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The effect of B_2O_3, PbO and P_2O_5 on the sintering and machinability of fluormica glass–ceramics

B. Eftekhari Yekta, S. Hashemi Nia, P. Alizadeh*

Ceramic Division, Materials and Energy Research Centre, Tehran, Iran

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Abstract

Sintering, crystallization and machinability behavior of the SiO_2–Al_2O_3–MgO–K_2O–B_2O_3–F glasses were investigated. The optimum fluormica glass–ceramics with desirable sintering behavior and machinability were obtained by addition of PbO and P_2O_5 glass formers. Various parameters, e.g. the morphology of the mica crystal, relative intensity of the mica phase, the particle size distribution of chips obtained by drilling, microhardness, and the strength differences of glass–ceramics before and after drilling ($\Delta\sigma$) were investigated and compared with naked eye experiments.

Keywords: Glass ceramics; Sintering; Machinability

1. Introduction

Fluorphlogopite glass–ceramic articles can be fabricated by melt-cast and sintering methods. The effect of various oxides on the type of precipitated mica phase, crystallization ability and their machinability have been extensively investigated in the melt cast one.[1–5] However, it seems that there is only few works in which the effect of various additives on the above-mentioned characteristics of sintered mica glass–ceramics have been discussed.[6]

The comparison of the glass–ceramic specifications prepared by melt-cast and sintering methods displayed that in the case of surface crystallization of glass, the later method would be preferred from point of crystallization and machinability views.[7] But the complete densification of compacted glass powder is a problem which should be considered in the pressure less sintering method. Otherwise, with increasing of firing temperature, the mica phase may be transformed to unwanted phases, weakens the machinability of specimen. Therefore, in the present work an attempt has been made to achieve mica glass–ceramics with maximum density and desirable machinability through the addition of B_2O_3, PbO and P_2O_5 to the base glass.

* Corresponding author.
E-mail address: p-alizadeh@merc.ac.ir (P. Alizadeh).
URL: http://www.Dr.Alizadeh.com.

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2. Experimental procedures

2.1. Glass preparation

Glasses were prepared by melting reagent-grade chemicals. The homogenized raw material powder was compacted under 2 MPa, and then melted in zircon crucibles at 1400 °C in an electric kiln for 1 h. The molten glasses were then quenched in cold distilled water. The chemical composition of the glasses is displayed in Table 1.

2.2. Methods of analysis

The frits obtained were ground in an electric hard porcelain mortar for 2 h and then ball-milled for 5 h, in aqueous media. The mean particle size of resulted powders was about 3 μm, which were obtained by a Laser particle size analyzer (Fritsch, Analysette 22). The crystallization temperature of the glasses was determined by simultaneous thermal analysis (STA) (Polymer Laboratories, model 1640) using 6 mg of glass powders in a platinum crucible in an air atmosphere with a heating rate of 20 °C/min.

The glass powders were mixed with 2.5 wt.% carboxy methyl cellulose and cold-pressed using a laboratory uniaxial hydraulic press into 55 mm × 13 mm × 5 mm bars at pressure of 49 MPa.

Table 1
Chemical composition of the glasses (wt.%)

Glass	SiO_2	Al_2O_3	MgO	K_2O	F	B_2O_3	PbO	P_2O_5
$GC_{B_2O_3\,1.77}$	42.37	17.15	20.17	8.45	10.08	1.77	—	—
GC	40.13	16.24	19.11	8.00	9.55	6.68	—	—
$GC_{B_2O_3\,11.16}$	38.33	15.51	18.25	7.64	9.12	11.16	—	—
$GC_{PbO\,6.68}$	40.13	16.24	19.11	8.00	9.55	—	6.68	—
$GC_{PbO\,4.45}$	40.13	16.24	19.11	8.00	9.55	2.23	4.45	—
$GC_{PbO\,2.97}$	40.13	16.24	19.11	8.00	9.55	3.71	2.97	—
$GC_{P_2O_5\,6.68}$	40.13	16.24	19.11	8.00	9.55	—	—	6.68
$GC_{P_2O_5\,4.45}$	40.13	16.24	19.11	8.00	9.55	2.23	—	4.45
$GC_{P_2O_5\,2.97}$	40.13	16.24	19.11	8.00	9.55	3.71	—	2.97

The sinterability of the glasses was investigated by sintering them for 120 min from glass softening point to 1100 °C with a heating rate of 20 °C/min in an electric furnace. The microstructure and the crystallinity were inspected using a scanning electron microscope (SEM) (Cambridge Stereoscan) and X-ray diffraction equipment (Siemens, D-500). Silicon powder was used as the standard material for quantity measurements. The bulk density of the sintered glass–ceramics was determined by the Archimedes method. The powder density of the glass–ceramics was measured by gas pycnometer (Micromeritics, model Accupyc 1330). A Vickers microhardness tester with a diamond pyramid (Buehler, Micromet 1) was used to measure the microhardness. The load was 500 g, and the loading time was 15 s.

