

Sintering behavior and mechanical properties of the mica–diopside machinable glass-ceramics

Parvin Alizadeh^{a,*}, Bijan Eftekhari Yekta^b, Tannaz Javadi^a

^a School of Engineering, Tarbiat Modares University, Tehran, Iran

^b Ceramic Division, Department of Materials, Iran University of Science and Technology, Tehran, Iran

Received 1 May 2007; received in revised form 4 October 2007; accepted 26 October 2007

Available online 3 January 2008

Abstract

The machinability of fluor-mica glass-ceramics is an attractive characteristic of these materials. However, the poor mechanical strength and hardness has limited their applications.

In this research, to overcome this problem, a glass frit in the system CaO–SiO₂–P₂O₅–MgO was gradually added to a mica-based frit. After sintering of compacted mixtures, simultaneous crystallization of diopside and mica occurred that led to improved mechanical properties. The sinterability of various samples was investigated and their microstructure and crystallinity were evaluated by electron microscopy (SEM) and X-ray diffraction (XRD). The presence of plate-like crystals of mica, spherical particles of apatite and fibrous inclusions of diopside was the microstructural specification of the optimum composition.

The four-point bending strength and the Vickers microhardness of samples were also determined.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Glass ceramics; Machinability; Sintering; Mica; Diopside

1. Introduction

Mica glass-ceramics with their unique machinable property have become an interesting subject for many researchers. The machinability of these glass-ceramics is related to an interlocking microstructure and the cleavage of plate-like mica makes them suitable for machining with high precision by ordinary tools.¹

As the main weak point of mica glass-ceramics is their poor mechanical properties, various works have been done to improve this issue. Grossman showed that the strength of samples changes with the variation of mica crystals diameter.² By using a hot press, Cheng has produced directional growth of mica crystals and has determined its effect on the strength.³ Baik claimed the existence of compression stress around the mica crystals which caused greater sample strength.⁴ Uno investigated the precipitation of a barium fluor-mica phase on the strength and fracture toughness.⁵ Addition of a second crys-

talline phase to the glass matrix has been the other approach adopted for this purpose.⁶

It is known that addition of a second rigid and strong phase can improve the mechanical properties of a material by several mechanisms. However, this can lead to demolishing of the machinability of the specimen. It seems that if the reinforcement phase itself has suitability for machining, it will be possible to improve both mechanical properties and machinability. According to previous experiences,⁷ while diopside-based glass-ceramics have desirable mechanical strength they can also be machined to some extent. Therefore, with respect to the above-mentioned properties, the influence of a glassy powder from the system CaO–SiO₂–MgO–P₂O₅, when added gradually to a mica-based glass-ceramic frit⁸ has been investigated.

2. Experimental procedures

2.1. Glass preparation

Glasses were prepared by fusing reagent grade chemicals. The chemical compositions of the two glasses are given in Table 1. The frits GM and GD were agents for its formation of

* Corresponding author.

E-mail address: p-alizadeh@modares.ac.ir (P. Alizadeh).

Table 1
Chemical analysis of glasses (by weight)

Glass	SiO ₂	CaO	Al ₂ O ₃	MgO	K ₂ O	F	B ₂ O ₃	P ₂ O ₅	Fe ₂ O ₃
GM	40.13	–	16.24	19.11	8.00	9.55	2.23	4.45	–
GD	29.12	45.35	–	4.30	–	–	–	16.23	5.00

fluor-mica and diopside crystalline phases during sintering procedure, respectively. Homogenized raw materials of GM and GD were melted in a platinum crucible at 1400 and 1430 °C, respectively in an electric kiln for 30 min. Molten glasses were then quenched in cold distilled water. The gained frits were ground in an electric hard porcelain mortar for 2 h. Mean particle size of the resulting powders was measured using a laser particle size analyzer (Fritsch, Analysette 22).

