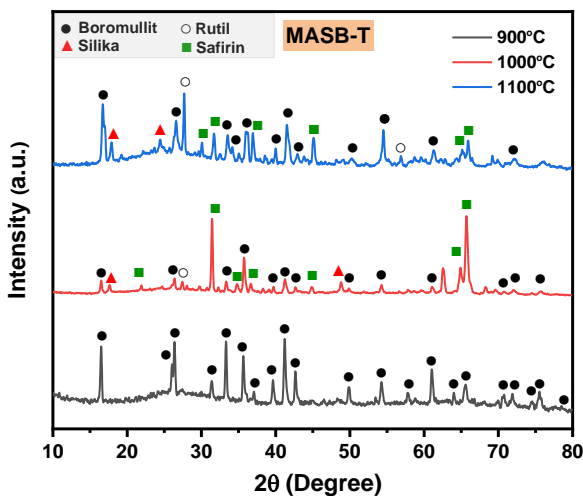


Figure 2. XRD results of MASB-T glass-ceramics.

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 spaces⁸. Shao et al. applied crystallization to the glass in the MgO-Al₂O₃-SiO₂-TiO₂ 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, respectively⁹. The results are in agreement with the work of Shao et al. The crystallization phases peak of MASB-Z that heat treated at 900-1100°C 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 CeO₂ additive on MgO-Al₂O₃-SiO₂-ZrO₂ glasses. When they crystallize these glasses at 1060°C for 1 hour, they reported that quartz, spinel and zirconia phases were present in the microstructure¹⁰.

When the XRD results of MASB-TZ for 900-1100°C (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-Al₂O₃-SiO₂-TiO₂-ZrO₂ 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 structure¹¹.

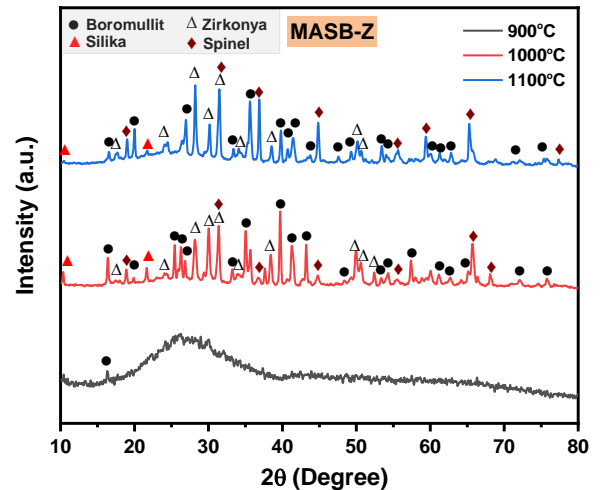


Figure 3. XRD results of MASB-Z glass-ceramics.

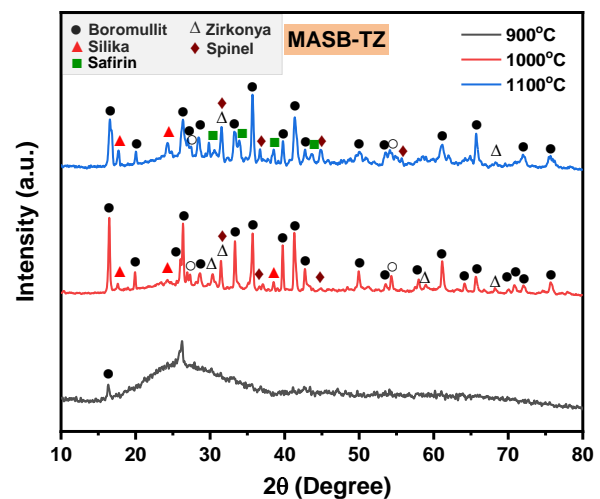


Figure 4. XRD results of MASB-TZ glass-ceramics.

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.

