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Investigation of Li_2O and TiO_2 Effects on MAS Glass-Ceramic Produced from Waste Material

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Abstract:

Among glass-ceramics, MgO-Al_2O_3-SiO_2 (MAS) system occupies an important place due to its good characteristics. In this study, the magnesite waste being an industrial waste was evaluated for the production of MAS glass ceramics and the properties of the glass-ceramics produced were examined. For this purpose, mixtures were prepared using magnesite waste, quartz, kaolin and alumina raw materials according to the chemical composition of cordierite. Furthermore, in the mixtures prepared with the additions of TiO_2 and Li2O added as a nucleating agent the effects of these additions on the crystallization temperatures were investigated. Crystallization temperatures of the glass samples were determined by the differential thermal analysis (DTA) and characterized by X-ray analysis (XRD). Subsequently, the glass-ceramic transformation was performed at 1000, 1050, 1100, 1150 and 1200°C for 1, 3, 5 and 10 hours. The products obtained were analyzed using X-ray (XRD) and scanning electron microscope (SEM). In addition, the microhardness of glass-ceramic products and their corrosion resistance in an acidic environment were measured and compared in this study.

***Keywords**: Crystallization; Differential thermal analysis (DTA); Glass-ceramics; Magnesite waste; MgO-Al_2O_3-SiO_2 (MAS) system.*

1. Introduction

Glass-ceramics are generally produced by creating special glasses, and mostly by melting them, and then by performing a controlled heat treatment to nucleate and precipitate the crystals in the glassy matrix [1]. Glass-ceramics that are formed of fine-grained and randomly oriented crystals in a glass matrix has a wide range of fields of application. They can be used in many applications such as cooking ceramics, building materials, optical materials, machinable ceramics, bio-ceramics, etc [2]. Besides its superior features, another advantage is the simple manufacturing process combined with a lower production cost [3]. Examples of general glass-ceramic systems can be the CaO-Al_2O_3-SiO_2 (CAS) system [4], the CaO-MgO-Al_2O_3-SiO_2 (CMAS) system [5,6], the Li_2O-Al_2O_3-SiO_2 (LAS) system [7,8] and the MgO-Al_2O_3-SiO_2 (MAS) system [9]. In the MgO-Al_2O_3-SiO_2 (MAS) system, glass ceramics with good mechanical properties can be obtained. Good thermal stability, good dielectric characteristics, high mechanical strength and thermal shock resistance can be listed among the characteristics of the MAS system [10]. Furthermore, added glass ceramics have

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attracted considerable attention in recent years due to their wide range of potential applications. Annealing of this system without using any additives causes surface crystallization. The addition of nucleating agents results in crystallized and fine-grained glass ceramics in volume [11]. Hardness, workability, conductivity, and other various characteristics of the MAS glass-ceramic depend on the composition and microstructure [12]. In the literature, the studies on MAS glass ceramics containing nucleating additions of Y_2O_3, ZrO_2 [9], TiO_2, ZnO [13], CaO [14], P_2O_5, NiO [15] are found. A mixture of TiO_2 and ZrO_2 or TiO_2 is widely used as the nucleating agents to produce high-strength glass-ceramics. However, the use of TiO_2 allows producing colored glass-ceramics from purple to blue due to its formation of Ti^{+3}. With the addition of ZrO_2, colorless glass-ceramic with high mechanical strength can be obtained in the MAS systems [11]. Wange et al. [16] produced MAS glass-ceramics using heat treatment at 800°C for 2 hours and at 1080°C for 3 hours in two stages with the addition of TiO_2, and obtained an elastic module of 139 GPa, a Vickers hardness of 9.5 GPa, and a fracture toughness of 4.3 $MPa.m^{1/2}$. In their study Chen et al. [17], applied a heat treatment at 760°C for 12 hours and at 930°C for 4 hours, again in two stages, to examine the effect of La_2O_3 addition on the MAS glass-ceramic system and found out that the hardness and density were increased with an increased addition of La_2O_3 as well as that the thermal diffusion coefficient of was increased. MAS glass-ceramics in which the main crystalline is as a phase based on a spinel composition with Mg-Al spinel ($MgAl_2O_4$) can be prepared. However, high concentrations of SiO_2 and Al_2O_3 cause high melting temperature and viscosity, which makes it difficult to prepare them. Therefore, the addition of fluxes, which are usually alkali oxides, enables the viscosity and melting temperature to be reduced, and in parallel with this, the crystallization behavior, the thermal diffusion coefficient, or decrease in transparency may also change. In their study Wang et al. [18], analyzed the effect of alkali oxides on the MAS glass-ceramic system and determined that the activation energy for viscous flow in a system with the addition of 2% Na_2O was 306.04 $kJ.mol^{-1}$, the melting temperature was about 1585°C, and the activation energy in a system with the addition 1% Li_2O was 284.01 $kJ.mol^{-1}$, the melting temperature was about 1508°C, and that both of them were decreased. They also noted that the addition of 1% K_2O causes a slight decrease in the activation energy for viscous flow and melting temperature, and reported them respectively, as being 288.78 $kJ.mol^{-1}$ and 1573°C.

Therefore, the study examined the effects of Li_2O and TiO_2 additions on the MAS glass-ceramics produced with additives. Furthermore, magnesite waste was used as a raw material for the glass-ceramics produced for this purpose. In this way, a waste substance was industrially evaluated, and it was aimed to reduce the production temperature with the addition of oxides, and additionally to improve the characteristic properties thereof. In other words, the effects of Li_2O and TiO_2 additions on the MAS glass-ceramic prepared using magnesite waste, quartz, kaolin and alumina raw materials were analyzed.

2. Materials and Experimental Procedures

In this study, waste magnesite was used as a source of MgO, and it was aimed to produce MAS-based glass ceramics that are economical and high mechanical properties and corrosion resistance by adding TiO_2 and Li_2O as nucleating agents. As initial raw materials, magnesite waste supplied from KUMAŞ Company; quartz, kaolin, alumina supplied from Akgün Company, and TiO_2 and Li_2CO_3 at a purity of 98.5% (as a source of Li_2O) supplied from Merck, were used. The results of X-Ray Fluorescence (XRF) spectrometry of the raw materials employed in the study are given in Table I, the compositions prepared and their codes are also given in Table II.