2.2. Mixing of two frits

The weight percent of prepared compositions from mixing of the two frits GM and GD were tabulated in Table 2. The glass powders were mixed with 2.5 wt.% PVA and cold pressed into 55 mm × 10 mm × 5 mm bars at a pressure of 50 MPa using a laboratory uniaxial hydraulic press. The sinterability of the mixed glasses was investigated by sintering for 240 min in an electric furnace from the glasses softening points up to 1000–1180 °C, at a heating rate of 10 °C min⁻¹.

2.3. Methods of analysis

Microstructure and crystallinity were inspected using scanning electron microscopy (Philips XL30) and X-ray diffraction equipment (Philips, X'Pert). Silicon powder was used as the standard for quantitative measurements. A Vickers microhardness tester with a diamond pyramid indenter (Buehler) was used to measure microhardness. The load was 500 g and the loading time was 30 s.

Four-point bending strength was measured using an Instron universal testing machine (model 5500 R). Five polished rectangular specimens (50 mm × 10 mm × 5 mm) were tested from each series of samples.

Table 2
Composition of prepared glasses from mixing of two frits

	Sample										
	M	M9D1	M8D2	M7D3	M6D4	M5D5	M4D6	M3D7	M2D8	M1D9	D
GM (%)	100	90	80	70	60	50	40	30	20	10	0
GD (%)	0	10	20	30	40	50	60	70	80	90	100

Table 3
Sintering temperature, linear shrinkage and relative density of prepared glass-ceramics

	Sample										
	M	M9D1	M8D2	M7D3	M6D4	M5D5	M4D6	M3D7	M2D8	M1D9	D
Sintering temperature (°C)	1120	1120	1120	1120	1140	1140	1140	1150	1180	1180	1000
Linear shrinkage (%)	22.3	18	18	17	14.7	17.8	18.15	18	18	18.7	16
Relative density (%)	98	96	95	95	93	94	94	95	94	94	98

3. Results and discussion

According to the Frenkel equation,⁹ the particle size of glass powder is a major and effective factor on the sintering rate of compacted glassy powder. On the other hand, it has been claimed that there is a threshold for glass particle size (7 μm): for larger glass particles, the amount of shrinkage is strongly decreased.¹⁰ Therefore, the particle size distributions of both milled glasses were measured and targeted at this amount. The optimum sintering temperature of samples was determined by considering the linear shrinkage and relative density (Table 3). It can be seen that while the optimum sintering temperature of GD by itself is the lowest, its addition gradually to GM led to increase of the sintering temperature for glass mixtures. As we know one of the reasons for sintering temperature raise, could be the change in amount of powder compaction during the addition of frit GD to GM. However, the results of experiment do not confirm the above-mentioned phenomenon. Whereas the total porosity of compacted powder of GM, GM5D5 and GD were relatively the same (26, 26 and 27%, respectively). It seems the increase of sintering temperature is related to crystallization behavior.

Figs. 1 and 2 show the XRD patterns of the sintered samples. As can be observed fluor-phlogopite and forsterite; apatite and diopside are the main crystalline phases precipitated during sintering in the M and D series, respectively. It can be seen that addition of GD to GM, led gradually to reduction of fluor-phlogopite, ultimately to zero in the sintered M4D6. Fluoroapatite appeared in the M8D2 specimen and gradually increased with GD. In an equal weight percent of the two glasses, i.e. in the M5D5, fluoroapatite, forsterite, fluor-phlogopite and diopside were the main four crystalline phases which can be observed. When the amounts of GD predominate, only fluoroapatite and diopside were crystallized, their amounts were increased with increasing GD.