The four-point bending strength was measured using Instron Universal Testing Machine, model 1196. Five polished rectangular specimens (50 mm × 10 mm × 5 mm) were tested for each series of samples. The machinability of drilled glass–ceramics was evaluated initially by naked eye observation and then determination of mean particle size of glass–ceramics chips after their drilling, using 2 mm conventional drills at drilling rate of 3.8 cm/min at 300 rpm. The comparison between drilled and undrilled specimens' bending strength was the third criterion of machinability.

3. Results and discussions

As there was not any clear crystallization peak in the DTA curve of the base glass GC (Fig. 1) and for the other glasses, the interval temperature of 850–1100 °C was adopted for sintering of the compacted glass powders. The linear shrinkage measurement of the above-mentioned specimens fired at interval temperatures showed that complete densification occurred at 1100 °C. Fig. 2 shows the variation of linear shrinkage of samples versus amounts of PbO and P_2O_5, respectively. According to our results, sinterability of glass was improved by the addition of more B_2O_3 (11.16 wt.%) but it reduced the relative intensity (I_{mica}/I_{Si}) of mica from 0.12 to 0.03 and therefore degraded the machinability. On the other hand, the decreasing of the amount of B_2O_3 (1.77 wt.%) caused a reduction of the sinterability of glass and prevents complete densification of the specimen. These experiments also display that even with complete substitution of B_2O_3 by PbO or P_2O_5, the mica still was precipitated in the glasses. This effect shows that B_2O_3 is not a necessarily component for mica structure formation.

As it can be seen, the optimum amounts of B_2O_3, PbO and P_2O_5 are 6.68, 2.97 and 4.45 wt.% in each glass series, respectively. Fig. 3 shows the XRD patterns of the above-mentioned specimens after sintering at 1100 °C. According to these figures, the same crystalline phases, i.e., mica, cordierite and aluminum magnesium spinel, precipitated in different glasses during sintering. However, from the results in Table 2, these glass–ceramics have different characteristics from point of views of machinability and other related parameters.

It can be elucidated that the addition of PbO and/or P_2O_5 to the base glass improves the machinability, confirmed by comparison of the mean particle size of chips (d_{50}) and the bending strength differences of drilled and

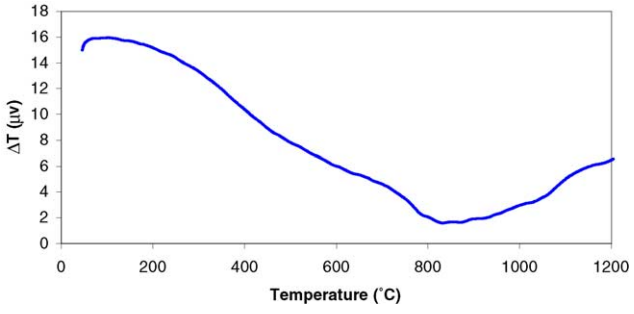

Fig. 1. DTA curve of the base glass (GC).

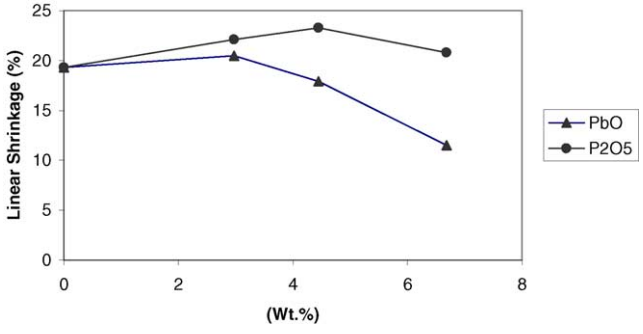

Fig. 2. Variation of linear shrinkage vs. PbO and P_2O_5 (wt.%).