The raw materials used were dry mixed through zirconia balls in a ball mill to form a homogeneous mixture. The homogeneously mixed compositions were melted in an electric

furnace at 1500°C for 2 hours in an alumina crucible. The molten glass is formed by being molded in a graphite die. After the process of forming, glass plates were holded at 600°C for 1 hour to relieve their stress, and then were cooled to room temperature. A single-stage heat treatment application and the production of glass-ceramics from the glass samples prepared, which comprise the stages of nucleation formation and growth, were performed at 1000°C, 1050°C, 1100°C, 1150°C and 1200°C temperatures for 1, 3, 5 and 10 hours. The experimental process followed in the production of MAS-based glass and glass-ceramics is given in Fig. 1.

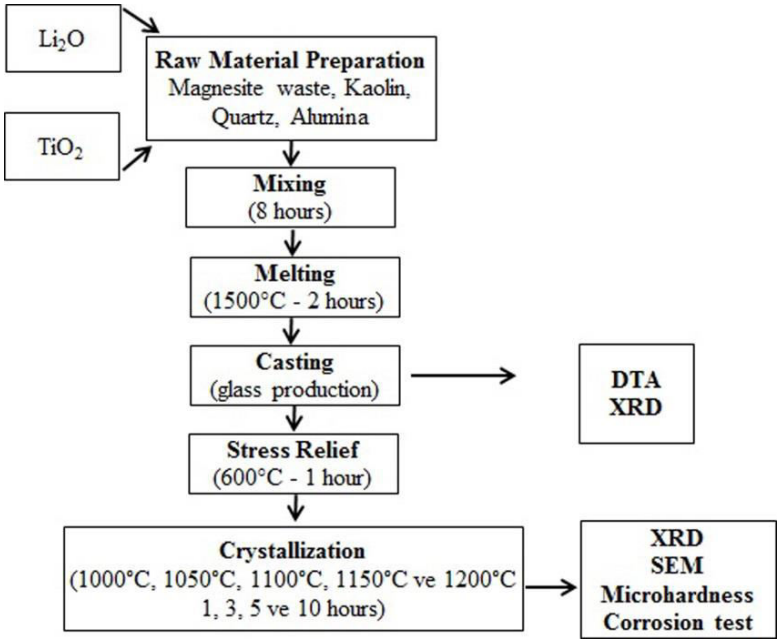

Fig. 1. Flow chart of experimental studies.

Tab. I Chemical analysis of raw materials.

	Magnesite waste	Kaolin	Quartz	Alumina
SiO_2	35,61	52,12	99,1	0,52
MgO	33,34	0,05	0,06	-
Al_2O_3	2,04	33,84	0,28	99,425
TiO_2	0,22	0,45	0,05	-
CaO	2,73	0,15	0,10	-
Na_2O	0,08	0,05	0,17	0,055
K_2O	0,02	0,13	-	-
Fe_2O_3	6,04	0,55	0,05	-
L.O.I*	19,77	12,45	0,19	-

* Loss on ignition

After glass production, glass products were milled and powdered in a porcelain mortar to determine the crystallization temperatures required for the transformation to the glass-ceramic material, and DTA analysis (NETZSCH) was applied. X-ray diffraction (XRD) analyses (RIGAKU) were performed to determine the amorphous and crystalline phases occurring in the glass and glass-ceramic samples produced. Microstructures of the glass-ceramics produced were examined using a JOEL scanning electron microscope (SEM). In order to determine the corrosion resistance of the glass and glass-ceramic samples produced, a corrosion test was performed in a 10% HNO_3 solution. Their corrosion resistance was

determined by calculating the total change in weight, for which the ratio of the weight loss to the initial weight was calculated as %. In addition, the microhardness values of the samples were determined as Vickers hardness with a time of 15 seconds under a load of 50 g using a Leica device.

Tab. II Prepared compositions and codes.

Compound (% wt.)	Raw materials					
	Magnesite waste	Quartz	Kaolin	Al_2O_3	Li_2O (excess)	TiO_2 (excess)
M	35	20	25	20	-	-
MLi	35	20	25	20	2,5	-
MTi	35	20	25	20	-	8
MLiTi	35	20	25	20	2,5	8