As it pointed out above, fluoroapatite was crystallized in the mixed glasses. It means that its constituents supplied from the two glasses, i.e. F⁻ ion from GM and Ca²⁺ and P⁵⁺ ions from GD. Therefore, it can be concluded that mutual diffusion of the above-mentioned constituents at the glass–glass interface and/or

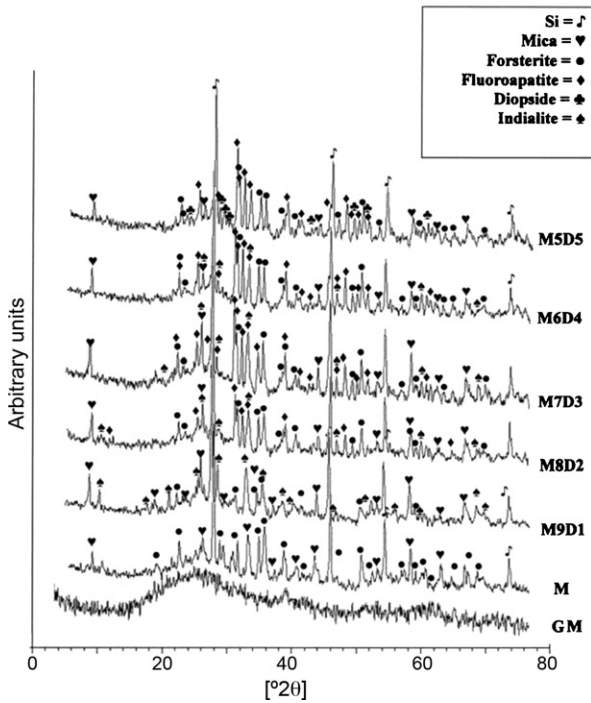


Fig. 1. XRD patterns of prepared glass-ceramics from M to M5D5.

unifying of the two glasses by viscous flow has been responsible for precipitation of fluoroapatite.

In order to investigate the crystallization behavior, the sample of M5D5 was examined. Fig. 3 shows the crystallization behavior of this sample during increasing of temperature. According to experimental results, fluoroapatite and chondrodite were crys-

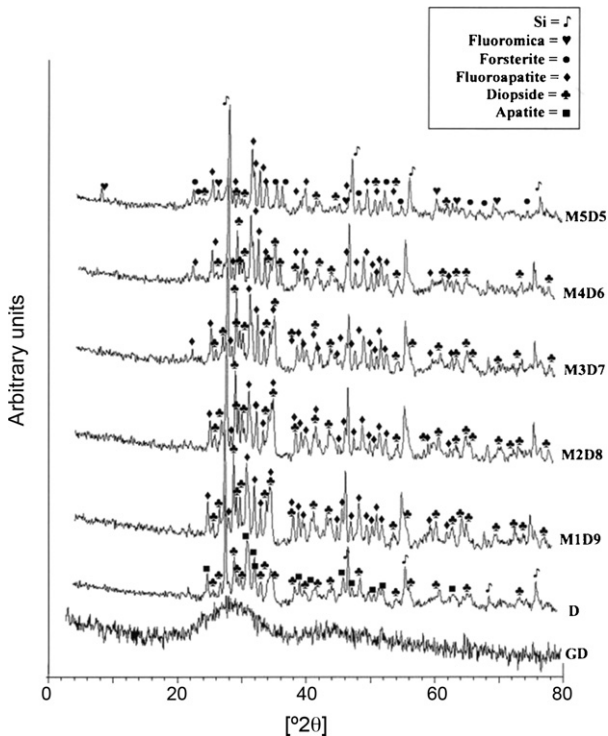


Fig. 2. XRD patterns of prepared glass-ceramics from D to M5D5.