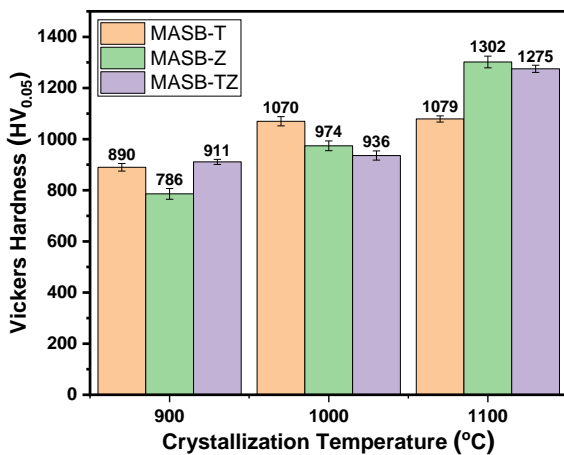


Figure 5. Vickers hardness values of MASB glass-ceramics.

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 TiO₂ 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.

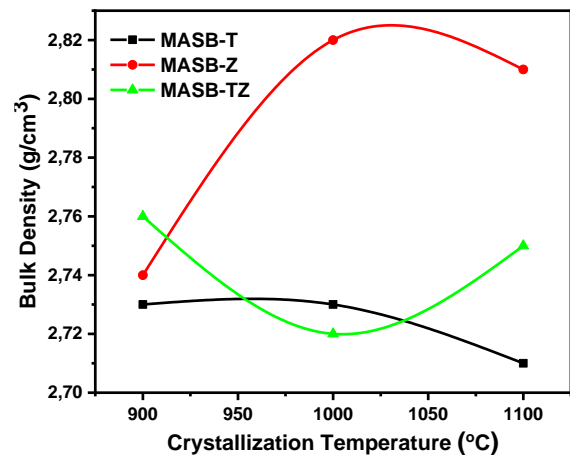


Figure 6. Archimedes density values of MASB glass-ceramics.

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 ZrO₂, which is used as nucleating agent, compared to TiO₂. 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 TiO₂ and ZrO₂ were used as nucleators in MASB-TZ glass-ceramics. This is why spinel and sapphirine are formed together at 1000°C. Because while TiO₂ additive promotes the formation of sapphirine, ZrO₂ 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 TiO₂ and ZrO₂ at 1100°C is between the density value of MASB-T containing only TiO₂ and MASB-Z containing only ZrO₂. This proves that ZrO₂ added to MASB glass-ceramics forms a denser material than TiO₂. Liu et al. have done structure, characterization and property analysis by adding Cr₂O₃ to the MASB system. The density values they found in their study ranged from 2.652 g/cm³ to 2.761 g/cm³ according to the change in the amount of nucleating additives¹².

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 TiO₂ nucleator after heat treatment at 900°C. Although no crystal phase can be detected in the image of glass-ceramic containing only ZrO₂, there is an amorphous appearance as indicated in the XRD analysis. In the MAS-TZ sample, where TiO₂ and ZrO₂ are used together, there are light coloured crystals precipitated in the glass phase. By increasing the temperature to 1000°C, the formation of dark-coloured dendritic crystals becomes evident, while light-coloured dendritic crystals are present with ZrO₂. However, the addition of TiO₂ encouraged the formation of rod-like structures. At 1100°C, 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.

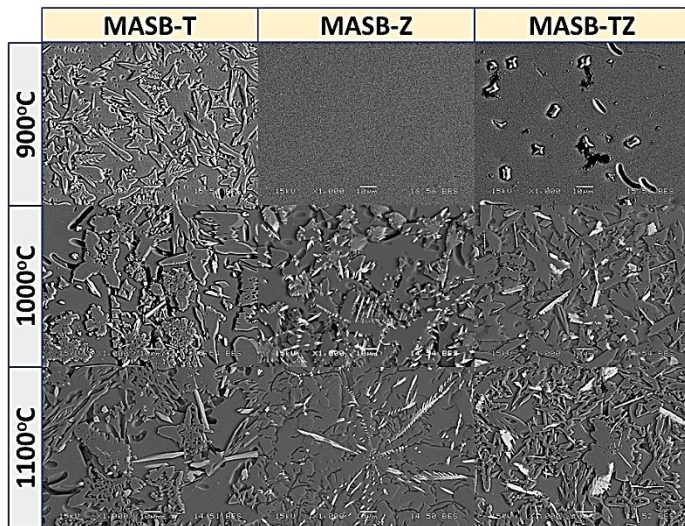


Figure 7. SEM images of MASB glass-ceramics.