3. Results and Discussion

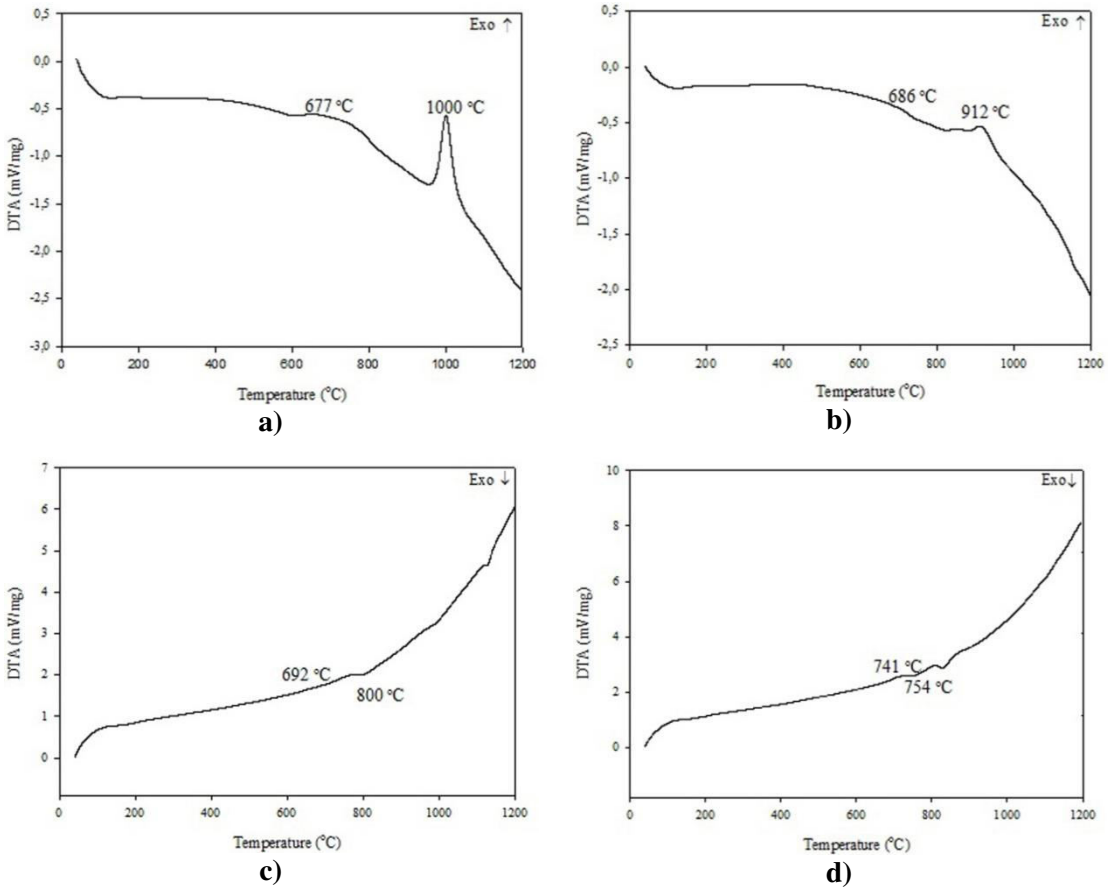

Fig. 2. DTA analysis of glasses produced in different compositions a) M, b) MLi, c) MTi, d) MLiTi.

In experimental was investigated and compared the glass-ceramic composition obtained from magnesite waste, quartz, kaolin and alumina raw materials, as well as the compositions containing the addition of Li_2O and TiO_2. The results of Differential Thermal

Analysis (DTA) are given in Fig. 2, which are obtained by increasing the temperatures of the prepared glasses to 1200°C under atmospheric conditions in order to determine their glass transition temperatures and the crystallization temperatures required for the production of glass-ceramics. Here, according to the data obtained from the DTA chart of the M coded glass (a), the glass transition temperature (Tg) was determined to be 677°C, and it seems that an exothermic reaction occurs at 1000°C. Therefore, this temperature may be determined as the crystallization temperature for this composition. When other graphics were examined, in the MLi coded glass (b) glass transition temperature (Tg) was determined to be 686°C, crystallization temperature was determined to be 912°C, in the MTi coded glass (c) glass transition temperature (Tg) was determined to be 692°C, crystallization temperature was determined to be 800°C, and in the MLiTi coded glass (d) glass transition temperature (Tg) was determined to be 741°C, crystallization temperature was determined to be 754°C. As can be seen from the DTA analyses, the additions of the Li_2O and TiO_2 increased the glass transition temperature of the glass while it decreased its crystallization temperature. Pavlikov et al. in their study carried out in the MgO-Al_2O_3-SiO_2 system [19], prepared various compositions and indicated in their DTA analyses that the crystallization temperatures of the compositions were about 1000°C, and that the oxide additions to the system decreased the crystallization temperature. In the study carried out by Shao et al. [20], they detected the glass transition temperature to be 780°C and the crystallization temperature to be 1000°C by adding 5-10% TiO_2 nucleating agent to the MAS system.

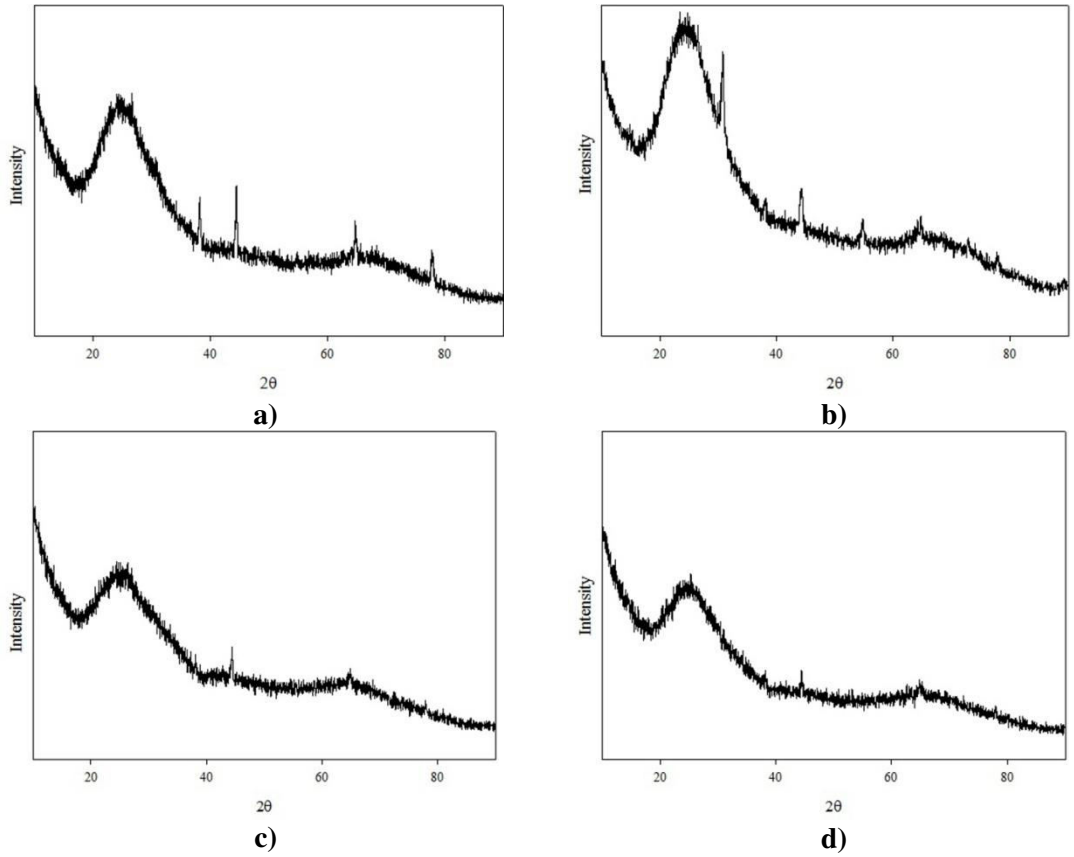

Fig. 3. XRD analysis of glasses produced in different compositions a) M, b) MLi, c) MTi, d) MLiTi.