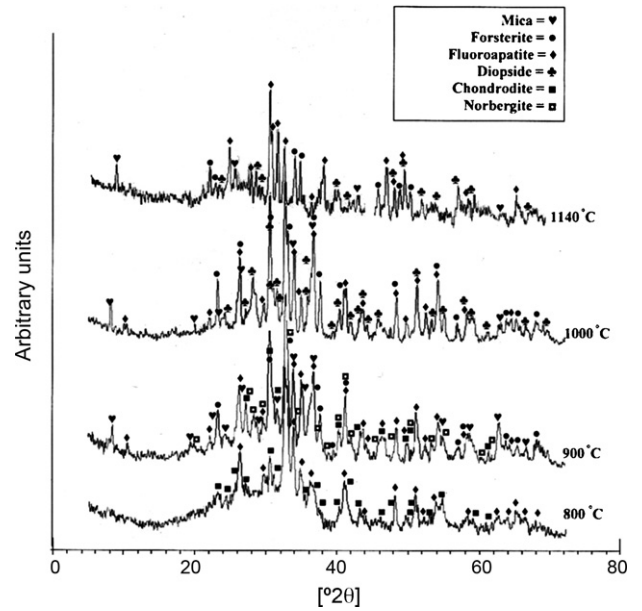


Fig. 3. XRD patterns of M5D5 glass-ceramic vs. the increase of temperature.

tallized at 800 °C. Increasing the firing temperature up to 900 °C led to formation of new phases: norbergite, forsterite, and fluor-phlogopite. Diopside was appeared at 1000 °C, while norbergite and chondrodite phases were disappeared. Finally at sintering temperature (1140 °C) only fluor-phlogopite, diopside and forsterite can be observed.

In general, the increasing of crystallized phase causes decrease of sintering. So, the crystallization of the glass before sintering causes reduce sintering rate.¹¹ Fig. 4 shows the trend of total intensity of all crystalline phases (fluor-phlogopite + fluoroapatite + forsterite + diopside) precipitated during sintering to silicon intensity with GD. According to the above result, it seems that increasing of GD in the mixture leads to enhancement of crystalline phase amounts. This occurrence will prohibit free flowing of the glass phase and so require increase in the sintering temperature of the specimens with GD.

Figs. 5 and 6 show the SEM microstructure of M and M9D1 glass ceramics, respectively. Accordingly, while the microstructure of M specimen consisted of spherical fluor-phlogopite crystalline phase dispersed in the glassy matrix, in the M9D1 it changes to plate-like shape. It has been said that the spherical-

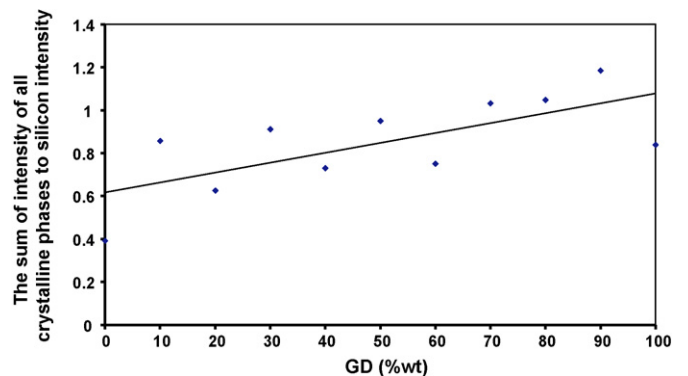


Fig. 4. The trend of total intensity of all crystalline phases to silicon intensity.

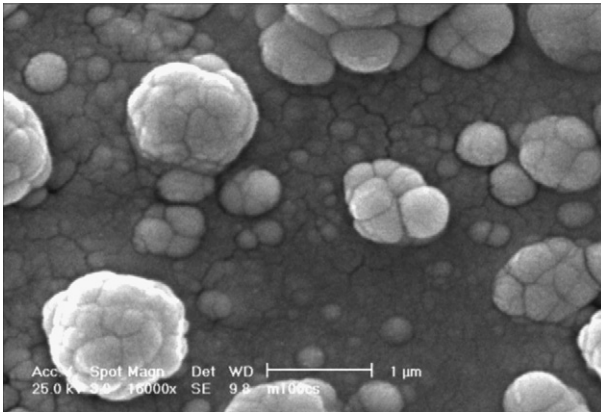


Fig. 5. SEM microstructure of spherical mica in sample M.