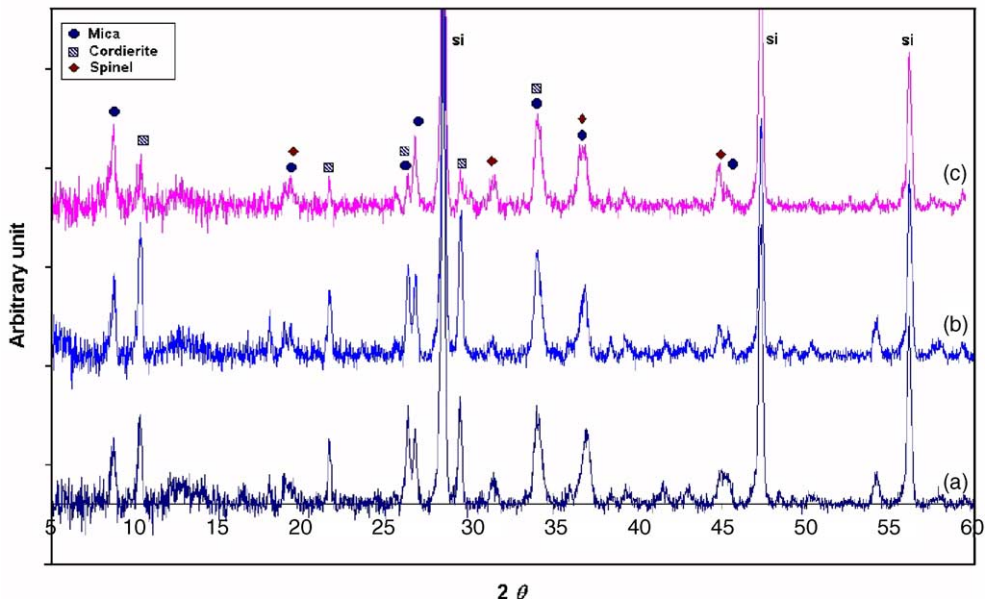

Fig. 3. XRD patterns of the sintered (a) GC, (b) $GC_{PbO\,2.97}$ and (c) $GC_{P_2O_5\,4.45}$ glass–ceramics at 1100 °C.

Table 2
Some characteristics of GC, $GC_{PbO\,2.97}$, $GC_{P_2O_5\,4.45}$ sintered glass–ceramics

Glass	I_{mica}/I_{Si}	Microhardness (GPa)	Bending strength (MPa)	$\Delta\sigma$ (MPa)	d_{50} (μm)	Eye observation
GC	0.12	2.13	50± 13.2	—	16.65	Acceptable
$GC_{PbO\,2.97}$	0.14	1.27	35± 8.8	7.12	9.22	Good
$GC_{P_2O_5\,4.45}$	0.15	0.85	41± 5.6	13.21	8.65	Excellent

undrilled specimens ($\Delta\sigma$). It is said that machinability of mica glass–ceramics related to two main conditions: mica volume percent and degree of interlocking of crystalline phases.[8–10] If we consider the ratio of I_{mica}/I_{Si} in Table 2, the first condition is fulfilled in the specimens $GC_{PbO\,2.97}$ and $GC_{P_2O_5\,4.45}$. However, the second condition is not satisfied with the above-mentioned glass–ceramic microstructures. While the glass–ceramic GC consisted of interlocked microstructure of platelet crystals with mean diameter of ∼5 μm (Fig. 4), the mica particles in $GC_{PbO2.97}$ and $GC_{P_2O_5\,4.45}$ glass–ceramics are spherical with a mean diameter of 2 and 1 μm, respectively (Figs. 5 and 6). These observations are compatible with the results obtained by Holand and Vogel[11] and Carl.[5] They showed that the machinability of these spherical shapes mica glass–ceramics is four to five times more than the platelet one, and concluded that the noted microstructure resulted due to occurrence of a limited phase separation in glass which leads to precipitation of mica directly from the glass phase and not from the intermediate phases, i.e., norbergite and conderdite. Also occurrence of a limited phase separation and the lack of

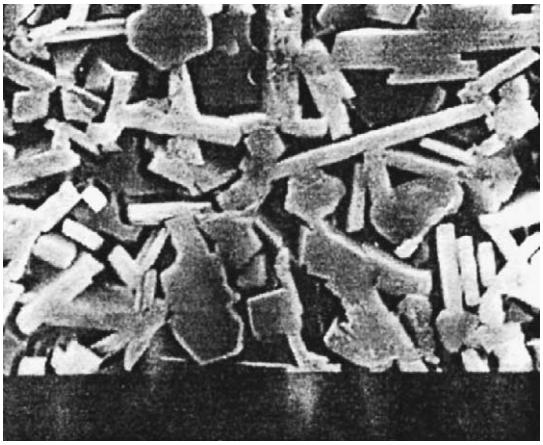

Fig. 4. SEM microstructure of the glass–ceramic GC (5000×).

