

Sintering Behavior and Machinability in Mica Glass-Ceramic of the System $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO--K}_2\text{O--B}_2\text{O}_3\text{--F}$

E. ERCENK* AND S. YILMAZ

Sakarya University, Engineering Faculty, Department of Metallurgical and Materials Engineering
Esentepe Campus, 54187 Sakarya, Turkey

Mica glass-ceramic was prepared by sintering method from in the $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO--K}_2\text{O--B}_2\text{O}_3\text{--F}_2$ system. The sintering behavior and machinability of a glass-ceramic composition were examined. The starting materials were mixed and milled in an alumina ball mill for 2 h. Then the powders were sieved to obtain grain sizes smaller than $75\ \mu\text{m}$. For the shaping process, disc samples were prepared by pressing at 100 MPa. The pressed discs were sintered at temperatures in the range from 900 to 1200 °C for 2 h in an electric furnace using a heating rate of 5 °C/min. X-ray diffraction analysis, scanning electron microscopy, and machinability tests for characterization were performed on sintered samples. The results showed that all samples exhibited similar phases formation and good machinability.

DOI: [10.12693/APhysPolA.125.629](https://doi.org/10.12693/APhysPolA.125.629)

PACS: 61.05.cp, 68.37.Hk, 81.20.Ev, 81.20.Wk, 81.05.Je, 81.05.Mh

1. Introduction

Glass-ceramics are normally obtained by a controlled crystallization process of suitable glasses. It can be produced from different waste or natural materials such as fly ash, high furnace slags, or natural volcanic rocks. Initially, glass base structures are transformed to glass-ceramics via controlled crystallization. The composition of the crystalline phases and the crystallite sizes define the properties of the final material. Ceramic base materials are not suitable for some applications due to the brittle properties of the ceramics and glass-ceramics against to mechanical effects as cutting and drilling [1]. Some modifications in chemical composition and production methods can provide better mechanical behavior as for these effects. One of the important materials about the improvement of machinability of the ceramics is mica base glass-ceramics. Mica containing glass-ceramics are used as high-quality electrical insulators and show high resistance to thermal shock and exhibit good machinability [2]. Mica glass-ceramics based on the $\text{SiO}_2\text{--MgO--MgF}_2\text{--K}_2\text{O}$ system are commercial and these materials exhibit unique properties, such as remarkable cleavage, flexibility, and elasticity, enabling therefore excellent machinability [3]. Commercial mica-type glass-ceramic, of which the main crystal is fluorophlogopite-type mica, also exhibits favorable properties; heat resistance, electrical insulating, and high mechanical strength [4].

In the present study, the effects of varying sintering/crystallization temperature on the crystal phases, the machinability and the microstructure properties of $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO--K}_2\text{O--B}_2\text{O}_3\text{--F}_2$ system were investigated. It had been made to achieve mica glass-ceramics with maximum density and desirable machinability through

the addition of B_2O_3 and Al_2O_3 to the base composition.

2. Experimental procedure

The chemical composition of the samples used in this work was 48% SiO_2 , 18% Al_2O_3 , 15% MgO , 10% K_2O , 5% B_2O_3 , and 4% F by weight. The raw materials such as SiO_2 , AlF_3 , Al_2O_3 , K_2CO_3 , MgCO_3 , and B_2O_3 were first ground and mixed by using a alumina ball mill for 2 h. The mixtures were sieved to a particle size fraction of $-75+45\ \mu\text{m}$ and then uniaxial pressing was employed to shape the samples. Cylindrical samples ($\varnothing\ 25\ \text{mm}$) were shaped under the 100 MPa load and then sintered at several temperatures between 900 and 1200 °C the heating rate of 5°/min for 2 h. For the crystalline phases observation, X-ray diffraction (XRD) analysis (Rigaku D/MAX, $\text{Cu}\ K_\alpha$ radiation) was used. The microstructural examinations by using scanning electron microscopy (SEM) (JEOL 6060) were performed at polished and etched surfaces, the solution of 5 vol.% HF for 1–2 min was used for etching process. Energy-dispersive spectrometer attachment (EDS) was employed for elemental analysis. Furthermore, machinability tests were applied to the disc shaped specimens using 5 mm diamond drills with 200 rpm drilling rate under uncontrolled load.