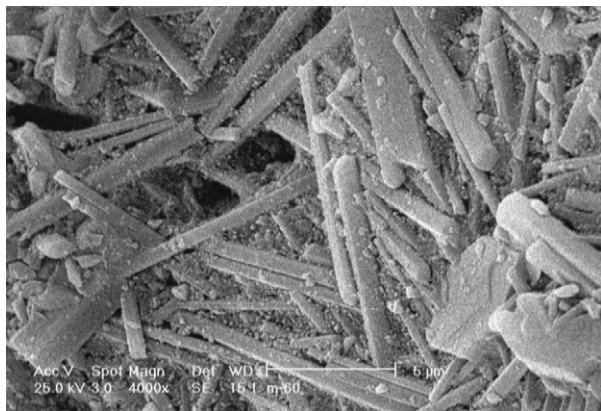


Fig. 6. SEM microstructure of plate-like mica in sample M9D1.

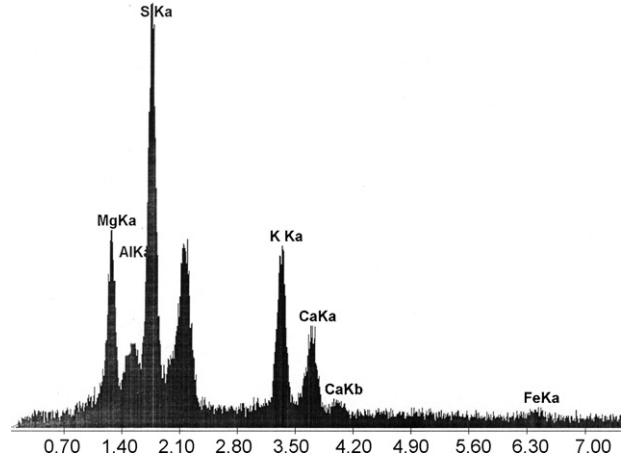


Fig. 8. EDAX analysis of mica solid solution in sample M9D1.

shaped mica originated from a limitation in liquid–liquid phase separation, which causes fluor-phlogopite precipitates directly from a homogeneous glass phase and not from transient phases like norbergite and chondrodite.¹² Holland and Vogel have attributed this morphology to substitution of Mg^{2+} by Al^{3+} in the octahedral positions of mica structure.¹³ As known previously,⁸ this factor had altered the morphology of mica crystals in the glass M to spherical kind. Therefore, we can conclude that addition of glass GD to GM reduces the total amounts of Al ions in the mixed composition, converting the shape to plate-like.

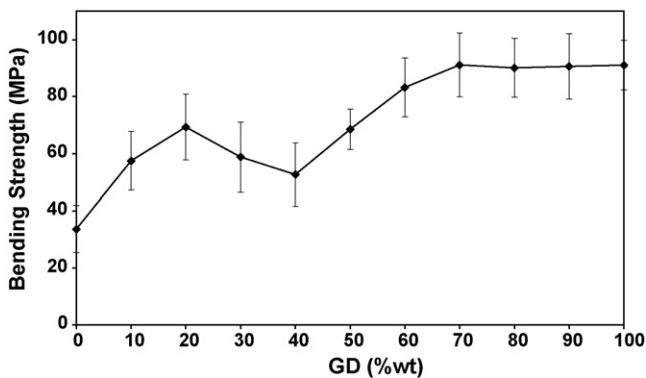


Fig. 7. Variations of bending strength vs. the increase of frit GD.