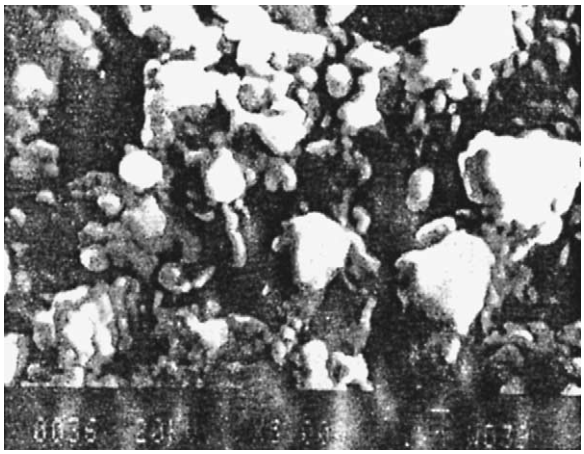

Fig. 5. SEM microstructure of the glass–ceramic $GC_{PbO\,2.97}$ (5000×).

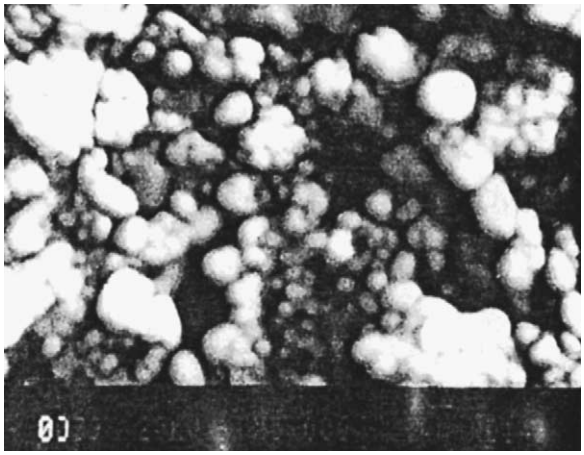

Fig. 6. SEM microstructure of the glass–ceramic $GC_{P_2O_5\,4.45}$ (5000×).

intermediate phases in the glass–ceramics $GC_{PbO2.97}$ and $GC_{P_2O_5\,4.45}$ were confirmed by SEM and XRD results.

The pronounced reduction of microhardness is another result that obtained by addition of PbO and P_2O_5 to the base glass (GC), which could be related to higher amounts of mica phase in these specimens and also to reduction of microhardness of residual glassy phases. It seems that reduction of microhardness in any form caused an improvement of specimen's machinability.

The formation of spherical mica in the glass–ceramics has been attributed to a low growth rate of crystals during heat-treatment.[12] It is pointed out that P_2O_5 and PbO shift the crystallization of glasses to higher temperatures so that at a specified heat-treatment, these oxides can delay the procedure of crystallization[13,14] and thereby improve the glass sinterability.[15] Therefore, it seems that similar procedure has been happen for $GC_{PbO\,2.97}$ and $GC_{P_2O_5\,4.45}$ specimens and made possible for the precipitation of spherical mica crystals to occur.

In spite of advantages which obtained by the addition of PbO and P_2O_5 to the base glass, addition of these oxides were somewhat associated with reduction of bending strength and microhardness. However, if the improvement of machinability to bending strength and microhardness was preferred, the use of the above oxides in machinable glass–ceramics is recommended.

4. Conclusions

1. The maximum densification temperature of the compacted glass powders were about 1100 °C. Fluormica crystals were the main crystalline phase which precipitated during sintering in different compositions.
2. The machinability of the sintered glass–ceramics improved by addition of 2.97 wt.% PbO and/or 4.45 wt.% P_2O_5 to the base glass. The improvement of machinability was attributed to more volume percent of precipitated mica, and less microhardness of PbO and P_2O_5 bearing glass–ceramics.
3. Addition of PbO and P_2O_5 to the base glass also changed the mica crystals morphology from platelet to spherical shapes.

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