Li_2O, which is an alkali metal oxide, has a reducing effect on the viscosity and melting temperature of the glass, reduces the network connectivity of titanium which can act as both a

modifier and a network builder within the structure, and thus facilitates network movement at a lower temperature, which results in a decrease in the crystallization temperature. In addition, it is believed that lower crystallization temperatures of the products produced with the additions of Li_2O and TiO_2 compared to the literature are caused by the presence of oxides in the magnesite waste used as a raw material, and by their role as a flux in the system, and this can be considered as a fairly great advantage.

In order to compare to the glass-ceramic samples produced, the results of the XRD analysis of the glass compositions obtained before crystallization are given in Fig. 3. When the XRD results are examined, it is seen that amorphous formations are found in all glass compositions produced as expected.

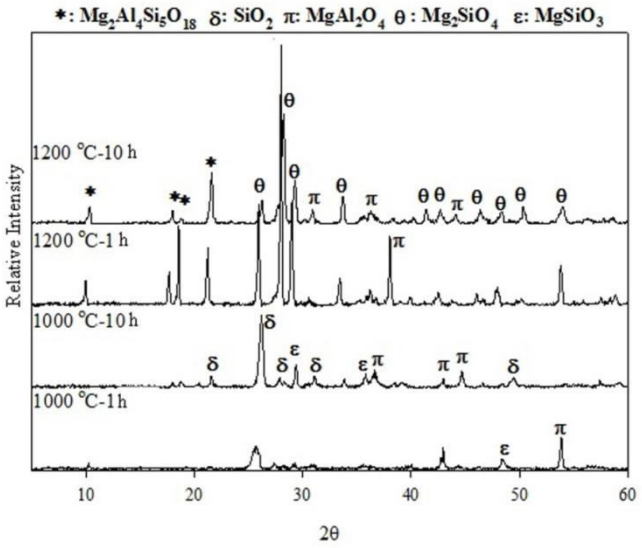

Fig. 4. XRD analysis after crystallization of glasses of composition M at different temperatures and times.

The glasses produced were crystallized by heat treatment in the temperature range of 1000 between 1200°C for 1, 3, 5 and 10 hours in an attempt to produce glass-ceramics. The XRD phase analyses of the glass-ceramics obtained as a result of this process are shown in Figs 4, 5, 6 and 7. Fig. 4 shows the phase analysis obtained after the heat treatment of the M coded glass-ceramics carried out in different temperatures and times, in which no addition of a nucleating agent has been made. As it can be seen, no amorphous phase was observed even after the crystallization process carried out at the lowest temperature and the shortest time (1000°C-1 hour). The phases formed as a result of crystallization at 1000°C were silica (SiO_2), spinel ($MgAl_2O_4$) and enstatite ($MgSiO_3$), and at this temperature it seems that a cordierite ($Mg_2Al_4Si_5O_{18}$) phase did not occur. There was also no cordierite phase after crystallization at 1050, 1100 and 1150°C. For this reason, phase analyses of these temperatures are not given here. Similarly, phase analyses of the highest and lowest temperatures and times are given for other compositions. The cordierite phase was first detected after the process of crystallization at 1200°C for 1 hour, in addition, the enstatite ($MgSiO_3$) phase was not observed at high temperature, it was replaced by forsterite (Mg_2SiO_4), which is a high-temperature form.

In the XRD analysis of the MLi coded sample after different temperatures and times which is given in Fig. 5, it is seen that lithium aluminum silicate ($LiAlSi_3O_8$), cordierite ($Mg_2Al_4Si_5O_{18}$) and forsterite (Mg_2SiO_4) phases occur at high temperatures in structures, and the cordierite phase was not observed at 1000°C.

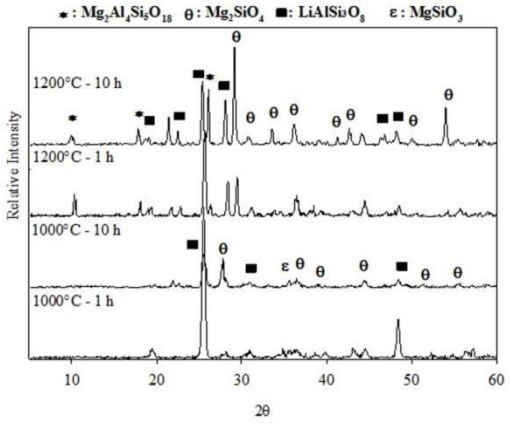

Fig. 5. XRD analysis after crystallization of glasses of composition MLi at different temperatures and times.

TiO_2 it is a very effective nucleating additive used in many glass-ceramic systems. This powerful effect of TiO_2 comes from its phase decomposition, heterogeneous nucleation, or role in the formation of an early crystalline nucleus in the glassy phase. Glass-ceramics in the systems MgO-Al_2O_3-SiO_2-TiO_2 are notable for their superior mechanical properties [21]. In Fig. 6, XRD analyses of the MTi composition are given, which contains only 8% TiO_2 as a nucleating additive. Here, magnesium dititanate ($MgTi_2O_5$) and enstatite ($MgSiO_3$) phases were formed at 1000°C, while the cordierite ($Mg_2Al_4Si_5O_{18}$) phase was also formed at 1200°C. In addition, it is observed that the peak intensities of the cordierite phase formed here were also higher compared to other compositions. Goel et al. [22] noted that a hexagonal, metastable $Mg_2Al_4Si_5O_{18}$ phase, which was similar to the cordierite composition, was formed after the crystallization at 850°C for 5 hours in the compositions that they prepared with the addition of 4.11% TiO_2 (mol%), but that the residual glassy phase still existed. They detected that the $MgTi_2O_5$ phase was formed at 950°C in 5 hours as well as this phase. They indicated that the hexagonal phase was transformed into the orthorhombic cordierite phase at 1150°C in 5 hours [23]. When the XRD analyses given in Fig. 5 and Fig. 6 are compared, in other words, when considering the effect of Li_2O and TiO_2 additions, we can say that the addition of TiO_2 increases the formation of the cordierite phase.