Fig. 7 shows the variation of bending strength of glass ceramics versus the frit GD. On the whole, with the exception of a shallow concave-shaped region in the near-middle of the graph, it can be observed an upward trend of strength with glass GD. It seems that introduction of high amounts of CaO by GD into the system is responsible for this behavior. Figs. 8 and 9 depict the EDAX analysis of plate-like shaped mica in the M9D1 and the overall changes in the relative intensity of two major and effective phases (fluor-phlogopite and diopside) as a function of added GD, in the sintered glass mixtures, respectively. Existence of calcium in the crystalline particle (Fig. 8) indicates a partially substitution of K^+ by Ca^{2+} in the crystalline particle. Since the coordination number of Ca^{2+} is lower than K^+ in this structure, and as the bonding strength of the former with oxygen (32 kcal) is greater than the latter with oxygen (12 kcal),¹⁴ the strength of cleavage bonding in the solid solution would be higher than to the previous potassium fluor-phlogopite. Therefore, according to Fig. 9 the strengthening of specimen up to M8D2 should be related to simultaneous increasing of mica amount and formation of solid solution. Oppositely, the subsequent reduction of strength up to M6D4 should be related to reduction of it. Afterwards, where the fibrous-shaped diopside (Fig. 10), with its higher elastic modulus, in the higher calcium containing mixtures (viz., M6D4) appears (Fig. 9), strengthening of sintered specimens occurs again.

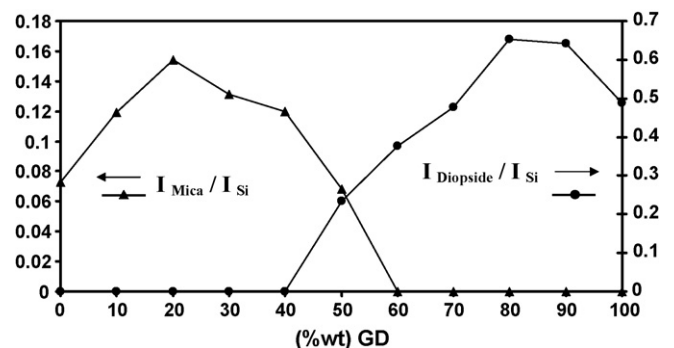


Fig. 9. Intensity of (a) mica crystals and (b) diopside crystals to intensity of silicon vs. the increase of frit GD.

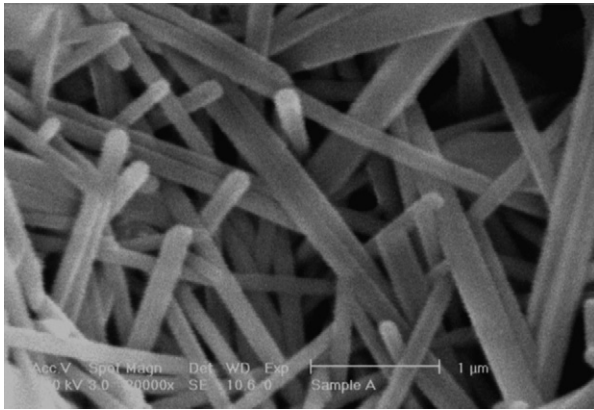


Fig. 10. Fibrous morphology of diopside phase in sample M1D9.

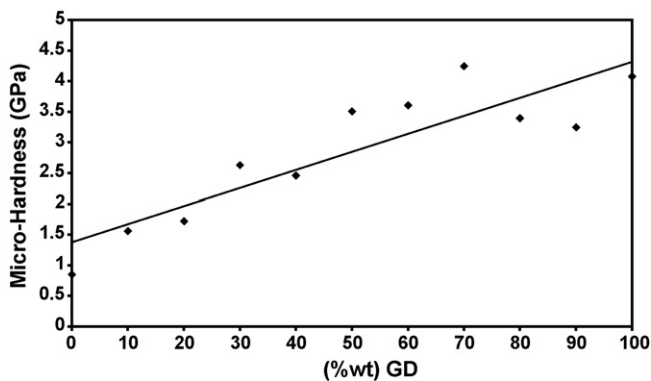


Fig. 11. Variations of Vickers microhardness vs. the increase of frit GD.

Fig. 11 depicts the trend of microhardness variation with glass GD. As it was expected the microhardness of glass-ceramics increases gradually with GD. The same reasons, which proposed in the previous subject, can also be explained for this behavior. It means that formation and increasing of potassium–calcium fluor-mica solid solution, instead of a less hard pure potassium one (in M–M8D2 interval); reduction of its amount (from M8D2 to M6D4), which substituted probably by a harder glassy phase; and ultimately coming into existence of diopside (from M6D4 to GD) are responsible for improvement of hardness with gradually addition of GD.