3. Experimental results

The XRD patterns of the samples sintered at temperatures in the range from 900 to 1200 °C are seen in Fig. 1. MgAl_2O_4 [spinel (ASTM card no: 01-082-2424)], SiO_2 [quartz (ASTM card no: 01-070-3755)], $\text{KMg}_3(\text{Si}_3\text{Al})\text{O}_{10}\text{F}_2$ [fluorophlogopite (ASTM card no: 00-016-0344)] and MgAl_2O_4 [magnesium dialuminium oxide (ASTM card no: 01-077-1193)] phases were determined by XRD in all samples. Especially, the phase called fluorophlogopite ($\text{KMg}_3(\text{Si}_3\text{Al})\text{O}_{10}\text{F}_2$) is significant for machinability. Increase in sintering temperature

*corresponding author; e-mail: ercenk@sakarya.edu.tr

caused weak fluorphlogopite peaks formation. This phase was observed in the XRD patterns of the samples sintered at 900 and 1000 °C; strongly, over the 1000 °C, not only these peaks but also all peak intensities decreased depending on temperature. Spinel ($MgAl_2O_4$), quartz, fluorphlogopite and magnesium dialuminium oxide phases overlapped with the high intensity lines. Machinable glass-ceramic as commercial trademark MACOR consists of fluorphlogopite mica in a borosilicate glass matrix. The XRD results are in good agreement with the literature [5]. It was probable that the crystallization temperatures were around 900–1000 °C and the increase in temperatures caused melting of the crystalline phases.

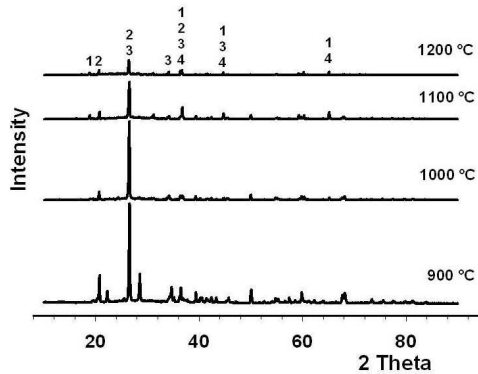


Fig. 1. XRD patterns of the samples depending on sintering temperature (1 — spinel, 2 — quartz, 3 — fluorphlogopite, 4 — magnesium dialuminium oxide).

Table exhibits detected crystalline phases and the macro images as to machinability test results. As one can see in Table, machinability test was performed for all samples, successfully. Any mechanical damage such as fracture was not observed during the machinability tests. Fluorphlogopite is a common phase for machinable glass-ceramics. It provides plastic deformation possibility for glass-ceramics in specific scale. Fluorphlogopite mica is not inclined to distortion and can bear big stress, tension, and compression [1–5]. In this study, fluorphlogopite was a major phase in all samples, other than this, magnesium dialuminium oxide, spinel, and quartz phases were detected for all sintering conditions. On the other hand, clinohumite and kalsilite phases were observed in the samples sintered at lower temperature. When the temperature increased to 1100 °C, these phases decomposed and transformed to the other phases.

In literature, kalsilite phases ($KAlSiO_4$) can be stable up to 950 °C; above this temperature, it can transform to the other phases in suitable conditions. For instance, kalsilite reacts with sufficient amorphous SiO_2 , the phase leucite happened when the glass compacts were sintered at 1000 °C [6]. Clinohumite $[Mg_9(SiO_4)_4(F,OH)_2]$ also is a silicate mineral belonging to humite group. The humite series of minerals have the general formula $n[Mg_2SiO_4][Mg(OH, F)_2]$. This group of minerals is classified as follows: norbergite, chondrodite, humite, and

TABLE

The macro images and crystalline phases versus sintering temperature.

Sintering temp.	Detected phases	Before	After
		machinability test	
900 °C	fluorphlogopite, clinohumite (traces), kalsilite (traces), magnesium dialuminium oxide, spinel, quartz		
1000 °C	fluorphlogopite, clinohumite (traces), magnesium dialuminium oxide, spinel, quartz		
1100 °C	fluorphlogopite, magnesium dialuminium oxide, spinel, quartz		
1200 °C	fluorphlogopite, magnesium dialuminium oxide, spinel, quartz		

clinohumite [7]. In general, this type of structure is observed in machinable glass-ceramics and presence of these phases can bring about fluorphlogopite formation. That these structures can be unstable at high temperature was presented in the literature [2]. The phase clinohumite decomposed at high temperature in this study. As can be seen in the macro images, firing shrinkage was observed depending on increase in temperature.

Figure 2 shows the SEM images and EDS analysis of the samples sintered at 900 and 1200 °C. The results obtained from EDS analysis deal with the XRD analysis results. For both of the samples sintered at 900 °C and 1200 °C, SiO_2 rich regions were determined, that can be read as an evidence about the presence of glassy and SiO_2 crystalline (quartz) phase in the glass-ceramic. EDS point analysis showed that the potassium elemental peaks were dense in the samples sintered at 900 °C, especially. It was indicated that the regions dominated by fluorphlogopite phase were diffuse in this structure. Apart from the fluorphlogopite, presence of magnesium and aluminium elements pointed that there were magnesium dialuminium oxide and spinel phases in the structure. On the other hand, strong Mg, F, K, and Al peaks in EDS results of this sample showed the formation of the clinohumite and kalsilite phases at 900 °C. It was confirmed by XRD analysis and these phases were decomposed by increase in temperature. Similar situations were detected in the samples sintered at 1200 °C. Fluorphlogopite, magnesium dialuminium oxide, spinel, quartz

phases were determined in this sample. In the EDS analysis of this sample, clear decreases in K and F peak intensities were observed. It can be seen that clinohumite and kalsilite phases decompose and transform to other

phases. Marked grains in this microstructure (Fig. 2b) are common images in mica glass-ceramic including fluor, it was presented by Höche et al. as mica plates [8].