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 TiO₂ was added at 900°C, 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 ZrO₂ at 1100°C; “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, ZrO₂ 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 ZrO₂ added as nuclei.

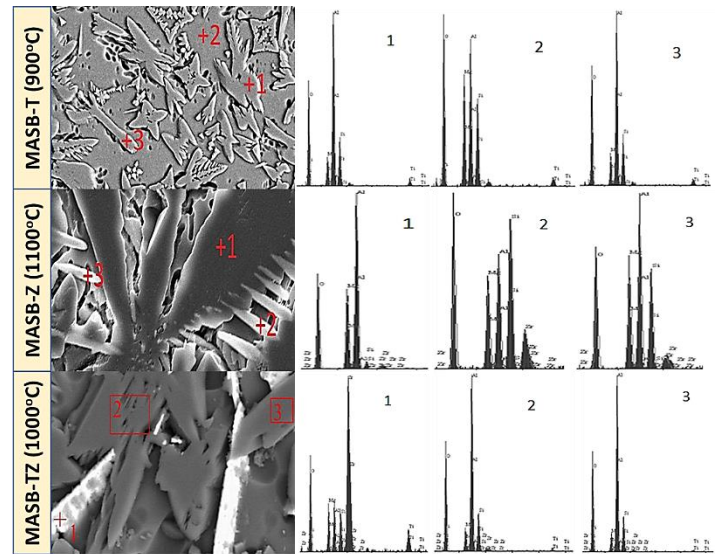


Figure 8. EDS Results of MASB glass-ceramic crystallized at different temperatures.

4. CONCLUSIONS

In the present study, the effect of TiO₂ and ZrO₂ 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 TiO₂ added sample. However, the spinel phase is the dominant phase only in the ZrO₂ doped sample. In addition, in samples where TiO₂ and ZrO₂ are used together, the dominant phases are sapphirine and spinel phases. From this point of view, it can be concluded that TiO₂, which is added to MASB glass-ceramics as a nucleator, promotes the sapphirine phase and ZrO₂ promotes the spinel phase. In addition, when the XRD results of the samples crystallized at 900°C are examined, the sample containing TiO₂ has a boromullite phase, while the sample containing ZrO₂ has an amorphous structure. However, peaks of boromullite phase started to occur at very low intensity in the sample where TiO₂ and ZrO₂ were added together. From this point of view, it can be concluded that the addition of TiO₂ to MASB glass-ceramics promotes the crystallization ability more than ZrO₂ at low temperatures.

When crystallized at high temperature, the hardest sample is the sample containing ZrO₂. The sample with the lowest hardness is the sample containing TiO₂. The hardness of the sample containing TiO₂ and ZrO₂ additives is intermediate. From this point of view, it can be concluded that the ZrO₂ additive added to the MASB glass increases the hardness more than the TiO₂ additive in case the crystallization temperature is high. However, since the material has better crystallization ability at low temperature with TiO₂ additive, the samples containing TiO₂ 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 ZrO₂ added samples is the highest. However, the density of the sample containing TiO₂ is at the lowest value. The density of the sample, which contains TiO₂ and ZrO₂ 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 ZrO₂.

- 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 TiO₂ is used as nucleating agent.
- As a result, TiO₂ 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 ZrO₂ was used as nucleating agent.

Competing Interests

The authors declare no competing interests. This study was conducted with grants (Grant No: 2021-7-24-7) from the Sakarya University Scientific Research Projects Coordinator Ship (BAPK).

Author Contributions

M. Tümer conducted the experimental work. B. Aydın contributed to the physical properties of the samples. Z.Y. Merkit contributed to the characterization of the samples. H.Ö. Toplan evaluated the results. N. Toplan conceived and supervised the project.

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