4. Conclusions

The sintering temperature of mixed glass compositions is influenced by the amounts of diopside-based glass quantity, which itself had the lowest sintering temperature. According to our results, this came from the enhancement of crystalline phase in the sintered specimens when diopside-based glass was added to the other one, gradually.

Fluoroapatite was a crystalline phase, which crystallized only in the sintered glass mixtures. As the constituents of this phase are supplied from the two glasses, it can be concluded that this phase has been formed by mutual diffusion of glass constituents and/or by unifying of the two glasses by viscous flowing during sintering procedure.

Addition of the diopside-based glass to the mica-based one led to change of mica morphology from spherical to plate-like shape. Formation of the plate-like mica with addition of diopside-based glass is due to encourage of liquid–liquid phase separation and reduction of Al^{3+} in the crystalline structure, which is compatible with some of the previous works.

Mechanical strength and microhardness variation with the diopside-based glass show an enhancement trend. According to our results, the changes of mica composition and incrementally formation of fibrous-shaped diopside were the main reasons for these behaviors.

References

- Baik, D. S., No, K. S., Chun, J. S. and Yoon, Y. J., Mechanical properties of mica glass-ceramics. *J. Am. Ceram. Soc.*, 1995, **78**(5), 1217–1222.
- Grossman, D. G., Machinable glass-ceramics based on tetrasilic mica. *J. Am. Ceram. Soc.*, 1972, **55**, 446–449.
- Cheng, K., Wan, J. and Liang, K., Enhanced mechanical properties of oriented mica glass-ceramics. *J. Mater. Lett.*, 1999, **39**, 350–353.
- Baik, D. S., A comparative evaluation method of machinability for mica-based glass-ceramic. *J. Mater. Sci.*, 1995, **30**, 1801–1806.
- Uno, T., High strength mica containing glass-ceramic. *J. Am. Ceram. Soc.*, 1991, **74**, 3139–3141.
- Tzeng, J. M., Duh, J. G., Chung, K. H. and Chan, C. C., Al_2O_3 and ZrO_2 -modified dental glass-ceramics. *J. Mater. Sci.*, 1993, **28**, 6127–6135.
- Alizadeh, P., Eftekhari Yekta, B. and Gervei, A., Effect of Fe_2O_3 addition on the sinterability and machinability of glass-ceramics in the system $MgO-CaO-SiO_2-P_2O_5$. *J. Eur. Ceram. Soc.*, 2004, **24**, 3529–3533.
- Eftekhari Yekta, B., Alizadeh, P. and Hashemi Nia, S., The effect of B_2O_3 , PbO and P_2O_5 on the sintering and machinability of fluoromica glass-ceramics. *J. Eur. Ceram. Soc.*, 2005, **25**(6), 899–902.
- Rbinovich, E. M., Preparation of glass by sintering. *J. Mater. Sci.*, 1985, **20**, 4259–4297.
- Panda, P. C., Effect of heating rate on the relative rates of sintering and crystallization in glass. *J. Am. Ceram. Soc.*, 1989, **72**, 2361–2364.
- Hamzawy, A. M., Crystallization behavior of fluorophlogopite glass-ceramics. *Ceramic-Silikaty*, 2001, **45**(3), 89–96.
- Holand, W. and Vogel, W., A new type of phlogopite crystal in machinable glass-ceramics. *Glass Technol.*, 1983, **24**, 318–322.
- Holand, W., Wang, P. and Naumann, K., Control of phase formation process in glass-ceramics for medicine and technology. *J. Non-Cryst. Solids*, 1991, **129**, 152–162.
- Varshneya, A. K., *Fundamental of Inorganic Glasses*. Academic Press, 1994, p. 34.