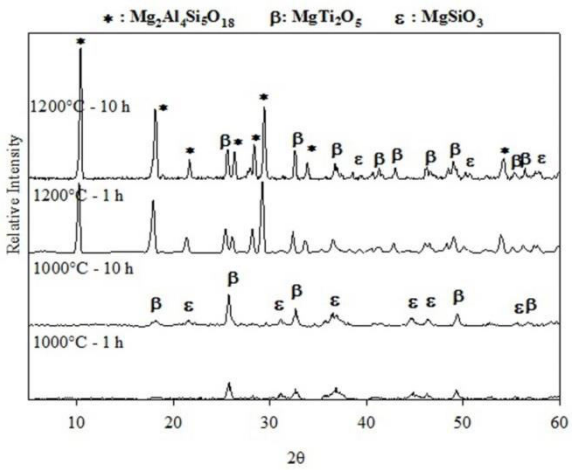

Fig. 6. XRD analysis after crystallization of glasses of composition MTi at different temperatures and times.

Here, the effects of using two nucleating agents individually and together with the addition of Li_2O and TiO_2 on the system were examined. Fig. 7 shows the XRD analyses of the MLiTi composition prepared with the addition of 2.5% Li_2O and 8% TiO_2, which were obtained after crystallization processes at different temperatures and times. Cordierite formations at low temperature have not been found here. After crystallization at 1200°C, lithium aluminum titanium oxide ($Li_2Al_2Ti_4O_{12}$), cordierite ($Mg_2Al_4Si_5O_{18}$), magnesium dititanat ($MgTi_2O_5$), enstatite ($MgSiO_3$), lithium silicate ($Li_2Si_3O_7$) and magnesium silicate (Mg_2SiO_4) phases have been detected. When this result is compared with the MTi composition given in Fig. 6, we can say that the addition of Li_2O reduces the formation of cordierite.

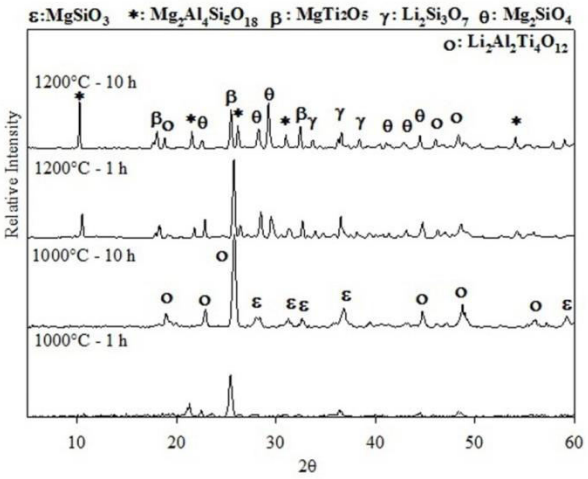

Fig. 7. XRD analysis after crystallization of glasses of composition MLiTi at different temperatures and times.

After initial weights of the glass and glass-ceramic samples produced to determine their corrosion resistances were measured, they were kept in a 10% HNO_3 solution for 20 days and then their weights were measured again. The ratio of the weight loss occurring in the glass-ceramic samples, which were obtained from the glasses prepared from the MLi, MTi and MLiTi compositions and by crystallization of these glasses at 1150 and 1200°C for 1, 3, 5 and 10 hours, to the weight prior to corrosion was calculated in percentages (%), and the results thereof are given in Table III.

Tab. III Corrosion test results of MLi, MTi and MLiTi coded glass and glass-ceramics.

Corrosive environment	Crystallization Conditions	Weight Loss (%)		
		MLi	MTi	MLiTi
10% HNO_3 by volume	Glass	3,45	1,98	2,85
	1150 °C- 1 saat	0,48	0,22	0,45
	1150 °C- 3 saat	0,4	0,14	0,41
	1150 °C- 5 saat	0,53	0,21	0,42
	1150 °C- 10 saat	0,5	0,12	0,4
	1200 °C- 1 saat	0,32	0,07	0,28
	1200 °C- 3 saat	0,37	0,08	0,27
	1200 °C- 5 saat	0,39	0,07	0,24
	1200 °C- 10 saat	0,33	0,1	0,29

As the desired phases were not achieved in the crystallization processes performed at the temperatures lower than 1150°C, corrosion tests were applied to the samples produced at 1150 and 1200°C. The weight loss - time graphs of corrosion tests are also given in Fig. 8. It can be seen from the graphs that the weight losses of the MTi composition at both crystallization temperatures are quite little compared to other samples. It is seen in Table III that the weight losses caused by soaking glasses in HNO_3 acidic solution in all three compositions are more than the weight losses of glass-ceramics. It is expected that the dissolution rates of glass-ceramics in their corrosion behavior were decelerated by multiple phases and crystal-glass interfaces. It was indicated that the crystal phase was substantially more durable in corrosive environments compared to the glass phase [23]. However, some minerals such as lithium metasilicate and disilicate phases demonstrate poor resistance to the treatment of acid solutions and decompose [24]. Therefore, it is seen that the weight losses of glass-ceramic systems containing Li_2O were higher compared to the MTi coded composition with the addition of TiO_2. The lowest weight loss was measured as 0.07% in the glass-ceramic samples obtained after crystallization of the MTi composition at 1200°C for 1 and 5 hours.