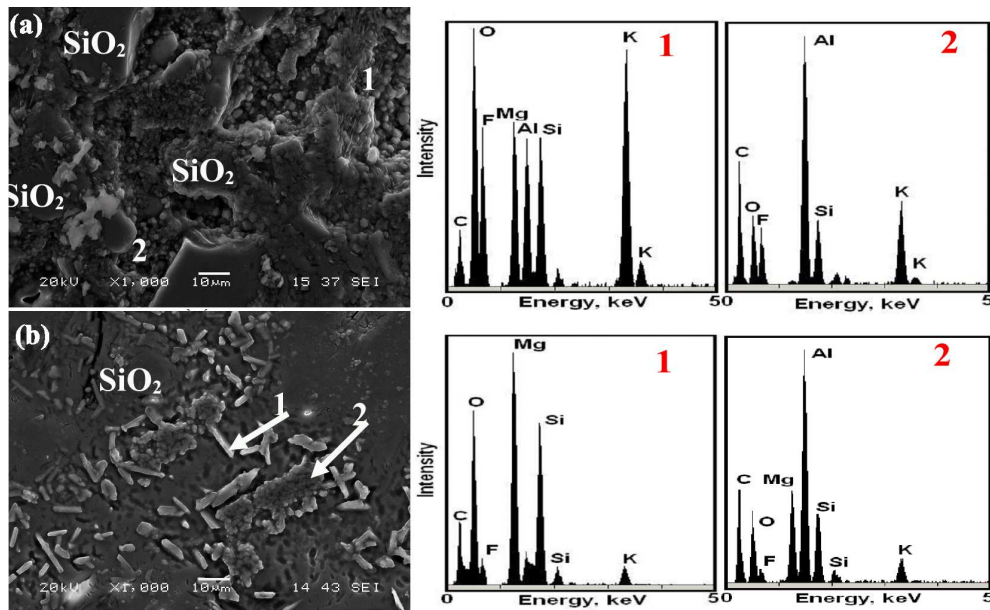


Fig. 2. SEM micrographs and EDS analysis of the samples depending on sintering temperature: (a) 900 °C, (b) 1200 °C.

4. Summary

The main object of this study was to produce machinable glass-ceramic materials by a sintering process in SiO₂-Al₂O₃-MgO-K₂O-B₂O₃-F₂ system. In this study SiO₂, Al₂O₃, K₂CO₃, MgCO₃, B₂O₃, and AlF₃ as fluor source was used. Fluorphlogopite, magnesium dialuminium oxide, spinel, quartz phases were detected in all sintered glass-ceramic sample. Fluorphlogopite is a common phase of this type material, especially. Apart from these phases, clinohumite and kalsilite phases were determined in the diffraction pattern of the samples sintered at 900 °C. These structures were decomposed or transformed due to increase in temperature. To observe machinability performance of the samples, drilling test was performed and it was detected that all samples were drilled without mechanical damage such as crack or fracture.

References

- [1] D.U. Tulyaganov, M.J. Ribeiro, J.A. Labrincha, *Ceram. Int.* **28**, 515 (2002).
- [2] A.M. Nassar, E.M.A. Hamzawy, F.M. Hafez, S.S. El Dera, C. Rüssel, *Ceram. Int.* **38**, 1921 (2012).
- [3] D.U. Tulyaganov, S. Agathopoulos, H.R. Fernandes, J.M. Ventura, J.M.F. Ferreira, *J. Europ. Ceram. Soc.* **24**, 3521 (2004).
- [4] S. Taruta, T. Ichinose, T. Yamaguchi, K. Kitajima, *J. Non-Cryst. Solids* **352**, 5556 (2006).
- [5] J. Henry, R.G. Hill, *J. Non-Cryst. Solids* **319**, 13 (2003).
- [6] J. Wu, Z. Li, Y. Huang, F. Li, *Ceram. Int.* **39**, 7743 (2013).
- [7] S. Lakshmi Reddy, N.C. Gangi Reddy, G. Siva Reddy, B. Jagannatha Reddy, R.L. Frost, *Spectrochim. Acta A* **65**, 684 (2006).
- [8] T. Höche, S. Habelitz, I.I. Khodos, *J. Cryst. Growth* **192**, 185 (1998).