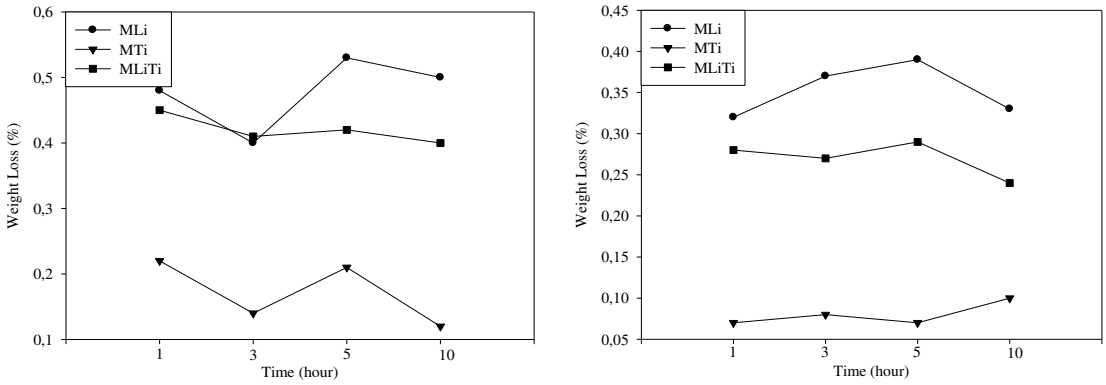

Fig. 8. Corrosion test graphs of MLi, MTi and MLiTi coded glass-ceramics obtained by crystallization at (a) 1150°C, (b) 1200°C.

Tab. IV Hardness values (Vickers) of MLi, MTi and MLiTi coded glass and glass-ceramics.

	MLi	**MTi**	**MLiTi**
Glass	1051	841	889
1150 °C-1h	1208	1307	1328
1150 °C-3h	1288	1316	1306
1150 °C-5h	1227	1300	1318
1150 °C-10h	1305	1321	1429
1200 °C-1h	1368	1365	1573
1200 °C-3h	1271	1464	1553
1200 °C-5h	1259	1478	1597
1200 °C-10h	1295	1474	1520

The hardness values of the glass-ceramic samples, which were obtained from the glasses prepared from the MLi, MTi and MLiTi compositions and by crystallization of these glasses at 1150 and 1200°C for 1, 3, 5 and 10 hours, were measured under a load of 50 g and with a resting time of 15 seconds by Vickers hardness value. The obtained values are given in Table IV and the graph of these results is given in Figure 9. When the data are examined; it is clearly seen that glass-ceramics has a higher hardness value than glasses in all of three compositions. When three compositions obtained after crystallization were compared with

one another, it is seen that the composition MLiTi had higher hardness values, that its highest hardness value was achieved as 1597 HV following a treatment at 1200°C for 5 hours. It was determined that the hardness values measured here were quite high in the MAS glass-ceramics with addition compared to the literature [11,17,25-27].

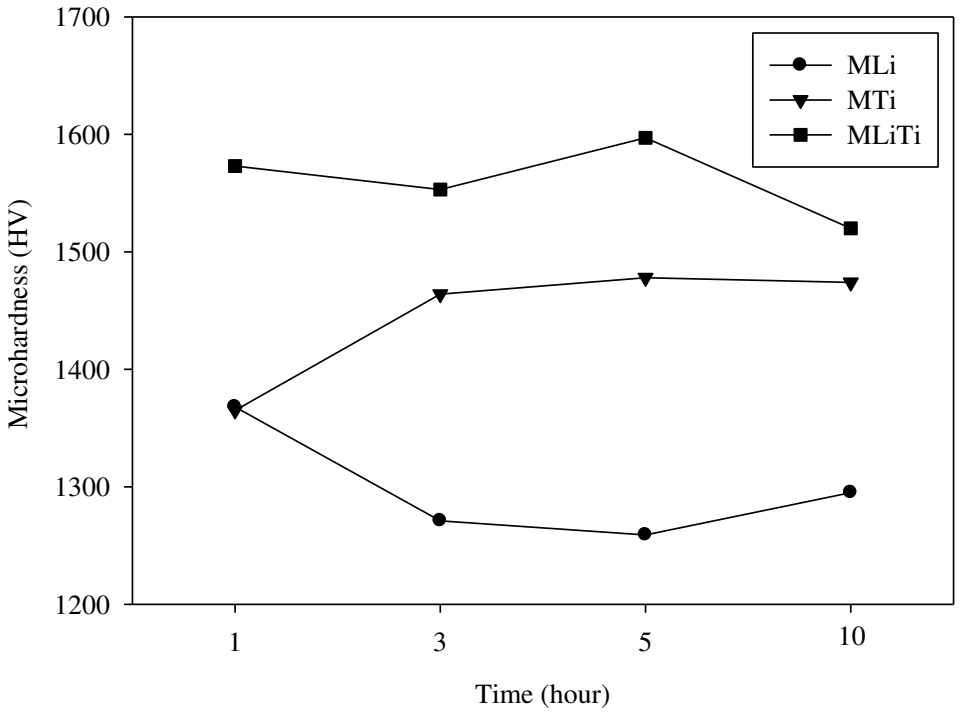

Fig. 9. Comparison of the hardness of MLi, MTi and MLiTi coded glass-ceramics obtained by crystallization at 1200°C.

SEM images obtained from the etched surface after different crystallization conditions for the compositions of MTi and MLiTi are given in Fig. 10 and Fig. 11. Here, microstructure analyses of the compositions of MTi and MLiTi, from which better results were obtained compared to the aforementioned analyses, were included, and microstructure images of the composition of MLi were not given. Considering all of the structures that were formed in general, it seems that they had quite small grain sizes. When Fig. 10 is examined, it is clearly seen that there was an increase in the size of the grain formed due to an increase in temperature and time. It can be seen that the grains formed around 200 nm after crystallization at 1150°C for 1 hour reached around 600 nm when the temperature rises to 1200°C. In the studies, it was observed that the TiO_2 addition reduced the grain size [16,18].
In general, when all of the images are examined, it can be said that the structure was homogeneous and non-porous. When looking at the images of the MLiTi coded samples given in Fig. 11, it is seen that they are larger in grain size than the MTi coded samples. This can be interpreted as the addition of TiO_2 was more effective in reducing the grain size of the formed nuclei than the addition of Li_2O. As a raw material, there are studies on glass-ceramic production from industrial solid wastes with high silica and alumina content due to low cost and high product performance [28]. Experimental results show that magnesite waste, which is a different industrial waste, has been successfully used in glass-ceramic production.

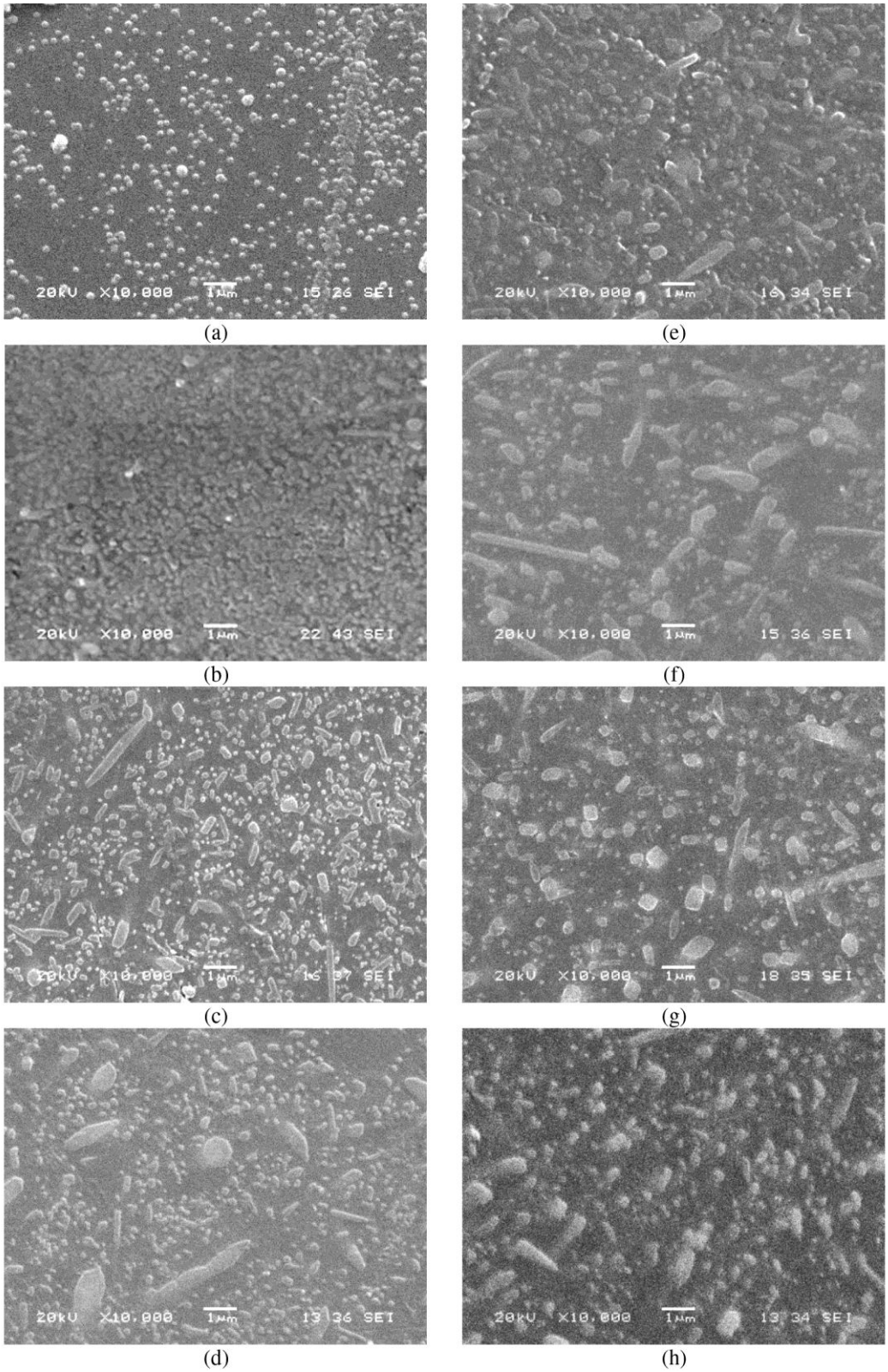

Fig. 10. SEM images of MTi coded glass-ceramics crystallized at different temperatures and times, at 1150°C a) 1 hour, b) 3 hours, c) 5 hours, d) 10 hours and at 1200°C e) 1 hour, f) 3 hours, g) 5 hours, h) 10 hours.

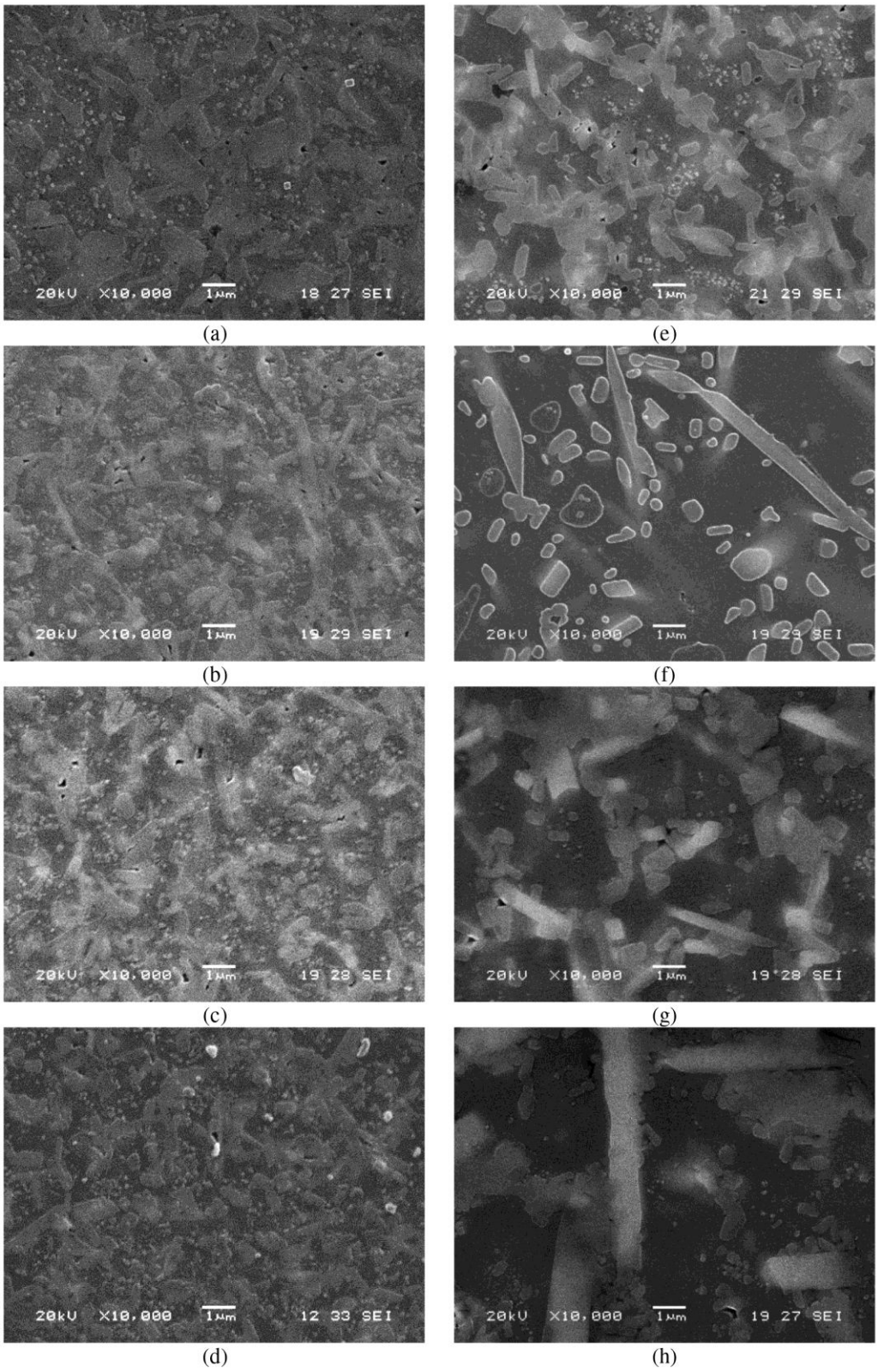

Fig. 11. SEM images of MLiTi coded glass-ceramics crystallized at different temperatures and times, at 1150°C a) 1 hour, b) 3 hours, c) 5 hours, d) 10 hours and at 1200°C e) 1 hour, f) 3 hours, g) 5 hours, h) 10 hours.

4. Conclusion

Glass-ceramic production from the waste material has been successfully carried out. In order to reduce expenditures, magnesite waste, which is a waste material, was used in the production of MAS-based glass-ceramic. Furthermore, in addition to the initial raw materials, TiO_2 and Li_2CO_3 (As a source of Li_2O) powders were used and their impacts were studied. The general results obtained:

- From the DTA results, it was found out that the addition of Li_2O and TiO_2 increased the glass transition temperature while it reduced the crystallization temperature.
- According to XRD analyses, the cordierite phase was formed in the compositions prepared and depending on the additive element to be added, spinel ($MgAl_2O_4$), lithium aluminum silicate ($LiAlSi_3O_8$), forsterite (Mg_2SiO_4), enstatite ($MgSiO_3$), magnesium dititanat ($MgTi_2O_5$), lithium aluminum titanium oxide ($Li_2Al_2Ti_4O_{12}$), lithium titanium oxide ($LiTi_2O_4$) phases were detected.
- When the microstructure images of the produced samples were examined, it was seen that the structure was nonporous and dense after crystallization, and the structures formed had quite small grain sizes.
- In corrosion tests carried out in a HNO_3 solution, it was determined that the MTi composition exhibited better results, so the addition of Li_2O reduced the corrosion resistance and the addition of TiO_2 increased the same.
- According to the micro hardness measurements, it was found out that the composition of the MLiTi with addition of 8% TiO_2 and 2.5% Li_2O had the highest hardness values. The highest hardness value in the MLi composition after a 1 hour crystallization at 1200°C was determined to be 1368 HV, in the MTi composition after a 5 hours crystallization at 1200°C was determined to be 1478 HV and in the MLiTi composition after a 5 hours crystallization at 1200°C was determined to be 1597 HV.

Acknowledgments

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Сажетак: *Међу стакло-керамикама, MgO-Al_2O_3-SiO_2 (MAS) систем заузима важно место због својих добрих карактеристика. У овој студији, мотпад на бази магнесита је коришћен за производњу MAS стакло керамике и испитиване су њене особине. За ову сврху, смеше су припремљене од отпада магнесита, кварца, каолина и алумине, сходно хемијском саставу кордијерита. У смеше је додат TiO_2 и Li_2O као агенси за нуклеацију и испитиван је њихов утицај на температуру кристализације. Температуре кристализације су одређене диференцијалном термијском анализом а састав је одређен рендгенском дифракцијом. Узорци су синтеровани на 1000, 1050, 1100, 1150 и 1200°C током 1, 3, 5 и 10 сати. Добијени узорци су карактерисани CEM и XRD анализама. Поред тога, у овој студији је мерена и упоређена микротврдоћа стаклокерамичких производа и њихова отпорност на корозију у киселој средини.*
Кључне речи*: кристализација, диференцијална термијска анализа (DTA), стакло-керамика, отпад, MgO-Al_2O_3-SiO_2 (MAS) систем.*